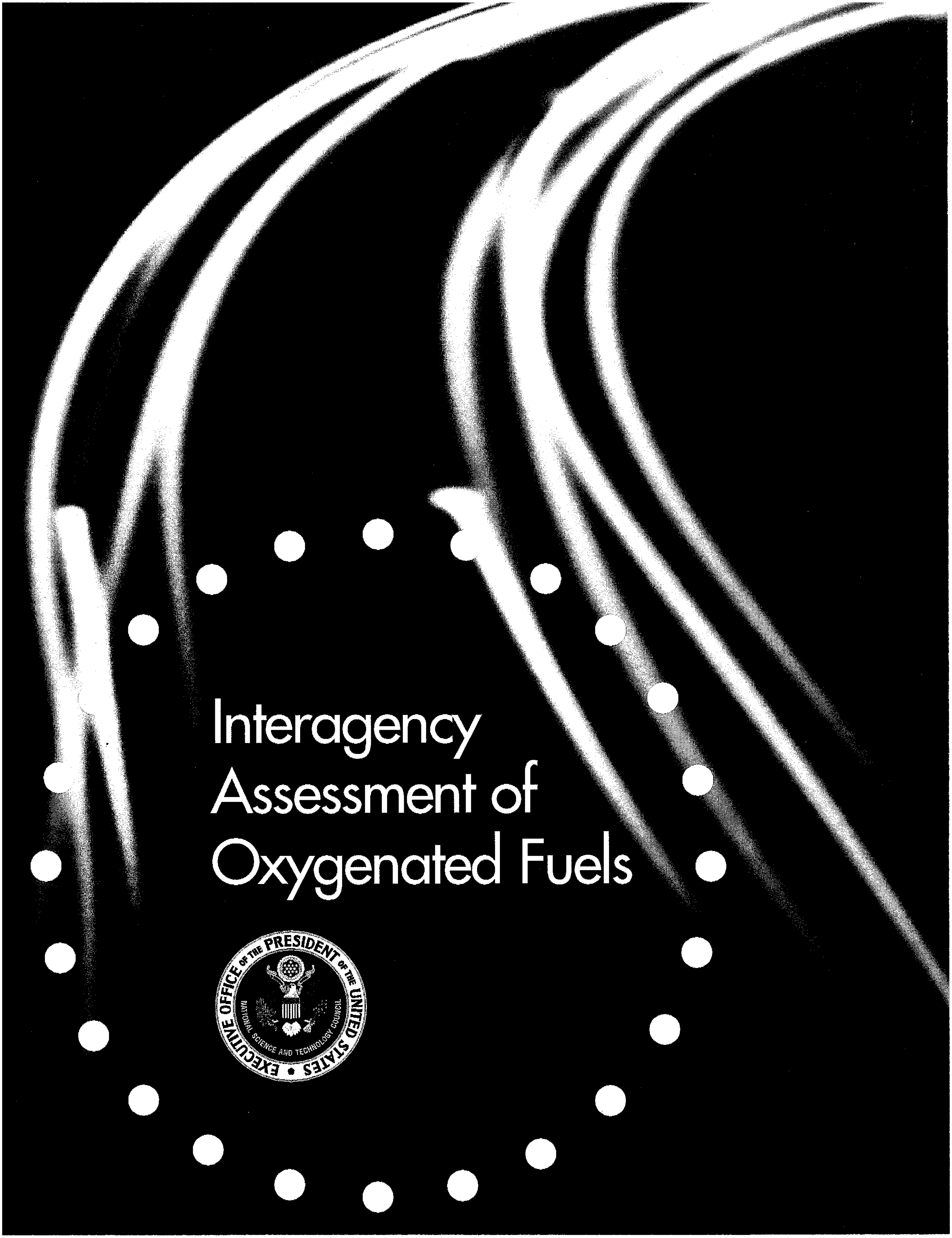

Interagency Assessment of Oxygenated Fuels

EXECUTIVE OFFICE OF THE PRESIDENT OF THE UNITED STATES
NATIONAL SCIENCE AND TECHNOLOGY COUNCIL

Interagency Assessment of Oxygenated Fuels

EXECUTIVE OFFICE OF THE PRESIDENT OF THE UNITED STATES

JUNE 1997

National Science and Technology Council

Committee on Environment and Natural Resources

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EXECUTIVE OFFICE OF THE PRESIDENT
NATIONAL SCIENCE AND TECHNOLOGY COUNCIL
WASHINGTON, D.C. 20500

June 1997

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.

John H. Gibbons
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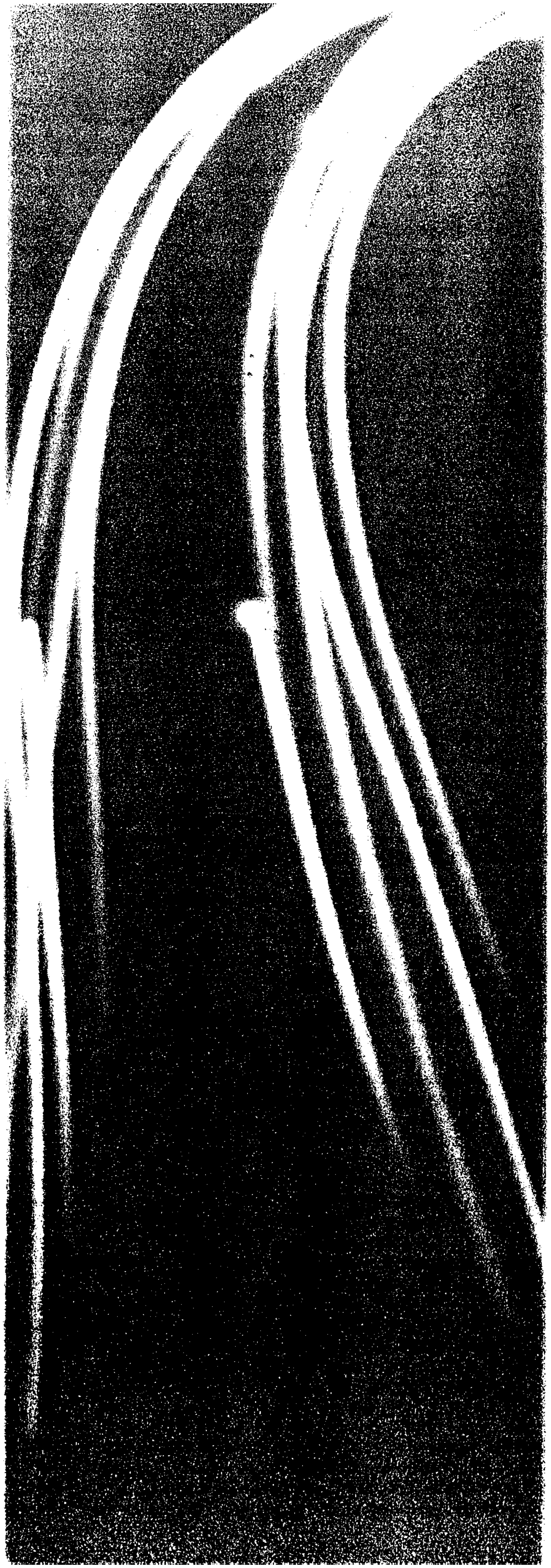

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PREFACE

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.

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.

- 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.

- 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.

- 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 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.

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FIGURES

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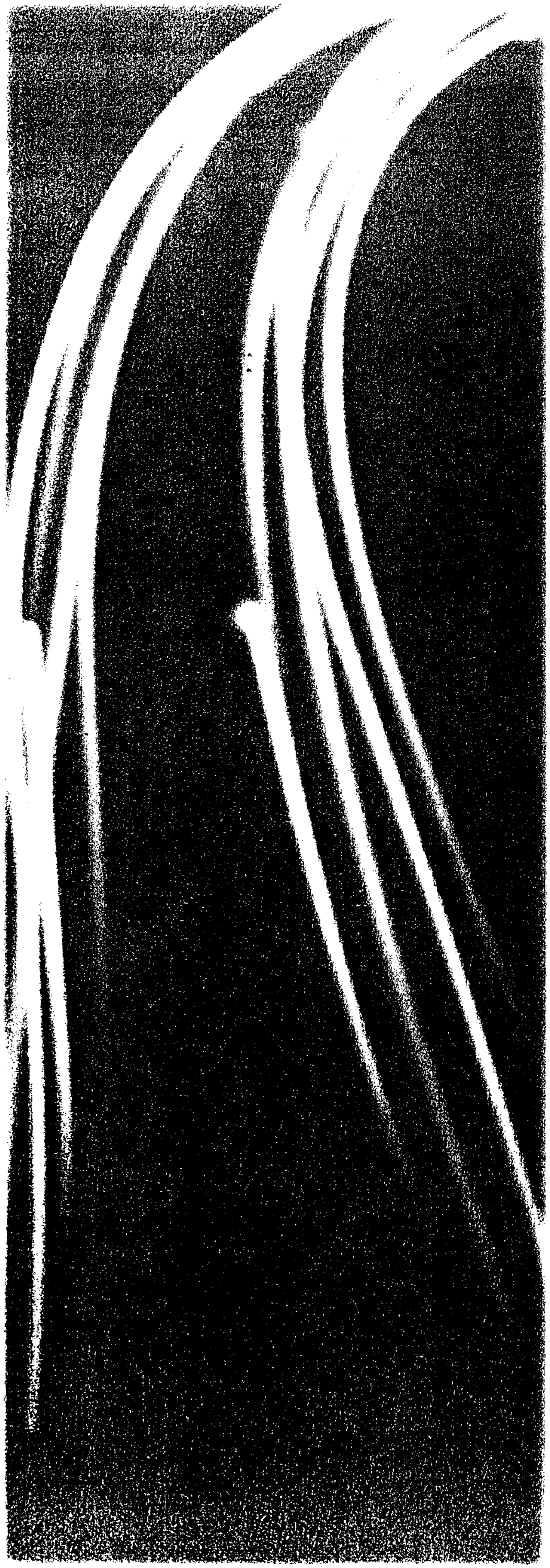

Air Quality Effects of the Winter Oxyfuel Program

1

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CONTENTS

SCOPE OF THE CHAPTER

The effects of the winter oxyfuel program on air quality are assessed in this chapter. The focus of the program is on carbon monoxide (CO) but other pollutants including volatile organic compounds (VOC), nitrogen oxides (NO and NO_2 designated as NO_x), particulate matter, and the toxic air pollutants (TAP), benzene, 1,3-butadiene, formaldehyde, and acetaldehyde are also affected to varying degrees. Data from vehicle emission studies, model predictions, and ambient air quality measurements are reviewed for this assessment.

BACKGROUND OF THE WINTER OXYFUEL PROGRAM

Carbon monoxide is a colorless, odorless, and poisonous gas produced by the incomplete combustion of carbon-containing fuels. Elevated levels of ambient CO have been shown to be a human health hazard (Morris *et al.*, 1995). The EPA has set National Ambient Air Quality Standards (NAAQS) for CO that specify upper limits of 35 ppm for a one-hour period and 9 ppm for an eight-hour period. Generally the eight-hour limit is the more restrictive and virtually all recorded exceedances in recent years involve violation of this limit. Monitoring stations are allowed one exceedance of the air quality standard per year. A second exceedance constitutes a violation. For this reason the second maximum value of CO has been adopted as an important indicator in air quality trend studies. In cities during the winter, on-road vehicles account for a large fraction of the emissions, up to 95% (USEPA, 1995a).

A network of air pollutant monitoring stations has found a persistent pattern of high levels of carbon monoxide (CO) during winter months in many U.S. urban locations. The winter peak values occur during months when temperature inversions trap pollutants near the ground and inhibit dispersion and dilution. The buildup of CO is aggravated in cold climates by increased CO emissions from cold vehicles. Figure 1.1 shows the monthly average CO concentrations over the last 14 years recorded at a monitoring site in downtown Denver, Colorado. At this highly polluted site the peak values occur typically during the months November through February, corresponding to the period of frequent inversions and low temperatures. The average winter CO concentrations at this site are about twice as large as the average summer values, which are indicated by the minima in the data.

Gasoline-fueled engines are a major source of carbon monoxide (CO) and other pollutants. Under ideal conditions, the complete combustion of a hydrocarbon fuel results in a product mixture of mainly carbon dioxide (CO_2) and water vapor in the exhaust stream. The effect of the combustion air/fuel (A/F) ratio on the exhaust composition can be understood with reference to Figure 1.2. This figure is a representative example of the effect of the air/fuel ratio on exhaust pollutant formation in a 1980 vintage engine. It should be noted that the figure gives the engine emissions, called engine out emissions, not the tailpipe emissions, which are considerably lower when a properly functioning catalyst system is used. The dashed line represents the air/fuel ratio with equivalent amounts of oxygen and fuel required for complete combustion. But even at this point 5 - 10% of the fuel carbon is emitted as CO.

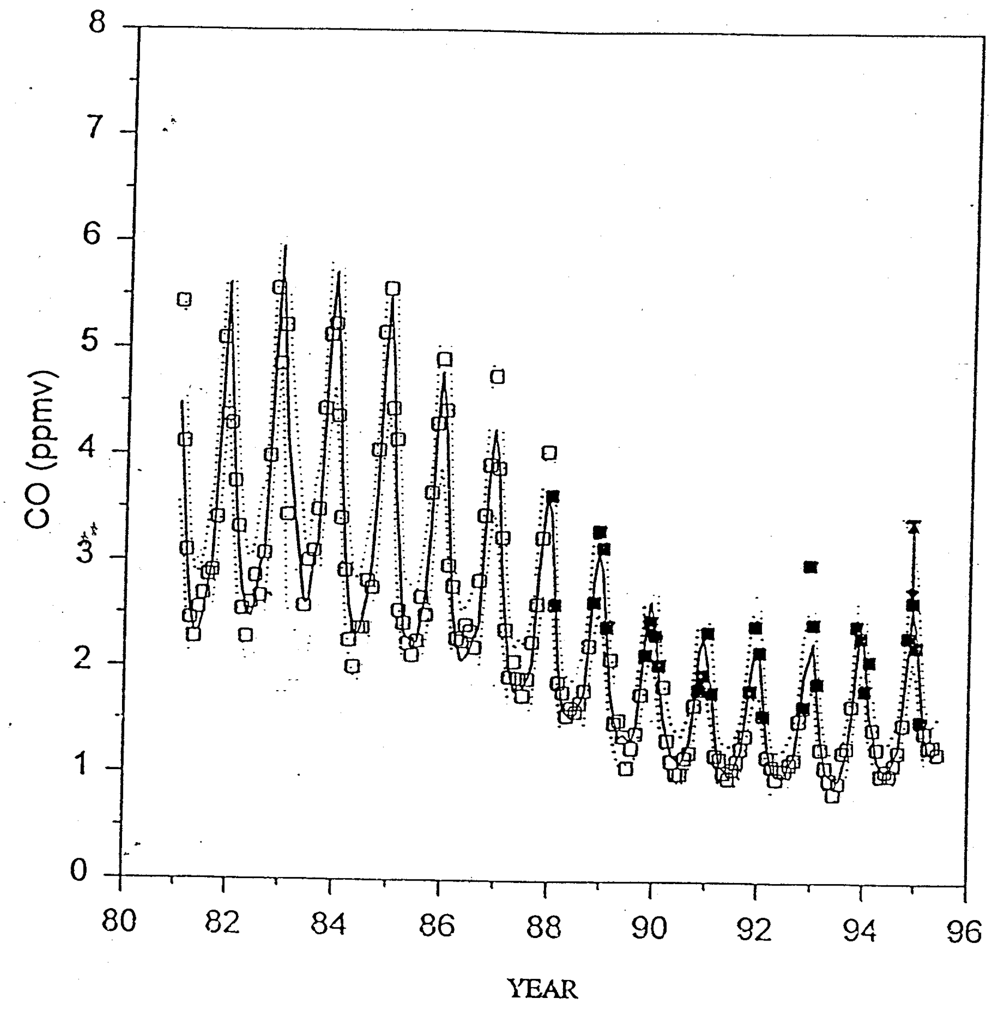

Figure 1.1 A 14-year record showing monthly average values of hourly average CO concentrations at the CAMP air quality monitoring site in Denver, Colorado. The filled symbols indicate the months during which oxyfuels have been used. The bar above the point at 95 shows what the ambient CO concentration would be if one assumes the measured value corresponds to a 24% reduction due to oxyfuels. (Figure courtesy of Larry Anderson)

Some fuel is not completely oxidized, because of limitations of combustion kinetics and quenching of the combustion by the cool metal surfaces of the engine cylinder. The result is incomplete oxidation of the fuel and the emission of CO and some residual organic compounds. About half of the emitted organic material is unburned fuel and half is partially oxidized fuel products. The engine operates in a fuel rich condition when started (cold start) and at an A/F ratio of about 13 for maximum power during a hard acceleration. Under the latter condition about 25% of the fuel carbon is emitted as CO. The nitric oxide (NO) pollutant (generally referred to here as NO_x) has an interesting inverse relationship with the CO and hydrocarbon (HC) pollutants. The NO increases under high A/F ratio (lean) conditions because it is made by the reactions of excess oxygen and nitrogen at high temperatures. Frequently the NO_x emissions are low when the CO and HC emissions are high.

Several actions have been taken to reduce vehicle emissions. The EPA has promulgated emission standards for gasoline fueled vehicles since 1968. A summary of these standards for selected years is given in Table 1.1. In addition to CO, the emissions of hydrocarbons (HCs) and NO_x are regulated, because they contribute to photochemical smog and ozone production. During the past 30 years vehicle manufacturers have responded to the emission regulations by installing emission control devices. Current technology includes a computer-controlled feedback system incorporating oxygen sensors, three-way catalysts, and fuel injection into closed loop and adaptive learning strategies. The concept of the closed loop technology is to measure the oxygen concentration in the exhaust system and to control the vehicle A/F ratio near the stoichiometric point to minimize pollutant emissions. Improved catalysts have also helped reduce emissions. The reduction in exhaust emissions, indicated by comparing the emission levels in the top line of Table 1.1 with the current standards in the bottom line is a factor of 10 for NO_x and about 25 for CO and HC.

Table 1.1 Vehicle exhaust emission standards in grams per mile (U.S. passenger cars, excluding California).

Model Year	Hydrocarbons	CO	NO_x
Pre-1968 (no standards)	11.0	80	4
1973/4	3.4	39	3.0
1977	1.5	15	2.0
1981	0.41	3.4	1.0
1996	0.41	3.4	0.4

Although the introduction and improvement of vehicle emission control devices has led to a decline in urban CO levels, many areas continued to exceed the NAAQS into the late 1980's. Beginning in January 1988, a program of adding an oxygenated organic compound to gasoline was instituted in the Denver, Colorado, area. In subsequent years many other regions in the U.S. that continued to exceed the NAAQS, called nonattainment areas, were required by EPA to adopt similar programs to reduce ambient CO levels. The concept behind the EPA oxyfuel program is to introduce additional oxygen into the combustion mixture by adding an oxygen-containing compound to the fuel. This is equivalent to shifting the A/F ratio in Figure 1.2 toward the right. The added oxygen has been shown to reduce the amount of CO in the engine exhaust in many studies. The additives are called oxygenates and the most common ones are an alcohol: ethyl alcohol (ethanol) or *tertiary*-butyl alcohol (TBA) or an ether: methyl *tertiary*-butyl ether (MTBE), ethyl *tertiary*-butyl ether (ETBE), *tertiary*-amyl methyl ether (TAME), or *tertiary*-amyl ethyl ether (TAEE).

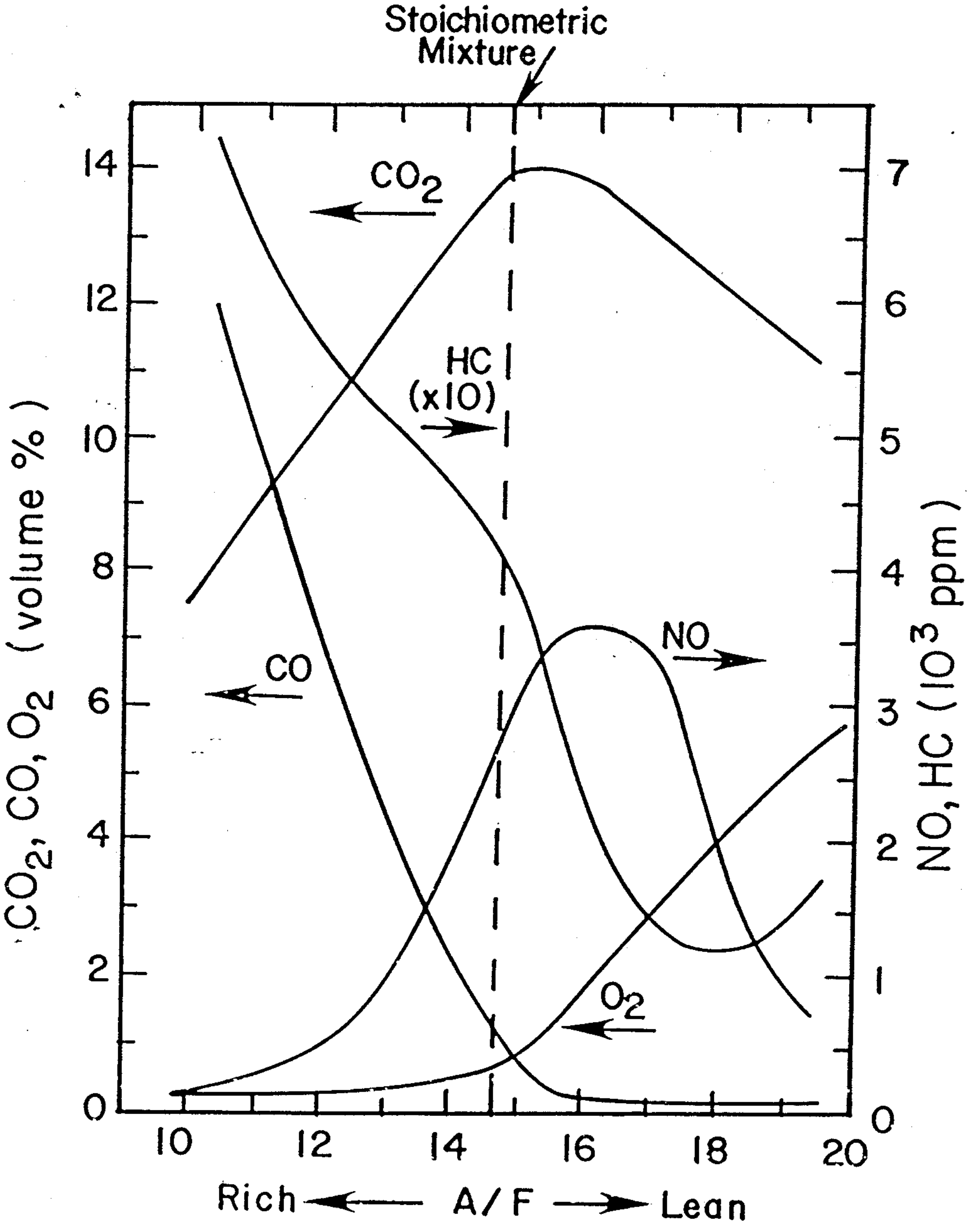

Figure 1.2 Typical gasoline engine pollutant emissions as a function of the intake air to fuel ratio (A/F). The ratio values are based upon mass. The stoichiometric point is a theoretical value at which the amounts of air and fuel are equivalent for complete oxidation of the fuel. Note the different scale for hydrocarbons (HCs) which is 10 times the value for nitric oxide (NO). Adapted from Kummer (1980).

Currently, ethanol and MTBE dominate the market. Adding about 15% by volume MTBE or about 7.8% by volume ethyl alcohol to a standard gasoline achieves a 2.7% by weight oxygen fuel. The amount of oxygen added to a fuel is relatively small, typically 2 to 3.5% by weight.

In this report, emission measurements are distinguished from ambient air quality measurements. Emission measurements are those which sample and measure gases and particles at the tailpipe. The emissions are the gases emitted by the vehicle after passing through any pollution control devices and may also include gases from fuel evaporation. Ambient measurements are those made in the atmosphere. These are characteristic of the gases we breathe in an urban environment. Some air quality measurements are made that are neither an emission measurement nor an ambient measurement, but are somewhere in between. For example, measurements made in a restricted environment such as a tunnel or parking garage are not strictly emission measurements or ambient measurements, although some information about both can be deduced from them.

EFFECTS OF OXYFUELS ON VEHICLE EMISSIONS

Introduction

An assessment of the effects of oxyfuels on vehicle emissions must take into account a complex array of variables affecting emissions. Firstly, the vehicle fleet itself is undergoing a continual change-over. In general the newer models emit less pollution because of improved emission control devices and the use of fuel injection, which makes it possible to provide tight control of A/F stoichiometry. In addition to significant model year changes, the emissions vary from vehicle to vehicle depending upon how it is maintained and operated and the quality of the fuel used.

Secondly, emission studies must be performed on a wide variety of fuel compositions. One of the most extensive studies of fuel effects on automobile emissions is the Auto/Oil Air Quality Improvement Research Program (AQIRP). In this program three domestic automobile manufacturers and 14 oil refining companies cooperated to test the effects of vehicle technology and fuel composition on vehicle emissions. The study has developed an extensive database for a matrix of fuels, vehicles, and operating conditions. Although the program is not specifically directed at studying oxyfuel effects, it provides a valuable database of carefully documented measurements.

Gasoline is a mixture of numerous different hydrocarbons, including alkanes, alkenes and aromatic compounds, which can be blended in many different combinations. Into these combinations oxygenates are added. In some cases oxygenated fuels are prepared by adding the oxygenate to a standard gasoline. This technique is referred to as splash blending. In other cases, the fuels are blended, usually at a refinery, to obtain certain properties, for example, the addition of oxygenates to increase a fuel's octane rating or to achieve important parameters, such as overall vapor pressure or to minimize emissions of certain pollutants. [Fuel vapor pressure is reported as Reid vapor pressure (RVP), the vapor pressure at 100 °F.] This technique is referred to as match blending.

Finally the ambient conditions of vehicle operation in oxyfuel areas cover a broad range. Elevation varies from sea level to one mile (Denver, Colorado) corresponding to pressures from 1 to 0.8 atmosphere. Temperatures also vary from around +80 ° to -40 °F (27 ° to

-40 °C). It is not surprising that no individual study has covered the broad range of variables required to characterize completely vehicle emission effects.

This report covers two types of studies used to obtain information on vehicle emissions: (1) dynamometer studies and (2) field studies. The dynamometer studies are usually conducted in a controlled laboratory environment at 75 °F, usually on a well maintained vehicle and under a standard format called the Federal Test Procedure (FTP). During the FTP, exhaust gas is sampled and analyzed during three phases of vehicle operation. The first phase (called Bag 1) represents cold start emissions, the second phase (called Bag 2) represents emissions under stable vehicle temperatures, and the third phase (called Bag 3) represents hot start emissions. Thus the effects of fuel composition on emissions can be quantified for each phase of operation and a standard driving cycle. Dynamometer studies have the advantage that many variables affecting emissions can be controlled and characterized and that the composition of the exhaust can be accurately quantified by a variety of laboratory instruments. A limitation of dynamometer studies is that it is practical to perform only representative tests and that tests are not made over the full spectrum of driving conditions. These limitations contribute to the uncertainty of predicting the emissions of the on-road vehicle fleet.

Field studies include both remote sensing and tunnel studies. The remote sensing studies employ a roadside detector that optically analyzes the exhaust of individual vehicles, typically for CO, HC, and CO_2. The CO_2 serves as a tracer for the exhaust plume and the pollutant concentrations are determined relative to the total amount of gaseous carbon species which is mainly CO_2. A camera can be synchronized with the exhaust analysis to identify the vehicle and subsequently to provide details of the engine and pollution control devices. The remote sensor has the advantage that a large number, on the order of 100,000, of on-road vehicles can be tested and characterized. It has a disadvantage that the range of vehicle operating conditions is limited, typically, to a hot stable mode and only a couple of emission constituents are measured. The tunnel studies involve the analysis of air sampled within a tunnel. This confined space allows the exhaust emissions of many vehicles to be analyzed collectively. Many exhaust components can be quantified. This measurement represents a population of on-road vehicles under real operating conditions. The disadvantages are that individual vehicles are not characterized and that the emissions represent a limited range of operating conditions, typically, the hot stable mode.

It is not possible, within the scope of this assessment, to evaluate the numerous studies of the effects of oxygenates on vehicle emissions. A few examples are cited here to illustrate representative studies and important issues.

Dynamometer Studies

CO Emissions. The Auto/Oil AQIRP study by Reuter *et al.* (1992) reports the effects of oxygenated gasolines and RVP on emissions from twenty 1989 model year vehicles. The test vehicles represented a broad range of engine sizes from 2 to 5.7 liter displacements and had between 10,000 and 29,000 miles on their odometers. The fuel inlet systems included two with carburetors, four with throttle body injection, ten with port fuel injection, and four with sequential fuel injection. All of the vehicles employed three-way catalyst systems and two vehicles also had oxidation catalysts. The fleet can be characterized as a relatively new, low emission group of vehicles. Eleven fuels were studied including four 3.7 wt % oxygen ethanol fuels, two 2.7 wt % oxygen MTBE fuels, and one 2.7 wt % ETBE fuel.

The tests were conducted according to the FTP. Some of the results are summarized in Table 1.2. The oxyfuel effects on the emissions are given as a percent change observed with the oxyfuels normalized to the oxygen content of the test fuel, that is, divided by the wt % oxygen content of the fuel.

Table 1.2 Summary of results from Auto/Oil AQIRP study (Reuter *et al.*, 1992) of oxyfuel effects on twenty 1989 model year vehicles exhaust emissions. This fleet is a relatively new, low emission group.

		% Change with Oxyfuel per wt % Oxygen[c]		
Emission[a]	**Mass Emission**[b] **(g/mi)**	**3.7% O_x EtOH**	**2.7% O_x MTBE**	**2.7% O_x ETBE**
CO	2.5	-3.6 ± 1.3	-3.4 ± 2.4	-5.4 ± 2.7
HC	0.21	-1.3 ± 0.7	-2.4 ± 1.3	-1.9 ± 1.4
NO_x	0.6	+1.4 ± 1.1	+1.3 ± 2.0	+2.0 ± 2.3
Benzene	9×10^{-3}	-3.1 ± 1.6	-4.1 ± 3.0	-3.5 ± 3.0
1,3-Butadiene	9×10^{-4}	-1.6 ± 1.5	-0.6 ± 2.9	-1.0 ± 3.1
Formaldehyde	1.5×10^{-3}	+5.2 ± 8.4	+5.9 ± 15.3	+6.3 ± 26.6
Acetaldehyde	1.4×10^{-3}	+43 ± 12	-0.3 ± 13	+95 ± 25

[a] HC = Total hydrocarbons

[b] Mass emissions are approximate average values for test fuels.

[c] The oxyfuel effects have been normalized to 1 wt % oxygen. The oxygen wt % of the test fuel is noted: 3.7% O_x means 3.7 wt % oxygen. The uncertainties represent 95% confidence limits.

Reuter *et al.* found a statistically significant reduction in CO, total HC and benzene emissions with all three fuel oxygenates compared to the non-oxygenated fuels. The NO_x emissions increased for all of the oxygenates, but the result was statistically significant for only the ethanol fuels, the fuel set with the highest oxygen content. The average effect for the complete fuel set was also found to be significant, about (+1.6 ± 1)% NO_x per wt % oxygen. Acetaldehyde emissions increased greatly for ethanol and ETBE fuels. The fleet average CO benefit for the 7 test oxygenate fuels is -3.8% per wt % oxygen. The effect of reducing the fuel RVP by 1 psi did not have a statistically significant effect for the oxygenate fuel set, although it did reduce the CO emissions by 10.4 ± 8.0% in the non-oxygenated fuel set. In general HC and CO emissions are reduced when fuels with lower RVP are used. An important result from a comparison of effects of the different oxygenates is that they all have quite similar benefits, when normalized to the wt % oxygen content. It is generally assumed that the oxygenates' effects are indistinguishable except for the special effects on aldehyde emissions as discussed later.

Another Auto/Oil study (Hochhauser *et al.*, 1991) compared the emission benefits of a 15% MTBE fuel in current and older vehicles. The current vehicles were the same 1989 model year group described by Reuter *et al.* (1992). The older vehicle group consisted of fourteen 1983-1985 model year vehicles with 42,000 to 79,000 odometer miles and 1.8 to 5.7 liter displacement engines. Twelve of these older vehicles had carburetors and two had throttle body injection. Four of the vehicles had three-way catalysts (TWC), four had oxidation catalysts (OC) and six had both TWC and OC. The older group of vehicles also had relatively low emission levels. The results of the study are summarized in Table 1.3. The mass emissions from the older group are from 2 to 2.4 times larger than the current fleet. The oxyfuel benefits are also larger for the older higher emitting vehicles. The effects of the oxyfuel on the current fleet are similar to the results reported in Table 1.2, as expected.

Table 1.3 Summary of results from Hochhauser *et al.* (1991) on the effects of a 15% MTBE fuel (2.7 wt % oxygen) on a current group of 1989 model year vehicles and a group of older 1983-1985 model year vehicles. Both groups included cars and light duty trucks and represent relatively low emitting vehicles.

Emission [a]	Mass emission [b] (g/mi)	% Change with oxyfuel per wt % oxygen [c]
CO		
Current Fleet	2.8	-4.1 ± 1.3
Older Fleet	6.2	-5.2 ± 1.4
HC		
Current Fleet	0.22	-2.2 ± 0.9
Older Fleet	0.53	-3.4 ± 1.1
NO_x		
Current Fleet	0.6	+0.5 ± 0.7
Older Fleet	1.2	+0.5 ± 0.7

[a] HC = Total hydrocarbons.

[b] Mass emissions are average values for test fuels.

[c] Note that the oxyfuel effects have been normalized to 1 wt % oxygen.
The uncertainties represent 95% confidence limits.

A study was carried out as a part of the Auto/Oil AQIRP series to examine fuel effects on high emitting vehicles (Knepper *et al.*, 1993). The effects of oxyfuels on high emitting vehicles are particularly important because there is evidence that, although they represent a small fraction of the on-road fleet, they are responsible for a disproportionately large amount of urban CO as discussed in the section on “Model Predictions.” A group of seven 1986-1987 model year vehicles were selected for their high emission characteristics. The vehicles were diagnosed to have various problems that caused them to run fuel rich. The Federal Test Procedure CO emissions ranged from 17 g/mi to 216 g/mi. The HC emissions were also quite high, ranging from 1.5 g/mi to 15 g/mi. The NO_x emissions tended to be low as expected for vehicles running in a fuel rich condition, averaging about 0.5 g/mi. The oxyfuel effects were tested with a 3.65 wt % oxygen ethanol fuel and 2.76 and 2.54 wt % oxygen MTBE fuels. The results are summarized in Table 1.4. Knepper *et al.* reported that the emission levels varied greatly due to unstable maintenance of the air/fuel ratio. The values given in Table 1.4 for percent changes were obtained from bar charts. In general the measurements had greater variability and much larger confidence limits than results from stable vehicles. The CO benefits are larger than observed in normally operating vehicles, averaging about -9.7% per wt % oxygen. The HC emissions were similarly reduced, averaging about -9.4% per wt % oxygen. The NO_x emissions increased, averaging about +9%, although the mass emission for NO_x remained generally low.

Table 1.4 Summary of results of Auto/Oil AQIRP study of oxyfuel effects on high emitting vehicles (Knepper *et al.*, 1993). This group of vehicles had mechanical defects causing them to run in a fuel rich condition.

Emission[a]	Mass Emission[b] (g/mi)	% Change with Oxyfuel per wt % Oxygen[c] 3.65% O_x EtOH	2.7% O_x MTBE
CO	149, 124	-7.4 ± 7.4	-12 ± 7
HC	12.0, 9.2	-6.8 ± 6.3	-12 ± 4
NO_x	0.39, 0.55	+5.8 ± 3	+12 ± 3

[a] HC = Total hydrocarbons.

[b] Mass emissions are fleet average for reference fuels. The first number is for the ethanol and 2.76 wt % oxygen MTBE fuels. The second number is for the 2.54 wt % oxygen MTBE fuel.

[c] The oxyfuel effects have been normalized to 1 wt % oxygen. The uncertainties represent 95% confidence limits.

A series of tests were conducted by EPA (Mayotte *et al.* 1994 a,b) to determine the effects of oxygenates and other fuel parameters on normal and high emitting vehicles characteristic of the general population. The vehicles were grouped according to the HC emission, where vehicles emitting <0.82 g/mi represent the normal emitter group. Although high HC emission levels often correlate with high CO emission levels, they do not always correlate, so the high HC emitting fleet may not be a high CO emitting fleet. In Phase I of the program (Mayotte *et al.*, 1994a) a fleet of twenty 1987-90 model year (MY) normal emitters and sixteen 1987-90 MY high emitters were studied using eight fuels, five of which were 2 wt % oxygen MTBE fuels and one of which was a 3.7 wt % oxygen ethanol fuel. In the Phase II study (Mayotte *et al.*, 1994b) twelve fuels were tested in thirty-nine vehicles, twenty-seven 1986-91 MY normal emitters and twelve 1986-89 MY high emitters. Ten of the fuels were reformulated blends containing 2.0% by weight oxygen MTBE and one was a 2.5% by weight oxygen MTBE/ethanol blend. The results are summarized in Table 1.5. In Phase I of the study the high emitters had significantly larger reductions in CO and HC emissions with oxygenate fuel than the normal emitters. In Phase II the normal and high emitters showed similar CO and HC emission effects with the oxygenated fuels. The fleet benefits are estimated to be in the range of 4 to 5% reduction in CO per wt % oxygen in these studies. The oxyfuel effects on NO_x emissions are small in all cases. The only statistically significant result was the highest oxygen content fuel produced an increase in NO_x emission in the Phase I normal emitter group.

Although the primary objective of the oxyfuel program is the reduction of winter CO emissions, relatively little is known about the effects of oxygenates on emissions at low operating temperatures. Vehicle testing at low temperatures poses special problems. A gasoline engine generates a large amount of heat, so a large cooling capacity is required in a test laboratory to simulate the operating conditions of a cold environment. The rate at which the engine and the catalytic converters of vehicle warm to obtain efficient operation is critically important for a test to represent realistic operating conditions.

Table 1.5 Summary of results of EPA study of normal and higher emitting vehicles (Mayotte *et al.* 1994a, b).

	% Change with Oxyfuel per wt % Oxygen			
	Phase I			
	Normal Emitters		**High Emitters**	
Emission[a]	**2% O_x MTBE**	**3.7% O_x EtOH**	**2% O_x MTBE**	**3.7% O_x EtOH**
CO	-2.4 ± 4.0	-2.3 ± 2.0	-8.0 ± 2.3	-6.8 ± 2.1
HC	-4.2 ± 2.8	-2.0 ± 1.5	-5.1 ± 1.8	-5.2 ± 1.5
NO_x	+1.0 ± 2.1	+1.5 ± 1.2	0 ± 5.2	-0.5 ± 3.3
	Phase II			
	Normal Emitters		**High Emitters**	
Emission	**2% O_x MTBE**	**2.5% O_x MTBE/EtOH**	**2% O_x MTBE**	**2.5% O_x MTBE/EtOH**
CO	-4.4 ± 2.7	-2.9 ± 1.9	-3.9 ± 2.1	-4.8 ± 2.4
HC	-4.4 ± 1.7	-1.4 ± 1.6	-3.3 ± 1.5	-1.5 ± 2.5
NO_x	-0.7 ± 1.5	-0.1 ± 1.2	-0.4 ± 1.6	-0.7 ± 3.6

[a] HC = Total hydrocarbons

[b] Oxyfuel effects have been normalized to 1 wt % oxygen. The uncertainties represent 90% confidence limits.

Hood and Farina (1995) have reviewed studies of oxyfuel effects on emissions from light duty vehicles at low ambient temperatures. One of the studies they reviewed was reported by Most (1989) and conducted under the auspices of the Coordinating Research Council. The test fleet consisted of sixteen vehicles representing a range of fuel inlet and emission control technologies: four 1979-1980 MY carbureted vehicles with OC; six 1983-1986 MY vehicles of which four were carbureted and two were fuel injected and all had TWC; and six 1986-1988 MY vehicles with fuel injection and adaptive learning, closed-loop TWC systems. The test fleet did not include any high emitters. The test fuels included 11.5 and 13 psi RVP fuels and oxygenate mixtures that were an 11% MTBE blend, and two 10% ethanol blends. The emission tests were conducted at sea level and 5000 ft altitude and at temperatures at 35 °, 50 ° and 75 °F. The emission test results are summarized in Table 1.6. The oxyfuel benefits have been normalized to 1 wt % oxygen. The oldest technology group, the carbureted OC vehicles, had the largest and most consistent reduction in CO emissions at all temperatures, typically about 9% reduction in CO per wt % oxygen. The middle technology group, the closed-loop, three-way catalyst vehicles, had reduced benefits from oxyfuels, typically about 3.4% CO reduction per wt % oxygen. The highest technology group, the adaptive learning vehicles, had mixed effects from oxyfuels, and in some cases showed small enhanced CO emissions with fuel oxygenates. The oxygenate effects on this group at 5000 ft were negative, where half of the test set indicated an increase in CO emissions with fuel oxygenate.

Table 1.6 Percent changes in average CO emissions from oxyfuels (13 PSI Fuel Set) under different ambient conditions of temperature and altitude. Reported by Most (1989). [Taken from Hood and Farina (1995)]

Fleet[a] Technology	**Temp. (°F)**	**CO % Change with Oxyfuel per wt % Oxygen[b]** **11% MTBE** **2% O_x**	**10% EtOH (Splash)** **3.66% O_x**	**10% EtOH (Matched)** **3.75% O_x**
		Sea level		
CL/AL/TWC	35	-2.8	-0.14	-4.0
CL/AL/TWC	50	-5.1	-3.2	-1.4
CL/AL/TWC	75	-4.1	-4.0	-0.21
CL/TWC	35	-1.8	-4.3	-3.8
CL/TWC	50	+1.4	-3.2	-3.5
CL/TWC	75	-3.8	-4.4	-1.5
		5000 ft altitude		
CL/AL/TWC	35	+1.3	+1.9	
CL/AL/TWC	50	-2.5	-5.9	
CL/AL/TWC	75	+6.1	-4.5	
CL/TWC	35	-5.9	-3.7	
CL/TWC	50	-9.4	-4.3	
CL/TWC	75	-0.3	-2.6	
COC	35	-13.2	-7.2	
COC	50	-6.5	-8.4	
COC	75	-9.8	-9.9	

[a] CL = closed loop, AL = adaptive learning, TWC = three-way catalyst, COC = carbureted with oxidation catalyst.
[b] The oxyfuel effects are normalized to 1 wt % oxygen.

Hood and Farina (1995) reviewed results from a study sponsored by the American Petroleum Institute (Lax, 1994). The study examined the effects of oxygenate and RVP onemissions from an eleven vehicle fleet at 35 °, 55 ° and 80 °F. The 1981 to 1989 MY test fleet was divided into six categories: one - OL/CARB/OC; one - CL/MPFI/OC; two - OL/CARB/TWC; one - CL/CARB/TWC; two - CL/TBI/TWC; and four - CL/MPFI/TWC, where OL = open loop, CARB = carbureted, OC = oxidation catalyst, CL = closed loop, MPFI = multi-port fuel injection, TWC = three way catalyst, and TBI = throttle body fuel injection. The fuel oxygenates included 10% ethanol (3.5 wt % oxygen), 15% MTBE (2.7 wt % oxygen) and 17.1% ETBE (2.7 wt % oxygen). The fleet average CO emission levels were about 5, 7, and 15 g/mi at 80 °, 55 °, and 35 °F, respectively. The fleet fuel effects are summarized in Table 1.7. For CO emissions, the oxyfuel benefits decreased by about a factor of 3 at the lowest temperature, 35 °F, compared to the effects at 55 ° and 80 °F. The HC emissions were consistently reduced by fuel oxygenate by about 3.5% per wt % oxygen at all temperatures except for the high oxygen fuel at 35 °F. The NO_x emissions were generally increased by the addition of fuel oxygenate. No distinct emission benefit of one oxygenate over the others was identified.

Table 1.7 Summary of oxyfuel effects from American Petroleum Institute (Lax, 1994) study [taken from Hood and Farina (1995)].

Temperature	Oxyfuel Effect per weight % Oxygen[a]					
	2.7 wt % O_x fuels			3.5 wt % O_x fuels		
(°F)	CO	HC	NO_x	CO	HC	No_x
35	-1.9	-3.7	-1.4	-1.8	-2.1	+0.9
55	-6.4	-3.4	+2.7	-6.3	-3.4	+2.7
80	-5.7	-3.8	+1.5	-5.6	-3.7	+1.5

[a] These data represent the 13 PSI fuel set.

Hood and Farina (1995) summarize the effects of oxygenates at low ambient temperature as follows: (Note the % benefits have been calculated assuming an average 3.1 wt % oxygen fuel.)

(1) At temperatures of 80 ° to 55 °F there are only small changes in vehicle exhaust emission levels. Vehicles with closed-loop controls experience CO and HC reductions in the ranges 1 to 4.5% per wt % oxygen and 1 to 4.8% per wt % oxygen, respectively. The CO reductions in open-loop control vehicles were greater, from 3.2 to 10% per wt % oxygen.

(2) At temperatures of 55 ° to 20 °F the CO and HC emissions generally increase relative to their levels at 75 °F. The oxygenates reduce CO and HC emissions but the effect on CO (on a percentage basis) is smaller than at 75 °F. Vehicles with closed-loop controls experience CO and HC emission reductions in the ranges 0.6 to 6.5% per wt % oxygen and 0.6 to 3.9%, respectively. Vehicles with open-loop controls experienced CO and HC emission reductions of 0.6 to 8.4% per wt % oxygen and 0.3 to 2.6% per wt % oxygen, respectively.

At temperatures below 20 °F very few data are available. The HC and CO emission rates show large increases of 2 to 6 times higher than at 75 °F. The available data fail to show consistent reductions with added oxygenate.

The reason for the low and sometimes negative oxygenate effects on CO emissions observed at low temperatures has not been identified. This is in contrast to most fuel-emission effects which can be understood in terms of chemical and engineering principles. Doyon *et al.* (1993) have discussed the effects of fuel volatility on vehicle CO and HC emission levels at low temperatures. Generally higher vapor pressure fuels are used during the winter season to compensate for the effect of low ambient temperatures decreasing fuel vapor pressure. It is possible that the oxygen present in the oxygenate is consumed by the excess hydrocarbon in the cooler fuel rich environment encountered at low temperatures. Thus the fuel oxygen oxidizes hydrocarbons to CO rather than oxidizing CO to CO_2. Therefore the oxygenate may enhance CO emissions.

Fuel vapor pressure and fuel sulfur content affect the CO and HC emission levels of vehicles. Mayotte *et al.* (1994a) reported an 11.3% reduction in CO emissions in the ombined normal and high emitting fleet, when the fuel RVP was reduced from 8.3 to 7.6

psi. A large effect of sulfur content on CO emissions was noted by Mayotte *et al.* (1994a) who found a 13.8% reduction in CO emissions in the combined normal and high emitting fleet, when fuel sulfur was decreased from 324 ppm to 112 ppm by weight. An Auto/Oil AQIRP study (Benson *et al.*, 1991) reported 13% CO, 16% HC and 9% NO_x reductions from a ten vehicle, 1989 MY, low emitting fleet, when the fuel sulfur content was decreased from 466 ppm by weight to 49 ppm. Sulfur is known to poison the catalyst thereby reducing its efficiency. Although RVP and sulfur influence the CO emissions of vehicles, their levels are not controlled in most winter oxyfuel areas. Fuel sulfur and RVP are controlled in California.

Other Emissions. Most dynamometer studies report the effects of oxyfuels on pollutant emissions other than CO. An important effect of all oxygenate fuels is achieved through dilution. For example, adding 8 to 15% by volume oxygenate to a base gasoline or blend lowers the benzene concentration proportionately. In some fuels, oxygenates have been used to replace benzene and other aromatics as octane enhancers. Since some emissions are unburned fuel components, the dilution effect directly lowers their levels. On the other hand the unburned oxygenates are found in the exhaust too. Sulfur emissions are also reduced by dilution. Sulfur dioxide can decrease catalyst performance and is a source of secondary atmospheric particles via oxidation to sulfuric acid.

Table 1.2 shows some representative effects of three standard oxygenates on total hydrocarbons and several critical pollutants at 75 °F for a fleet of twenty relatively clean 1989 vehicles. These results can be summarized as follows: The HC emissions generally decrease with added fuel oxygenate. The NO_x emissions increase with fuel oxygenate. Benzene emissions are reduced by fuel oxygenate. The 1,3-butadiene emissions are reduced but not significantly except for the ethanol fuel with the highest oxygenate content. The formaldehyde emission did not change significantly, although most studies find MTBE increases formaldehyde emissions (Hood and Farina, 1995). Acetaldehyde emissions increase greatly with ethanol and ETBE fuels. The data in Table 1.3 show that the effects of oxygenates on HC and NO_x emissions from older, higher emitting vehicles are similar to the effects observed on the clean fleet (Table 1.2).

In general one would expect NO_x emissions to increase with the addition of oxygenate to a fuel. The addition of oxygenate is equivalent to increasing the air/fuel ratio in Figure 1.2. NO_x emissions are found to be less affected by oxygenates at low temperatures (Hood and Farina, 1995). This may be related to the increased HC emissions at lower temperatures. The effects of low temperatures on toxics and other emissions are not well characterized.

In developing the California wintertime oxygenates program, the California Air Resources Board staff evaluated the available data on the effect of fuel oxygen on motor vehicle emissions and concluded that adding levels of oxygen higher than 1.8 to 2.2 wt % to gasoline would lead to NO_x emission increases. They estimated that implementing a wintertime oxygenate program with 2.7 wt % oxygen as specified in the Clean Air Act could increase NO_x emissions by about 4 to 8% (CARB, 1992). The effect of oxygenates on NO_x emissions appears to be nonlinear and is discussed further in the section on "Model Predictions."

Ambient particulate matter concentrations are affected by both direct emissions and by secondary products formed by the atmospheric oxidation of VOC, SO_2, and NO_x

emissions. Direct particle emissions from gasoline-fueled vehicles are small and the effect of oxyfuels is not known. The effects of NO_x, VOC and SO_2 on particle formation in the winter urban environment are not well known.

Field Studies

Bishop and Stedman (1989, 1990) used remote sensing to evaluate the effects of oxyfuels on vehicle emissions in Denver, Colorado. At the time of their initial study (Bishop and Stedman, 1989) a 1.5 wt % oxygen fuel was required and the Colorado Department of Health predicted a vehicle CO emission reduction of (11.7 ± 2.5)% using the EPA MOBILE 3 Model. Bishop and Stedman analyzed CO emissions from about 60,000 vehicles at a freeway on-ramp during and after the oxyfuel season. They found a (6 ± 2.5)% reduction in emitted CO that could be attributed to oxyfuel. The vehicles sampled for this result were probably in the hot stable operating mode.

In a second study Bishop and Stedman (1990) analyzed emissions from Denver vehicles at two locations, a freeway on-ramp and an off-ramp before, during, and after the Colorado oxyfuel season, 1 November 1988 through 28 February 1989. During this period Colorado required a 2.0 wt % oxygen fuel. The Colorado Department of Health used the EPA MOBILE 3 Model to estimate a 15.3% reduction in vehicle CO emissions. Bishop and Stedman analyzed more than 117,000 individual measurements of which about 4,900 vehicles were identified by make and model. They reported a decrease in average CO emissions of (16 ± 3)%. They also found that between 7 and 10% of the vehicles were responsible for 50% of the CO emissions. Their results showed that newer vehicles tended to have much lower CO emission levels than older vehicles but the emission levels seemed to level off for pre-1976 vehicles. The CO reduction corresponds to (8 ± 1.5)% per wt % oxygen.

An even more comprehensive remote sensing study in Denver was reported by PRC (1992). In this study the following factors were accounted for: gasoline composition, ambient temperature and pressure, vehicle speed, vehicle age, vehicle emission control technology, and the vehicle operating mode, e.g., cold start vs. hot running modes. A total of about 80,000 measurements were made at three locations, a freeway exit ramp and two parking garages. The study was conducted between October 1991 and April 1992. The fuel from selected in-use vehicles was sampled and analyzed. The Colorado oxyfuel program at this time required 2.0 wt % oxygen in November and 2.6 wt % oxygen in December through February. The study found an average 0.3% oxygen one month before the program, 2.64% oxygen during the program, and 0.4% oxygen about 35 days after the program.

The PRC study found that there was about a 25% reduction in CO emissions and a 14% reduction in HC emissions that could be attributed to oxyfuels at the off-ramp site. The CO reduction corresponds to about -10% CO per wt % oxygen. These vehicles are probably operating in a hot stable mode. When broken down into MY groups, the report concluded that each group receives approximately the same percentage benefit from oxyfuels. The newer vehicles have, on average, lower emissions, so the average reduction in CO mass emission decreases as the average age decreases. Vehicles emitting more than 3.5% CO (3.5% of the total gaseous carbon emissions are CO) were classified as high emitting vehicles. It was found that high emitting vehicles were 3.2% of the 1983 (MY) and newer population and they contribute 33.4% of the CO outside of the oxyfuel program. It was concluded that the 50% of the vehicles emitting the least CO realize very little CO reduction due to oxyfuel usage and that the 10% of the vehicles that emit the most CO contribute more than half of the total CO and account for most of the reduction realized by oxyfuel use. No significant effect of ambient temperature on emissions from hot stable vehicles was found.

A remote sensing study in Raleigh, NC, was reported by Rhudy *et al.* (1995). The study was made before, during, and after the 1994-95 winter oxyfuel program which requires 2.7 wt % oxygen fuels. Carbon monoxide emission measurements were made on approximately 180,000 vehicles with more than 2,000 individual vehicles measured at least once during each of the three measurement periods. The study found no significant reduction in CO that could be attributed to the oxyfuel program. This finding may be flawed because of the lack of control over important variables, notably the ambient and vehicle operating temperatures. Nevertheless, the conclusion contradicts the findings of all other similar studies. This measurement program is to be continued with improved controls.

A recent field study of oxyfuel emission effects was conducted by Kirchstetter *et al.* (1996) in the Caldecott tunnel in the San Francisco Bay area in August and October, 1994. In this area a 2.0 wt % oxygen fuel is required from 1 October to 31 January. The oxygenates in use were 80% MTBE and 20% ethanol. The pollutant concentrations were measured in August, when the average oxygen content of the fuel was only 0.3 wt % (due to the use of oxygenates as octane boosters), and in October. The vehicles sampled were operating in the hot stabilized mode. The vehicles passing through the tunnel had the following populations: 70% passenger cars, 30% pickup trucks and small vans, and 0.2% heavy duty trucks and buses, during both sampling periods. The typical speeds were 40 to 50 mph on a 4.2% uphill grade. Two potential complications of this study are that the CO emissions were not measured after the winter oxyfuel season and that the slight uphill grade could cause some vehicles to run in a power demand mode with a rich air/fuel ratio. The latter condition would result in an enhanced oxyfuel benefit.

Kirchstetter *et al.* report that during the oxyfuel period, CO emissions were reduced by (21 ± 7)%, VOC emissions were reduced by (18 ± 10)%, benzene emissions were reduced by (25 ± 17)%, NO_x emissions and acetaldehyde emissions did not change significantly, and formaldehyde emissions increased by (13 ± 6)%. The acetaldehyde and formaldehyde effects are consistent with the use of primarily MTBE oxygenate. Speciated profiles are reported for a large number of VOCs. This study reports a substantial CO reduction of 14 to 28% that can be attributed to a 1.7 wt % oxygen fuel or about -(12 ± 4)% CO per wt % oxygen. A study in August 1995 (R. Harley, personal communication, 1996) found the CO emission factor during the non-oxyfuel period was reduced by about 14% compared to the previous August. Based on this the reported CO decrease should be adjusted to about (19 ± 7)%.

The remote sensing and tunnel studies find larger oxyfuel benefits than the dynamometer FTP studies. The reason for this difference may be related to the fact that the remote sensing and tunnel measurements test emissions during the hot stable mode of vehicle operation. Rapp *et al.* (1993) analyzed the effects of certain fuel properties, including oxygenate, on emissions during specific modes of vehicle operation for the same twenty vehicle fleet described in the Auto/Oil AQIRP study by Reuter *et al.* (1992). The HC, CO, and NO_x emissions were measured during nine different operating modes, which are part of the FTP. The results from this analysis could be useful in comparing data from tunnels and remote sensing, which observe vehicles operating generally in a single mode, with data from the standard emission test, the FTP. The tunnel study by Kirchstetter *et al.* (1996) states that the vehicles travel at steady speeds of 40-50 mph. This range can be compared to results for 30 mph and 55 mph cruise modes, for which oxyfuel benefits of 9.6% and 0.9% CO reduction per wt % oxygen, respectively, were reported by Rapp *et al.* These figures represent the largest and smallest CO benefits found in the study, which is surprising considering the two cruise modes are rather similar. The average effect for the two modes is a 5.4% CO reduction per wt % oxygen, which is 59% larger than 3.4% CO reduction per wt % oxygen reported for the FTP. The 30 mph cruise result of -9.6% CO per wt % oxygen is possibly representative of the urban freeway on/off ramp traffic and is nearly 3 times larger than the FTP benefit. This analysis indicates that the tunnel study (Kirchstetter *et al.*, 1996) and the remote sensing studies (Bishop and Stedman, 1989, 1990; PRC, 1992) may overestimate the oxyfuel benefit compared to the FTP result. However, it should be noted that in the study of Rapp *et al.* (1993), the fleet was a relatively clean and low emitting group of vehicles. It is not reasonable to attempt to quantitatively apply the factors from the vehicle mode study to an on-road fleet.

A comparison also can be made between the tunnel and remote sensing results with the Bag 2 emissions from the hot stable phase of the FTP. Data reported by Hochhauser *et al.* (1991) for the Auto/Oil AQIRP 1989 MY current (low emitting) and older fleets give the ratios of the Bag 2 to the composite (FTP) oxyfuel benefits as 2.10 and 1.14, respectively. These ratios also indicate that the hot stable phase emissions have larger oxyfuel CO reductions than the FTP results shown in Table 1.3. They are increased by 110% for the current fleet and 14% for the older fleet. These factors cannot be applied directly to the tunnel and remote sensing results, but they further indicate that those types of measurements are likely to overestimate the overall oxyfuel benefits.

Summary of Vehicle Emissions Studies

The emission studies reported here are presented as representative examples of efforts to quantify the effects of fuel oxygenates on vehicle emissions. For the purpose of predicting the effect of oxygenate usage on urban air quality, the FTP dynamometer studies provide the most useful available data. These studies measure the emission effects over a range of vehicle operating conditions. Unfortunately these studies have some very important limitations: (1) A relatively small number of vehicles are studied and these are not necessarily representative of the on-road fleet and specifically the fraction that emits the largest amount of pollution. (2) The studies with the best controls on fuel composition, such as the Auto/Oil AQIRP studies, do not necessarily represent the effects of the fuels sold to the consumers in winter oxyfuel areas. Most FTP emission studies seek to isolate the effects of specific fuel parameters known to influence vehicle emissions, such as the concentrations of sulfur, aromatics, oxygenates, olefins, and paraffins as well as volatility factors. In the real world these factors are not controlled individually. In most winter oxyfuel program areas the only significant specification for the fuel is the wt % oxygen. It is known that RVP as well as the concentrations of sulfur and aromatics also strongly influence CO emissions, for example. Therefore the applicability of the fuel parameters derived from the carefully controlled studies reported above to the fuels sold in winter oxyfuel program areas is unproven. (3) The FTP test cycle does not necessarily represent real urban driving conditions. Although the FTP cycle does provide a valuable standard for comparing fuel and vehicle effects, it is not possible that any single standard is appropriate to driving in all cities and conditions. For example, there is tremendous variability possible in factors such as terrain, traffic patterns, traffic speed, traffic congestion, and travel distance which complicate any attempt to devise a representative driving urban cycle. An extremely important factor that has not been investigated adequately is the effect of low temperatures on oxygenated fuel performance. It is known that the amounts of CO and HC pollutant emissions rise dramatically with decreasing temperature. The few low temperature studies reported indicate that the effectiveness of fuel oxygenate at reducing CO emissions decreases dramatically at low temperatures. Improvements in vehicle technology, specifically air/fuel ratio control and catalyst efficiency, have led to recent generations of vehicles that emit much less pollution. These cleaner cars not only emit much less CO per mile traveled but also have a lower percentage reduction in emissions in response to the use of fuel oxygenate. Therefore these clean vehicles account for a relatively small improvement in air quality, when using oxygenated fuel (PRC, 1992). In a vehicle with a properly functioning oxygen sensor, the feedback control of the air/fuel ratio acts to defeat the purpose of adding oxygenate to the fuel. The vehicles that will benefit the most from oxyfuels are high emitters, generally older vehicles or newer vehicles with broken emission control systems (PRC, 1992).

Some of the important conclusions from vehicle emission studies are as follows:

- Carbon monoxide exhaust emissions from vehicles operating at temperatures of 50 °F and higher are reduced by oxyfuels by about 2 to 10% per wt % oxygen in FTP tests. For most vehicles the reductions are about 3 to 6%. The CO emission reduction is generally smaller in vehicles with newer technology: fuel injected, adaptive learning, closed loop, three-way catalysts; and larger in vehicles with older technology: carbureted, oxidation catalysts. Malfunctioning, high CO emitting vehicles operating fuel rich also experience larger CO reduction benefits from oxyfuels.

- The vehicle emission database at low temperatures is inadequate. Oxyfuel effects on vehicle CO emissions are uncertain at temperatures below 50 °F. Low temperature studies show some benefits down to 20 °F in some vehicles, but generally the results are not conclusive. Some studies report an increase in CO emission with oxyfuels at low temperatures. It has not been demonstrated that oxyfuels will significantly improve air quality at low temperatures.

- Hydrocarbon exhaust emissions from vehicles are reduced by 1 to 7% per wt % oxygen by oxyfuels. Generally the benefits are lower in new technology vehicles and larger in older and higher emitting vehicles.

- Nitrogen oxide exhaust emissions are not changed significantly by low concentrations of oxygenates but some studies show an increase in NO_x emissions with oxygenate concentrations higher than about 2 wt % oxygen.

- Fuel oxygenates decrease vehicle emissions of the toxics, benzene and 1,3-butadiene.

- Fuel oxygenates increase emissions of toxic aldehydes. Ethanol and ETBE increase acetaldehyde emissions by large amounts. MTBE increases formaldehyde emissions.

- Some but not all remote sensing and tunnel studies find a large reduction in CO emissions attributable to oxyfuel use in on-road vehicles. The reported CO benefits are about 10% per wt % oxygen. Since the sampled vehicles are operating in a hot stable mode, this benefit is likely to be larger than the FTP benefit.

- Fuel vapor pressure and sulfur content have been shown to strongly influence CO emissions, but these variables are not employed as a part of the CO emission control strategy in most areas.

MODEL PREDICTIONS

Introduction

The data collected from emission studies are used to develop computer models for predicting pollutant emission levels. The major EPA models for evaluating vehicle emissions and fuels are the MOBILE Model and the Complex Model. The California Air Resources Board (CARB) has developed the CARB EMFAC and Predictive models for similar purposes. The models are used to predict emissions for studies of photochemical ozone and oxidant production, for particle concentrations, and for other ambient air quality issues. An advantage of the models is that they can be used to predict effects such as the changes in vehicle emissions from using an oxyfuel. They give the user a number. The disadvantages are that one has very little sense of the uncertainty in the number or of the most important parameters defining the uncertainty. The parameters that affect the CO emissions from vehicles have been found to be many and complex. The varying effects of vehicle emission control technology, vehicle age and condition, fuel composition, and ambient temperature defy generalization. The ability of any present model to predict reliable emission levels at low temperatures is doubtful, because comprehensive emission data do not exist.

Kirchstetter *et al.* (1996) compared their measured emission rates with some values predicted by the CARB EMFAC7F Model. They compared the mass ratios for CO/NO_x and VOC/NO_x and found that the model agreed well with the observed VOC/NO_x ratio but was low by nearly a factor of two in predicting the CO/NO_x ratio. Unfortunately, few such detailed data sets which examine oxyfuel effects exist for testing the model predictions.

EPA Models

The MOBILE Model is designed by EPA specifically for use by the states in the preparation of the highway mobile source portion of emission inventories required under the Clean Air Act. The MOBILE 5a Model is the standard tool currently available to make fleetwide estimates of the effects of oxygenated fuels for purposes of area-wide inventories. It estimates emission levels in grams of pollutant per vehicle mile (g/mi) under a wide variety of conditions, such as altitude, ambient temperature, average travel speed, operating modes, fuel volatility, mileage accrual rates, and different fleet compositions. It also takes into account the impact of numerous emission control regulations and in-use vehicle emission reduction programs. The model can predict emissions for calendar years 1960 through 2020. Because the model takes into account such a wide variety of conditions and programs over an extended period of time, it accounts for their effects with varying levels of sophistication and accuracy.

The basis for the MOBILE Model series is the on-going Emission Factor testing program conducted by EPA since the early 1970's. In this program, in-use vehicles are solicited from their owners and the emissions of these vehicles are measured in contractor and EPA laboratories. Since 1990, data have also been collected at state run Inspection and

Maintenance (I/M) stations, where vehicles arrive for mandatory, periodic emission inspections. The database derived from these testing programs has been used by EPA to develop estimates of the in-use performance of highway vehicles for use in the MOBILE Models. Some of this analysis has appeared in journals and technical papers (Barth, 1984; Bruetsch, 1981; Becker and Rutherford, 1979; Darlington, 1981; Glover and Brzezinski, 1989; Harvey and Michael, 1985; Lorang, 1984; Lorang *et al.* 1982; Michael, 1981, 1982, 1983, 1984; Montalvo and Hare, 1985; Pidgeon, 1984; Shelton, 1983, 1984; USEPA, 1983, 1984, 1985, 1988).

The adjustments to the basic emission levels estimated in the MOBILE Model to account for oxygenated fuels are fairly simple. These adjustments account for differences in the technologies in the vehicle fleet and the changes in the composition of the fleet in different areas and different calendar years. The model assumes a linear relationship between fuel oxygen level and percent emission benefit for vehicles of any particular baseline (non-oxy) emission level. The linearity constant depends on baseline emission level and vehicle fuel delivery technology. For example, for 1981 and later model years, there are a series of oxygenate benefit/emission level parameters derived from studies of oxyfuel benefits on a fleet of 273 vehicles. These parameters are integrated into MOBILE 5a. A representative series of parameters is given in Figure 1.3. Pre-1981 vehicles have parameters accounting for vehicle age, technology, and CO emission level. The technology factor accounts for the fuel inlet system but does not explicitly identify the exhaust emission control system. The figure shows that the magnitude of the emission benefit per fuel weight % oxygen increases with vehicle emission level reflecting the EPA test programs which found higher benefits on higher emitters and leveling off at the highest emission levels. In general the CO reduction factors are quite large, rising to almost 10% per wt % oxygen at an emission level of about 15 g CO/mi. Few of the emission studies in the previous section indicated a benefit as large as 10% per wt % oxygen.

Since the largest CO reduction benefit is realized by the vehicles with the highest emission levels (g CO/mi), the predicted reduction in fleet CO emissions from oxyfuel usage is weighted heavily toward the high emitter benefit. For example, a “fleet” of 10 vehicles consisting of 9 relatively clean vehicles with an average CO emission level of 4 g/mi and one high emitting vehicle with an emission level of 60 g/mi has a fleet emission level of 96 g/mi. Assuming an average oxyfuel benefit of 5% CO reduction per wt % oxygen for the 9 clean vehicles and a 10.5% CO reduction per wt % oxygen for the high emitter, a 3.1 wt % oxygen fuel is predicted to reduce the fleet CO emission from 96 g/mi to 70.9 g/mi, or -26.1%. Thus the fleet benefit from oxyfuel use is equivalent to an average of 8.4% CO reduction per wt % oxygen, which is much larger than the individual benefit experienced by 90% of the vehicles in the hypothetical fleet.

Because the model predicted reduction in vehicle fleet CO emissions due to oxyfuels is heavily weighted by the effects on the higher emitting vehicles, the distribution of higher emitting vehicles in the fleet population is a critically important factor. Vehicle emission levels are assessed by EPA using the EPA IM240 test. It should be noted that the IM240 test employed to obtain emission data for the MOBILE 5a Model represents vehicles in warm to hot modes of operation, although the IM240 test is intended to be a FTP surrogate. The tests involve vehicles brought in for inspection. Since inspection is not required of new vehicles during the first two years, unless there is a change of ownership, the effects of new vehicles on the emission distribution is presumably accounted for separately. Figure 1.4 shows representative emission measurement data used in the MOBILE 5a Model giving the percentage of the total fleet emissions versus the percent of the fleet population as diamonds connected by a line. These data represent a fleet with an Inspection/Maintenance Program. The figure shows that the highest emitting 15% of the fleet accounts for about 50% of the CO emissions.

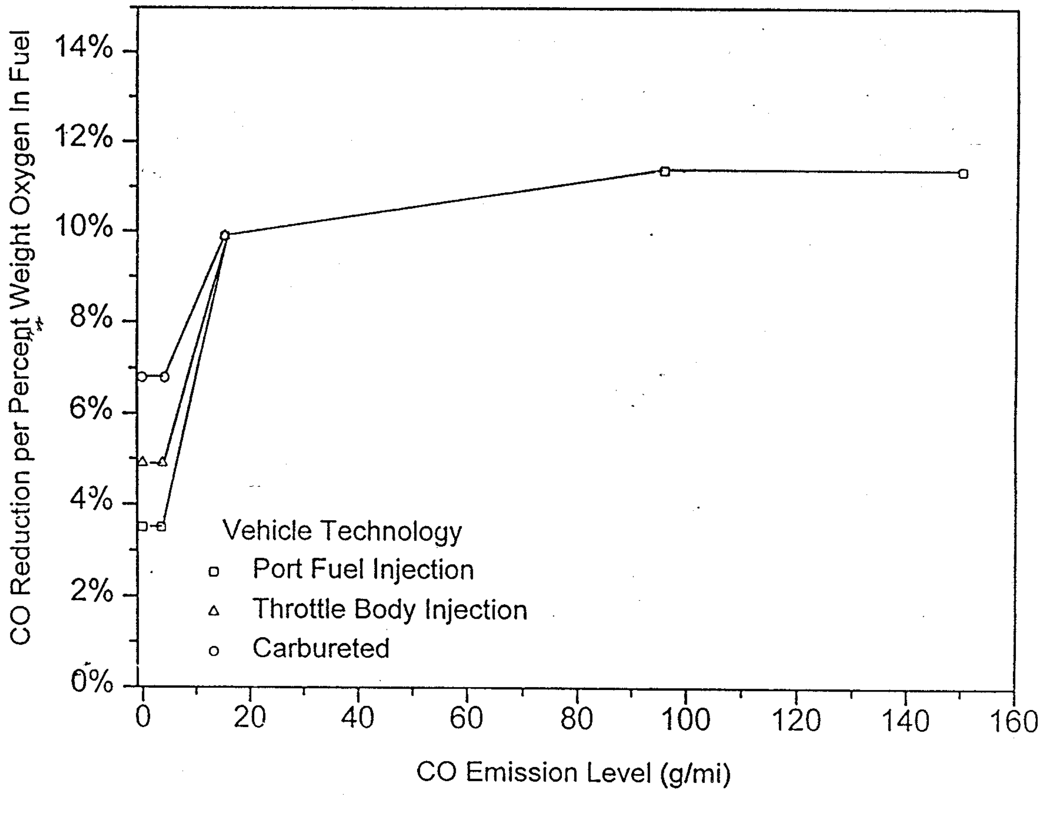

Figure 1.3 This figure shows representative data used as input for the EPA MOBILE 5a Model indicating the percent reduction in CO emissions per percent by weight oxygen fuel versus the vehicle CO emission level. These data are derived from emission studies of 273 1981 and later model year vehicles. At very low emission levels the parameters depend only upon the fuel inlet technology. As the emission levels increase to about 15.3 g CO/mi, the lines merge. The Figure shows that the % CO reduction increases as the emission level increases.

This figure can be compared with results from an analysis of roadside emission tests conducted in California in 1989. Lawson (1993) examined data from low-idle (~1000 rpm) emission measurements of 4,421 vehicles at locations throughout California. The results from his analysis are shown as circles in Figure 1.4. He reports a relatively small fraction of the vehicles, about 10%, accounts for about 62% of the emissions. In general his results show a small fraction of the vehicle population accounts for the bulk of the emissions from vehicles in the idle mode of operation.

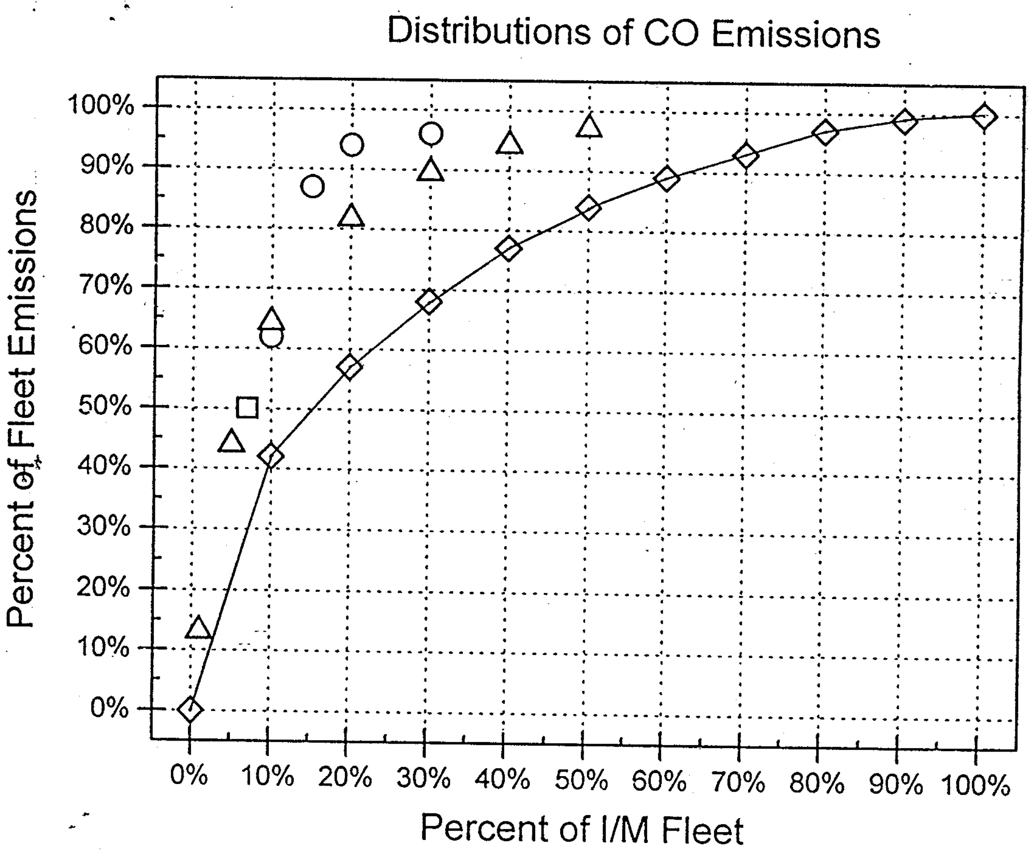

Figure 1.4 The diamonds and line in this figure show a fleet distribution of CO emissions for model years 1976-1993 vehicles. These data represent a fleet with an Inspection/ Maintenance Program. The distribution is based on EPA testing of in use vehicle fleets in Phoenix, AZ and Hammond, IN using a 4 minute transient emission inspection (IM240) developed from the Federal Test Procedure. The symbols O (open circle) represent data reported by Lawson (1993) for 4,421 vehicles inspected in California. The study was conducted in 1989 on vehicles operating in a low-idle mode. The symbols □ (open square) represent data reported by Zhang *et al.* (1995) from remote sensing measurements of about 87,200 vehicles in the U.S. during 1991-92. The vehicles in this study were measured while operating on the road and leaving or entering an urban freeway. The symbols △ (open triangle) represent data reported by Shepard *et al.* (1995) from 17,182 remote sensing on-road measurements in suburban Detroit. (The EPA data are courtesy of J.R. Cook, EPA.)

A similar result was found in a remote sensing study conducted between June 1991 and June 1992 and reported by Zhang *et al.* (1995). They made on-road measurements of operating vehicles in three U.S. cities, Chicago, IL, Denver, Colorado, and Los Angeles, CA. The measurement sites included slight uphill and flat surfaces that were city streets or freeway on-ramps or off-ramps. The results can be summarized as follows: in Chicago 8,733 vehicle tests show 7.5% of the vehicles account for 50% or more of the CO emissions; in Denver 35,945 vehicle tests show 6.7% of the vehicles account for 50% or more of the CO emissions and in Los Angeles 42,546 vehicle tests show 7% of the vehicles account for 50% or more of the CO emissions. The results of these measurements are indicated by the square symbol on Figure 1.4.

A 1992 study in suburban Detroit by EPA and General Motors (GM) produced 23,979, and 17,182 measurements, respectively, of CO emissions using adjacent remote sensors (Shepard *et al.*, 1995). The analysis excluded unidentified vehicles, diesel-fueled vehicles, and heavy duty trucks. The GM group included vehicles from 1964-1993 model years. The distribution of CO emission rates from the GM data set are plotted as triangles in Figure 1.4 for comparison with the other sets. The EPA sensor produced a distribution similar to the GM results. It should be noted that these results as well as those reported by Lawson (1993) and Zhang *et al.* (1995) represent vehicles operating in the hot stable mode and therefore do not account for emissions over the full range of modes covered in the FTP, the EPA standard for vehicle emissions tests. On the other hand, the IM240 test used to produce the data indicated by the line is conducted on hot stable vehicles as well. The measurements made in Chicago and Denver were made on vehicles traveling on urban freeways, while the California measurements were made on an urban street. The agreement among these data sets indicates similar distributions are found in various locations.

Because the remote sensing method employed by Zhang *et al.* (1995) and Shepard *et al.* (1995) is a transient test of a vehicle's emissions, they may not detect some vehicles with high emission levels during other parts of the driving cycle. It is likely that some vehicles emit large amounts of CO in an erratic manner or during certain operating conditions such as a hard acceleration. To the extent that these vehicles qualify as high emitters, they may not be identified as such by the remote sensing technique. This is a weakness of any method that samples emissions for only a single mode of vehicle operation. The effect of this limitation will be to under-represent the population of high emitters in the fleet distribution.

Although the studies by Lawson (1993), Zhang *et al.* (1995), and Shepard *et al.* (1995) do not represent FTP tests, they find similar results for two different modes of operation. The idle and remote sensing distributions indicate a population with a very large fraction of the total CO emissions, about 50%, coming from a small fraction, about 7%, of the vehicles. Because the highest emitting fraction of the fleet tends to receive the greatest benefit from oxyfuels, this distribution indicates a small benefit in terms of grams of CO per mile for most of the vehicle fleet and a large benefit for a small fraction of the fleet. This concept is examined quantitatively in the PRC (1992) report. The EPA emission distribution in Figure 1.4 indicates a population in which about 15% of the vehicles account for about 50% of the emissions. A distribution with too many high emitters will result in an overestimate of the oxyfuel CO reduction benefit when coupled to the emission level data in Figure 1.3. The MOBILE 5a data indicate that the cleanest 50% of the fleet accounts for about 16% of the CO emissions. By contrast the idle and remote sensing studies indicate that about 50% of the fleet emits less than 5% of the total CO. The difference between the two sets of distributions is significant.

The effect of ambient temperature on vehicle emissions can be predicted with the MOBILE 5a Model. Emission studies have shown that the amount of CO and HC emissions increase with decreasing temperature, particularly the amount contributed by the cold start mode. After a vehicle has warmed up, the fuel inlet and pollution control systems are expected to function nearly the same as at 75 °F, the emission test standard temperature. As the ambient temperature decreases, the time required to reach standard temperature operation increases. At very low temperatures standard operation may not be obtained during the vehicle operation. The MOBILE 5a Model does not include a correction for the effect of temperature on the oxyfuel benefit, because the quantity and quality of low temperature emission data are judged to be inadequate to derive low temperature parameters for the oxyfuel benefits. Therefore, the 75 °F series of oxyfuel parameters, such as those shown in Figure 1.3, are applied to the low ambient temperature emissions levels. The available low temperature data indicate that those parameters will greatly overestimate the CO reduction at low temperatures.

Sample runs were performed with the MOBILE 5a Model for a variety of scenarios to illustrate the predicted benefits of a 3.1 wt % oxygen oxyfuel on vehicle CO emissions. These results are shown in Table 1.8. All of the model runs are representative of the FTP, the EPA standard operating cycle for vehicle emission testing. The emission levels indicate the total amount of CO emission per FTP cycle per vehicle divided by the effective number of miles the vehicle traveled. The predicted oxyfuel benefits are given as the total % reduction and the % reduction per wt % oxygen. The predicted benefits are large, about -28%, and vary little for the different scenarios. The baseline calculations show that the emission levels decrease greatly from 1980 to 1994, but the oxyfuel benefit increases slightly during that period. One might expect an opposite trend, a decreasing benefit with the newer fleets, because the newer technology vehicles generally show less benefit from oxyfuels. The effect of an I/M Program on the CO emission factor is predicted to be substantial, reducing emissions by about 30%, but the oxyfuel benefit on the I/M fleet is still large – 27.8%. The benefits of I/M programs are not the focus of this assessment, but a study by Lawson (1993) was not able to observe an effect of California's I/M Program on reducing tampering or emissions as measured by the idle test. The 35 °F prediction indicates an increased CO emission level as expected. The predicted oxyfuel benefit is not significantly changed, because the MOBILE 5a Model uses 75 °F data for predicting oxyfuel effects at all temperatures.

The 1994 baseline CO emission rate given in Table 1.8, 21 g/mi, is the predicted fleet average. Using this average value, the EPA distribution in Figure 1.4 indicates that more than 50% of the fleet has an emission level of about 14 g/mi or larger. The data in Figure 1.3 show that this corresponds to a predicted oxyfuel benefit of about 10% reduction in CO emission per wt % oxygen. The minimum CO reductions shown in Figure 1.3 are experienced by only about 10% of the MOBILE 5a fleet. The emission distributions indicated by the remote sensing and low idle distributions in Figure 1.3, on the other hand, indicate that about 75% of the fleet is relatively clean, with an average emission level of about 2.8 g/mi, assuming a fleet average CO emission level of 21 g/mi. This emission level is comparable to the Auto/Oil AQIRP 20 vehicle clean fleet the evaluated in Table 1.2. The dirtiest 7% or so of the remote sensing and low idle groups account for about half of the total CO emissions and average about 150 g CO per mile, assuming a fleet average

Table 1.8 MOBILE 5a Model predictions of the effects of 3.1 wt % oxygen oxyfuel on light duty gasoline vehicle CO emissions. (Courtesy of D. Brzezinski, EPA.)

	Emission Level (g/mi)		**% Change**	
Run Description[a]	**no oxyfuel**	**with oxyfuel**	**Total**	**per wt % oxygen**
1980 Baseline	55.3	40.4	-26.9	-8.7
1990 Baseline	25.4	18.3	-28.0	-9.0
1994 Baseline	21.3	15.2	-29.0	-9.4
1994 with I/M[b]	14.8	10.7	-27.8	-9.0
1994 35 °F[c]	42.8	30.6	-28.6	-9.2
1994 5500 Feet[d]	23.4	16.6	-29.0	-9.4

[a] Unless noted otherwise, the predictions correspond to vehicle operation at 75 °F at sea level and under the Federal Test Procedure.

[b] I/M indicates the effects of a state Inspection/Maintenance Program.

[c] Calculations indicate performance at 35 °F.

[d] Calculations indicate performance at an altitude of 5500 feet.

emission rate of 21 g/mi as estimated by the MOBILE 5a Model. The large MOBILE 5a Model predicted CO reduction, 9.4% per wt % oxygen, implies a fleet with a large fraction of vehicles in the high emitting category. This result is not consistent with the fleet emission distributions indicated by the field data (Lawson, 1993; Zhang *et al.*, 1995; Shepard *et al.*, 1995).

The EPA Complex Model for Reformulated Gasoline (RFG) was originally developed in conjunction with Federal reformulated gasoline regulations to elucidate the relationships among individual fuel parameters and pollutant emissions. This model is a compliance model and was developed specifically to identify fuels that would meet the RFG rule requirements for VOC, NO_x, and toxic emission reductions. The VOC and NO_x emissions relate to photochemical air pollution problems, which peak during the summer season. Most of the data on which the Complex Model is based were collected since 1990 on a sample of vehicles selected to be representative of the 1990 model year (mostly fuel-injected) passenger vehicles [Auto/Oil AQIRP 1, 1990; Auto/Oil AQIRP 2, 1991; Auto/Oil AQIRP 6, 1991; Auto/Oil AQIRP 8, 1992; Auto/Oil AQIRP 9, 1992; Mayotte et al, 1994a,b]. These emissions data were collected at typical summertime conditions. The number of high emitting vehicles and the ratio of exhaust and non-exhaust emissions for 1990 model year passenger cars were derived from the MOBILE Model.

The application of the Complex Model to estimating oxyfuel emission effects for the on-road fleet is limited by several factors: (a) The Complex Model is constrained by statute to vehicle technologies which are representative of 1990 model year. (b) The Complex Model emissions data base is for summertime conditions. (c) Carbon monoxide emissions were not a focus of the original Complex Model development. Nevertheless, EPA believes that the Complex Model is a useful tool for estimating the on-road fleet emission effects of oxyfuels for the following reasons (D. Korotney, personal communication, 1996): (1) The Complex Model is based on much of the same data that are considered the most reliable for up-to-date emissions estimates, a sampling of which is described in the above section "CO Emissions." (2) Despite the fact that the Complex Model is constrained to

1990 MY technologies, model years 1986-1991 are represented in its database. EPA estimates that this selection of technologies represents 30 to 50% of the current on-road fleet. (3) The MOBILE 5a Model does not provide estimates of the effects of fuel oxygenate on fleetwide NO_x emissions. EPA believes that the Complex Model is a reliable alternative as discussed below. (4) The Complex Model uses a weighting of the emission effects of normal and high emitting vehicles as a means of representing the emitter class distribution of the in-use fleet. EPA believes this approach allows the very limited data on high emitters to be properly accounted for in the fleet emissions inventory. (5) A carbon monoxide supplement to the Complex Model was developed in 1995 using the same database and statistical regression procedure that was used for the VOC, NO_x, and toxics portion of the model. Thus the Complex Model for CO can be used as a check on the MOBILE Model estimates for CO. (6) Since the Complex Model was built upon a large data set comprised of a wide variety of fuel compositions and vehicles, EPA believes its usefulness for estimating the effect of fuel parameter changes on emission is not limited to RFG.

Table 1.9 summarizes Complex Model predictions of fleetwide exhaust emissions effects for five different oxygenated fuels compared to a base fuel. The fuel parameters for the six fuels are given in the top of the table. The predicted percent changes in emissions normalized to 1 wt % oxygen are given in the bottom part of the table. The mass emissions for the base fuel are also given. There are two notable differences between the MOBILE 5a Model and the Complex Model predictions for CO. The fleet average CO emission, 11.9 g/mi, is about half of that predicted by the MOBILE 5a Model. The Complex Model predicted reductions in CO for the various oxygenate blends are much smaller than those predicted by the MOBILE Model, ranging from about 2 to 4 times smaller. These dramatic differences reflect the effects of improved vehicle technology and the fact that the 1990 technology vehicles do not emit as much CO and do not respond as much to fuel oxygenate as most of the earlier vehicles. In general the fuel effects predicted by the Complex Model are comparable to those reported by Reuter *et al.* (1992) for the 1989 model year group and summarized in Table 1.2. The average CO emission level from the Complex Model is almost five times larger than the Reuter *et al.* study level but the effects of fuel oxygenate are comparable.

The most striking difference between the effects found in Table 1.2 and in some of the other emission studies reviewed here compared to the Complex Model results concerns NO_x, where the emission studies indicate an increase in NO_x emission with fuel oxygenate and the model predicts no effect or a small decrease in NO_x emission. This discrepancy is not as important to the winter oxyfuel program as it is to the Reformulated Gasoline Program, as the latter requires by statute that the NO_x emission can not be increased by RFG. The limited emission studies reviewed here indicate an increase in NO_x emissions when fuel oxygenate is used. This observation is consistent with the expected effect of fuel enleanment as shown in Figure 1.2. The EPA stands behind the accuracy of the Complex Model prediction that fuel oxygen increases do not increase NO_x emissions for this in-use fleet, even for oxygen levels above 2.7 wt % (D. Korotney, private communication). It should be noted that the analysis upon which the Complex Model is based involves a more detailed review of a larger data base. If the addition of oxygenate does not increase fleetwide NO_x emissions, it suggests some effect other than enleanment is influencing the emission. For example, if the oxygenate reduces the combustion temperature or improves the catalyst performance, the simple enleanment effect may not account for the NO_x emission.

A CO emissions model developed by Rao (1996) reports the effects of various fuel parameters on CO exhaust emissions. The database used to develop this model is identical to the database used to develop EPA's Complex Model. Rao's model gives emission effects for both normal and high emitting vehicles, where the high emitters are classified based on total HC emissions. He notes that 29 of the 32 high HC emitters studied would be classified as high CO emitters. The average CO emission for the 32 vehicle high emission group is 31.5 g/mi. For a 3.5 wt % oxygen fuel he finds a 3.3% reduction in CO per wt % oxygen for normal emitters and a 1.8% reduction for high emitters. The reason for the smaller reduction in CO emission found in high emitting vehicles is not identified and is the opposite of the effect shown in the MOBILE 5a Model benefits shown in Figure 1.3. Rao's model also indicates that reducing fuel sulfur from 339 ppm by wt to 139 ppm decreases CO emissions by 9.6% and 8.0% in normal and high emitters, respectively. This effect is comparable to what is predicted for standard levels of fuel oxygenate, 2.7-3.1 wt % oxygen. It should be noted that this model is applicable to nominal 1990 MY technology vehicles.

Table 1.9 Complex Model predictions of the effects of MTBE and ethanol oxygenated fuels on on-road fleet exhaust emissions. (Courtesy of D. Korotney, EPA.)

	Fuel Parameters					
		A	**B**	**C**	**D**	**E**
Fuel	**Base**	**15% MTBE**	**15% MTBE + d[a]**	**10% EtOH + R[a]**	**10% EtOH + R + d[a]**	**10% EtOH + d[a]**
Wt % O_x	0.0	2.7	2.7	3.5	3.5	3.5
Sulfur (ppm)	324	324	276	324	291	291
RVP (psi)	10.6	10.6	10.6	10.6	10.6	11.6
E200 (%)	47.3	47.3	55.1	47.3	52.6	52.6
E300 (%)	82.3	82.3	84.9	82.3	84.1	84.1
Aromatics (Vol. %)	30.6	30.6	26.6	30.6	27.8	27.8
Olefins (Vol. %)	13.4	13.4	11.7	13.4	12.3	12.2
Benzene (Vol. %)	1.35	1.35	1.18	1.35	1.23	1.23

Fuel	**Base**	**A**	**B**	**C**	**D**	**E**
Emission	**Mass Emissions (g/mi)**	**Percent Changes (Per wt % Oxygen)**				
CO	11.9	-4.4	-2.7	-2.7	-3.6	-2.2
VOC	0.46	-2.6	-0.4	-0.4	-1.6	-0.6
NO_x	0.68	-0.9	-0.004	-0.003	-0.5	-0.3
Benzene	0.024	-8.5	-4.1	-4.0	-6.4	-6.4
1,3-Butadiene	0.0048	-7.1	-2.8	-2.7	-5.0	-5.0
Formaldehyde	0.0046	+6.0	+4.9	0.0	+0.5	+0.5
Acetaldehyde	0.0023	-3.7	-2.9	+40	+39	+40

[a] d = effect includes dilution, R = RVP is controlled.

Summary of Model Predictions

Models are used to provide inventories of urban vehicle emissions and to assess the effects of fuels and vehicles on urban air quality. Studies of on-road vehicle emissions and urban air quality data have identified discrepancies between the model predictions and the observations [Pierson *et al.*, 1990; Fujita *et al.*, 1992; Cadle *et al.*, 1993; Lawson, 1993; Pierson, 1995; Kirchstetter *et al.*, 1996; Pierson *et al.*, 1996; Robinson *et al.*, 1996]. These studies can lead to refinements in the models. Accurate models require vehicle emission data that are representative of the on-road vehicle fleet, of realistic urban driving patterns and conditions, and of the fuels used by consumers. The previous section of this chapter has shown that the data required to predict the temperature effects of the winter oxygenated fuel program are inadequate. Although the models are critically important to air quality programs such as the winter oxygenated fuel program it seems that few critical tests are devised to evaluate the accuracy or reliability of the model predictions.

The predictions of fuel oxygenate effects on fleetwide CO emissions from the MOBILE 5a Model and the Complex Model can be compared. The CO emission reduction predicted by the MOBILE Model is three times larger than the Complex Model prediction, 9.4% per wt % oxygen compared to a 3.1% average for five different oxygenated fuels. The emission data reviewed here indicate that the MOBILE 5a Model significantly overestimates the oxyfuel effect on CO emissions. The differences between the MOBILE and Complex Model predictions can to some extent be attributed to vehicle emission control technology, since the latter model is focused on newer technology vehicles. The MOBILE 5a Model, however, does not show a significant change in predicted oxyfuel effects from 1980 to 1994.

Some of the important conclusions regarding model predictions can be summarized as follows:

- The EPA MOBILE 5a Model appears to significantly overestimate the benefits of oxyfuels on fleetwide CO emissions. The model predicted benefit for high emitters is very large and the fleet distribution has a large population of high emitters.

- The EPA Complex Model estimates a fleetwide reduction in CO emissions that is about one third of the value predicted by the MOBILE 5a Model. The Complex Model is focused on 1990 model year technology representing vehicles with lower CO emission levels and smaller oxyfuel CO reductions than the MOBILE Model.

- The EPA Complex Model estimates a negligible effect of fuel oxygenate on fleetwide NO_x emissions at oxygenate levels up to 3.5 wt % oxygen. This estimate does not agree with the conclusion drawn from the emission studies reviewed in this assessment, but is based upon an analysis of a larger data set.

- No existing EPA model is capable of accurately predicting oxyfuel effects at temperatures below about 50 °F. The emission data available for assessing the effects of low temperature on oxyfuel performance is inadequate and has not been incorporated into the MOBILE 5a or Complex Models.

- Much of the data upon which the EPA MOBILE 5a Model is based have not been published in the peer-reviewed literature.

AMBIENT AIR QUALITY EFFECTS OF OXYFUELS

Introduction

In this section the effects of the winter oxyfuel program on ambient air quality are assessed. Because the oxyfuel program is intended to improve air quality by reducing the ambient concentration of CO, its direct effect on air quality is the most important measure of the program's effectiveness. The EPA MOBILE 5a Model is the instrument used by the states to predict the CO reduction expected from oxyfuel use within the oxyfuel program areas. Recognizing the limitations of the model, it is the standard against which the observed changes in ambient CO concentrations will be compared. The urban areas with oxyfuel programs during the winter of 1995-6 as well as the areas that are considering redesignation or are not continuing the program are listed in Table 1.10. It can be seen that all of the geographical regions of the U.S. are represented. In spite of the fact that many areas are or have been involved in the winter oxygenated fuel program, relatively few studies have been reported that attempt to measure the effect of the program on air quality.

The target pollutant of the program is CO, but it is possible that other air pollutants such as NO_x, VOCs, toxics (benzene, 1,3-butadiene, formaldehyde, acetaldehyde, and polycyclic organic matter), particles and ozone are also affected. All of these materials, except ozone, are directly emitted by vehicles. Some particles grow or are formed from primary and secondary pollutants such as SO_2, sulfuric acid, NO_x, nitric acid, and polar organic compounds. In some cases these pollutants are produced by the oxidation of the primary vehicle emissions. Other sources besides motor vehicles also contribute these pollutants to the urban atmosphere.

Winter Photochemistry

The approximate lifetimes for the toxics and the oxyfuel components in the urban atmosphere during the winter months are of interest in considerations of the air quality effects. Removal of atmospheric contaminants occurs by several mechanisms including OH-radical attack and direct photodecomposition during the daylight hours, NO_3-radical attack at night, and by dry and wet deposition. For most of the pollutants considered here, the first process, OH-attack, is often the most important (Atkinson, 1994).

Unfortunately, no measurements of urban OH radical concentrations during wintertime are available. For the purpose of estimating an approximate upper limit to the amount of winter photochemistry, a crude analysis is made using the available information. These estimates are intended to represent a reasonable upper limit of winter urban photochemistry and therefore are not intended to be representative of the average level of photochemistry, which is likely to be very low and negligible in areas other than the southern latitudes. It should be noted that the estimates given here are different from the estimates given in the chapter on Water Quality, where lifetimes are calculated based on the global average OH concentration, and not a winter urban scenario.

The rate coefficients for the gas-phase reactions of the OH radical with the pollutants (Atkinson, 1994) can be combined with estimated ambient OH radical concentrations to obtain an estimate of the pollutant lifetimes. It is expected that during wintertime the ambient OH radical concentrations will decrease markedly with increasing latitude because

Table 1.10 Areas with winter oxygenated fuel programs in 1995; Areas considered for redesignation for 1995; and Areas previously redesignated.

Areas with Oxygenated Fuel Programs		
Area	Control Period	Fuel Type
New York/No. NJ./Connecticut	10/1 - 4/30	2.7 RFG
Minneapolis/St. Paul, MN	10/1 - 1/31	2.7±
Albuquerque, NM`	11/1 - 2/28	3.1
El Paso, TX	11/1 - 2/28	2.7
Colorado Springs, CO	11/1 - 2/28	3.1
Denver/Boulder, CO	11/1 - 2/28	3.1
Ft. Collins, CO	11/1 - 2/28	3.1
Missoula, MT	11/1 - 2/28	2.7
Provo/Orem, UT	11/1 - 2/28	2.7
Las Vegas, NV	10/1 - 2/28	3.1
Reno, NV	10/1 - 1/31	2.7
Phoenix, AZ	10/1 - 2/28	3.1
Los Angeles, CA	10/1 - 2/28	2.0 RFG
Chico, CA	10/1 - 1/31	2.0
Modesto, CA	10/1 - 1/31	2.0
San Diego, CA	11/1 - 2/28	2.0 RFG
Sacremento, CA	10/1 - 1/31	2.0
San Francisco, CA	10/1 - 1/31	2.0
Stockton, CA	10/1 - 1/31	2.0
Anchorage, AK	11/1 - 2/28	2.7±
Grant's Pass, OR	11/1 - 2/28	2.7±
Klamath Co., OR	11/1 - 2/28	2.7±
Medford, OR	11/1 - 2/28	2.7±
Portland, OR /Vancouver, WA	11/1 - 2/28	2.7±
Seattle, WA	11/1 - 2/28	2.7±
Spokane, WA	9/1 - 2/28	2.7±

Areas considering redesignation or that will not implement oxygenated fuel programs		
Area	**Control Period**	**Fuel Type**
Baltimore, MD	11/1 - 2/28	2.7% RFG Area
Boston, MA	11/1 - 2/28	2.7% RFG Area
Raleigh-Durham, NC	11/1 - 2/28	2.7% RFG Area
Hartford, CT	11/1 - 2/28	2.7% RFG Area
Philadelphia, PA	11/1 - 2/28	2.7% RFG Area
Washington, DC	11/1 - 2/28	2.7% RFG Area
Fairbanks, AK	11/1 - 2/28	2.7%
Salt Lake City, UT	11/1 - 2/28	2.7%

Oxyfuel areas previously redesignated	
Area	**Date of Redesignation**
Greensboro, NC	Sept. 2, 1994
Raleigh-Durham, NC	Aug. 1, 1995
Syracuse, NY	Sept. 23, 1993
Cleveland, OH	Feb. 5, 1994
Duluth, MN	April 14, 1994
Memphis, TN	July 26, 1994

of the reduced intensity and duration of sunlight. Goldstein *et al.* (1995) deduced a summer/winter ratio for OH concentrations of about 9 ± 2 at northern mid-latitudes. Indirect measurements in the downwind portion of the Los Angeles basin in late October 1994 (Gupta, 1995) suggest a 12-hr average daytime OH radical concentration of approximately 1×10^6 molecule cm^{-3} (to within a factor of 2-3). It appears that a 24-hr average OH radical concentration in the Los Angeles air basin of around 5×10^5 molecule cm^{-3} is a reasonable wintertime limit. Significantly lower OH concentrations are expected in the winter months of December and January. For comparison this value is a factor of 2 lower than the global average tropospheric OH concentration (diurnally, seasonally and annually averaged) of Prinn *et al.* (1995). The OH radical concentrations for cities at higher latitudes are expected to be lower than this value for Los Angeles. For Denver we estimate the winter average OH is a factor of 2 to 5 times lower than the Los Angeles value. With rate constants (cm^3 $molecule^{-1}$ s^{-1} units) for MTBE (2.9×10^{-12}), ETBE (8.8×10^{-12}), ethanol (3.3×10^{-12}) and TAME (5.5×10^{12}) at 298 K (the rate constants are not very temperature dependent), the corresponding lifetimes for a 24-hr average OH radical concentration of 5×10^5 molecule cm^{-3} are: 8 days for MTBE, 2.6 days for ETBE, 7 days for ethanol and 4 days for TAME. The lifetimes for Denver are estimated to be 2 to 5 times larger than these values. These lifetimes are sufficiently long that the photochemistry of these fuel oxygenates can to a first approximation be neglected. Their fate will be transport out of the urban region and oxidation in the free troposphere. During a 1-day time period, about 12% of the MTBE will react with OH at a radical concentration of 5×10^5 molecule cm^{-3}. At higher latitudes, the lifetimes are longer and the photooxidation even less significant.

The products of the gas-phase oxidation of MTBE, ETBE, ethanol and TAME have been investigated at room temperature and atmospheric pressure (Atkinson, 1994, and references therein; Smith *et al.*, 1995). The reaction of MTBE with the OH radical in the presence of NO leads to the formation of *tertiary*-butyl formate (with a 76% yield), formaldehyde, methyl acetate and acetone (Atkinson, 1994 and references therein), ETBE reacts to form *tertiary*-butyl formate, *tertiary*-butyl acetate, ethyl acetate, acetone, acetaldehyde and formaldehyde (Atkinson, 1994, and references therein). Ethanol reacts to form mainly acetaldehyde plus a small amount of formaldehyde and glycolaldehyde (Atkinson, 1994); and TAME reacts to form *tertiary*-amyl formate, methyl acetate, acetaldehyde, acetone (minor), formaldehyde, and a number of other organics and organic nitrates in low yield (Smith *et al.*, 1995).

These products of the tropospheric degradations of the oxygenates are expected to react with the OH radical and, for formaldehyde, acetaldehyde and acetone, to photolyze (Atkinson, 1994, and references therein; Smith *et al.*, 1995). Rate constants for the gas-phase reactions of the OH radical with these products have been measured (Atkinson, 1989, 1994, and references therein; Smith *et al.*, 1995). Based on these OH radical reaction rate constants, the calculated lifetimes of *tertiary*-butyl formate, methyl acetate and *tertiary*-butyl acetate are >30 days at a 24-hr average OH radical concentration of 5×10^5 molecule cm^{-3}; the calculated lifetimes of ethyl acetate and *tertiary*-amyl formate are 14 days and 4 days, respectively, for the same OH radical concentration. Formaldehyde, acetaldehyde and acetone also undergo photolysis (Atkinson *et al.*, 1992), with photolysis being calculated to dominate over the OH radical reaction for formaldehyde, to be of similar importance as the OH radical reaction for acetone, and to be less important than the OH radical reaction for acetaldehyde. The lifetimes of acetone and acetaldehyde are expected to be approximately 50 days for acetone and 1.4 days for acetaldehyde, for a 24-hr average

OH radical concentration of 5 x 10^5 molecule cm^{-3}. For formaldehyde, the photolysis lifetime at zenith solar angles of 40 to 70 degrees range from about 5 to 16 hours (Rogers, 1990). Hence, apart from formaldehyde and acetaldehyde which are also emitted in vehicle exhaust and are photooxidation products of other fuel VOCs (Atkinson, 1994), the reaction products of the oxygenates MTBE, ETBE and TAME are fairly long-lived under wintertime conditions.

Concentrations of MTBE averaging about 4 ppb have been measured in the summer in Los Angeles, CA (B. Zielinska, personal communication). Goldan *et al.* (1995) measured MTBE concentrations in Boulder, Colorado of up to about 10 ppb and averaging around 2 ppb during February 1991. In both cases the ambient MTBE can be attributed to an oxygenated gasoline source. Using the OH radical concentration of 5 x 10^5 molecule cm^{-3} averaged over a 24-hr period, and neglecting losses of the products with the OH radical, the amount of *tertiary*-butyl formate formed from 4 ppb MTBE over a 1-day period is about 0.4 ppb.

The lifetimes of the oxygenates and their atmospheric reaction products depend largely on the ambient OH radical concentration, for which no direct data are available during wintertime months and which can not be accurately estimated. Based on an estimated 24-hr average OH radical concentration of 5 x 10^5 molecule cm^{-3} for the Los Angeles area suggests that the lifetimes of MTBE, ETBE, ethanol and TAME due to chemical reaction range from a few days to a week or so, and that advection out of the urban area will dominate over chemical reaction. In fact, the physical loss processes of wet and dry deposition to the Earth's surface may also be significant for these oxygenates. The atmospheric reactions of these oxygenates are calculated to lead to low concentrations of reaction products in the urban environment. For example, the formation of approximately 0.4 ppbv of *tertiary*-butyl formate is estimated over a 1-day time period from MBTE at previously measured ambient MTBE concentrations of about 4 ppbv. Winter photochemistry is even less significant at northern latitudes, for example, in Denver it is likely to be negligible during the winter oxyfuel season.

Trends in Ambient CO

The EPA reports regularly on the national trends in air quality. The report for 1994 trends (USEPA, 1995b) gives the 20-year record shown in Figure 1.5 which indicates a decline of about 60% in the second 8-hour maximum concentration during the 1975-1994 period. During the past 10 years average CO concentrations have decreased about 28% (USEPA, 1995a).

The decline in ambient CO concentrations has had a remarkable effect on the number of exceedances of the EPA 8-hour 9 ppm standard. Table 1.11 shows a count of the number of exceedances during the period from 1985 to 1994. The drop in the number of exceedances during the past 10 years is even more dramatic than the decrease in CO levels, having decreased by over a factor of 10. It should be noted that this is not a count of all of the recorded CO exceedances of the 8-hour standard. The only selection criterion for this count was that to be included a station must have a full 10-year record of data. Table 1.12 gives an accounting of all of the stations reporting exceedances in 1993 and 1994. During this period the number of exceedances seems to have leveled off. This may be due in part to weather conditions, such as temperature inversions, which can strongly influence the frequency of exceedances. There is also the effect of increasing vehicle miles traveled counteracting the reduction in CO emissions per mile. The data in Figure 1.1 may also indicate this effect of the leveling off of the decline in recent years.

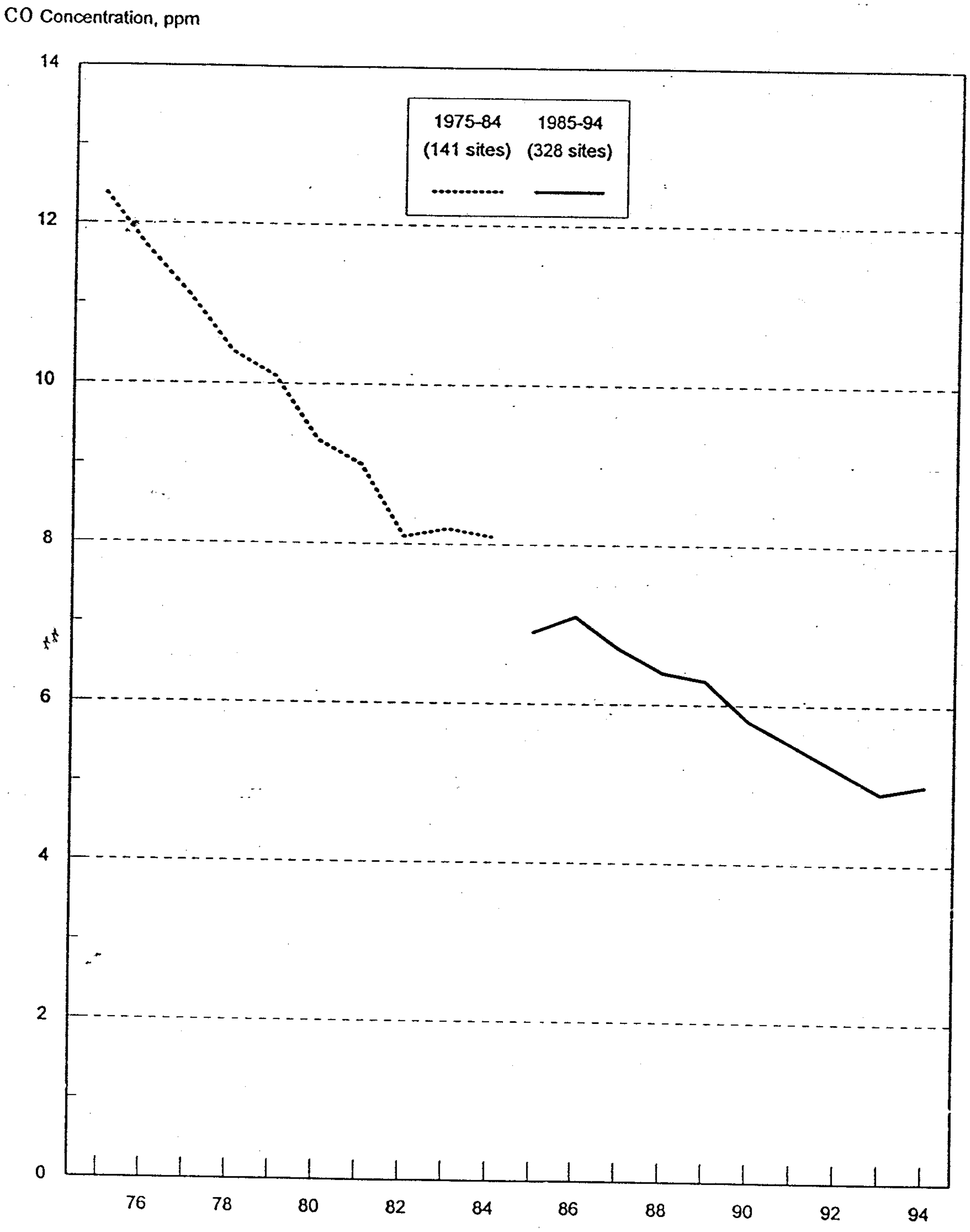

Figure 1.5 Twenty-year trend in CO second maximum 8-hour concentration (USEPA, 1995b). The break in the line around 1984 is due to a change in the number of monitoring sites.

Table 1.11 Count of the total number of exceedances of the 9 ppm 8-hour standard from the 1985-1994 record of all urban stations.*

Year	85	86	87	88	89	90	91	92	93	94
No. of exceedances	778	690	429	359	373	215	125	69	38	60

*Only stations with a full 10-year record (277 stations) are counted. Most urban areas have several stations so it is possible that single exceedance events are counted more than once. The purpose of this table is to show the general 10-year trend.

Since an exceedance involves a 9-ppm concentration threshold, the decline in urban CO concentrations has steadily moved many urban peak values below this limit. EPA data show that the decrease in CO occurred in suburban and rural areas as well (USEPA, 1995b). Because motor vehicles account for most of the CO emissions, it is reasonable to attribute the decline in CO to improvements in vehicle technology in response to the EPA mandated standards in vehicle emissions. The decline started well before the period of oxyfuel usage, which generally began in 1992 and has been limited mostly to winter months.

Table 1.12 Count of all reported exceedances* of the 8-hour 9 ppm standard reported by about 550 urban stations in 1993 and 1994.

Area	**1993**	**1994**
Los Angeles, CA	22	38
Fairbanks, AK	8	7
Imperial, CA	—	10
Steubenville, OH / Weirton, WV	4	7
Las Vegas, NV - AZ	3	5
Anchorage, AK	4	2
Denver, CO	4	4
El Paso, TX	3	1
Phoenix - Mesa, AZ	0	6
Jersey City, NJ	0	3
Newark, NJ	0	2
Detroit, MI	0	2
Provo - Orem, UT	2	1
Miscellaneous	6	8
Total	56	93

*This is not a count of violations, because each area is allowed one exceedance per year and because single events may have been counted by more than one station within an area. Note the Imperial, CA monitor was not in operation in 1993 but accounted for 10 exceedances in 1994.

Since the oxyfuel program was initiated to improve air quality and specifically to reduce winter ambient CO levels, one may expect to find a quantitative improvement in CO air quality that can be attributed to the use of oxygenated fuels. One way to assess the effects of oxygenate fuel additives on ambient air quality is to compare records of measurements made before, during, and after periods of oxygenate usage. Unfortunately such a straightforward analysis is complicated by a number of factors acting to introduce variations in ambient CO concentrations.

Meteorology in general is the single most significant variable with which one must contend to measure the effectiveness of the program using ambient data. Temperature inversions are a major contributor to the winter buildup of CO. Therefore the frequency and duration of inversions are important variables affecting winter air quality measurements. Lower temperatures cause a large increase in vehicle emissions. The data in Table 1.8 show that the average CO emission from vehicles doubles when the temperature drops from 75 °F to 35 °F. In evaluating records from urban monitoring stations, other variables may also interfere with the analysis. As described above there is a long-term downward trend in CO over the last decade or so that is attributable to EPA mandated exhaust emission standards, reduced vehicle emissions and a turnover in the vehicle fleet. This trend is being counteracted by a steady increase in vehicle miles traveled, driven by increasing populations and numbers of vehicles. Measurements at specific monitoring sites may be affected by local changes in traffic patterns, by rerouting streets and freeways, and even by changes in traffic light sequencing.

One factor favoring an observable reduction in ambient CO levels is that the predictions indicate a large effect. The MOBILE 5a Model predicts a reduction in CO emissions of about 9.4% per wt % oxygen as shown in Table 1.8. The EPA Air Quality Trends report (USEPA, 1995a) states that in cities automobile exhaust can contribute as much as 95% of all CO emissions and that transportation sources account for 78% of the nation's total CO. The Colorado report on the oxygenated gasoline program (Livo and Miron, 1995) states that mobile source emissions contribute approximately 80% of the total CO emissions in the Colorado Front Range inventories. Thus a factor of (80 ± 10)% seems reasonable for the fraction of winter urban ambient CO contributed by gasoline-fueled vehicles. The MOBILE 5a predicted emission benefit of 9.4% reduction in CO emission per wt % oxygen reduces to an ambient benefit of about 7.5% CO reduction per wt % oxygen. Based on this prediction the 3.3 wt % oxygen fuel used in Colorado would reduce ambient CO by about 24%. To indicate the magnitude of this change, a bar is added to the ambient CO data in Figure 1.1 above the year 95. The top of the bar shows the concentration of CO that would have been experienced without oxyfuel, assuming oxyfuels did reduce ambient CO by 24%. Such a large effect should be readily observable in the ambient CO record, in spite of the confounding effects of meteorology and trends.

California Studies

The state of California has experienced some of the most serious air quality problems due in part to motor vehicle pollution. In the winter of 1992-3 California implemented a modified version of the EPA mandated winter oxyfuel program to reduce ambient CO concentrations. The California oxyfuel program was modified to reduce the required oxygen content from the EPA mandated 2.7 wt % oxygen to 1.8 to 2.2 wt % oxygen, because of possible effects of oxyfuel usage on NO_x emissions (CARB, 1992). Eight metropolitan areas were classified as non-attainment because of CO violations. The winter oxyfuel period for these areas generally fall within the months from October through February.

Dolislager at the California Air Resources Board (CARB) has developed and applied methods of analyzing ambient air quality data to examine the effects of the oxyfuel program on CO concentrations. In his first study (Dolislager, 1993) ambient air quality data in four metropolitan regions, Concord, San Jose, and Vallejo in the San Francisco Bay Area Basin; North Long Beach, Lynwood, and Los Angeles in the South Coast Air Basin; El Cajon in the San Diego Air Basin; and Stockton and Bakersfield in the San Joaquin Valley Air Basin, were analyzed. It was noted that the air quality in the 1992-3 winter, which was the first oxyfuel season, was greatly improved over previous years, for example, CO was reduced over 30% compared to the 1991-2 winter. However it was also noted that the weather in 1992-3 was unusually wet compared to the previous winters and that wet weather is accompanied by greater atmospheric mixing and dispersion. In an effort to eliminate the effects of meteorology, Dolislager developed an analysis in which the ambient concentrations of hydrocarbons (HCs) and nitrogen oxides (NO_x) are used as atmospheric tracers. Like CO, the winter urban HC and NO_x come mainly from vehicle exhaust. By assuming that the HC and NO_x emissions were not significantly changed by the use of oxyfuels, their ambient concentrations provide an independent indication of the effects of meteorology on air quality. Thus changes in ambient CO relative to these tracers give a measure of the effect of oxyfuel usage. Trends in the CO, HC, and NO_x concentrations from the prior winters of 1985-6 through 1991-2 were determined and incorporated into the analysis. The results based upon the HC tracer were somewhat more variable than those based upon the NO_x tracer. Hydrocarbon emissions are found to be reduced by fuel oxygenate in most emission studies, so they are not expected to be a reliable tracer. Some reduction of CO was found in all four air basins studied. The author concluded that the California 1992-3 winter oxyfuel program accounted for a 6 to 10% reduction in ambient CO.

In a subsequent report Dolislager (1996) made a similar analysis of the effect of the winter oxyfuel programs from 1992-3 through 1994-5 based on data from the following monitoring sites: San Jose and Vallejo in the San Francisco Bay Area Basin; Anaheim, Burbank, Costa Mesa, Hawthorne, La Habra, Los Angeles, Lynwood, Pasadena and Reseda in the South Coast Air Basin; Sacramento in the Sacramento Valley Air Basin; Fresno, Modesto and Stockton in the San Joaquin Valley Air Basin. The CO data showed reductions of about 30, 10, and 35%, respectively, for these three oxyfuel winter periods compared to earlier years. NO_x was used as a tracer of the confounding effect of meteorology. From this analysis he concluded that a 5 to 10% reduction in ambient CO could be attributed to the usage of oxyfuel. The accuracy of the analyses reported by Dolislager is heavily dependent upon the assumption that the NO_x emissions are not affected by the 2% by weight oxygen in the fuel. If the fuel oxygenate increases NO_x emissions, he will overestimate the CO effect but if NO_x emissions are decreased he will underestimate the benefit. The tunnel study by Kirchstetter *et al.* (1996) supports this assumption for vehicles operating in the hot stabilized mode. A study by Born *et al.* (1994) also finds the effect of oxyfuels (at the 2 wt % oxygen level) on NO_x emissions is small in California vehicles. On the other hand, there does appear to be a significant change in HC and VOC emissions that can be attributed to the use of oxyfuel (PRC, 1992; Kirchstetter *et al.*, 1996; Born *et al.*, 1994). The 5 to 10% reduction in ambient CO by Dolislager corresponds to an oxyfuel benefit of 2.5 to 5% per wt % oxygen.

CDC Study of 11 Western States

Mannino and Etzel (1996) published a study evaluating ambient CO concentrations in 11 western states. They analyzed data from 62 monitors for the period 1986 through 1992. The data set included five areas with winter oxyfuel programs from two seasons up to five seasons: Phoenix (3) and Tucson (2), AZ; Las Vegas (3) and Reno (3), NV; and Colorado (5), where the number in parenthesis indicates the number of oxyfuel seasons. The oxyfuels in use in these areas ranged from 1.5 to 2.7 wt % oxygen. The data set also included areas outside of the oxyfuel areas as a control for comparison. Summer (May through August) as well as winter (November through February) periods were analyzed to test for trend effects. Hourly CO concentration data were analyzed to determine the changes in the mean daily CO concentration, the 1-hour maximum daily CO concentration, and the 8-hour maximum daily CO concentration. Analyses for the effects of temperature and wind were also made. The analyses found that the winter season mean daily ambient CO concentration in areas not using oxyfuels was reduced by (10.3 ± 11.5)% in 1989-91 compared to 1986-88. For the same period, the areas with an oxyfuel program showed a decrease in mean daily CO of (20.5 ± 7.9)%, where the uncertainties represent one standard deviation. The net reduction in mean daily CO concentration that can be attributed to oxyfuel usage is about 10%. The amount of oxygenate in the oxyfuels used ranged from 1.5 to 2.7 wt % oxygen, the average being 2.3 wt % oxygen. The observed decrease in ambient CO found in this study is therefore about 4.3% per wt % oxygen.

Colorado, Arizona , New Mexico, and Nevada Studies

The state of Colorado has the longest term oxyfuel program. It started as a two-month program in January 1988 with a 1.5 wt % oxygen additive and an EPA MOBILE Model predicted 12% reduction in ambient CO and has evolved to a current four-month program with a 3.1 to 3.3 wt % oxygen fuel and a model predicted 30% reduction in CO emissions (Livo and Miron, 1995) and an estimated 24% reduction in ambient CO. Anderson and coworkers (Anderson *et al.*, 1994, 1995) have attempted to find evidence of the reported reductions in CO levels by treating the record of ambient CO concentrations since about 1981 with a statistical analysis. The analysis method "a Structural Time Series Analysis" fits a quantity that varies with time, in this case the ambient CO concentrations, with a multi-term expression that accounts for the various independent factors contributing to the variation of CO with time. One term in the expression is associated with the time period during which oxyfuels are in use. The magnitude of this term is a measure of the effect of the oxyfuel program on ambient CO. Two data sets from several different sites in the Colorado oxyfuel program area were subjected to analysis: (1) the monthly average CO and (2) the monthly maximum 8-hour average CO. Figure 1.1 shows a sample of the type of data they analyze. The Colorado oxyfuel seasons are indicated by the filled symbols on the figure. In an analysis of data through 1993, they reported (Wolfe *et al.*, 1994) that they could not find a statistically significant oxyfuel effect. As a further test, they showed that their analysis should detect a 10% CO reduction at about the 80% confidence level. They also analyzed data from four other western cities with winter oxyfuel programs, Albuquerque, NM; Phoenix, AZ; Las Vegas and Reno, NV. In recent years all of these areas have had a winter program using at least a 2.7 wt % oxygen fuel. In general these data showed more variability and scatter. Only data from Phoenix showed a statistically significant reduction in CO due to oxyfuel usage.

A new study from this group (Wolfe *et al.*, 1996) extends and updates their earlier analyses of Denver area data. They analyzed monthly data from three CO monitors for 1981 through June 1995. They combined the results from two different types of statistical analyses, a Structural Time Series Analysis and an ARIMA analysis. They report an oxyfuel reduction in ambient CO of (7 ± 10)%, where the uncertainty represents the 95% confidence limits. This reduction in CO corresponds to about a (2.3 ± 3.3)% CO reduction per wt % oxygen.

Several important factors affecting ambient CO are not explicitly accounted for in their analysis. Meteorology is the most important, because it plays a dominant role in the winter CO maxima. They contend that by averaging over such a large time scale this effect should "average out". A second possible systematic error could come from changes in driving patterns, particularly vehicle miles traveled, during the winter months. More recently they have attempted to assess the role of urban vehicle counts on CO levels (Anderson, 1995, personal communication) and find no significant effect. On the other hand one might expect a small complement to the oxyfuel CO reduction in the Denver area, because during periods of high ambient CO, there are designated no-driving and no-wood burning days. This program discourages driving and prohibits most wood burning, which is a small contributor to ambient CO.

Alaska Study

Anchorage, AK, initiated an oxyfuel program during the winter of 1992-3. The ambient CO concentrations during that period declined by about 20 to 30%, an unusually large amount compared to variations observed in previous years. Heil (1993) developed a model to predict CO concentrations from weather observations, such as wind, temperature, pressure, and cloud cover, from CO emission estimates and from other variables. The idea was to compare the model predictions before and after oxyfuel implementation to determine if there was a residual effect that could be attributed to the oxyfuel. Heil concluded that of the observed 27% reduction in CO during the winter of 1992-3, about 16% was due to the variables in the model, mostly weather. The residual 11% decline in CO could be due to oxyfuel usage, but a propagation of uncertainties in the model and in the input parameters led her to conclude that it was unclear whether or not the oxyfuel program contributed to the decline in CO. If the 11% decline in CO is attributed to the use of a 2.7 wt % oxyfuel, the residual reduction in ambient CO corresponds to 4.1% per wt % oxygen.

North Carolina Studies

Three North Carolina counties (Durham, Forsyth, and Wake), with a history of violating the CO air quality standard, and eight neighboring counties were mandated by EPA to sell only oxygenated fuel during the 1992-3 winter season, November through February. The ambient CO data for selected stations in the oxyfuel program area covering a four-year period including the first oxyfuel season were analyzed by Vogt (1994). As a control these data were compared with ambient CO data from selected urban areas (Fayetteville and Charlotte) outside the oxyfuel program.

A general downward trend in urban CO was reported. The reduction in the observed maximum values was found to be greatest during the 1992-3 oxyfuel season. The study concluded that this change was not statistically significant, although some local improvements may have been realized. It was noted that changes in meteorology introduced a confounding factor in analyzing the air quality data.

A second report by Vogt *et al.* (1994) took a closer look at the weather patterns during the high CO seasons. They analyzed data from two oxyfuel seasons 1992-3 and 1993-4 as well as some prior years. They focused on several parameters including atmospheric stability, wind direction, wind speed, temperature and precipitation. They concluded that any benefit in CO reduction from oxyfuel usage was masked by the influence of meteorological conditions.

A statistical analysis of CO trends from about 1987-9 to 1994 was made by Cornelius (1995) in an effort to find an effect that could be attributed to the North Carolina oxyfuel program. Ambient CO records were analyzed for oxyfuel areas and non-oxyfuel areas including, Raleigh, Durham, Greensboro, Winston-Salem, Charlotte, and Fayetteville. Meteorological data, notably precipitation events, were included in the analyses. The trends in ambient CO were determined for the years prior to the implementation of the oxyfuel program and were extrapolated into the oxyfuel seasons to generate predicted CO levels with which the observed levels were compared. Several areas were exempted from the oxyfuel program beginning with the 1994-5 winter season. All of the sites experienced generally declining CO trends. No quantitative factors were assigned to an oxyfuel effect for any area. In Raleigh, Durham, and Greensboro a reduction of CO during the oxyfuel season beyond the trend was observed, but it was concluded that this could be attributed to either weather or oxyfuel usage. In Winston-Salem the observed ambient CO levels showed no effect that could be attributed to oxyfuel usage.

Utah Study

Keislar *et al.* (1995) made a study of ambient CO concentrations to determine the effects of the oxyfuel program in Provo, Utah. Their approach was to measure CO and CO_2 concentrations at a number of test and control sites before, during, and after the local oxyfuel season, 1 November 1994 to 19 January 1995. The test sites included two street intersections, one mid-block location and one parking garage in Provo. Similar locations in Salt Lake City, which is geographically close but outside the Provo oxyfuel area, were monitored as a control during the test period. In addition the background CO and CO_2 concentrations were monitored. They used five separate numerical techniques to investigate the change in background corrected CO/CO_2 concentration ratios from Provo, after normalization to the Salt Lake City control. They report that their results show that nearly all of the observed CO at the study site can be attributed to mobile sources. Although their measurements are made on whole air samples, their analysis method corrects for the background concentration. Therefore this study is more an analysis of the emission effect of oxyfuels than of the effect on the urban ambient CO level. The test fleet is probably a mix of cold and hot vehicles. The Provo oxyfuel sales indicate that 30 to 35% of the fuel was a 15% by volume MTBE blend and the remainder was a 7.8% by volume ethanol blend. Both contain about 2.7% oxygen by weight.

Although some reduction in CO is observed at the Provo sites during the oxyfuel season, Keisler *et al.* state that no reduction is significant at the 95% confidence level for more than one numerical analysis technique. They report an upper limit of 9-10% mean reduction at the 80% confidence level in the observed CO/CO_2 ratios for morning rush hour samples. Two of the analysis methods found reductions of 15% and 35% in the parking garage at the 82 and 91% confidence levels, respectively. The latter they characterize as cold start data. Keislar *et al.* report that the sensitivity of their method of measuring an oxyfuel effect suffered, because of the use of differences and ratios of individual measurements. Keislar (personal communication, 1995) indicates that some of the background measurements may have been contaminated by local emissions. In that case, their report will underestimate the benefit of the oxyfuel and the reduction would be greater than 10%. The reported 10% upper limit corresponds to the vehicle CO emission benefit. If the ambient concentration benefit is assumed to be 80% of this, the ambient benefit is about 3% per wt % oxygen.

Other Ambient Air Quality Effects

The primary reason for the winter oxyfuel program is to reduce ambient CO concentrations, but emission studies show some effects on other emitted pollutants as well. Unfortunately, there are very few studies of the effects of the winter oxyfuel program on ambient air quality other than the CO studies. Anderson *et al.* (1994, 1995) have reported measurements of formaldehyde (CH_2O) and acetaldehyde (CH_3CHO) in Denver, Colorado, since 1988. They find the winter concentrations of these toxic gases are correlated with ambient CO and conclude that vehicles are an important source of both compounds. Vehicle emission studies find that ethanol gives an enhanced acetaldehyde emission and MTBE gives an enhanced formaldehyde emission. Their data (Anderson *et al.*, 1995) show a steady increase in the formaldehyde to acetaldehyde ratio during the winters from 1988 to 1992-3. During this period the winter oxygenate was changing from about 95% market share MTBE and 5% ethanol to about 55% market share MTBE and 45% ethanol. Thus direct vehicle emission effects are expected to exhibit an opposite trend, i.e., with acetaldehyde concentrations increasing relative to formaldehyde concentrations. The reason for this discrepancy is not understood but may involve unknown factors in the emissions and sources, in atmospheric loss mechanisms (such as heterogeneous reactions), or in the sampling and measurement of the aldehydes. The winter concentrations of these gases are around 4 to 6 ppbv for formaldehyde and 2 ppbv for acetaldehyde in recent years (Anderson *et al.*, 1995).

The Utah Division of Air Quality conducted a study during the 1994-5 winter oxyfuel season in Utah County (Provo) to determine the effect of oxyfuel usage on the concentration of small particles, PM_{10}, in the urban atmosphere (Olson, 1995). PM_{10} refers to particles with diameters of 10 μm or less. These particles are drawn into the lungs and are suggested to be a human health hazard. Particles were sampled and analyzed in both Utah County and in Salt Lake County, which is not an oxyfuel area, as a control during and after the oxyfuel season. Utah County used a 2.7 wt % oxygen fuel during the test period. Unusual meteorology was experienced during the 1994-5 oxyfuel season and there were few atmospheric inversions, which usually account for high levels of small particles. The unusual meteorology also caused some contamination of the Salt Lake County control area with particles from Utah County. An analysis and extrapolation of the data indicated that under extreme conditions of very high particle densities, oxyfuel usage could contribute a small increase in small particle concentration. Cooper *et al.* (1995) have proposed that increases in vehicle NO_x and aldehyde emissions caused by fuel oxygenates may enhance the formation of small particles during winter oxyfuel periods.

There are numerous stations making air quality measurements in many urban sites, but no other studies or reports or attempts to assess oxyfuel effects on winter air quality are known. Therefore one must rely upon emission studies and models to estimate the effects of other pollutants on air quality.

Summary of Ambient Air Quality Effects of Oxyfuels

Table 1.13 summarizes the results from studies of the effects of the winter oxygenated fuel program on urban CO concentrations. They are listed in the approximate order in which they are rated to provide a quantitative measurement of the oxygenated fuel effect, with the best studies at the top. The best studies account for the effects of trends and meteorology. The ambient CO analyses are rated as the most significant measurement of the effectiveness of the program, to reduce urban CO concentrations. As described above five analyses were unable to find a statistically significant reduction in CO that could be attributed to the oxyfuel, while four found reductions that generally fall in the range of 5 to 10%. It is not clear whether or not the studies not finding a measurable oxyfuel effect would be capable of detecting a 5 to 10% reduction in CO. All of the studies report a steady downward trend in CO and problems from the confounding effects of meteorology in extracting an oxyfuel effect. Several of the studies observe that the winter of 1992-3, the first year of the oxyfuel program, was an unusually rainy season and was accompanied by an unusually large drop in CO concentrations. Since the rainy weather is characterized by more than usual dispersion of pollution, a decrease of about 20% in the ambient CO observed that season is attributed to the weather (Heil, 1993 and Dolislager, 1996).

Table 1.13 Summary of studies analyzing ambient CO data to measure the effectiveness of the winter oxyfuel program. The studies are ranked with the ones rated the most quantitative listed first.

Study	Winter Years	Area	Wt % Oxygen	Reported CO Reduction
Dolislager (1996)	1992 to 1995	CA	2	5 to 10%
Mannino and Etzel (1996)	1989 to 1991	AZ CO NV	1.5 to 2.7	~10%
Wolfe *et al.* (1996)	1989 to 1995	CO	2 to 3.1	(7 ± 10)%
Heil (1993)	1992/3	AK	2.7	<11%
Vogt *et al.* (1995)	1992 to 1994	NC	2.7	not detectable
Cornelius (1995)	1992 to 1994	NC	2.7	not detectable

The first column gives the reference for the study.
The second column indicates the years of data analyzed.
The third column indicates the states covered in the analysis.
The fourth column indicates the level of oxygenate used.
The CO reductions reported should be considered an upper limit to the oxyfuel contribution, because other CO reduction programs may also contribute to the reduction as described in the text.

The MOBILE 5a Model predicted reductions in CO emissions range from about 16% in California areas where fuel oxygenate concentration increases by about 1.7 wt % oxygen during the winter oxyfuel season to about 30% in Colorado where a 3.1 to 3.3 wt % oxygen fuel is used. These emission predictions can be adjusted by a factor of 0.8 to account for an estimated 80% (to 95%) of the urban CO coming from gasoline-fueled vehicles. Thus one expects reductions in ambient CO due to oxyfuels of from 13% to 24%. A reduction of 7 to 8% is representative of the effects reported in Table 1.13 and this falls below the predicted reductions by a factor of two to three. It should be noted that the observed reductions in ambient CO are consistent with the predicted oxyfuel effects from the Complex Model. The data in Table 1.9 lead to estimated reductions in ambient CO of about 4 to 8%, which are consistent with the observations summarized in Table 1.13.

The areas with winter oxygenated fuel programs generally have implemented other programs to reduce the winter CO levels. These include Inspection/Maintenance programs, which EPA believes is very effective at reducing CO emissions as indicated by the MOBILE 5a Model prediction of about -27% in Table 1.8. Other programs attempt to reduce urban vehicle traffic by encouraging mass transit, car pool, and van pool commuting. In Colorado wood burning fires are prohibited during periods of high CO and wood burning fireplaces are forbidden in new construction and remodel projects. These types of programs have the potential of augmenting reductions in CO concentrations in oxyfuel program areas. Therefore the observed reductions in ambient CO reported in Table 1.13 should be viewed as upper limits to the oxyfuel effect as they may overestimate the oxyfuel benefit by neglecting contributions from other CO reduction programs.

Some of the important conclusions regarding ambient air quality studies can be summarized as follows:

- Measurements of urban CO concentrations have been examined by a number of researchers to assess the effects of the winter oxyfuel program. The reported reductions in CO that are attributed to oxyfuels range from undetectably small up to about 10%. Variations in CO concentrations due to meteorology make it difficult to accurately measure small changes. The observed CO reduction is about one half to one third of the effect predicted by the EPA MOBILE 5a Model but is consistent with the effect predicted by the EPA Complex Model. The measured reduction represents an upper limit to the CO effect of oxyfuels because other CO reduction programs may contribute to the observed decrease.

- The effects of oxyfuels on ambient air pollutants other than CO are uncertain. Very little has been done to study ambient air pollutants such as toxics and particles. Most information on oxyfuel effects on other pollutants are derived from vehicle emission studies and models.

- A very small fraction of the ambient CO measurement data available has been analyzed for oxyfuel effects. The benefits of oxyfuels on ambient air quality have not been proven in cold climate areas.

- The fate of the oxygenate vapors in the atmosphere is assessed. During the winter the level of atmospheric chemistry (photochemistry) that normally oxidizes pollutants is very low in most areas. Some of the oxygenate is expected to be scrubbed from the atmosphere by precipitation. The fate for most of the vapors appears to be dispersion and dilution from the urban atmosphere into the free troposphere where it is slowly, on a time scale of weeks and months, photooxidized.

SUMMARY AND CONCLUSIONS

This chapter evaluates vehicle emission data, vehicle emission models, and ambient air quality studies to assess the effects of the winter oxyfuel program on air quality. The focus is upon carbon monoxide, a poisonous gas emitted in gasoline fueled vehicle exhaust. Vehicle emission studies at about 50 °F and higher temperatures find that adding an oxygenate to the fuel reduces CO emissions. For most vehicles the CO reductions fall in the range of about 3 to 6% per wt % oxygen. The standard emission test used to derive these emission effects is conducted at 75 °F. Emission data for winter temperatures below about 50 °F are very limited and inadequate for a reliable prediction of oxyfuel effects. The available data indicate a decreased effectiveness of the fuel oxygenate at low temperatures. Some vehicles at low temperatures have been found to respond to fuel oxygenate with increased CO emissions.

Emission studies show that the pollutant emissions from vehicles have been steadily declining for over two decades. EPA mandated reductions in vehicle emissions and improved emission control technology largely account for the decline. The CO emissions from new 1996 model year vehicles, for example, are about twenty five times less than from new 1970 vintage vehicles. The current generation of vehicles employs oxygen sensors in the exhaust and computer controlled fuel injection to regulate the engine air/fuel ratio. This coupled with high efficiency catalysts greatly reduces the pollutant emissions. The oxygen sensor in the exhaust stream of vehicles decreases the effectiveness of adding fuel oxygenate to reduce CO emissions. Therefore recent generations of vehicles have both lower CO emission levels and lower oxyfuel effectiveness than most older vehicles.

The EPA MOBILE 5a Model is used by states to predict the effects of oxygenate on vehicle emissions and gives predicted reductions of about 9.4% per wt % oxygen. This corresponds to a predicted 25% reduction in CO emissions in areas using a 2.7 wt % oxygen fuel. The model appears to overestimate the effect of oxyfuels on CO emissions by a factor of two or so, in part because it employs very large CO reduction parameters, about 10-11% per wt % oxygen for high emitting vehicles, and an on-road fleet distribution with a large population of high emitting vehicles. The MOBILE Model has no correction for oxyfuel effects at temperatures below 75 °F. The EPA Complex Model was developed to characterize emissions from 1990 model year vehicles, but EPA believes it has some value predicting fuel effects for the present on-road fleet. The Complex Model is also based on 75 °F emission studies. It predicts an oxyfuel reduction in CO that is about one third of the value predicted by the MOBILE 5a Model.

It has not been proven that either the MOBILE 5a Model or the Complex Model is capable of accurately predicting the emissions of the on-road fleet. The standard emission test protocol, the Federal Test Procedure, is unlikely to accurately represent the broad range of conditions that affect vehicle emissions in urban driving. Also the emission levels of the on-road fleet are not known accurately. It is concluded that the most reliable assessment of on-road vehicle emissions is made by examining ambient air quality data.

Relatively few attempts have been made to test the effect of the winter oxyfuel program on urban air quality. The studies that have been conducted, find that the observable reduction in CO that can be attributed to winter oxyfuels ranges from an effect that could not be quantified to a reduction of about 10%. The observed reduction is considered an upper limit because other air quality improvement programs, such as Inspection/Maintenance programs, are conducted parallel to the oxyfuel programs and are likely to contribute some CO reduction. The larger CO reductions are found in warmer climates, California and the southwestern states. Attempts to measure the effectiveness of the program are confounded by meteorology which can cause large year-to-year variations in urban CO concentrations of up to about 20% (Heil, 1993 and Dolislager, 1996). Cold weather and inversions tend to increase ambient CO levels, whereas windy weather and precipitation tend to decrease ambient CO levels. In addition there has been a steady decline in urban CO concentrations for over two decades. This trend is attributed largely to the effects of EPA mandated reductions in vehicle emissions and the resultant developments in vehicle emission control technology.

The studies of ambient CO concentrations with the best accuracy and controls report the oxyfuel effect is in the range of 5 to 10%. If a value of 7 or 8% is taken as representative of the observed reduction in urban CO attributable to winter oxyfuels, this is a factor of two to three times smaller than the value predicted by the EPA MOBILE 5a Model but is comparable to the prediction of the EPA Complex Model.

The effects of oxyfuels on some other vehicle pollutant emissions have been studied. The emissions of most volatile organic compounds are reduced by fuel oxygenate, notably the toxic compounds 1,3-butadiene and benzene. On the other hand, the emissions of a toxic aldehyde, either formaldehyde or acetaldehyde depending upon the specific oxygenate used, are increased by fuel oxygenate. The emission studies reviewed here indicate that nitrogen oxide emissions increase with oxygenate addition, particularly at levels of oxygenate above about 2 wt % oxygen. Although this observation conforms to the combustion engineering expectation of enleanment, the emission data analysis performed to develop the Complex Model indicates a negligible effect of oxygenate on NO_x emissions.

Two of the major findings of this assessment are that emission data are inadequate to assess the effects of fuel oxygenate at low temperatures, i.e., winter conditions, and that the available analyses of air quality data do not support the large CO reduction predicted by the EPA MOBILE Model. The same issues were identified three years ago at a conference on MTBE and other oxygenates (USEPA, 1995c) sponsored by the Environmental Protection Agency, the American Petroleum Institute and the Oxygenated Fuels Association.

To answer the question of whether the winter oxyfuel program reduces CO in cold weather areas, a carefully designed and conducted analysis of the ambient air quality data is required. Studies that do not account for the effects of the year-to-year trends and meteorology are of limited value. An analysis of data for months within the oxyfuel season and for some months out of the oxyfuel season is required to establish trends before and during the oxyfuel years. As a control for the effects of meteorology, a similar analysis should be made of CO data for adjacent urban areas without an oxyfuel program. Another valuable test of the oxyfuel program could be made on the data from areas that have discontinued the program. In these areas the oxyfuel off-on-off seasons provide a unique data set for examining the ambient air quality effects of oxyfuels. There is a very large volume of data from urban CO monitors that has never been critically analyzed to test for a benefit.

If it is assumed that the winter oxyfuel program reduces urban CO by about 10%, which is a reasonable upper limit from the available studies, the magnitude of the reduction in urban CO concentration can be estimated. EPA data for the areas with winter oxyfuel programs indicate an average CO concentration of about 1.4 ppmv during the last quarter of 1994 and the first quarter of 1995 (J.R. Cook, personal communication). The average CO reduction would be about 0.14 ppmv or less. For comparison the air quality monitors that report urban CO concentrations measure concentration with an accuracy of ±20%, or ±0.28 ppmv at the 1.4 ppmv level. The global (clean air) background CO concentration is about 0.1 ppmv.

The reported reduction in the ambient CO from the winter oxyfuel program could provide some basis for evaluating the program. Because the winter oxyfuel program is intended to reduce the number of exceedances of the CO air quality standard, it would be useful to have a measure of the number of exceedances that have been avoided by the program. And finally the most important issue concerns human health effects. The approximate 10%

reduction in ambient CO found in this assessment could be useful input for evaluating the health benefits of the program.

At the end of each of the previous sections there is a brief summary of the conclusions of that section. The major findings of this assessment are as follows.

Vehicle Emission Effects

- CO exhaust emissions from vehicles operating at temperatures of 50°F and higher are reduced by oxyfuels by about 2 to 10% per wt % oxygen in Federal Test Procedure studies. For most vehicles the reductions are about 3 to 6% per wt % oxygen which corresponds to about 8 to 16% CO reduction for a 2.7 wt % oxygen fuel. The CO emission reduction is generally smaller in vehicles with newer technology: fuel injected, adaptive learning, closed loop, three-way catalysts; and larger in vehicles with older technology: carbureted and oxidation catalysts. Malfunctioning, high CO emitting vehicles operating fuel rich also experience larger CO reduction benefits from oxyfuels.

- The low temperature vehicle emission database is inadequate. Oxyfuel effects on vehicle CO emissions are uncertain at temperatures below 50°F. Low temperature studies show some benefits down to 20 °F in some vehicles, but generally the results are not conclusive. Some studies report an increase in CO emission with oxyfuels at low temperatures. It has not been demonstrated that oxyfuels will significantly improve air quality at low temperatures.

- Hydrocarbon exhaust emissions from vehicles are reduced by 1 to 7% per wt % oxygen by oxyfuels. Generally the benefits are lower in new technology vehicles and larger in older and higher emitting vehicles.

- Nitrogen oxide exhaust emissions are not changed significantly by low concentrations of oxygenates but studies reviewed in this assessment show an increase in NO_x emissions with oxygenate concentrations higher than about 2 wt % oxygen.

- Fuel oxygenates decrease vehicle emissions of the toxics, benzene and 1,3-butadiene.

- Fuel oxygenates increase emissions of toxic aldehydes. Ethanol and ETBE increase acetaldehyde emissions by large amounts. MTBE increases formaldehyde emissions.

- Some but not all remote sensing and tunnel studies find a large reduction in CO emissions attributable to oxyfuel use in on-road vehicles. The reported CO benefits are about 10% per wt % oxygen. Since the sampled vehicles are operating in a hot stable mode, this benefit is likely to be larger than the FTP benefit.

- Fuel vapor pressure and sulfur content have been shown to strongly influence CO emissions, but these variables are not employed as a part of the CO emission control strategy in most areas.

Model Predictions

- The EPA MOBILE 5a Model is used by EPA and the states to predict the effects of the winter oxyfuel programs on urban fleet emissions. It appears to overestimate the benefits of oxyfuels on fleetwide CO emissions by about a factor of two. The model predicted benefit for high emitters is very large and the fleet distribution has a large population of high emitters. The model predicted CO reduction is much larger when compared to ambient air data.

- The EPA Complex Model is used to assess the effects of fuel composition and vehicle technology on vehicle pollutant emissions. EPA believes it can be used to predict fuel effects on the emissions of the on-road fleet. The Complex Model estimates a fleetwide reduction in CO emissions from oxyfuel that is about one third of the value predicted by the MOBILE 5a Model. The Complex Model is focused on 1990 model year technology representing vehicles with lower CO emission levels and smaller oxyfuel CO reductions than the MOBILE 5a Model.

- The EPA Complex Model estimates a negligible effect of fuel oxygenate on fleetwide NO_x emissions at oxygenate levels up to 3.5 wt % oxygen. This estimate does not agree with the conclusion drawn from the emission studies reviewed in this assessment but is based upon an analysis of a larger data set.

- No existing EPA model is capable of accurately predicting oxyfuel effects at temperatures below about 50 °F. The emission data available for assessing the effects of low temperature on oxyfuel performance is inadequate and has not been incorporated into the MOBILE 5a or Complex Models.

- Much of the data upon which the EPA MOBILE 5a Model is based have not been published in the peer reviewed literature.

Air Quality Effects of Oxyfuels

- Carbon monoxide concentration data for some urban areas have been examined by several researchers to assess the effects of the winter oxyfuel program on ambient air quality. The reported changes in CO that are attributed to oxyfuels range from an effect that could not be quantified up to about a 10% reduction. Variations in CO concentrations due to meteorology make it difficult to accurately measure small changes of the order of 10%. The observed reductions in CO are upper limits and correspond to about one half to one third of the effect predicted by the EPA MOBILE 5a Model but are consistent with the effect predicted by the EPA Complex Model. The measured reduction may represent an upper limit to the CO effect of oxyfuels because other CO reduction programs in winter oxyfuel areas may contribute to the observed decrease.

- Urban concentrations of CO have been declining for about two decades with a rate of about 2.8% per year for the last 10 years. This decrease is attributed largely to stringent EPA mandated vehicle emission standards and to improved vehicle emission control technology, although other air quality programs such as Inspection/Maintenance may also contribute.

- The effects of oxyfuels on ambient air concentrations of pollutants other than CO are uncertain. Very little has been done to assess oxyfuel effects on ambient air concentrations of pollutants such as toxics and particles. Most information on oxyfuel effects on other pollutants is derived from vehicle emission studies and models which may not be directly applicable to the ambient air effects of the on-road fleet.

- A very small fraction of the ambient CO measurement data available has been critically analyzed for oxyfuel effects. The benefits of oxyfuels on ambient air quality have not been proven in cold climate areas.

- The fate of the oxygenate vapors in the atmosphere is assessed here. During the winter the level of atmospheric chemistry (photochemistry) that normally oxidizes pollutants is very low in most areas. Some of the oxygenate is expected to be scrubbed from the atmosphere by precipitation. The fate for most of the vapors appears to be dispersion and dilution from the urban atmosphere into the free troposphere where it is slowly, on a time scale of weeks and months, photooxidized.

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REFERENCES

Anderson, L.G., P. Wolfe, R.A. Barrell, and J.A. Lanning, 1994, The effects of oxygenated fuels on the atmospheric concentrations of carbon monoxide and aldehydes in Colorado, in Alternative Fuels and the Environment, edited by F.S. Sterrett, Lewis Publishers, Boca Raton.

Anderson, L.G., P. Wolfe, and J.A. Lanning, 1995, The effects of oxygenated fuels on carbon monoxide and aldehydes in Denver's ambient air, Proceedings of the Conference on MTBE and Other Oxygenates: A Research Update, held in Falls Church, VA, July 26-28, 1993, U.S. Environmental Protection Agency Technical Report, EPA/600/R-95/134.

Atkinson, R., 1989, Kinetics and mechanisms of the gas-phase reaction of the hydroxyl radical with organic compounds, J. Phys. Chem. Ref. Data, Monograph 1: 1-246.

Atkinson, R., 1994, Gas-phase tropospheric chemistry of organic compounds, J. Phys. Chem. Ref. Data, Monograph 2: 1-216.

Atkinson, R., D.L. Baulch, R.A. Cox, R.F. Hampson, Jr., J.A. Kerr, and J. Troe, 1992, Evaluated kinetic and photochemical data for atmospheric chemistry, Supplement V, J. Phys. Chem. Ref. Data, 21: 1125-1568.

Auto/Oil AQIRP,1990, Technical Bulletin No. 1: Initial mass exhaust emissions results from reformulated gasolines, Auto/Oil Air Quality Improvement Research Program.

Auto/Oil AQIRP, 1991, Technical Bulletin No. 2: Effects of fuel sulfur levels on mass exhaust emissions, Auto/Oil Air Quality Improvement Research Program.

Auto/Oil AQIRP, 1991, Technical Bulletin No. 6: Emissions results of oxygenated gasolines and changes in RVP, Auto/Oil Air Quality Improvement Research Program.

Auto/Oil AQIRP, 1992, Technical Bulletin No. 8: Effects of fuel sulfur on mass exhaust emissions, air toxics, and reactivity, Auto/Oil Air Quality Improvement Research Program.

Auto/Oil AQIRP, 1992, Technical Bulletin No. 9: Comparison of effects of MTBE and TAME on exhaust and evaporative emissions, air toxics, and reactivity, Auto/Oil Air Quality Improvement Research Program.

Barth, E.A., 1984, Effects of Reid vapor pressure on hydrocarbon evaporative emissions, U.S. Environmental Protection Agency Report, EPA-AA-TEB-84-3.

Becker, J.P. and J.A. Rutherford, 1979, Analysis of Oregon's Inspection and Maintenance Program, Air Pollution Control Association Paper No. 79-7.3.

Benson, J.D., V. Burns, R.A. Gorse, A.M. Hochhauser, W.J. Koehl, L.J. Painter, R.M. Reuter, 1991, Effects of gasoline sulfur level on mass exhaust emission - Auto/Oil Air Quality Improvement Research Program, SAE Technical Paper Series No. 912323.

Bishop, G.A., and D.H. Stedman, 1989, Oxygenated fuels, a remote sensing evaluation, SAE Technical Paper Series No. 891116.

Bishop, G.A., and D.H. Stedman, 1990, On-road carbon monoxide emission measurement comparisons for the 1988-1989 Colorado oxy-fuels program, Environ. Sci. and Technol., 24: 843-847.

Born, G.L., S.V. Lucas, R.D. Scott, T.H. DeFries, and S. Kishan, 1994, Effect of use of low oxygenate gasoline blends upon emissions from California vehicles, Final Report, Contract No. A932-159, prepared for California Air Resources Board and South Coast Air Quality Management District.

Bruetsch, R.I., 1981, Carbon monoxide and non-FTP ambient temperature, U.S. Environmental Protection Agency Technical Report, EPA/AA/CTAB/TA/81-7.

Cadle, S.H., R.A. Gorse, and D.R. Lawson, 1993, Real-world vehicle emissions: A summary of the Third Annual CRC-APRAC On-Road Vehicle Emissions Workshop, J. Air & Waste Manage. Assoc., 43: 1084.

CARB, 1992, Request for a waiver of the minimum oxygen content requirements for wintertime gasoline requirements, pursuant to Federal Clean Air Act section, 211(m)(3)(A), California Air Resources Board, California Wintertime Oxygenates Program, Technical Support Document.

Cooper, J.A., B.C. Patterson, and D.A. Drerup, 1995, Comments on results from the State of Utah's 1994-1995 winter study of the effects of oxygenated gasoline on PM_{10}, TRC Environmental Corporation Report, Tigard, Oregon.

Cornelius, W.L., 1995, Effects of North Carolina's oxygenated fuel program on ambient carbon monoxide concentration, Report to the North Carolina Department of Environment, Health, and Natural Resources Air Quality Section.

Darlington, T., 1981, Emission effects of inspection and maintenance at cold temperatures, U.S. Environmental Protection Agency Technical Report, EPA-AA-IMA-81-24.

Dolislager, L.J., 1993, Did the wintertime oxygenated fuels program reduce carbon monoxide concentrations in California?, Proceedings of the 10th International Symposium on Alcohol Fuels, Colorado Springs, CO, November 7-10.

Dolislager, L.J., 1996, The effect of California's Wintertime Oxygenated Fuels Program on ambient carbon monoxide concentrations, submitted to: J. Air & Waste Manage. Assoc.

Doyon, J., K. Mitchell, and T. Mayhew, 1993, The effect of gasoline composition on vehicle tailpipe emissions at low ambient temperature, SAE Technical Paper Series No. 932669.

Fujita, E.M., B.E. Croes, C.L. Bennett, D.R. Lawson, F.W. Lurmann, and H.H. Main, 1992, Comparison of emission inventory and ambient concentration ratios of CO, NMOG, and NO_x in California's South Coast Air Basin, J. Air & Waste Manage. Assoc., 42: 264.

Glover, E.L. and D.J. Brzezinski, 1989, MOBILE4 exhaust emission factors and Inspection/Maintenance benefits for passenger cars, U.S. Environmental Protection Agency Technical Report, EPA-AA-TSS-I/M-89-3

Goldan, P.D., M. Trainer, W.C. Kuster, D.D. Parrish, J. Carpenter, J.M. Roberts, J.E. Yee, and F.C. Fehsenfeld, 1995, Measurements of hydrocarbons, oxygenated hydrocarbons, carbon monoxide, and nitrogen oxides in an urban basin in Colorado: Implications for emission inventories, J. Geophys. Res., 100: 22,771-22,783.

Goldstein, A.H., S.C. Wofsy, and C.M. Spivakovsky, 1995, Seasonal variations of nonmethane hydrocarbons in rural New England: Constraints on OH concentrations in northern midlatitudes, J. Geophys. Res., 100: 21,023-21,033.

Gupta, P., 1995, The contribution of methylnitronapthalenes to the vapor-phase mutagenicity observed in ambient air samples collected at Redlands, CA, M.S. Thesis, University of California, Riverside, March 1995.

Harvey, C.A., and B. Michael, 1985, Exhaust and evaporative emissions of high mileage passenger cars, U.S. Environmental Protection Agency Technical Report, EPA-AA-TSS-PA-85-1.

Heil, C.L. 1993, Assessment of the Anchorage oxygenated fuels program on ambient carbon monoxide concentrations, Master of Environmental Quality Science Thesis, School of Engineering, University of Alaska, Anchorage.

Hochhauser, A.M., J.D. Benson, V. Burns, R.A. Gorse, W.J. Koehl, L.J. Painter, B.H. Rippon, R.M. Reuter, and J.A. Rutherford, 1991, The effect of aromatics, MTBE, olefins, and T_{90} on mass exhaust emissions from current and older vehicles - The Auto/Oil Air Quality Improvement Research Program", SAE Technical Paper Series No. 912322.

Hood, J., and R. Farina, 1995, Emissions from light duty vehicles operating on oxygenated fuels at low ambient temperatures: A review of published studies, SAE Draft for Fuels and Lubricants Meeting in Toronto, SAE Paper No. 952403.

Keislar, R.E., J.L. Bowen, E.M. Fujita, and D.R. Lawson, 1995, Effect of oxygenated fuels on ambient carbon monoxide concentrations in Provo, Utah, Final Report prepared by the Desert Research Institute for Geneva Steel Company.

Kirchstetter, T.W., B.C. Singer, R.A. Harley, G.R. Kendall, and W. Chan, 1996, Impact of oxygenated gasoline use on California light-duty vehicle emissions, Environ. Sci. and Technol., 30, 661-670.

Knepper, J.C., W.J. Koehl, J.D. Benson, V.R. Burns, R.A. Gorse, Jr., A.M. Hochhauser, W.R. Leppard, L.A. Rapp, and R.M. Reuter, 1993, Fuel effects in Auto/Oil high emitting vehicles", SAE Technical Paper Series No. 930137.

Kummer, J.T., 1980, Catalysts for automobile emission control, Prog. Energy Combust. Sci., 6:177-199.

Lawson, D.R., 1993,'Passing the Test - Human behavior and California's smog check program", , J. Air & Waste Manage. Assoc., 43, 1567-1575.

Lax, D., 1994, The effects of fuel RVP and fuel blends on emissions at non-FTP temperatures, American Petroleum Institute, Health and Environmental Sciences Dept., Vol. 1: Summary Report, API Publication 4533.

Livo, K.B., and W. Miron, 1995, 1995 Oxygenated Gasoline Program, Air Pollution Control Division Annual Oxygenated Gasoline Report to the Colorado Air Quality Control Commission, Colorado Department of Public Health and Environment.

Lorang, P.A., J.T. White III, and D.J. Brzezinski, 1982, In-use emissions of 1980 and 1981 passenger cars: Results of EPA testing, SAE Technical Paper Series No. 820975.

Lorang, P.A., 1984, Emissions of in-use vehicles: Update on the U.S. experience, U.S. Environmental Protection Agency Technical Report, EPA-AA-TSS-85-5.

Mannino, D.M., and R.A. Etzel, 1996, Are oxygenated fuels effective? An evaluation of ambient carbon monoxide concentrations in 11 western states, 1986 to 1992, J. Air & Waste Manage. Assoc., 46, 20.

Mayotte, S.C., C.E. Lindhjem, V. Rao, and M.S. Sklar, 1994a, Reformulated gasoline effects on exhaust emissions: Phase I: Initial investigation of oxygenate, volatility, distillation and sulfur effects, SAE Technical Paper Series No. 941973

Mayotte, S.C., C.E. Lindhjem, V. Rao, and M.S. Sklar, 1994b, Reformulated gasoline effects on exhaust emissions: Phase II: Continued investigation of the effects of fuel oxygen content, oxygenate type, sulfur, olefins and distillation parameters, SAE Technical Paper Series No. 941974.

Michael, R.B., 1981, A study of the effectiveness of mechanic training for vehicle emissions Inspection and Maintenance programs, U.S. Environmental Protection Agency Technical Report, EPA-AA-IMS-81-11.

Michael, R.B., 1982, Disablement testing of 1981-1982 model year vehicles with closed-loop emission control systems, U.S. Environmental Protection Agency Technical Report, EPA-AA-TSS-82-5.

Michael, R.B., 1983, The emission effects of misfueling five 1981-1982 model year automobiles with 10 continuous tankfuls of leaded gasoline, U.S. Environmental Protection Agency Technical Report, EPA-AA-TSS-83-2.

Michael, R.B., 1984, Misfueling emissions of three-way catalyst vehicles, SAE Technical Paper Series No. 841354.

Montalvo, D.A. and C.T. Hare, 1985, Crankcase emissions with disabled PCV systems, U.S. Environmental Protection Agency Report, EPA 460/3-84-011.

Morris, R.D., E.N. Naumova, and R.L. Munasinghe, 1995, Ambient air pollution and hospitalization for congestive heart failure among elderly people in seven large U.S. cities, Am. J. Pub. Health, 85: 1361.

Most, W.J., 1989, Coordinating Research Council study of winter exhaust emissions with gasoline/oxygenate blends, SAE Technical Paper Series No. 892091.

Olson, R. N., 1995, A study of the effects of oxygenated gasoline on particulate concentrations in Salt Lake and Utah counties during the winter season, 1994-5, State of Utah, Department of Environmental Quality, Division of Air Quality, Report No. AMC-126-95.

Pidgeon, W.M., 1984, Effect of evaporative canister removal and Reid vapor pressure on hydrocarbon evaporative emissions, U.S. Environmental Protection Agency Report, EPA-AA-TEB-84-04.

Pierson, W.R., 1995, Automotive CO emission trends derived from measurements in highway tunnels, , J. Air & Waste Manage. Assoc., 45: 831-832.

Pierson, W.R., A.W. Gertler, and R.L. Bradow, 1990, Comparison of the SCAQS tunnel study with other on-road vehicle emission data, J. Air & Waster Manage. Assoc., 40: 1495-1504.

Pierson, W.R., A.W. Gertler, N.F. Robinson, J.C. Sagebiel, B. Zielinska, G.A. Bishop, D.H. Stedman, R.B. Zweidinger, and W.D. Ray, 1996, Real-world automotive emissions — Summary of studies in the Fort McHenry and Tuscarora mountain tunnels, Atmos. Environ., 30: 2233-2256.

PRC Environmental Management, Inc., 1992, Final Report of the Performance Audit of Colorado's Oxygenated Fuels Program, prepared for the Colorado State Auditor. The Executive Summary of this report was published separately: C.E. Lyons and R.J. Fox, 1993, Quantifying the air pollution emissions reduction effectiveness and costs of oxygenated fuels, SAE Technical Paper Series No. 930374.

Prinn, R.G., R.F. Weiss, B.R. Miller, J. Huang, F.N. Alyea, D.M. Cunnold, P.J. Fraser, D.E. Hartley, P.G. Simmonds, 1995, Atmospheric trends and lifetime of CH_3CCl_3 and global OH concentrations, Science, 269: 187-192.

Rao, V., 1996, Development of an exhaust carbon monoxide emissions model, SAE Technical Paper Series No. 961214.

Rapp, L.A., J.D. Benson, V.R. Burns, R.A. Gorse, Jr., A.M. Hochhauser, J.C. Knepper, W.J. Koehl, W.R. Leppard, L.J. Painter, R.M. Reuter, and J.A. Rutherford, 1993, Effects of fuel properties on mass exhaust emissions during various modes of vehicle operation, SAE Technical Paper Series No. 932726.

Reuter, R.M., R.A. Gorse, Jr., L.J. Painter, J.D. Benson, A.M. Hochhauser, B.H. Rippon, V.R. Burns, W.J. Koehl, and J.A. Rutherford, 1992, Effects of oxygenated fuels and RVP on automotive emissions - Auto/Oil Air Quality Improvement Program, SAE Technical Paper Series No. 920326

Rhudy, S.A., M.O. Rodgers, and N. Vescio, 1995, Seasonal measurements of motor vehicle emissions by remote sensing: Raleigh, North Carolina Oxygenated Fuels Program, submitted to: J. Air & Waste Manage. Assoc.

Robinson, N.F., W.R. Pierson, A.W. Gertler, and J.C. Sagebiel, 1996, Comparison of MOBILE 4.1 and MOBILE 5 predictions with measurements of vehicle emission factors in Fort McHenry and Tuscarora mountain tunnels, Atmos. Environ., 30: 2257-2267.

Rogers, J.D., 1990, Ultraviolet absorption cross sections and atmospheric photodissociation rate constants of formaldehyde, J. Phys. Chem., 94: 4011-4015.

Shelton, J.C., 1983, A study of exhaust emissions from thirty-five high mileage 1979 passenger cars, U.S. Environmental Protection Agency Report, EPA-AA-TEB-83-5.

Shelton, J.C., 1984, A study of exhaust emissions from forty high mileage 1981 passenger cars, U.S. Environmental Protection Agency Report, EPA-AA-TEB-84-5.

Shepard, S., J. Heiken, and J. Fieber, 1995, Analyses of Michigan and Rosemead remote sensing data sets, comparison of MOBILE 5a fleet emissions to Michigan remote sensing data, and comparison of EMFAC7F fleet emissions to Rosemead remote sensing data, Systems Applications International Technical Memorandum.

Smith, D.F., C.D. McIver, and T.E. Kleindienst, 1995, Kinetics and mechanism of the atmospheric oxidation of tertiary amyl methyl ether, Int. J. Chem. Kinet., 27: 453-472.

U.S. Environmental Protection Agency, 1983, Anti-tampering and anti-misfueling programs to reduce in-use emissions from motor vehicles, U.S. Environmental Protection Agency Report, EPA-AA-TSS-83-10.

U.S. Environmental Protection Agency, 1984, Fleet characterization data used for MOBILE3, U.S. Environmental Protection Agency Report, EPA-AA-TEB-84-2.

U.S. Environmental Protection Agency, 1985, MOBILE3 sensitivity analysis, U.S. Environmental Protection Agency Report, EPA-AA-TEB-EF-85-3.

U.S. Environmental Protection Agency, 1988, Derivation of technology specific effects of the use of oxygenated fuel blends on motor vehicle exhaust emissions, U.S. Environmental Protection Agency Technical Report, EPA-AA-TSS-PA-88-1.

U.S. Environmental Protection Agency, 1995a, Air Quality Trends, U.S. Environmental Protection Agency Report, EPA-454/F-95-003.

U.S. Environmental Protection Agency, 1995b, National Air Quality and Emissions Trends Report, 1994, U.S. Environmental Protection Agency Report, EPA-454/R-95-011.

U.S. Environmental Protection Agency, 1995c, Proceedings of the Conference on MTBE and Other Oxygenates: A Research Update, held in Falls Church, VA, July 26-28, 1993, U.S. Environmental Protection Agency Technical Report, EPA/600/R-95/134.

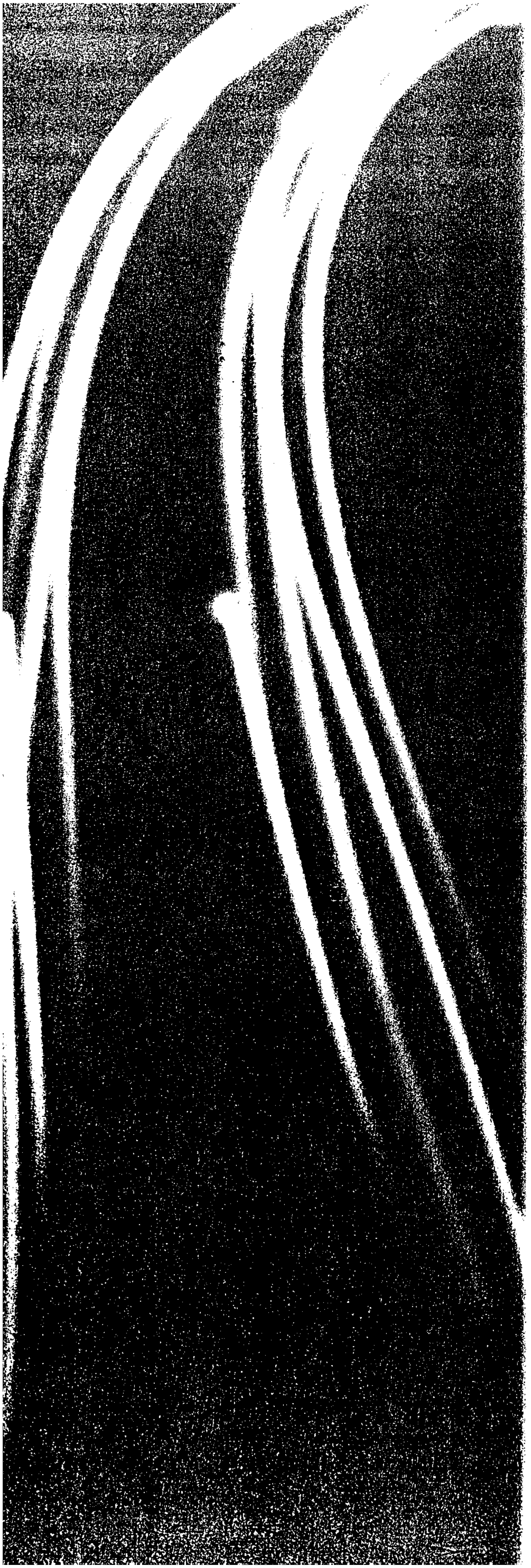
Vogt, D., 1994, An evaluation of the effect of North Carolina's 1992-93 oxygenated fuel program on ambient carbon monoxide levels in urban areas, Special Report No. 80 by the State Center for Health and Environmental Statistics, North Carolina Department of Health and Environmental Resources.

Vogt, D., T. Anderson, G. Murray, 1994, Summary of the evaluation of the effect of North Carolina's oxygenated fuel program on ambient carbon monoxide levels in urban areas:, North Carolina Department of Health and Environmental Resources Report, Raleigh, NC.

Wolfe, P., L.G. Anderson, J.A. Lanning, and R.H. Jones, 1994, A structural time series assessment of the effectiveness of the oxygenated fuel program in reducing carbon monoxide concentrations in five western U.S. cities, Air and Waste Management Association 87th Annual Meeting, Cincinnati, Ohio, Paper 94-WP91.04.

Wolfe, P., L.G. Anderson, J.A. Lanning, and R.H. Jones, 1996, Techniques for assessing the effectiveness of oxygenated fuels, paper to be presented at the Air and Waste Management Association 89th Annual Meeting, Nashville, Tennessee, June 23-28, Paper 96-WP89.06.

Zhang, Y., D.H. Stedman, G.A. Bishop, P.L. Guenther, and S.P. Beaton, 1995, Worldwide on-road vehicle exhaust emissions study by remote sensing, Environ. Sci. and Technol., 29, 2286-2294.



Fuel Oxygenates and Water Quality

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

Introduction and Scope

At the request of the U.S. Environmental Protection Agency (USEPA), the Office of Science and Technology Policy, Executive Office of the President, has coordinated an interagency assessment of the scientific basis and efficacy of the Nation's winter oxygenated gasoline program. This program mandates that compounds referred to as oxygenates be added to gasoline in select metropolitan areas across the United States to reduce the amount of carbon monoxide in the atmosphere in the winter. Many other areas of the United States have voluntarily chosen to use oxygenated fuels to abate air pollution and in severe ozone non-attainment areas reformulated gasoline is required. Fuel oxygenates are also used to enhance the octane of conventional gasolines-a practice that started in the late 1970's and continues today.

Methyl *tert*-butyl ether (MTBE) is the most commonly used fuel oxygenate. The U.S. production was estimated to be 8.0 billion kilograms in 1995. Essentially all of MTBE produced is used for fuel oxygenation. Ethanol (EtOH) is the second most used oxygenate in gasoline blending. EtOH production in the U.S. was estimated to be 4.3 billion kilograms in 1994. No data are available to estimate the portion of this production used in gasoline. Gasoline in carbon monoxide non-attainment areas must contain no less than 2.7 percent oxygen by weight. By volume, this requirement for MTBE and EtOH corresponds to 14.8 and 7.3 percent, respectively. Oxygenates in limited commercial use include ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), and diisopropyl ether (DIPE). Methanol (MeOH) is only being used as an oxygenate in a limited test program in California. *Tert* -butyl alcohol (TBA) has been added to gasoline in the past and is another potential fuel oxygenate, but is not currently produced for this purpose.

The purpose of this chapter is to address water-quality issues arising from the production, distribution, storage, and use of fuel oxygenates and their movement in the hydrologic cycle. It summarizes the scientific literature, data, and agency information on the sources, concentrations, behavior, and fate of fuel oxygenates, and their aqueous degradation products, in ground water and surface water. It also assesses the implications for drinking-water quality and aquatic life. Recommendations for further data-base compilation, monitoring, reporting of information, follow-up assessments, reports, and research efforts are also noted. Although the scope of this chapter is intended to cover all oxygenates and aqueous degradation products, little to no data and few scientific publications are available on the occurrence and behavior of oxygenates and their degradation products in ground water, surface water, and drinking water, except for MTBE. Some monitoring data are available for MTBE, however, these data sets are limited in scope.

Sources and Releases

Like hydrocarbon components of gasoline, fuel oxygenates are introduced to the environment during all phases of the petroleum fuel cycle, but the major sources of these compounds are likely associated with the distribution, storage, and use of oxygenated gasoline. Releases of gasoline containing oxygenates to the subsurface from, for example, underground storage tanks, pipelines, and refueling facilities provide point sources for entry of oxygenates as well as gasoline hydrocarbons into the hydrologic cycle. Urban and industrial runoff and wastewater discharges also represent potential sources of oxygenates to the environment. Water in contact with the spilled gasoline at the water table or in the unsaturated zone will solubilize oxygenates along with aromatic hydrocarbon constituents (e.g., benzene, toluene, ethylbenzene, and xylenes commonly referred to as BTEX). Such water can contain high oxygenate concentrations, for example, MTBE concentrations as high as 200,000 micrograms per liter[1] have been measured in ground water at a site of gasoline leakage. 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.

Petroleum storage tanks represent the largest populations of potential point sources of alkyl ether oxygenates to natural waters. For example, in 1988 the USEPA estimated that there were about 2 million underground storage tanks (USTs) at over 700,000 facilities. In the last several years, USTs have been removed at many facilities, and the current EPA UST universe is an estimated 415,000 UST facilities (about 195,000 are service stations) with about 1.2 million tanks. USEPA's statistics show that slightly over 300,000 sites have been identified with contamination levels that require corrective action. Cleanup has been completed at about 130,000 of these sites. Because of the inherent difficulty in determining leak rates, leak durations, and the use of oxygenates in the released gasoline, it is difficult to develop a reliable estimate of past or current annual release of fuel oxygenates from these sources. USEPA and State requirements exist and require that USTs be fully upgraded to meet stringent release prevention and detection standards by December 1998. The concurrent improvement in the physical condition of USTs and release-detection capabilities, coupled with a reduction in the population of tanks, should contribute to a considerable reduction in the annual volume of oxygenated gasoline released to natural waters from this subset of point sources.

Estimated releases of MTBE, MeOH, and TBA during industrial activity are mostly to the atmosphere and are reported to the USEPA in annual Toxics Release Inventory (TRI) submissions by manufacturers. The release of MTBE to the environment is almost entirely associated with its production, distribution, storage, and use as a fuel oxygenate, whereas releases of MeOH and TBA occur from various other industrial and commercial uses. Industrial releases of other fuel oxygenates ETBE, TAME, DIPE, and most notably EtOH are not included in the TRI.

Annual estimates of exhaust emissions from vehicles, evaporative losses from gasoline stations and vehicles, and releases from storage tanks have not been reported in the scientific literature but are perceived to be important sources of oxygenates (as well as other fuel components) released to the environment. Fuel oxygenates in the atmosphere, because of the dispersive effect of weather patterns and occurrence in precipitation, are considered a non-point source to the hydrologic cycle.

Occurrence in Air and Water and Significance to Drinking Water and Aquatic Life

The Clean Air Act, Clean Water Act, and Safe Drinking Water Act do not require the monitoring of fuel oxygenates in air, ground water, surface water, or drinking water. Therefore, comprehensive data to document the occurrence of fuel oxygenates in the major

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[1] One microgram per liter is approximately equivalent to one part per billion.

compartments of the hydrologic cycle across the Nation are not available from these programs.

MTBE and other fuel oxygenates are not included in routine ambient air monitoring done by local and State agencies. An exception is the State of California, which just recently began to monitor for MTBE and other volatile organic compounds (VOCs) in ambient air. Air-quality data have been collected for MTBE in six cities as part of special studies. These data are not sufficient to provide a national perspective, however, MTBE was found in urban air and the median concentrations within these urban areas ranged between 0.13 and 4.6 parts per billion by volume. Concentrations of MTBE in air near known sources of MTBE (gasoline stations, roadways, parking lots and garages, and so forth) are higher, and in many cases considerably higher than ambient urban air.

Little data exist on the occurrence of any of the fuel oxygenates in surface-water bodies including streams, rivers, lakes, and reservoirs. Similarly, little data exist on oxygenate occurrence for drinking water derived from surface water.

Storm water was sampled and analyzed for MTBE in 16 cities during 1991-95. These studies were completed by various U.S. Geological Survey (USGS) Districts to characterize storm-water runoff in cities with population exceeding 100,000. These projects were not specifically designed to determine the occurrence and sources of MTBE or other oxygenates, or other VOCs originating from gasoline. Northeastern States and California, high-use areas of MTBE oxygenated gasoline, were not sampled in the USGS studies. The compilations, however, do provide insight on the occurrence of MTBE in storm water in select cities. MTBE was detected in about 7 percent of 592 storm-water samples. When detected, concentrations ranged from 0.2 to 8.7 micrograms per liter, with a median of 1.5 micrograms per liter. Eighty-three percent of the detectable concentrations occurred during the winter season. Statistical evaluation comparing MTBE concentrations for samples collected during an April 1 to September 30 time period versus an October 1 to March 31 time period yielded statistically significant differences. MTBE was detected both in cities using oxygenated gasoline to abate carbon monoxide non-attainment and in cities presumed to have used MTBE in gasoline for octane enhancement.

Water-quality criteria for oxygenates to protect aquatic life have not been established. For the alkyl ether oxygenates, chronic aquatic toxicity data are lacking, and only limited information exists on acute toxicity and bioconcentration. Considerably more acute toxicity studies have been completed for EtOH and MeOH. The maximum concentration of MTBE detected in storm water reported above is about five orders of magnitude below the median lethal concentration for the most sensitive species investigated to date. More toxicity studies of aquatic animals and plants, bioaccumulation information, and ambient levels in surface water are needed before the significance of MTBE to aquatic life can be assessed.

Two data sets provide information on the occurrence of MTBE in ground water and drinking water derived from ground water. Limited or no data are available for any other fuel oxygenate. The first data set was collected as part of the USGS's National Water-Quality Assessment Program. MTBE was included on a list of analytes for ground-water samples collected in 20 major basins across the country during 1993-94. In addition, retrospective efforts of this Program have summarized MTBE occurrence data from a few State and regional ground-water assessment programs. The second data set was assembled during the preparation of this report as USEPA requested, through its 10 Regions, information on drinking-water programs that have analyzed for MTBE. In response to this request, data on the occurrence of MTBE in public drinking-water supplies derived from ground water were provided by seven States, and four States provided data on private wells. It is likely that a significant number of large water utilities monitor for constituents such as MTBE as part of routine scans for VOCs, therefore, additional information on MTBE occurrence may exist but could not be compiled in the timeframe of this assessment.

At least one detection of MTBE has occurred in ground water in 14 of 33 States surveyed. These 14 States are located throughout the United States. MTBE was detected in 5 percent of over 1,500 wells sampled. Most of the detections occur in shallow ground water in urban areas. Ninety-nine percent of the samples from wells screened in shallow ground water in agricultural areas did not have MTBE. About 98 percent of the wells screened in deeper aquifers or deeper parts of shallow aquifers did not have detections of MTBE, and of the remaining 2 percent that had detections of MTBE, the highest concentration reported was 7.9 micrograms per liter. The mechanism for occurrence in the deeper wells is unknown. MTBE's presence in drinking water for one or more utility was reported in six of the seven States that provided data for public water supplies derived from ground water, and MTBE was reported in all four of the States that provided data for private drinking-water wells.

Because only a few States have information on MTBE in drinking water, it is not possible in this preliminary assessment to describe MTBE concentrations in drinking water nationwide. A Federal drinking-water standard has not been established for MTBE, however, the USEPA has issued a draft lifetime health advisory of 20 to 200 micrograms per liter. The health advisory is expected to be revised in 1997. MTBE has been detected in 51 public drinking-water systems to date based on limited monitoring, however, when detected, the concentration of MTBE was generally low and nearly always below the lower limit of the current draft USEPA health advisory. This indicates that the consumption of drinking water was not a major route of exposure for these few systems. Additional MTBE monitoring data for drinking water are needed, from both the States which provided information for this preliminary assessment and from States that were unable to provide said information, before the significance of drinking water as a route of exposure can be assessed for the Nation.

In the past, routine monitoring of ground water at gasoline USTs has focused on BTEX compounds and, as such, little monitoring information is available for fuel oxygenates. Past and recent releases from UST, however, are perceived to be an important source for the entry of high concentrations of fuel oxygenates to ground water. A California Senate Advisory Committee has initiated a request to collect MTBE concentration data for ground water at UST sites. This information should be helpful in understanding MTBE water-quality concerns from USTs. At least 10 States have established an action level and/or clean-up level for MTBE at sites where gasoline releases have occurred and are being remediated. MTBE monitoring data may be available from these and other States, and this information would provide insights on the potential significance of oxygenate releases from USTs, as well as MTBE concentrations in ground water at these sites.

Studies have been conducted to establish taste and odor thresholds for oxygenates in water. These studies provide useful information regarding the potential impacts on the palatability of drinking water, and the ability for the public to detect MTBE-containing water before it is ingested. These studies indicate that the taste threshold for MTBE, ETBE, and TAME are 39 to 134, 47, and 128 micrograms per liter, respectively. Similarly, the odor detection threshold of MTBE, ETBE, and TAME in water are 45 to 95, 49, and 194 micrograms per liter, respectively. The above-noted taste and odor threshold values for MTBE fall in the range of the USEPA's draft health advisory.

Behavior and Fate of Fuel Oxygenates in the Hydrologic Cycle

Water in contact with spilled gasoline at the water table or in the unsaturated zone will solubilize oxygenates along with aromatic hydrocarbon constituents. Water that is equilibrated with an oxygenated fuel can contain very high concentrations of the oxygenate. For example, for a gasoline that is 10 percent by weight MTBE, the concentration of MTBE in water in chemical equilibrium with the gasoline at room temperature would be on the order of 5,000,000 micrograms per liter and the total BTEX hydrocarbon concentration would be on the order of 120,000 micrograms per liter. Ground-water MTBE concentrations as high as 200,000 micrograms per liter have been observed in wells near gasoline spills. The fact that measured concentrations are typically lower than solubility levels for gasoline oxygenated with MTBE is due either to dilution by uncontaminated water or depletion of MTBE from the gasoline source. Alcohol oxygenates could occur at high concentrations in water adjacent to spilled gasoline because of the high solubility of alcohols, however, there are no published studies that report alcohol concentrations in ground water from releases of oxygenated fuels.

While oxygenated gasolines can lead to high concentrations of fuel oxygenates in water, these concentrations are typically not high enough to increase either the water solubilities (co-solvent effect) or the transport rates of the BTEX compounds. Gasolines containing very high amounts of ethers and alcohols are capable of causing this effect, but such fuels are not in widespread use.

MTBE and other alkyl ether oxygenates are much less biodegradable than BTEX hydrocarbons in ground water. Furthermore, the alkyl ether oxygenates sorb only weakly to soil and aquifer materials, therefore, their transport by ground water will not be retarded to any significant extent. These factors explain why MTBE has been observed to persist at higher concentrations and advance ahead of BTEX plumes in ground water at gasoline spill sites. Conversely, EtOH would be expected to degrade much more rapidly than BTEX hydrocarbons, therefore, EtOH is not expected to persist much beyond the source area and the immediate contaminant plume at a gasoline spill site. It should be noted, however, that no data exist on the occurrence of EtOH in ground water to verify the hypothesis of EtOH's non-persistence and non-migration at spill sites.

Abiotic degradation processes including hydrolysis, direct photolysis, and indirect photolysis are not expected to significantly alter the concentration of MTBE in natural waters.

Because of their occurrence in the atmosphere, and favorable and rapid partitioning to water, fuel oxygenates will occur in precipitation in direct proportion to their concentrations in air. Changes in the ambient air concentration of MTBE, due to increased or decreased usage of oxygenated gasoline, for example, will affect the level of MTBE in precipitation. Cooler temperatures imply larger concentration of MTBE in precipitation for a given atmospheric concentration. Assuming a concentration of 1 part per billion by volume MTBE in the atmosphere, the concentration of MTBE in precipitation would increase almost tenfold, from about 0.2 to 1.5 micrograms per liter, if the temperature decreases from 20 to 0 degrees Celsius. Based on this range of proportionality and MTBE atmospheric concentration data collected in a few cities, precipitation for general urban atmospheres could contain sub-microgram per liter to about 3 micrograms per liter of MTBE. Theory predicts that precipitation concentrations will be higher near roadways, parking lots and garages, and gasoline stations that consistently experience higher air concentrations of MTBE. Available data suggest that the alkyl ether oxygenates have lifetimes in the atmosphere that range from 4 days to 2 weeks. The main degradation pathway seems to be reaction with hydroxyl radical to form *tert*-butyl formate. In summary, the atmospheric source of alkyl ether oxygenates in urban areas is believed to be continual, and results in low concentrations of MTBE in water relative to point sources such as USTs. The atmospheric source is also areally extensive due to the dispersive effect of weather patterns.

Precipitation inputs oxygenates directly to streams, rivers, lakes, and reservoirs as it falls on these surface-water bodies or enters surface water through overland runoff and storm-water drainage. While they are volatile from water, the alkyl ether oxygenates, such as MTBE, in large rivers and some streams will not be lost quickly by volatilization. Precipitation falling on land and recharging aquifers, together with diffusion of oxygenates from the atmosphere through the unsaturated zone, inputs oxygenates to shallow ground water. From shallow ground water it is possible that dissolved alkyl ether oxygenates will move deeper into an aquifer system toward wells and surface-water discharge areas. The concentration of an oxygenate in ground water along a particular flow path depends upon the age of ground water, that is its residence time in the aquifer from recharge location, and the rate of biodegradation reactions. Dissolved MTBE and other alkyl ether oxygenates would advance deeper into the aquifer system than BTEX compounds because they are less degradable than BTEX compounds, however, the significance of this deeper migration is uncertain because of the paucity of in-situ monitoring and degradation studies.

Remediation

The chemical properties of oxygenates relative to BTEX compounds provide insight on the anticipated performance and costs of remediation techniques typically applied to remove BTEX at gasoline spill sites. The presence of MTBE and other alkyl ether oxygenates does not prevent the application of conventional (active) remedial methods (air stripping, carbon adsorption, and soil-vapor extraction) for fuel spills but it does raise the cost. For example, the alkyl ether oxygenates can be removed from water using aeration, but only with much higher air/water ratios than required for BTEX removal. The alcohol oxygenates cannot be removed from water by aeration in a cost-effective manner. Similarly, vacuum extraction and air-sparging techniques will be much less efficient for alkyl ether oxygenates than for BTEX, and infeasible for alcohol oxygenate remediation. The application of intrinsic (passive) bioremediation, an emerging, relatively inexpensive approach to the management of conventional gasoline spills, may be limited because of the slowness with which alkyl ether oxygenates are biodegraded and the tendency of these compounds to migrate from release sites. For contaminant plumes containing EtOH or MeOH, however, intrinsic bioremediation, or enhancements to in-situ bioremediation will remain effective.

Recommendations

This chapter has sought to provide an initial assessment of the water-quality consequences of the use of oxygenates in gasoline. The actions outlined in the specific recommendations given below will allow a more comprehensive understanding of those consequences. Specific recommendations are given for MTBE and the other alkyl ether oxygenates largely because of their extensive commercial use and their persistence in, and migration with ground water. Ethanol, the only alcohol currently in wide-scale commercial use as a gasoline oxygenate, is expected to undergo rapid biodegradation in ground water and surface water, except when concentrations are high enough to be toxic to microorganisms.

At the present time, sufficient monitoring data are not available in the Nation to characterize human exposure to the alkyl ether oxygenate compounds by the consumption of drinking water. Typical oxygenate concentrations are not known either for treated drinking waters, or for the surface- and ground-water sources of that drinking water, except for select States. Similarly, little information is available on either the concentrations of oxygenates in surface water to which aquatic animals and plants are typically exposed, or on the toxicities of those compounds to a broad range of aquatic species.

In order that resources directed to implement the recommendations outlined below be used wisely and efficiently, it is recommended that an ad hoc panel representing the public and private sectors develop a comprehensive and interdisciplinary monitoring, research, and assessment plan to determine the significance of the use of alkyl ether fuel oxygenates on drinking-water quality and aquatic life. The plan should identify lead agencies and organizations for various topics, and provide the necessary details which were beyond the scope of this initial assessment, such as: defining specific goals; establishing the timing and relative priority of research and monitoring needs; developing coordination between industry and various local, State, and Federal agencies; creating a national data base for analytical determinations; and selecting data sets for entry into the data base. Some components of the plan, such as monitoring and creating the national data base should be piloted for select cities and States to further work out details, such as common field sampling and analytical methods, and to make appropriate modifications if deemed necessary. Selecting cities and States that are actively engaged in monitoring for alkyl ether oxygenates in air and water would allow for the timely completion of the suggested pilot phase, with minimal additional expenditure.

Three broad recommendations are made based on this initial assessment:

1. Obtain more complete monitoring data and other information that would: (a) enable an exposure assessment for MTBE in drinking water, (b) characterize the relation between use of MTBE and other alkyl ether oxygenates in gasoline and water quality, and (c) identify and characterize major sources of MTBE to the environment.
2. Complete additional behavior and fate studies to expand current knowledge.
3. Complete aquatic toxicity tests to define the threat posed to aquatic life and establish, if warranted, a Federal water-quality criteria.

Completing the exposure assessment for MTBE in drinking water should be given priority. Monitoring of MTBE in drinking water for this purpose should initially be targeted to high MTBE use areas, and to those environmental settings that are otherwise thought to be most susceptible to contamination. State and Federal agencies and large public water utilities are encouraged to start voluntary monitoring of MTBE in drinking water immediately so that the drinking-water exposure assessment can be completed. Essential elements of each of the three recommendations are described below.

Better Characterize Ambient Concentrations, Oxygenated Gasoline Use, Sources to the Environment, and Relations Between Gasoline Use and Water Quality

- Add the alkyl ether oxygenates MTBE, ETBE, TAME, and DIPE to existing VOC analytical schedules and as USEPA routine target analytes for drinking water, wastewater, surface water, ground water, and remediation studies. This inclusion will provide considerable additional information on the occurrence of these oxygenates in water at little additional expense.

- Create a national data base of analytical determinations of the alkyl ether oxygenates in air, and in ground, surface, and drinking waters. The data base should also include, for example, information on sampling dates, locations, detection limits, analytical method, quality control, and the reporting agency. Carefully selected monitoring data obtained by Federal, State, and local agencies should be reported for inclusion in the data base. The difficulty and limited success in compiling monitoring data from the States for this preliminary assessment illustrates the need for the recommended data base. The goal should be to assemble a data base that allows exposure assessments for the alkyl ether oxygenates in drinking water and for aquatic life in surface water. The USEPA in late 1970's and 1980's completed similar drinking-water assessments for other VOCs.

- Characterize the seasonal volumes of gasoline containing the alkyl ether oxygenates that are sold in the major regions and cities of the Nation. Such usage information is presently unavailable in any systematic form and at the necessary scale, and this lack of data prevents attempts to correlate water-quality data with actual seasonal use. Establishing relations between the use of MTBE (and other alkyl ether oxygenates) and the oxygenate's presence in ground water and surface water will enable the identification of those hydrologic and geologic settings that are most susceptible to contamination.

- Determine the annual releases of the alkyl ether oxygenates to air, land, and water from all sources (e.g., industrial releases, refueling losses, auto emissions, and storage-tank releases), both point and non-point in nature. Presently, estimates of this information are available only for MTBE, TBA, and MeOH, for some sources, and only for those industries which must file annual TRI reports. Precise estimates of annual releases will be difficult to make from currently available information but order-of-magnitude estimates should be made to identify major "data gaps" and to identify the primary source(s) of the alkyl ether oxygenates for air, surface water, ground water, and drinking water. Once characterized, the feasibility of further reducing these primary sources of fuel oxygenates to the environment should be determined.

- Annually review the information specified above and when adequate information is available, prepare interpretive report(s) on the water-quality consequences of the use of MTBE and other alkyl ether oxygenates. At a minimum, the report(s) should cover: (1) exposure assessment for drinking water and aquatic life; (2) relation between oxygenated fuel usage and the seasonal occurrence of alkyl ether oxygenates in surface water, for various climatic and hydrogeologic settings, and (3) the significance of various sources of fuel oxygenates to air, surface water, ground water, and drinking water. The continued need to collect information on alkyl ether oxygenates should be re-assessed after the above-noted report(s) is completed.

Expand the Current Understanding of the Environmental Behavior and Fate of Alkyl Ether Oxygenates

- Characterize, via field monitoring in select cities and regions of the Nation, the occurrence, movement, and mass fluxes of alkyl ether oxygenates between ambient air, precipitation, surface water, the unsaturated zone, and shallow and deep ground water. This monitoring is needed to: (1) determine the significance of urban atmospheres as non-point sources of contamination of alkyl ether oxygenates to surface and ground water; (2) identify climatic and hydrogeologic settings where movement of alkyl ether oxygenates in the hydrologic cycle will be of concern; and (3) evaluate the influence of drainage and storm-water management programs on contaminant movement. These studies should also determine the importance of overland runoff in altering the levels of alkyl ether oxygenates in urban streams and rivers, and in water recharged to shallow aquifers.

- Conduct additional laboratory and field research on the degradation of the alkyl ether oxygenates in the different compartments of the hydrologic cycle, under a variety of environmental conditions. Information is needed on degradation half-lives and pathways. It is especially important to clarify exactly how persistent the alkyl ether oxygenates can be in soil and ground water under a range of redox conditions, and to identify all of the important degradation products for possible monitoring and behavior/fate research. The potential for plants to uptake and otherwise alter the concentration of alkyl fuel oxygenates in the root zone should be determined.

- Conduct further theoretical modeling on the movement of the alkyl ether oxygenates from land surface to shallow ground water. This research should: (1) test the hypothesis that the frequent occurrence of MTBE in shallow urban ground water at low concentrations can be due to recharged precipitation or overland runoff; (2) identify the associated predominant transport mechanisms; and (3) provide insights on the climatic and hydrogeologic factors that favor such movement of alkyl ether oxygenates in the unsaturated zone.

Expand the Current Understanding of the Aquatic Toxicity of Alkyl Ether Oxygenates

- Initiate studies of the chronic toxicity of alkyl ether oxygenates to a broad range of aquatic animals and plants indigenous to surface waters. Additional acute toxicity tests should also be completed for the same species. These studies are needed to: (1) define the extent of any threat posed by the alkyl ether oxygenates to aquatic life; and (2) collect sufficient information to form the basis of a Federal water-quality criteria, if warranted.

SCOPE OF THE CHAPTER

This chapter summarizes the scientific literature, data, and agency information on the sources, concentrations, behavior, and fate of fuel oxygenates, and their aqueous degradation products, in ground water and surface water; and assesses implications for drinking-water quality and aquatic life. Conclusions and recommendations are also noted.

The chapter is intended to cover all oxygenates currently in commercial use in the United States including methyl *tert*-butyl ether (MTBE), ethanol (ETOH), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), and diisopropyl ether (DIPE) and their aqueous degradation products. Information also is presented for methanol (MeOH) and *tert*-butyl alcohol (TBA). These latter chemicals are included because they: (1) have been used in gasoline in the past (Conrad, 1995); (2) are being used currently in pilot programs; or (3) may be used in the future.

Little to no data are available on the occurrence of fuel oxygenates in ground water, surface water, and drinking water. Some data are available for MTBE, however, these data sets are limited in scope. The paucity of monitoring data for fuel oxygenates in natural waters is due to their lack of historical use (e.g., alkyl ether oxygenates) or their difficulty of analysis in water (e.g., alcohols). The available data sets for MTBE are discussed in this chapter and are a composite of monitoring results obtained from States and by the U.S. Geological Survey (USGS) as part of the National Water-Quality Assessment (NAWQA) Program, and other USGS District studies. Concentrations of MTBE detected in water are compared to U.S. Environmental Protection Agency's (USEPA) draft drinking-water lifetime health advisory. Also, the aquatic toxicity, taste and odor properties, environmental behavior, fate, and remediation of fuel oxygenates are discussed.

SOURCES, RELEASES, AND MOVEMENT OF FUEL OXYGENATES IN THE HYDROLOGIC CYCLE

Sources and Releases of Fuel Oxygenates

The origin of fuel oxygenates in natural waters can be classified as occurring from either point sources or non-point sources. A point source is a discharge from a discrete point location. Examples include an effluent discharged to a stream via a pipe, a leaking fuel tank, or a spill. In contrast, a non-point source is areally extensive, and is often associated with land use. Examples include agricultural runoff, urban runoff, automotive (mobile) emissions, and atmospheric deposition.

Point Sources. Point sources of fuel oxygenates include: (1) releases from storage tanks, pipelines, and landfills and dumps; (2) spillage at industrial plants and refueling facilities; and (3) accidental spilling during transport. These are the sources cited most often by State agencies in cases of MTBE contamination of soil and ground water. Other point sources of fuel oxygenates include evaporative emissions during fuel handling, such as refueling at gasoline stations, "water bottom" releases from storage tanks, municipal effluents, and industrial releases to air, land and water, and deep-well injection. Estimates of industrial releases of some fuel oxygenates are reported annually in the Toxics Release Inventory

(TRI) and are discussed in the section on "Industry Releases of MTBE, TBA, and MeOH."

Storage-Tank Releases. There is a large population of storage tanks that may contain oxygenated gasoline, and that could be point sources of oxygenate releases to soil and ground water. The USEPA estimated in 1988 that there were over 2 million underground storage tanks (USTs) at over 700,000 facilities, and that 95 percent of these tanks are used to store petroleum fuels (Lund, 1995). There are currently an estimated 195,000 retail service stations (National Petroleum News, 1995), and an estimated 220,000 non-retail UST facilities (Lund, 1995). Combined, these facilities have about 1.2 million tanks. Gasoline usage represents approximately 80 percent of the volume of motor-fuels consumption, thus many of these tanks have stored gasoline. MTBE has been used in some gasolines since 1979, and other oxygenates have come into use in recent years. It is expected that many of these tanks have contained oxygenated gasoline at some time in their history.

USEPA statistics indicate that over 300,000 sites have been identified with soil or ground-water contamination that would require corrective action (USEPA, 1995a). Corrective action has been completed at more than 130,000 of these sites, and is underway at almost all of the others. The number of these sites that may have released gasoline containing oxygenates is not known. Because of the inherent difficulty in determining leak rates, leak durations, and concentration of oxygenates in the gasoline stored in a UST, it is difficult to develop a reliable estimate of past or current annual releases of fuel oxygenates from these sources.

Monitoring and remediation activities are required at release sites, but typically focus on the hydrocarbons benzene, toluene, ethylbenzene, and xylenes (BTEX compounds) that represent known environmental and health hazards. A limited number of States require monitoring for MTBE as part of the UST corrective-action programs including Florida, Maine, Maryland, Massachusetts, Michigan, New Mexico, New York, North Carolina, South Carolina, Vermont, and Wisconsin (Oliver et al., 1995). Additional data on UST-related impacts from oxygenated gasoline should be forthcoming. A California Senate Advisory Committee has initiated a request to collect data on MTBE concentrations in ground water at UST sites in that State (John Farr, letter of August 1995). Up to this time there was not a State requirement to analyze for MTBE in regular monitoring programs at UST-release sites.

Also, USEPA and State requirements exist and require that UST systems be fully upgraded to meet stringent release prevention and detection standards by December 1998. A survey reported in National Petroleum News (1994) indicates that about 55 percent of all USTs had been upgraded to meet USEPA's 1998 new tank standards. USTs meeting these standards are at a greatly reduced risk of having a release. Also, all current USTs are required to have release detection systems capable of detecting a release within a 30-day period. Finally, USEPA estimates that over 700,000 USTs have been removed in the last 8 years. This concurrent improvement in the physical condition of the UST tank population and release-detection capabilities, coupled with a substantial reduction in the population of tanks, should contribute to a considerable decrease in the annual volume of gasoline released to the environment.

It is estimated that in the Nation's marketing, transportation, and refining industries, there are approximately 14,000 aboveground storage tank (AST) facilities with an estimated 70,000 tanks (API, 1989). Between 30 to 40 percent of ASTs are used for gasoline storage. There are no known industry-wide estimates or surveys of the frequency of releases from ASTs. A 1994 American Petroleum Institute (API) survey of 299 facilities shows that about 40 percent had identified subsurface contamination and were engaged in some form of corrective action to address ground-water impacts of fuel releases (API, 1994a).

In addition to leaks, historic waste-management practices at ASTs may also have contributed to releases of MTBE or other oxygenates at these facilities. As noted in Davidson et al. (1995), water that collects at the bottom of large storage tanks (referred to as "water bottoms") used to be routinely drained into the diked area around the tank, subsequently recharging local ground water or evaporating to the atmosphere. Because of its high solubility, concentrations of MTBE in this water can be very high. One industry study of wastewater at AST facilities measured MTBE concentrations of 280,000 µg/L (micrograms per liter) (API, 1994b). Another study has found concentrations ranging from 1,800,000 to 9,000,000 µg/L (Butillo et al., 1994). An API study of AST facilities (API, 1994b) notes that water bottoms are now treated with other wastewaters generated at these facilities and are no longer released to ground water. As with USTs, specific estimates regarding current or past annual releases of MTBE or other oxygenates are not available.

Point-source releases of gasoline containing MTBE may result in concentrations of MTBE above the draft drinking-water lifetime health advisory of 20 to 200 µg/L. Several authors have reported drinking-water systems affected by MTBE but have not specified the source of MTBE (Anderson, 1986; Angle, 1991; Davidson, 1987; Davidson *et al.*, 1995; Jaremn, 1987; Mason, 1987; McQuillan, 1987; Smith, 1987; Zibrua, 1987). 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 storage tank (Haslam, 1996; Rodriguez, 1997; Komex•H_2O Science, 1997). In other instances, contaminated ground water was treated to remove MTBE and then used for drinking water (Garrett *et al.*, 1986; McKinnon and Dyksen, 1984; New York State Department of Health and U.S. Department of Health and Human Services Public Health Service, 1995). Underground storage tank improvement programs underway by the States and USEPA should result in a reduction in the release of gasoline and fuel oxygenates to ground water from these potential sources (40 CFR 280.200 - 280.230 and 281.39, July 1, 1996).

<u>Industry Releases of MTBE, TBA, and MeOH.</u> The industry-wide release of MTBE, TBA, and MeOH to air, land, and water, and disposal by deep-well injection are summarized in Table 2.1 for 1993, the most current TRI reporting year. Estimates of releases of chemicals by manufacturing facilities meeting certain size and chemical-release thresholds are required to be reported in the annual TRI; however, Federal facilities were not required to report releases in 1993. Storage-tank releases at manufacturing facilities that must report are also included in the TRI and noted in the environmental compartment in which disposal takes place (land, air, surface water, etc.) (USEPA, 1993a). The 1993 TRI includes reports from 23,000 facilities for 316 chemicals and 20 chemical categories. TRI does not mandate that facilities monitor their releases, and therefore the quantities of reported releases are estimates (USEPA, 1995c). For MTBE, a total of 136 facilities (see Appendix 1)

consisting of 22 Standard Industrial Classification codes reported MTBE releases for that year. About half (78/136) of the reporting facilities were petroleum refineries. These refineries collectively accounted for 83.8 percent of the MTBE released by industry in 1993, or about 1,440,000 kg. Also, nearly all of the estimated release of

Table 2.1: *Estimated releases of MTBE, TBA, and MeOH for the United States for report year 1993.*

[MTBE, methyl *tert*-butyl ether; TBA, *tert*-butyl alcohol; MeOH, methanol. Source: U.S. Environmental Protection Agency, 1993b]

Release to	Reported releases (kilograms per year) by:		
	Petroleum refineries	All other facilities	Total
	Methyl *tert*-butyl ether		
Atmosphere	1,398,026	274,571	1,672,597
Underground injection	288	3,979	4,267
Land	184	2	186
Water	41,799	74	41,873
Total releases	1,440,297	278,626	1,718,923
Percent	83.8	16.2	100
Number of facilities	78	58	136
	***Tert*-butyl alcohol**		
Atmosphere	40,498	705,127	745,625
Underground injection	253	138,410	138,663
Land	0	158	158
Water	5	79,051	79,056
Total releases	40,756	922,746	963,502
Percent	4.2	95.8	100
Number of facilities	8	59	67
	Methanol		
Atmosphere	369,895	77,544,790	77,914,685
Underground injection	9,670	12,645,520	12,655,190
Land	401	779,716	780,117
Water	17,134	4,523,137	4,540,271
Total releases	397,100	95,493,163	95,890,263
Percent	0.4	99.6	100
Number of facilities	67	2,198	2,265

MTBE by industry, about 97 percent, occurred to the atmosphere. It is important to note that the MTBE released by industry, as tallied from the TRI, represents only a small fraction of the total amount of MTBE produced. For example, the estimated release of MTBE by industry in 1992 in the United States accounted for only 0.03 percent of the MTBE that was produced (Squillace et al., 1995a). As noted previously, some sources of MTBE, such as automotive emissions and evaporative losses, evaporative losses at gasoline stations, accidental spills, and so forth are not well documented but could be important sources of oxygenates to the environment. Until these and other releases are accurately determined, it is not possible to put the industrial TRI release data for MTBE within a total release perspective.

The estimated release of TBA and MeOH to the environment by industry in 1993 was 963,500 and 95,890,000 kg, respectively. Similar to MTBE, the majority of the reported estimated releases of TBA and MeOH were to the atmosphere. In contrast to MTBE, petroleum refineries represented a very small amount, 4.2 and 0.4 percent, respectively, of the amount of reported industrial releases for TBA and MeOH (see 2.1). Non-industrial releases of TBA and MeOH also are not well known and thus a comparison of releases associated with the petroleum fuels industry to total releases is not possible. Industrial releases of other fuel oxygenates, including EtOH, ETBE, TAME, and DIPE are not included in the TRI.

Non-Point Sources. As previously noted, fuel oxygenates can enter natural waters from non-point sources, as well as from point sources. Many of the point sources characterized above, as well as exhaust and evaporative emissions from automobiles and trucks, will ultimately cause fuel oxygenates, like other volatile organic chemicals (VOCs), to enter the atmosphere, which can then act as a non-point source to water. The process of chemicals moving in the hydrologic cycle is subsequently described in the sections of this chapter on "Movement of Fuel Oxygenates in the Hydrologic Cycle" and "Behavior in the Ambient Hydrologic Cycle." Research on the atmospheric deposition of fuel oxygenates has not been reported in the scientific literature; however, the importance of this process has been extensively investigated for other VOCs and other chemical classes. Preliminary compilations on the occurrence of MTBE in urban storm-water runoff are discussed in the section on "MTBE in Urban Storm Water" and exhaust emissions of MTBE have been reported elsewhere (Calvert et al., 1993; Hoekman, 1992; Kirchstetter et al., 1996; Stump et al., 1990). The subjects of atmospheric deposition, storm-water runoff, and vehicular emissions as non-point sources of fuel oxygenates in water are discussed in the sections on "Partitioning Between Environmental Compartments" and "Behavior in the Ambient Hydrologic Cycle."

Movement of Fuel Oxygenates in the Hydrologic Cycle

MTBE and other fuel oxygenates are expected to move with water in the hydrologic cycle primarily because of their release to air, water, and land, and their favorable partitioning to water. A schematic depicting the movement of fuel oxygenates in the environment is shown in Figure 2.1. As shown, fuel oxygenates are released to the atmosphere from various point and non-point sources and, once present in the atmosphere, are expected to occur in precipitation because of partitioning from the gas phase to the water phase. Precipitation can then introduce oxygenates directly to streams, rivers, and lakes as it falls on these surface-water bodies, or enters through overland runoff and storm-water drainage. Precipitation falling on land and moving through the unsaturated zone (recharge), and the diffusion of the oxygenates from the atmosphere through the unsaturated zone, are potentially areally extensive, low-level sources of oxygenates to shallow ground water (Squillace et al., 1995a, 1995b, 1996). Dissolved oxygenates that are resistant to degradation can move deeper in aquifers as ground water flows towards wells or natural discharge areas, such as surface water. The extent, if any, to which fuel oxygenates undergo chemical or biological transformation to less harmful substances or chemicals of concern must be understood for each compartment of the hydrologic cycle. This topic is more fully addressed in the section on "Behavior in the Ambient Hydrologic Cycle."

Releases from gasoline storage sites represent important sources of fuel oxygenates to ground water because water in contact with the spilled product, at the water table or within the unsaturated zone, will solubilize the oxygenates as well as the BTEX compounds of the gasoline. Concentrations of oxygenates in ground water near such point sources would be high relative to concentrations in storm water and shallow ground water, that originated from precipitation containing MTBE.

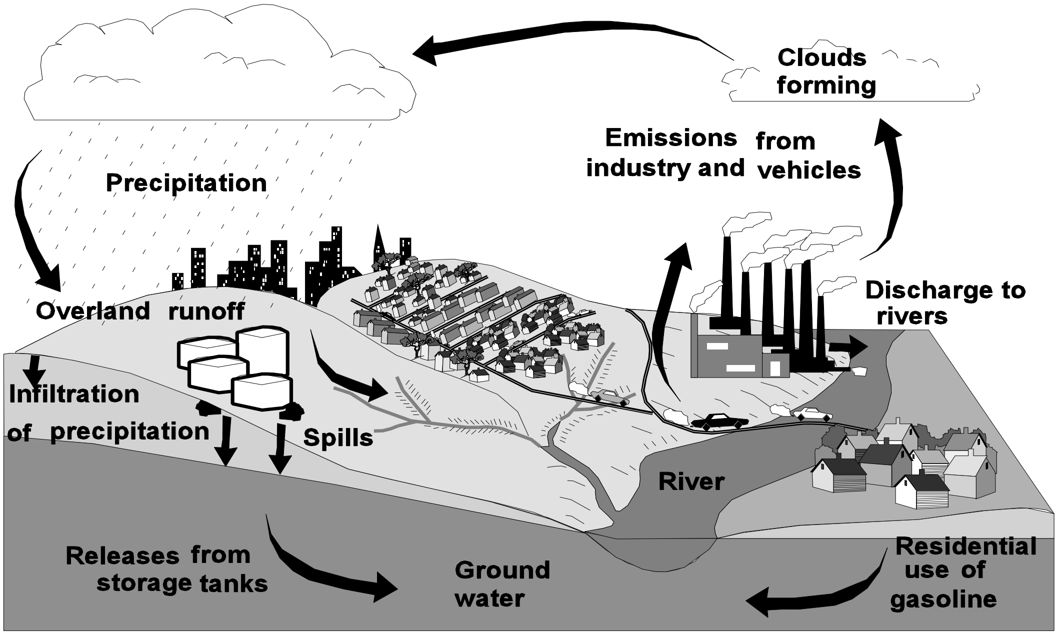

Figure 2.1. The movement of fuel oxygenates in the environment (adapted from Squillace *et al.*, 1995a)

OCCURRENCE AND SIGNIFICANCE OF FUEL OXYGENATES IN WATER

The occurrence of MTBE in ground water, storm water, and drinking water has been reported previously (Angle, 1991; Barks, 1994; Davidson, 1995a, 1995b; Davidson et al., 1995; Delzer et al., 1996; Dey et al., 1991; Garrett, 1987; Garrett et al., 1986; Lopes et al., 1995; McKinnon and Dyksen, 1984; New York State Department of Health and U.S. Department of Health and Human Services, 1995; Post, 1994; Squillace et al., 1995a, 1995b, 1996; Tangley, 1984; and U.S. Environmental Protection Agency, 1986, 1987a, 1987b). Collectively, these investigations document that MTBE occurs in water, especially in areas where this fuel oxygenate is extensively used, and where releases of MTBE to air, water, and land occur. These studies, especially the USGS's recent finding of MTBE's occurrence in shallow urban ground water (Squillace et al., 1995a), have increased national interest in better defining the occurrence and source(s) of fuel oxygenates in ground water, surface water, and drinking water, as well as the transport, biodegradation, fate, and remediation of these chemicals. Little information on the occurrence of other oxygenates in natural waters and drinking waters has been reported in the scientific literature.

Information on drinking-water standards, health advisories and guidelines, and ground-water action levels and protection standards for fuel oxygenates that have been set by the USEPA and the States is presented in this section. Also included is a summary of (1) taste-and-odor properties, (2) aquatic toxicity, (3) analytical methods, and (4) past monitoring in ambient air, storm water, ground water, and drinking water. Finally, recently compiled data on the occurrence of MTBE in urban storm water, drinking water provided from ground water and surface water, and in ground water is presented, along with a discussion of the significance of reported MTBE concentrations.

Drinking-Water and Ground-Water-Protection Regulations

The USEPA has not established a Federal drinking-water standard for any of the fuel oxygenates; however, the agency has issued a draft health advisory for MTBE (USEPA, 1995b). A drinking-water standard is a legally enforceable requirement that includes a maximum contaminant level for the protection of human health that public water supplies cannot exceed.

Health advisories describe non-regulatory concentrations of drinking-water contaminants at which adverse health effects would not be anticipated to occur over specific exposure durations, with a margin of safety. Health advisories serve as informal technical guidance for protecting public health when contamination situations occur. They are not to be construed as legally enforceable Federal standards. Health advisories for MTBE for various durations are reported elsewhere (USEPA, 1995b). The draft drinking-water lifetime health advisory for MTBE is 20 to 200 µg/L, and it is expected to be revised by the USEPA in 1997. The range reflects the uncertainty of the carcinogenicity of MTBE. Health advisories have not been developed by the USEPA for other fuel oxygenates.

Eleven States have established or are promulgating a standard, health advisory/guideline, or action level for MTBE in drinking water (see Table 2.2). An action level is the concentration, when exceeded in ground water, that triggers remediation or other appropriate action. The regulated level varies from State to State, and ranges between 35 to 230 µg/L. Vermont and New York have set standards for MTBE in drinking water at 40 and 50 µg/L, respectively.

At least ten States have established action levels and clean-up levels for MTBE in ground water (see Table 2.3). A clean-up level is the maximum concentration of a contaminant that can remain after remediation has occurred. As shown in Table 2.3, the action levels vary between 40 to 240 µg/L, and the clean-up levels vary between 12 to 700 µg/L (for a drinking-water designation). Some States do not distinctly set action levels or clean-up levels, but rather use standards or health advisory/guidance levels for drinking water to decide when remediation of ground water is needed and the clean-up level to be achieved. A comparison of standards, health advisories/guidelines, action levels, clean-up levels, and

Table 2.2: *Summary of MTBE drinking-water standards, health advisories/guidelines, and action levels established or being promulgated by select States.*

[MTBE, methyl *tert*-butyl ether. µg/L, micrograms per liter]

State	Type of requirement	Regulatory level (µg/L)	Reference	Remarks
California	Interim action level	35	(1,2)	Risk assessment is currently being updated.
Connecticut	Health advisory/guideline	100	(3)	Started about 1980.
Kansas	Health advisory/guideline	100	(3)	Not specific for MTBE; applies to total VOCs.
Illinois	Health advisory/guideline	230	(4)	--
Massachusetts	Health advisory/guideline	50	(3)	--
Maine	Health advisory/guideline	50	(3)	--
New Hampshire	Health advisory/guideline	200	(3)	--
New Jersey	Health advisory/guideline	50	(5)	
	Standard (proposed)	70	(5, 6)	Standard expected to be promulgated in 1996.
New York	Standard	50	(7, 8)	Not specific for MTBE; applies to unspecified organic contaminants.
Rhode Island	Health advisory/guideline	40	(3)	--
Vermont	Standard	40	(3)	--

[1] State of California, Division of Drinking Water and Environmental Management memo of 31 Oct 1995.

[2] State of California, Pesticide and Environmental Toxicology Section, memo of 19 Feb 1991.

[3] Chemical Communication Subcommittee, 1990.

[4] Illinois Environmental Protection Agency, 1994.

[5] New Jersey Drinking Water Quality Institute, 1994.

[6] New Jersey DEP letter of July 24, 1995.

[7] New York DOH letter of July 6, 1995.

[8] New York State Department of Health, 1995.

Table 2.3: *Summary of MTBE ground-water action and clean-up levels established or being promulgated by select States.*

[MTBE, methyl *tert*-butyl ether. μg/L, micrograms per liter]

State	Regulatory level (μg/L)		Reference	Remarks
	Action level	Clean-up level		
Florida	--	50	Oliver, 1995	--
Maine	--	50	Association for Environmental Health of Soils, 1994; Benjamin and Belluck, 1994	Applies to stringent sites only. Site-specific remediation standards applied to other sites.
Massachusetts	Not specified in regulation	[a]700/[b]50,000/[c]50,000	Oliver, 1995	a - Actual/potential drinking water supply; b - Source of vapor emissions to building; c - Everywhere.
Michigan	Same as cleanup criteria	[d]240/[e]690	Oliver, 1995	d - Residential; e - Industrial/commercial.
New Mexico	100	100	Oliver, 1995; Benjamin and Belluck, 1994	--
New York	50	[f]50	Oliver, 1995	f - Clean-up level is the action level, or when not achievable, site specific.
North Carolina	>200	>200	Association for Environmental Health of Soils, 1994; Benjamin and Belluck, 1994	--
South Carolina	Site specific	40 (Recommended)	Oliver, 1995	--
Vermont	40	Site specific	Oliver, 1995	--
Wisconsin	60	12	Oliver, 1995	--

other information is summarized in Figure 2.2. Similar information for other oxygenates has not been compiled to date.

Taste and Odor Thresholds

The introduction of the oxygenated gasoline program in November 1992 resulted in complaints about the smell of gasoline. In an attempt to understand the nature of the complaints, industry assessed the taste and odor thresholds of the neat ethers and then of oxygenate-gasoline mixtures. The work was completed by TRC Corporation, and was sponsored by ARCO Chemical Company and the American Petroleum Institute. Three reports were issued (TRC Environmental Corporation, 1994; Vetrano, 1993a, 1993b). Standard protocols were used in which trained adult volunteers sipped water or smelled air containing known concentrations of the oxygenates being tested. The data were then used to calculate the taste threshold for water and odor thresholds for water and air. The taste threshold of MTBE in water for two studies was 39 and 134 µg/L. Taste thresholds for ETBE and TAME were 47 and 128 µg/L, respectively.

Odor thresholds are characterized by two numbers, a detection threshold and a recognition threshold. The detection threshold is the level at which people can notice a difference between the smell of clean water and the smell of water containing the test material, and the recognition threshold is the level at which they can describe the smell. In general, the recognition threshold is about twice the detection threshold. The odor threshold data for alkyl ether oxygenates in water are summarized in 2.4. The relative standard errors associated with these measurements were found to range up to about 15 percent but for brevity are not included. As shown in Table 2.4, the odor-detection threshold of MTBE for two studies was 45 and 95 µg/L, and ETBE and TAME have reported detection thresholds of 49 and 194 µg/L, respectively. The above range for MTBE is not unusual and reflects the results of two studies done at different times and by different panels. The odor-detection threshold for MTBE in water falls within the range of the draft drinking-water lifetime health advisory for MTBE of 20 to 200 µg/L (see Figure 2.2). Odor thresholds in air are not discussed in this chapter; the reader is referred to the previously noted reports for this information.

Table 2.4: *Odor thresholds for fuel oxygenates in water.*

[MTBE, methyl *tert*-butyl ether; ETBE, ethyl *tert*-butyl ether; TAME, *tert*-amyl methyl ether; µg/L, micrograms per liter]

Fuel oxygenate	Odor threshold (µg/L)		Reference
	Detection	Recognition	
MTBE	95	193	Vetrano, 1993a
MTBE	45	55	TRC Environmental Corporation, 1994
ETBE	49	106	Vetrano, 1993a
TAME	194	443	Vetrano, 1993b

Aquatic Toxicology of Oxygenates

Because it will not be included in the health effects chapter, aquatic toxicological information on fuel oxygenates is summarized below. Both published information and information available from industrial studies not yet published in the peer-reviewed literature are included.

Water-quality criteria to protect aquatic life have not been established by the USEPA. When developing numerical criteria for the protection of aquatic life, acute and chronic toxicity and bioconcentration data are used. The minimum data set for criteria derivation consists of eight families or organisms, and acute and chronic testing must be available using the same species in the same dilution of water, for the most sensitive life stages of a given species. Plant toxicity is also a factor considered when developing water-quality criteria. For the alkyl ether oxygenates, chronic-toxicity data for aquatic animals and plants are lacking, and limited information exists on acute toxicity and bioconcentration. For EtOH and MeOH, considerably more aquatic toxicity studies have been completed, especially to assess acute toxicity.

USEPA's AQUIRE data base was searched for toxicity data on fuel oxygenates and articles cited therein, and industrial studies were subsequently reviewed for additional information on toxicity. Only studies with an AQUIRE documentation code of 1 or 2 were used. The available information is summarized in Table 2.5. Median lethal concentrations, LC_{50}, and median effective concentrations, EC_{50}, are given in this table. LC_{50} and EC_{50} represent the estimated concentration that is expected to be lethal and to cause other effects, in 50 percent of the test species, respectively. Effects described in EC_{50} studies include, for example, behavior, growth, immobilization, reproduction, and equilibrium. Many study results were available for EtOH and MeOH in AQUIRE and, as such, entries in Table 2.5 for these oxygenates are for the test species that had the lowest and second lowest concentrations for LC_{50} and EC_{50} only. For other fuel oxygenates, all studies completed to date are listed.

Based on the species tested to date, TBA and MTBE appear to have lower toxicity than other fuel oxygenates with LC_{50} ranges of 2,450 to 6,410 and 672 to >1,000 mg/L (milligrams per liter), respectively. Greater toxicity has been reported for other oxygenates, for at least one test species, including: TAME, 14 mg/L for shrimp; ETBE, 37 mg/L for shrimp; MeOH, 37 mg/L for mussel; DIPE, 92 mg/L for fathead minnow; and EtOH, 454 mg/L for scud.

As is shown in Table 2.5, non-lethal effects have been studied for EtOH, MeOH, TBA, TAME, and DIPE. MeOH and TBA have lower toxicity, whereas greater toxicity has been reported for TAME, 0.11 mg/L for freshwater algae; EtOH, 2.0 to 2.5 mg/L for water flea; and DIPE, 476 mg/L for fathead minnow. The reader is reminded the acute toxicity values noted above and listed in Table 2.5 are reported in milligrams per liter, not micrograms per liter; the latter unit is used in most instances in this chapter.

Monitoring and Analysis of Fuel Oxygenates

Monitoring. The Clean Air Act (CAA), Clean Water Act (CWA), and Safe Drinking Water Act (SDWA) do not require the monitoring of fuel oxygenates in air, ground water, surface water, or drinking water and, as such, national monitoring data sets are not available for these chemicals with two exceptions. First, MTBE was measured in ground water in 1993-95 as part of the NAWQA program, and preliminary findings have been reported (Squillace et al., 1995a, 1995b, 1996). Second, MTBE was measured in storm water as part of USGS

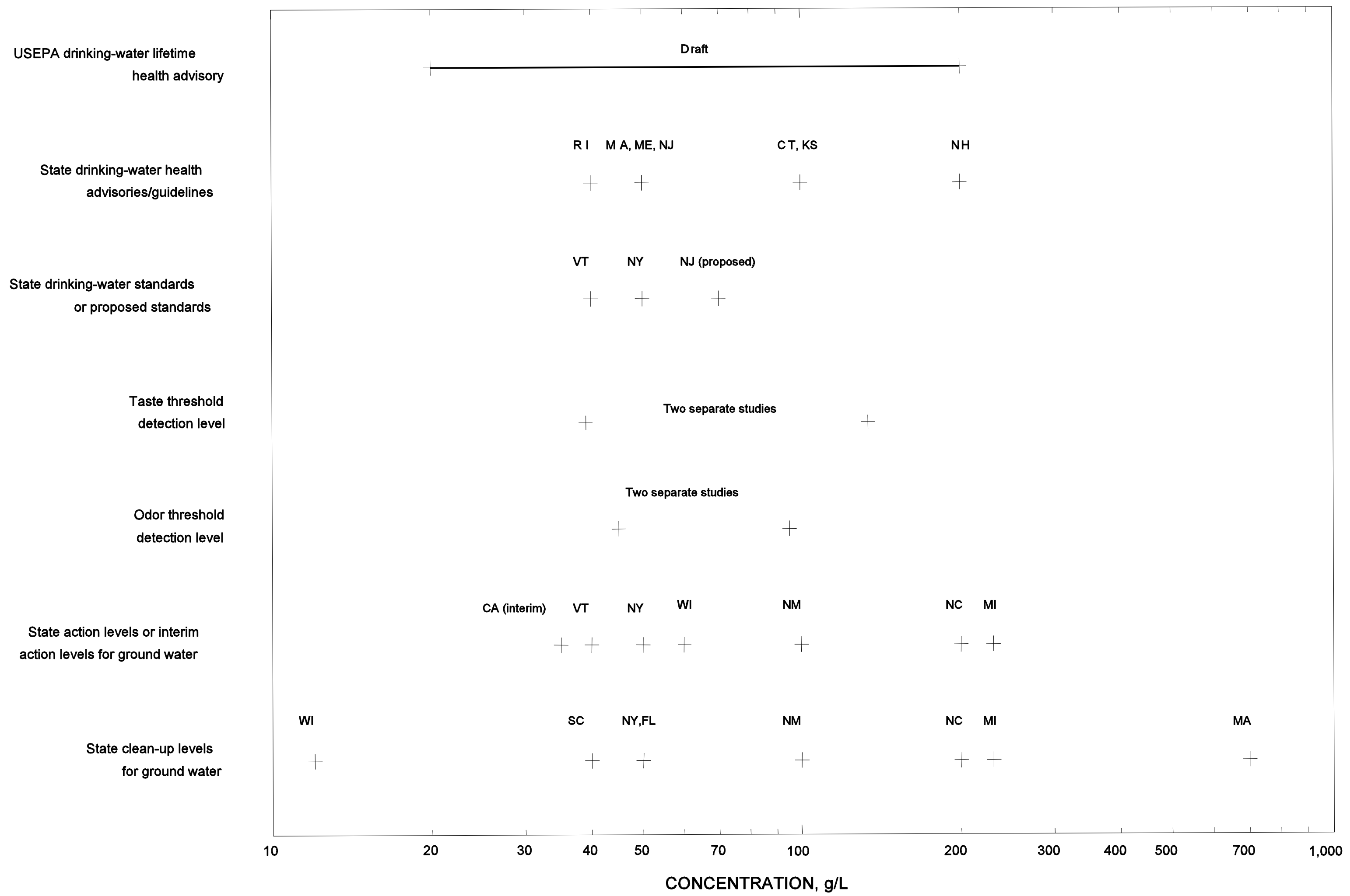

Figure 2.2. Comparison of MTBE health advisories/guidelines, drinking-water standards, taste and odor thresholds, action levels, and clean-up levels.

Table 2.5: *Acute toxicity of fuel oxygenates to freshwater aquatic life.*

[EtOH, ethanol; MeOH, methanol; TBA, *tert*-butyl alcohol; MTBE, methyl *tert*-butyl ether; ETBE, ethyl *tert*-butyl ether; TAME, *tert*-amyl methyl ether; DIPE, diisopropyl ether. BEH, behavior; GRO, growth; IMM, immobilization; PHY, physical; REP, reproduction; EQU, equilibrium, change in ability to maintain balance; mg/L, milligrams per liter]

Fuel oxygenate	Test species	LC$_{50}$[1] (mg/L)	EC$_{50}$[2] (mg/L)	Reference
EtOH[3]	*Hyalella azteca* (Scud)	[4]454		Cowgill and Milazzo, 1991
EtOH[3]	*Daphnia magna* (Water flea)	[5]8,210		Bowman *et al.*, 1981
EtOH[3]	*Daphnia magna* (Water flea)		[6]2.0-[7]2.5 (PHY)	Lagerspetz *et al.*, 1993
EtOH[3]	*Ceriodaphnia dubia* (Water flea)		[8]26 (REP)	Cowgill and Milazzo, 1991
MeOH[3]	*Anodonta imbecillis* (Mussel)	[6]37		Keller, 1993
MeOH[3]	*Lepomis macrochirus* (Bluegill)	[9]15,400		Poirier *et al.*, 1986
MeOH[3]	*Oncorhynchus mykiss* (Rainbow trout)		[6]13,000-[9]13,200 (EQU)	Poirier *et al.*, 1986
MeOH[3]	*Lepomis macrochirus* (Bluegill)		[6]16,000-[7]16,100 (EQU)	Poirier *et al.*, 1986
TBA	*Carassius auratus* (Goldfish)	[7]>5,000		Bridie *et al.*, 1979
TBA	*Daphnia magna* (Water flea)		[6,7]5,504 (IMM)	Kuhn *et al.*, 1989
TBA	*Chironomus riparius* (Midge larvae)	[6]5,800		Roghair *et al.*, 1994
TBA	*Pimephales promelas* (Fathead minnow)	[9]6,410	[9]4,430 (BEH)	Geiger *et al.*, 1988
TBA	*Xenopus laevis* (Clawed toad)	[7]2,450		De Zwart and Slooff, 1987
MTBE	*Bleak* (European fish)	[9]>1,000		Bengtsson and Tarkpea, 1983
MTBE	*Nitocra Spinipes* (Harpacticoid copepod)	[9]>1,000		Bengtsson and Tarkpea, 1983
MTBE	*Pimephales promelas* (Fathead minnow)	[9]706		Veith *et al.*, 1983a, 1983b

Table 2.5: *Acute toxicity of fuel oxygenates to freshwater aquatic life.-Continued*

Fuel oxygenate	Test species	LC_{50}[1] (mg/L)	EC_{50}[2] (mg/L)	Reference
MTBE	*Pimephales promelas* (Fathead minnow)	[9]672		Geiger *et al.*, 1988
ETBE	*Cyprinodon variegatus* (Sheepshead minnow)	[9]>2,500		Boeri *et al.*, 1994a
ETBE	*Mysidopsis bahia* (Shrimp)	[9]37		Boeri *et al.*, 1994b
TAME	*Selenastrum capricornutum* (Freshwater algae)		[9]0.11 (GRO)	API, 1995a
TAME	*Daphnia magna* (Water flea)		[7]100 (IMM)	API, 1995b
TAME	*Mysidopsis bahia* (Shrimp)	[9]14		API, 1995c
TAME	Oncorhynchus mykiss (Rainbow trout)	[9]580		API, 1995d
DIPE	Pimephales promelas (Fathead minnow)	[9]92		Veith *et al.*, 1983a, 1983b
DIPE	Carassius auratus (Goldfish)	[7]380		Bridie *et al.*, 1979
DIPE	Lepomis macrochirus (Bluegill)	[9]7,000		Dawson *et al.*, 1977
DIPE	Pimephales promelas (Fathead minnow)	[9]786	[9]476 (BEH)	Geiger *et al.*, 1988

[1] LC_{50}, the median lethal concentration, is the estimated concentration that is expected to be lethal to 50 percent of the test animals or plants. Only those studies with an AQUIRE documentation code of 1 and 2 are included.

[2] EC_{50}, the median effective concentration, is the estimated concentration that is expected to cause an effect other than death for 50 percent of the test animals or plants. Only those studies with an AQUIRE documentation code of 1 and 2 are included.

[3] Entries for EtOH and MeOH are for the test species that had the lowest and second lowest concentrations for LC_{50} and EC_{50}. For other fuel oxygenates, all studies completed to date are listed.

[4] 216-hr; [5] 18-hr; [6] 48-hr; [7] 24-hr; [8] 168-240-hr; [9] 96-hr.

cooperative projects with some of the Nation's larger cities, which completed monitoring as part of obtaining national permits for discharges of municipal storm-water runoff, and preliminary findings have been prepared (Delzer et al., 1996). Although used extensively as a fuel oxygenate, the lack of monitoring for EtOH is apparently a result of: (1) the difficulty of analyzing for this chemical in the aqueous phase, and (2) the ease of microbial degradation, which results in a short half-life in water. MTBE and MeOH are included on the CAA Hazardous Air Pollutant List, and information on these two oxygenates in urban air may become available via this voluntary program in the future. Also, MTBE is on the USEPA's Drinking Water Priority List, which means that it is a possible candidate for future Federal regulation and monitoring.

Some States have monitored for MTBE in public water systems, or a subset of systems, including Connecticut, Illinois, New Jersey, Rhode Island, and Texas. Other States, for example, Iowa, New York, Missouri, Rhode Island, and Wisconsin have completed monitoring of private wells and public water-supply systems. In some cases, the sampling program was conducted where contamination of ground water by MTBE was known to have occurred or was suspected. Although information on monitoring being completed by State agencies was sought as part of this assessment, additional information is needed to better characterize MTBE monitoring being completed by the States. Also, a number of large water utilities may monitor for MTBE as part of routine VOC monitoring, and the availability of this information needs to be determined. Very little monitoring of other fuel oxygenates in water has been completed by State agencies or water utilities.

MTBE and other fuel oxygenates are not included in routine ambient air monitoring done by local, State, and Federal agencies. An exception is the State of California, which just recently began to monitor for MTBE and other VOCs in ambient air. Air-quality data have been collected for MTBE, as part of special studies in Fairbanks, Alaska; Stamford, Conn.; Albany, N.Y.; Milwaukee, Wis.; Boston, Mass.; and Houston, Tex. (Table 2.6). Additional air-quality studies have been completed to determine human exposure, mostly at or near blending and distribution facilities, and gasoline stations (Johnson et al., 1995; McCoy and Johnson, 1995; NATLSCO, 1995). Some air-quality data are available for EtOH (Kelly et al., 1993; McCoy and Johnson, 1995), ETBE (Allen and Grande, 1995), and MeOH (Kelly et al., 1993), and none is known to exist for other fuel oxygenates.

The median concentration of MTBE in ambient air ("area" entries in Table 2.6) for the six cities listed in this table ranged between 0.13 to 4.6 ppb-v (parts per billion by volume), with the highest median value measured in Fairbanks, Alaska. Excluding Fairbanks, the maximum concentration measured in ambient air was 4.1 ppb-v in Milwaukee, Wisconsin. The median ambient air levels of MTBE in Milwaukee, Albany, Stamford, Boston, and Houston were typically at or below 1 ppb-v. While informative, air quality monitoring of fuel oxygenates completed to date is inadequate to characterize concentrations expected in ambient air across the United States. As shown in Table 2.6, concentrations of MTBE in air near gasoline stations, roadways, parking lots and garages, and blending and distribution facilities are higher, and in many cases considerable higher than ambient urban air.

Analysis. The widespread usage of fuel oxygenates will require that additional monitoring be performed. Analytical methods for EtOH, MeOH, and TBA in water have not been developed by the USEPA or USGS. However, alkyl ether oxygenates can be analyzed

Table 2.6: *Statististical summary of MTBE concentrations in urban air.*

[MTBE, methyl *tert*-butyl ether. Concentrations are parts per billion by volume (ppb-v); to convert to micrograms per cubic meters, multiply ppb-v values by 3.604]

City/State or special study		Mini-mum	Median	Maxi-mum	Reference	Remarks
Milwaukee, Wis.	Area (n=11)[1]	0.0	0.13	4.13	Allen and Grande, 1995	
	Gas station (n=6)	0.25	1.59	4.58		Sampled at perimeter of gas station.
	Parking lot (n=8)		2.05			Average concentrations of the 8 samples.
	Roadway[2] (n=12)	0	0.50	1.06		
	Gas station (n=19)	50	70	2,930		Sampled at breathing zone while refueling.
Fairbanks, Alaska (Phase I: Dec. 1-12, 1992)	Area (n=2)	2.0	4.0	6.0	Roy Zweidinger, USEPA, written commun., 1995	Phase I was immediately prior to the phase out of 15% MTBE in gasoline.
	Gas station (n=1)	54	54	54		
	Roadway (n=7)	3.0	5.0	12.0		
Fairbanks, Alaska (Phase II: Dec. 18-22, 1992)	Area (n=11)	1.7	4.6	28	Roy Zweidinger, USEPA, written commun., 1995	Phase II was during the phase out of 15% MTBE in gasoline.
	Gas station (n=1)	37.4	37.4	37.4		
	Roadway (n=7)	4.2	9.7	17.9		
Fairbanks, Alaska (Phase III: Feb. 2 - Mar. 5, 1992)	Area (n=9)	0.2	0.9	2.5	Roy Zweidinger, USEPA, written commun., 1995	Phase III was after the phase out of 15% MTBE in gasoline.
	Gas station (n=5)	1.7	3.2	13.8		
	Roadway (n=9)	0.6	1.4	3.4		
Albany, N.Y. (May 5-27, 1993)	Area (n=6)	0.1	0.25	0.7	Roy Zweidinger, USEPA, written commun., 1995	MTBE was used in premium gasoline only.
	Gas station (n=6)	6.5	17.7	54.0		

Table 2.6: *Statistical summary of MTBE concentrations in urban air--Continued.*

City/State or special study		Mini-mum	Median	Maxi-mum	Reference	Remarks
Stamford, Conn. (Apr. 13-14, 1993)	Area (n=4)	0.3	0.85	2.8	Roy Zweidinger, USEPA, written commun., 1995	Another area where 15% MTBE in gasoline was used.
	Gas station (n=3)	2.1	5.5	7.4		
	Parking garage (n=4)	18.6	35.1	49.4		
	Area (x=1/22)[3]	<0.2	<0.2	0.49	Kelly *et al.*, 1993	Sampled at former Toxic Air Monitoring Study site.
Houston, Tex.	Area (x=8/22)	<0.2	<0.2	2.8	Kelly *et al.*, 1993	Sampled at former Toxic Air Monitoring Study site.
Service station personnel exposure (long-term samples)	Attendant (Winter)	30	200	500	NATLSCO, 1995	Geometric means are used instead of the median values in this publication.
	Mechanic (Winter)	20	120	2,600		
	Attendant (Summer)	30	80	420		
	Mechanic (Summer)	20	30	180		
Area samplers	Blending - neat MTBE (x=32/38)	60	419	9,893	McCoy and Johnson, 1995	
	Blending - fuel mixtures (x=10/19)	40	200	2,100		
	Distribution (fuel) (x=3/4)	20	60	100		

Table 2.6: *Statistical summary of MTBE concentrations in urban air--Continued.*

City/State or special study		Mini-mum	Median	Maxi-mum	Reference	Remarks
New Jersey service stations Stage II full-service	Perimeter (x=15/16)	1	3	36	Johnson *et al.*, 1995	Stage II is a vapor recovery system used during refueling.
	Pumps (x=4/4)	120	440	1,600		
	Breathing zone (x=4/4)	84	245	520		
New York service stations Stage II self-service	Perimeter (x=24/24)	2	7	83	Johnson *et al.*, 1995	Stage II is a vapor recovery system used during refueling.
	Pumps (x=6/6)	14	48	80		
	Breathing zone (x=6/6)	77	205	780		
Connecticut service stations self-service	Perimeter (x=38/40)	1	14	140	Johnson *et al.*, 1995	
	Pumps (x=9/10)	9	170	1,500		
	Breathing zone (x=10/10)	170	1,500	2,600		

[1] n = number of samples.
[2] Roadway is defined as sites near highways or intersections of highways.
[3] x = number of detections/number of samples.

by purge and trap gas chromotography/mass spectrometry (GC/MS). USEPA Method 524.2 is one of the two required methods for the analysis of VOCs in drinking water, and it is the preferred method for measuring MTBE[2]. The other USEPA drinking water method for VOCs is 502.2. A revised version of Method 524.2 will officially replace the current version after July 1996. The estimated detection limit for reagent water spiked with 0.4 µg/L of MTBE for revised Method 524.2 is 0.09 µg/L (USEPA, 1992). Also, many laboratories have successfully used USEPA SW846 Methods, 8020 and 8240, to measure MTBE in water samples collected for remediation studies. Because existing GC/MS methods can be used, adding the alkyl ether oxygenates to monitoring programs should have only a minimal effect on cost.

MTBE was added as an analyte on routine VOC water schedules by the USGS in October 1991, and ETBE, TAME, and DIPE were added as target analytes in 1996. The method and its performance have been reported elsewhere (Raese et al., 1995; Squillace et al., 1995b, 1996). The estimated detection limit for reagent water spiked with 0.2 µg/L of MTBE is 0.06 µg/L (Raese et al., 1995). Methods used by the USGS to collect, preserve, and ship water samples are described elsewhere (Koterba et al., 1995).

Analytical results for MTBE described in the next two sections were completed by the USGS and a variety of States. USGS's analyses have a reporting level of 0.2 or 1.0 µg/L, whereas the reporting level for analyses done by the States are often unknown, and when known are usually similar to that noted for the USGS's analyses.

MTBE in Urban Storm Water

Storm water has been analyzed for MTBE and other non-oxygenate constituents in 16 cities and metropolitan areas from 1991 to 1995 (see Figure 2.3). These studies were completed by various USGS Districts to characterize storm-water runoff in cities with a population exceeding 100,000. These cities are required by provisions of the CWA to obtain National Pollution Discharge Elimination System (NPDES) permits for discharges from municipal separate storm-sewer systems. These projects were not specifically designed to assess the occurrence of fuel oxygenates in storm water, and many of the cities studied were not using MTBE in either oxygenated gasoline or reformulated gasoline during the sampling period. Also, MTBE may or may not have been used to enhance the octane of conventional gasoline in these cities. The compilations characterized herein provide some insights on the occurrence, or lack of occurrence, of MTBE in storm water in select cities in select States. MTBE was the only oxygenate analyzed. It is important to note that Northeastern States and California, high-use areas of MTBE oxygenated gasoline, were not sampled in the USGS investigations and, as such, the concentration of MTBE in storm water for these States has yet to be characterized.

The design of each study varied depending upon the requirements of each USEPA Region and the extent of monitoring desired by each municipality. A wide variety of conveyance types, such as culverts, concrete pipes, lined ditches, and channels was sampled. Some of the conveyances were open to the atmosphere and others were not. The drainage area of sampled sites was typically very small, with a range of 0.014 to 27.7 km^2 (kilometers

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[2] Drinking-water monitoring for MTBE is not required because a Federal drinking-water standard has not been established. Some States may complete MTBE analysis, however, because of existing or proposed State requirements.

squared). Most sampling sites had a predominant land use including highway, residential, commercial and industrial. Laboratory procedures (Raese et al., 1995) and preliminary study findings (Delzer et al., 1996) are reported elsewhere.

Compilations for All 16 Cities. Summary statistics were calculated on the occurrence and concentration of MTBE for each of the 16 cities where monitoring was completed (Appendix 2). The timeframe in which samples were collected in each city is also presented in Appendix 2. Tallies are provided for the entire calendar year and for the periods Oct. 1 to Mar. 31 and Apr. 1 to Sept. 30, to correspond with the expected seasonal use and non-use of MTBE in carbon monoxide non-attainment areas, respectively.

A total of 592 storm-water samples were collected and analyzed for MTBE and other VOCs (see Table 2.7), and about half were collected during each period. MTBE was detected in 6.9 percent of the 592 samples, or 41 detections. One or more detections were found for Birmingham, AL; Phoenix, AZ; Denver, CO; Colorado Springs, CO; Atlanta, GA; Dallas-Fort Worth, TX; San Antonio, TX; and Baton Rouge, LA. Eighty-three percent of the 41 detections occurred during the Oct. 1 to Mar. 31 period when MTBE would be used in greater volumes in carbon monoxide non-attainment areas, if it were the oxygenate of choice.

Table 2.7: *Occurrence of MTBE in storm water for all 16 cities where monitoring was completed.*

[MTBE, methyl *tert*-butyl ether]

Time period	Number of samples	Number of detections	Percent occurrence	Percent of total detections in the indicated time period
Apr. 1 - Sept. 30	305	7	2.3	17
Oct. 1 - Mar. 31	287	34	11.8	83
Entire year	592	41	6.9	--

The partitioning of MTBE from atmospheric gases to precipitation is very dependent upon air temperature and air concentrations of MTBE (Squillace et al., 1995b, 1996). The higher percent detection of MTBE in storm water during the winter season is attributable, in part, to the more favorable partitioning from air to precipitation, because of lower winter temperatures. Shorter atmospheric half-lives, lower atmospheric levels, reduced MTBE volumes in gasoline, and increased volatility from water during the summer season may also contribute to the observed difference in MTBE's occurrence in storm water between the two periods.

Concentrations of MTBE in storm water for all samples analyzed ranged from below the reporting level to 8.7 µg/L, with a median below the reporting level (Table 2.8). For just those samples in which MTBE was detected, the concentration ranged from 0.2 to 8.7 µg/L, with a median of 1.5 µg/L. As shown in Table 2.8, the median

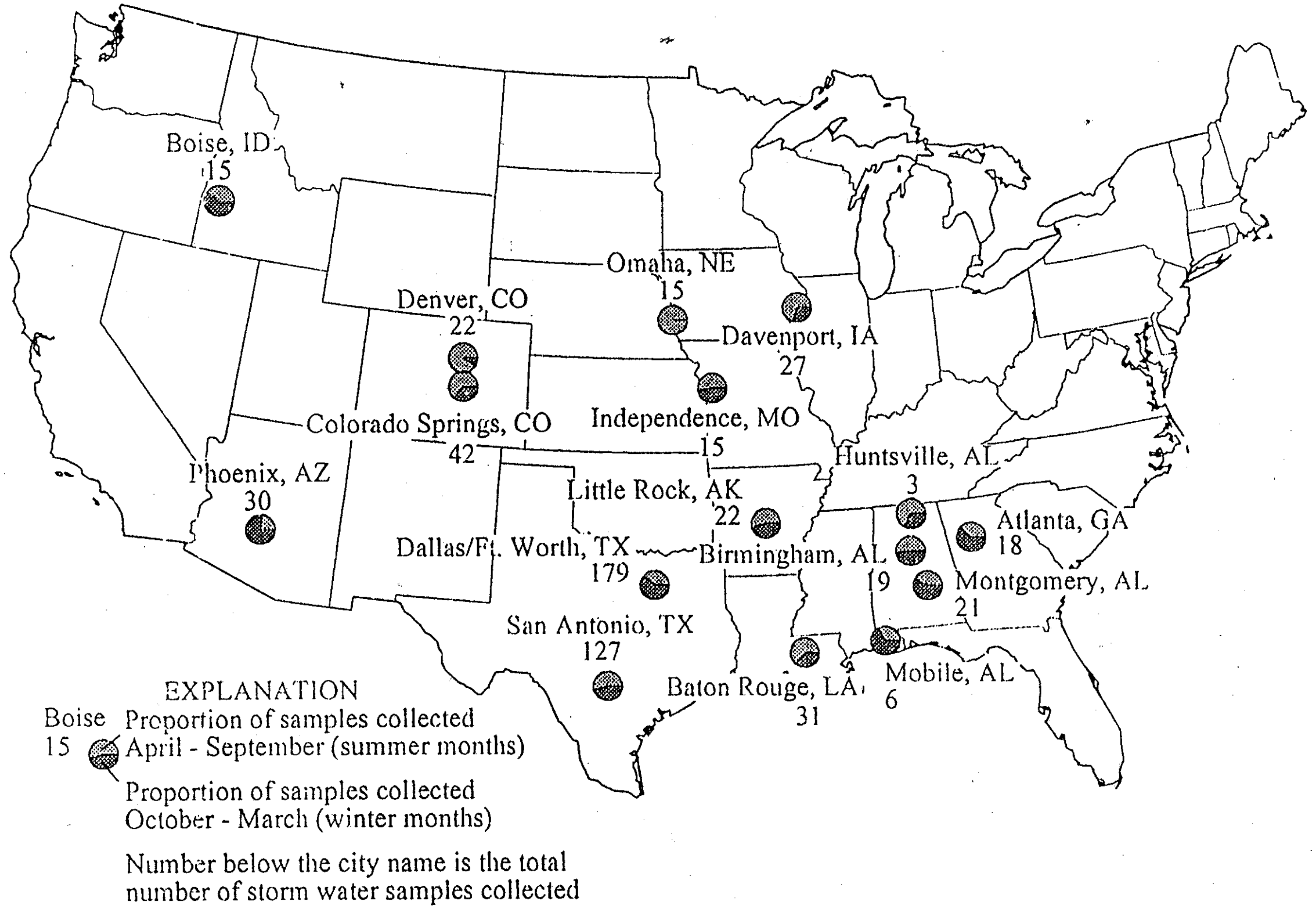

Figure 2.3. Cities and metropolitan areas where MTBE was sampled in urban storm water, 1991-95.

concentrations of MTBE detections were 1.8 µg/L during Apr. 1 to Sept. 30, and 1.5 µg/L during Oct. 1 to Mar. 31. The range of concentrations found was less during the Apr. 1 to Sept. 30 period when MTBE's use in reformulated gasoline and oxygenated gasoline is not expected to occur, except in severe ozone non-attainment areas. None of the cities where sampling was completed are so classified.

Table 2.8: *Concentration of MTBE in storm water for all 16 cities where monitoring was completed.*

[MTBE, methyl *tert*-butyl ether. µg/L, micrograms per liter]

	For all samples analyzed			
Time period	**Number of samples**	**Concentration (µg/L)**		
		Minimum1	**Median[1]**	**Maximum**
Apr. 1 - Sept. 30	305	<0.2	<1	3.4
Oct. 1 - Mar. 31	287	<0.2	<1	8.7
Entire year	592	<0.2	<1	8.7

	For samples with detection of MTBE			
Time period	**Number of samples**	**Concentration (µg/L)**		
		Minimum	**Median**	**Maximum**
Apr. 1 - Sept. 30	7	0.4	1.8	3.4
Oct. 1 - Mar. 31	34	0.2	1.5	8.7
Entire year	41	0.2	1.5	8.7

[1] Eighty-three percent of the storm-water samples were analyzed with a reporting level of 1.0 µg/L, 11 percent were analyzed at reporting level of 0.2 µg/L, and 6 percent of samples were diluted prior to analysis with varied reporting levels.

The median and mean concentrations of MTBE for all samples were shown to be statistically different during the Oct. 1 to Mar. 31 period, in comparison to the Apr. 1 to Sept. 30 period. The Wilcoxon rank sum test (one-sided p-value = 0.0000) and a modified t-test based on Tukey's bi-weight estimator (one-sided p-value = 0.0002) were used to establish the aforenoted statistical inferences. These tests are described elsewhere (Helsel and Hirsch, 1992).

The use of MTBE in oxygenated gasoline was confirmed by State air-pollution officials in Phoenix, AZ; Colorado Springs, CO; and Denver, CO; during the period when USGS's storm-water monitoring was completed. State officials also confirmed that MTBE was not being used in oxygenated fuel programs during the USGS sampling period for the other 13 cities listed in Appendix 2. MTBE may have been used in some of these latter cities as an octane enhancer, although this could not be confirmed. The detection of MTBE in Birmingham, AL; Baton Rouge, LA; Atlanta, GA; Dallas-Fort Worth, TX; and San

Antonio, TX; may be attributable to the use of MTBE as an octane enhancer in these cities. In total, 25 of the 41 MTBE detections, or 61 percent, occurred in cities that were not using oxygenated gasoline or reformulated gasoline.

Fuel oxygenates found in municipal storm water can originate from various point and non-point sources. Gasoline spills on land surfaces can enter storm water, and this source can potentially increase the levels of fuel oxygenates in storm water. Spills are transient events, however, and they would not be comprehensively characterized by the grab-sampling design used in the storm-water studies described above. This may explain, in part, why low levels of MTBE were found in these studies.

Compilations for Select Cities where MTBE was Used Seasonally in Oxygenated Gasoline. As noted previously, the use of MTBE in oxygenated gasoline was confirmed by State air-pollution officials in Phoenix, AZ, Colorado Springs, and Denver, CO, during the period when USGS's storm-water monitoring was completed. The occurrence and concentration of MTBE in storm-water samples for these three cities are summarized in Table 2.9. For each of the three cities, detections in storm-water samples occurred only during the period when oxygenated gasoline was in use. Again, the more favorable partitioning of MTBE to precipitation during colder temperatures, longer atmospheric half-lives in the winter, increased volume of MTBE in gasoline during the oxygenated gasoline season, and decreased volatility from storm water at winter temperatures may explain, in part, the strong seasonal detection pattern. MTBE was detected in 16 of 40 samples, or 40 percent of samples that were collected during the period when MTBE was used in oxygenated gasoline. The concentration of MTBE detections ranged from 1.0 to 4.2 µg/L, with a median concentration of 1.5 µg/L (Appendix 2).

MTBE in Ground Water and in Drinking Water Derived from Ground Water

The characteristics of the programs surveyed and used for this assessment, as well as the sources of the MTBE concentration data, are summarized in Appendices 3 and 4, by State, for ground water and for drinking water, respectively. The programs in Appendix 3 were compiled from (1) results of sampling by the NAWQA Program and (2) retrospective data compiled by the NAWQA Program for occurrence assessment. The information in Appendix 4 was compiled from responses to a request by USEPA's headquarters through the 10 EPA Regions to the States for information on drinking-water programs that have analyzed for MTBE. Samples collected in the NAWQA Program are from individual wells at or near the well head, regardless of the type of well. All drinking-water supplies that are listed in Appendix 4 have ground water as their source water, except for two Wisconsin drinking-water systems and at least one Rhode Island system, which used surface water as the source water.

Ground water and drinking water derived from ground water have been analyzed for MTBE in a number of States. MTBE has been analyzed in 1,516 wells in 33 States as part of 90 ground-water-resource assessment programs or studies (Table 2.10, Appendix 3). At least one detection of MTBE has occurred in 14 of the 33 States and in 25 of 90 assessment programs. From the data gathered by the USEPA request, seven States indicated that

Table 2.9: *Occurrence and concentration of MTBE in storm-water samples for select cities where MTBE was used seasonally in oxygenated gasoline.*

[MTBE, methyl *tert*-butyl ether. µg/L, micrograms per liter]

Study area	Time period	Number of samples	Number of detections	Percent occurrence	Median concentration of detections (µg/L)
Phoenix, Ariz.	Apr. 1 - Sept. 30	7	0	0	1.0
	Oct. 1 - Mar. 31	23	5	22	
	Entire year	30	5	17	
Colorado Springs, Colo.	Apr. 1 - Sept. 30	27	0	0	1.6
	Oct. 1 - Mar. 31	15	10	67	
	Entire year	42	10	24	
Denver-Lakewood-Aurora, Colo.	Apr. 1 - Sept. 30	20	0	0	1.5
	Oct. 1 - Mar. 31	2	1	50	
	Entire year	22	1	5	
All three cities	Apr. 1 - Sept. 30	54	0	0	1.5
	Oct. 1 - Mar. 31	40	16	40	
	Entire year	94	16	17	

MTBE had been sampled in public drinking-water systems and provided results of that sampling (Table 2.10, Appendix 4). Two of the seven States cited above also provided results on private drinking-water wells. In addition, two other States provided results of private well sampling. Six of the seven States reported at least one detection of MTBE in public water systems (Table 2.10). Also, all four States that provided MTBE results for private wells had at least one detection.

Ground Water. MTBE has been detected in ground water as a result of sampling of observation, monitoring, and water-supply wells (at the well head) by the NAWQA Program and other ground-water assessment programs (Appendix 3). Most of these ground-water-resource assessment programs were conducted by the NAWQA Program. The design of studies by NAWQA involves a well-selection strategy that results in a spatially distributed random sampling of a targeted ground-water resource. This approach, therefore, avoids skewing the characterization of water quality toward, for example, contamination plumes (Gilliom et al., 1995; Lapham et al., 1995; Scott, 1990; Squillace et al., 1995b, 1996).

Detections for All Programs Sampled. Detections of MTBE in ground water occurred in Colorado, Connecticut, Georgia, Massachusetts, New Jersey, New Mexico, Nevada, New York, Pennsylvania, Texas, Virginia, Vermont, Washington, and Wisconsin. Overall, about 5 percent (76 detections out of 1,516 samples) of the wells sampled in all networks had a detection of MTBE (Table 2.10). Most of the detections (27 percent of the shallow urban wells sampled–55 detections out of 204 samples) occur in shallow ground water in urban areas (described as NAWQA land-use studies in urban areas) and nearly half of these detections occurred in one urban area, Denver, CO. Only about 1.5 percent of samples from wells screened in shallow ground water in agricultural areas had detections of MTBE (7 detections out of 524 samples). One detection of MTBE occurred from seven samples of shallow ground water beneath an undeveloped land-use setting in Vermont. About 1.7 percent of the wells screened in deeper aquifers or deeper parts of shallow aquifers (13 detections out of 781 samples) had MTBE. The largest concentration of MTBE from deeper ground water was 7.9 µg/L from a well in New York State. These conclusions regarding frequency of detections are essentially the same as those reported by Squillace et al. (1995b, 1996).

The reason(s) for the frequent detection (23 of 29 wells) of MTBE in Denver's shallow ground water is not known. However, contributing factors likely include: (1) extended period of oxygenate use, (2) shallow depth from land surface to ground water, and (3) high vertical hydraulic conductivity. The alluvial aquifer sampled in Denver, and the overlying unsaturated zone, consist of very conductive sand and gravel, and the median depth to ground water is only 4.3 meters (Squillace et al., 1996). Further, MTBE has been used in Denver's oxygenated gasoline program since 1989 (and potentially longer to enhance the octane of conventional gasoline). Aquifers with similarly shallow depth to water and high vertical conductivity exist elsewhere in the Nation, and with extended use of MTBE or other alkyl ether oxygenates, these aquifers may also demonstrate a high frequency of occurrence pattern similar to MTBE in Denver's alluvial aquifer. As explained elsewhere, the high frequency of detection of MTBE in Denver's shallow ground water can not be

Table 2.10: *Summary information for MTBE in ground water and in drinking water derived from ground water for the States surveyed.*

[MTBE, methyl *tert*-butyl ether. NK, not known]

	Number of States	Number of programs	Number of wells (w) or drinking-water systems (s) sampled	Number of States surveyed	Number of programs surveyed	Number of wells (w) or drinking-water systems with a detection of MTBE	Percent of wells (w) or drinking-water systems with a detection of MTBE
				In which there was at least one detection of MTBE			
Ground water							
Ground-water resource assessment	33	90	1,516 (w)[1]	14	25	76 (w)[1]	5 (w)
Drinking water derived from ground water							
Public	7	8	NK[2]	6	7	NK[2]	NK[2]
Private	4	4	NK[2]	4	4	NK[2]	NK[2]

[1] Includes sampling of several springs.

[2] The total number of systems or wells sampled was not reported for each State.

explained by the inclusion of six existing wells that were installed upgradient of point-source releases to define the quality of ambient ground water (Squillace et al., 1996).

The samples from the deeper ground water that had detections of MTBE indicate that MTBE can reach deeper ground water. The occurrence of MTBE in these deeper wells does not in itself explain the mechanism for migration. Possible reasons for the detections of MTBE in deeper ground water include, for example, short, natural ground-water flow paths between recharge areas and deeper ground water, faulty well construction resulting in vertical movement of recently recharged ground water along the well bore to deeper ground water, use of dry wells to rapidly recharge storm-water runoff, or nearby pumping that induces recently recharged ground water to deeper ground water (see the section on "Environmental Behavior and Fate of Fuel Oxygenates" for discussion of the environmental behavior and fate of MTBE in ground water).

Detections for Only Those Programs Where MTBE was Found. Results of monitoring ground water for MTBE for those 25 programs that had at least one detection of MTBE are given in Appendix 5 and the number of detections and percent occurrence are summarized in Table 2.11. Concentrations of MTBE in all samples with concentrations at or above the reporting level used for the summaries in Table 2.11 are given in Appendix 6. In those programs in which there was at least one detection of MTBE (Table 2.11), detection of MTBE occurred in 14 percent (76 of 540) of the wells and only seven wells had concentrations of MTBE that exceeded 10 µg/L. Concentrations of MTBE were below the reporting level in 90 percent of the private and 92 percent of the public-supply wells. None of the samples from private and public-supply wells had concentrations that exceeded 10 µg/L. Detections of MTBE in concentrations in excess of 20 µg/L, the lower limit of the draft drinking-water lifetime health advisory range, occurred at only a small percentage of other types of wells (Table 2.11).

Drinking Water. USEPA does not have the authority to require monitoring or data reporting for MTBE, and consequently the data reported by State agencies was voluntary (Appendix 4). Also, the data reported only represents a fraction of the drinking-water programs in which MTBE has been sampled, and the level of detail of the information reported varies among the States. The reader must also be made aware that the data in Appendix 4 and summarized in Table 2.10 for drinking water may be biased. A number of the sampling programs were conducted when contamination from a nearby point source was known or suspected. For example, in the New Jersey Department of Health data set, where samples were collected in response to consumer complaints, 19 of 31 samples had detections. Three of the eight public water-system sampling programs listed in Appendix 4 are known to have been conducted in response to known or suspected contamination. Also, all private well-sampling programs in Appendix 4 are known to have been conducted in response to consumer complaints.

Because of the small size of the data set for drinking water available for this assessment (only a few programs in a total of nine States), the interpretation of MTBE occurrence is limited only to presence and absence in those States reporting data. It is not possible to describe MTBE occurrence nationwide in drinking water. These data do verify, however, previously published reports that MTBE has been detected in drinking water (Davidson,

Table 2.11: *Summary of non-detection and detection of MTBE for several ranges of concentrations for different types of wells sampled as part of ground-water assessment in programs that had at least one detection of MTBE.*

[MTBE, methyl *tert*-butyl ether. Number of detections (percent detections of total for each well type); RL, reporting level; μg/L, micrograms per liter]

Well type	**Number of wells sampled**	**< RL[1]**	**>= RL to <10 μg/L**	**>= 10 to <20 μg/L**	**>= 20 to <=200 μg/L**	**> 200 μg/L**
Monitoring/observation	170	128 (75)	38 (22)	0 (0)	2 (~1)	2 (~1)
Private	106	95 (90)	11 (10)	0 (0)	0 (0)	0 (0)
Public supply	25	23 (92)	2 (8)	0 (0)	0 (0)	0 (0)
Other/not known	239	218 (91)	18 (8)	1 (<1)	1 (<1)	1 (<1)
All well types	540	464 (86)	69 (13)	1(<1)	3 (<1)	3 (<1)

[1] RL is 0.2 μg/L with the exception of two programs (see appendix 5).

1995a, 1995b; New York State Department of Health and U.S. Department of Health and Human Services, 1995; Post, 1994; Squillace et al., 1995a, 1995b, 1996; USEPA, 1986, 1987a, 1987b).

Results of monitoring drinking water for MTBE for those programs in Appendix 4 that had at least one detection of MTBE are given in Table 2.12, separated into public supplies and private supplies. The MTBE concentration measured in the most recent sampling event was used for the compilations in this table for those public systems or private wells that have been sampled multiple times. The approach of comparing the number of detections to total number of samples was not used as it would have inappropriately combined samples from single sampling events with those of multiple sampling events.

Table 2.12 does not summarize the data provided by Rhode Island for public water systems or private wells and by Texas for private wells. This is because of the lack of information necessary to determine if the data represent multiple samples from a system or well, or single samples from a number of systems or wells.

MTBE was detected in 51 public drinking-water systems in Colorado, Iowa, Illinois, New Jersey, and Texas (Table 2.12). Nearly all of the systems, 47 of 51 (92 percent), with detections of MTBE were at concentrations less than 20 µg/L, the lower limit of the USEPA draft health advisory. Concentrations as high as 63 µg/L in Iowa and 770 µg/L in Illinois have been detected, however (Appendix 7). MTBE was detected in private wells in Indiana, Missouri (Table 2.12), Rhode Island, and Texas. MTBE in five of the six private wells reported from Indiana and Missouri exceeded 200 µg/L, and the concentration of MTBE in the 6th well was within the range of 20 to 200 µg/L. MTBE concentrations in the two private wells in Indiana were 5,400 and 40 µg/L. MTBE concentrations in the four private wells in Missouri, using the latest sampling date, were 1,900, 1,100, 780, and 1,500 µg/L (Appendix 7). It is known from the data provided in Appendix 7 that public drinking-water systems in Rhode Island and private wells in Rhode Island and Texas have had detections of MTBE. However, because the number of unique systems or wells sampled from these two States was not identified, these data could not be included in the analysis in Table 2.12.

Because only a few States have information on MTBE in drinking water, it is not possible in this preliminary assessment to describe MTBE concentrations in drinking water nationwide. A Federal drinking-water standard has not been established for MTBE, however, the USEPA has issued a draft lifetime health advisory of 20 to 200 µg/L. The health advisory is expected to be revised in 1997. MTBE has been detected in 51 public drinking-water systems to date based on limited monitoring, however, when detected, the concentration of MTBE was generally low and nearly always below the lower limit of the current draft USEPA health advisory. This indicates that the consumption of drinking water was not a major route of exposure for these few systems. Additional MTBE monitoring data for drinking water are needed, from both the States that provided information for this preliminary assessment and from States that were unable to provide said information, before the significance of drinking water as a route of exposure can be assessed for the Nation.

Table 2.12: *Occurrence and concentration ranges of MTBE in drinking water for those programs in which there was at least one detection of MTBE.*

[MTBE, methyl *tert*-butyl ether. NK, not known; µg/L, micrograms per liter]

State	Number of systems with detections[1]	Reporting level (µg/L)	Number of systems with detections of MTBE within indicated ranges of concentration			
			> reporting level to 10 µg/L	>=10 to <20 µg/L	>=20 to <=200 µg/L	>200 µg/L
			Public water systems			
New Jersey	35	NK	34	1	0	0
Iowa	1	NK	0	1	0	0
Illinois	7	NK	3	1	2	1
Texas	7	NK	5	1	1	0
Colorado	1	0.2	1	0	0	0
			Private wells			
Missouri	4	NK	0	0	0	4
Indiana	2	NK	0	0	1	1

[1] When multiple detections were reported for a single system or well, the most recent sample was used in this compilation. This table only includes those States where the number of unique public water systems or private wells could be identified. Public water-system data from the State of Rhode Island are not presented in this table, but Appendix 7 indicates MTBE has occurred in at least one public water system. Private well data for the States of Texas and Rhode Island are also not presented in this table, but Appendix 7 indicates MTBE has occurred in at least one private well in each State.

Occurrence and Variability of MTBE In Ground Water Over Time. An important issue relative to MTBE and other fuel oxygenates that remains unanswered is whether or not the frequency of detection and concentrations of these compounds in ground water will increase, remain constant, or decrease with time. This section focuses on existing monitoring data that provide an indication of temporal changes that may occur in wells in which MTBE has been detected. While the environmental behavior and fate of oxygenates in the subsurface is addressed later in this chapter, it is important to note that relative to the BTEX compounds, MTBE and other alkyl ether oxygenates are significantly less degradable.

Despite the extensive literature on UST releases and their impacts on ground water, case studies of the impacts on ground water over time of gasoline containing oxygenates are quite limited. When the source of MTBE in ground water is from a gasoline release, it is expected that the mass of residual gasoline at the water table or in the soil will remain a continuous source for years or possibly decades, depending on the size of the release and remedial efforts to remove the source. A recent study in North Carolina (Daniel, 1995) provides monitoring data for shallow ground water for 11 sampling events over a 26-month period (1/93 - 4/95) at a site where a small gasoline UST had been removed in 1990. Approximately 70 cubic meters of contaminated soil were also removed at that time, but some residual contamination remained present in the area of the water table. Multiple observation wells show consistent concentrations of MTBE over the entire sampling interval. For example, a well close to the area directly affected by the UST had concentrations that varied between 1,200 to 6,800 µg/L (well #3), and a well further downgradient (#17) had concentrations from 66 to 320 µg/L during that same period. Both wells also had measurable concentrations of BTEX from the release. No drinking-water wells were impacted at this site.

Figure 2.4 provides a detailed example of UST impacts on private water-supply wells, in this case MTBE concentrations in three private wells in Missouri, close to a UST that had released gasoline to a fractured bedrock aquifer. Although the tank had been removed before the sampling period shown, residual gasoline remained at or below the water table. Consistent detections of MTBE occurred in the three wells throughout the approximately 3-year periods of sampling, although concentrations and temporal variability differ among the three wells, especially well 3 (Figure 2.4). The range of MTBE concentrations reported was 700 to 14,000 µg/L, 510 to 17,000 µg/L, and 13 to 2,600 µg/L for wells 1, 2, and 3, respectively. These examples show that MTBE can remain at detectable levels near the source for years, although concentrations might vary by as much as several orders of magnitude during that time. The State of Connecticut has collected monitoring data over several years for its public water supplies and private wells. They have indicated that they are aware of multiple instances where MTBE continues to be detected, but that the data are not readily accessible, and were not included in this assessment.

Data characterizing MTBE and DIPE contamination of a New Jersey municipal water supply are presented in McKinnon and Dyksen (1984). The MTBE data reported in this reference are the earliest documentation of detections of MTBE in ground water found by the panel. McKinnon and Dyksen report that more than 25 water samples were collected

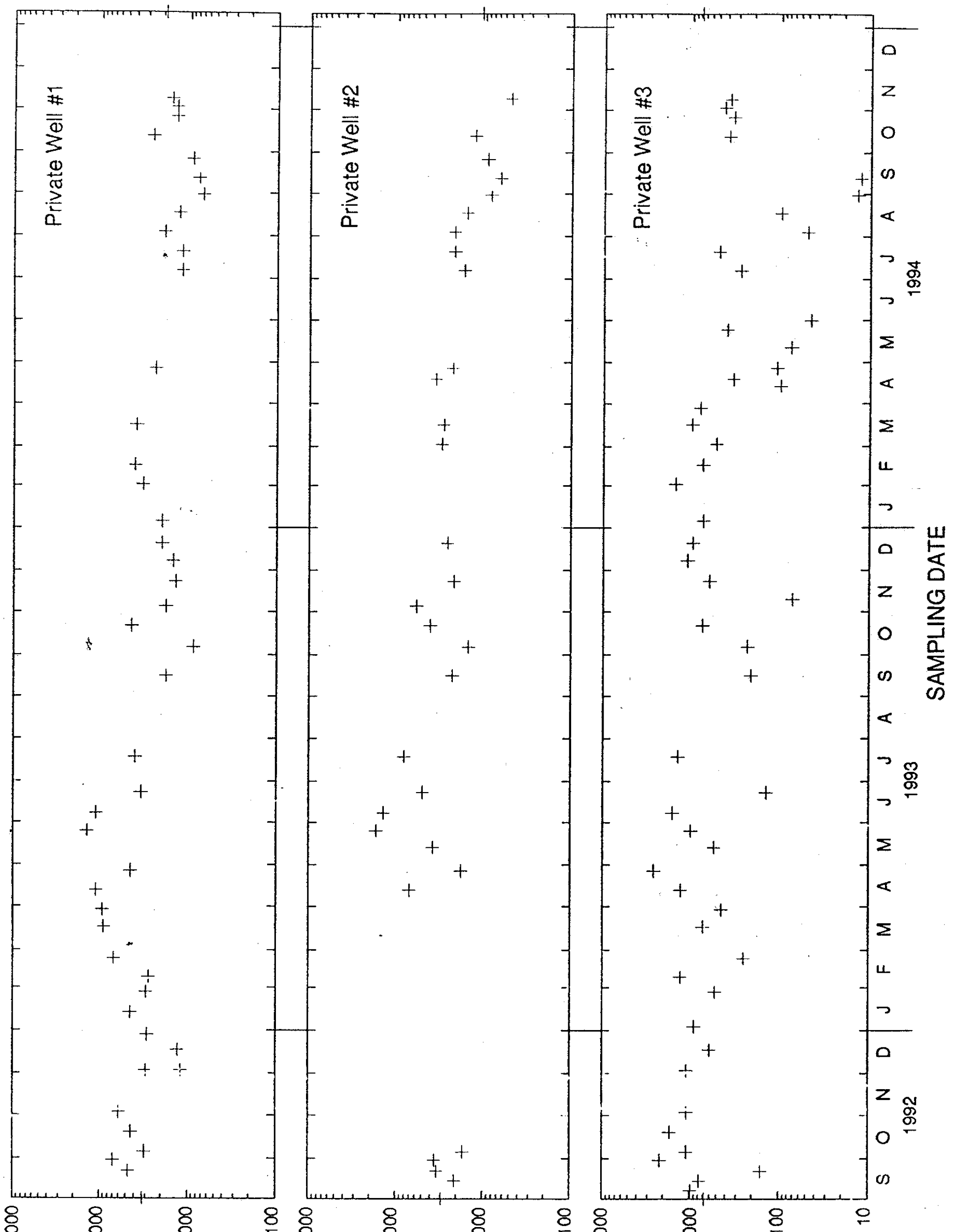

Figure 2.4. Temporal variation of the concentration of MTBE in three private wells in Missouri, 1992-95, which were contaminated by an underground storage tank.

from one well over a 29-month period from November 1980 to April 1983. DIPE concentrations in October 1980 ranged from 70 to 100 µg/L but decreased to below the detection limit by January 1983. MTBE concentrations ranged from 25 to 40 µg/L in October 1980 and declined to less than 10 µg/L by January 1983.

Limited temporal data on MTBE also were obtained for public-supply wells in Iowa, Illinois, and New Jersey. For these systems, MTBE concentration data are available for a sampling period of less than one year (Appendix 7). It is expected that regular monitoring of MTBE concentrations will continue at these facilities, and will provide further characterization of temporal changes.

A short-term data set that demonstrates continued areally extensive occurrence of MTBE in ground water, and its variability over time, is from an areally distributed network of 14 shallow urban wells sampled twice as part of the NAWQA Program in Denver, CO. These fourteen wells were sampled in July 1993 and in August 1995 (Table 2.13).

In the July 1993 sampling, 13 of the 14 shallow urban wells had detections of MTBE, ranging in concentration from 0.2 to 23,000 µg/L. In one well, MTBE was not detected above the reporting level of 0.2 µg/L. In the August 1995 sampling, MTBE was not detected above the same reporting level in three wells. Concentrations of MTBE ranged from 0.2 to 4,940 µg/L for the other 11 wells. MTBE was re-detected in August 1995 in 11 of the 13 wells in which it was detected in July 1993. Thus, the frequency of detection of MTBE did not change markedly. Also, for the 11 wells in which MTBE was detected during both sampling events, the concentration of MTBE decreased in six wells, remained the same in one well, and increased in four wells. Therefore, the number of wells in which concentrations increased over time was about equal to the number of wells in which concentrations decreased. Finally, changes in concentrations of at least one order of magnitude occurred in several wells between sampling events, with concentrations increasing in some of the wells and decreasing in other wells (Table 2.13). However, the median concentration of MTBE in all wells with concentrations above the reporting level remained essentially the same: 1.4 µg/L in July 1993 and 1.1 µg/L in August 1995. It is not known if all of the differences in concentration of MTBE at each well between the two sampling dates represent actual increases or decreases in concentration of MTBE in ground water at the screened interval. Some of the difference could be attributable to other factors; for example, difficulty in obtaining representative samples.

MTBE in Drinking Water Derived from Surface Water

In addition to the information provided by States on MTBE occurrence in drinking water derived from ground water, Wisconsin and Rhode Island provided data on drinking water derived from surface water. In Wisconsin, sampling was conducted during April 1995 at two drinking-water systems with surface-water sources. MTBE was not detected in either system (Appendix 4). In Rhode Island, an unknown number of surface-water samples have been analyzed for MTBE, and one detection of MTBE occurred at a system that used surface water as a source. The detection occurred in a sample collected in January 1994, and the concentration of MTBE was 1 µg/L (Appendix 7).

Table 2.13: *Concentration of MTBE in wells sampled in July 1993 and in August 1995 as part of the NAWQA Program in Denver, Colo.*

[MTBE, methyl *tert*-butyl ether. µg/L, micrograms per liter]

Well number	MTBE concentration measured in July 1993, in µg/L	MTBE concentration measured in August 1995, in µg/L
2	5.1	554
3	0.7	<0.2
4	0.2	3.6
5	3.5	3.7
7	1.4	0.2
15	<0.2	<0.2
16	0.3	0.3
17	1.3	0.7
19	800	70
20	33	<0.2
22	0.5	0.2
24	0.4	1.1
29	3.2	0.4
30	23,000	4,940

Significance of Measured Levels of MTBE for Drinking Water and Aquatic Life

The use of MTBE as an oxygenate and octane enhancer in gasoline has resulted in the compounds occurrence in the hydrologic cycle. This has been demonstrated for air, storm water, and ground water. Oxygenates with similar physical and chemical properties also would be highly mobile and potentially could be found in drinking-water supplies and affect aquatic life. The ease with which these chemicals move through the hydrologic cycle is of concern to some officials who are responsible for public and environmental health. The effect that MTBE and other alkyl ether oxygenates may have is difficult to ascertain because: (1) uncertainty exists about the carcinogenicity of these chemicals; (2) no data exist on the chronic effects that oxygenates may have when aquatic organisms are exposed to small concentrations; (3) few aquatic animals and plants have been tested for acute toxicity; (4) no data exist on synergistic effects of oxygenates with other chemicals that may co-occur; and (5) more data are needed on the sources, spatial distribution, pathways, and trends of concentrations in the environment. These and other unknowns have lead to established and proposed regulatory levels for MTBE in drinking water, for example, that vary from 20 to 230 µg/L (see Figure 2.2).

Existing data on the concentration on MTBE, described in the section on "MTBE in Ground Water and in Drinking Water Derived from Ground Water," indicate that drinking water supplied from ground water is a potential route for humans to be exposed to this chemical. Nearly all concentrations of MTBE measured in drinking-water systems to date were below 20 µg/L, the lower limit of USEPA's current draft lifetime health advisory, and below taste and odor thresholds. This indicates that the consumption of drinking water was not a major route of exposure for these few systems. The use of MTBE, however, has increased dramatically over the past 10 years. The continued increasing use of this oxygenate could increase its occurrence and spatial distribution in ground water, and thereby affect the occurrence and possibly the concentration of MTBE in drinking water derived from ground water.

As noted in the section, "*Drinking Water*," it is not possible to describe MTBE's occurrence in drinking water nationwide from available information. Although nearly all detections in public water-supply systems to date have been below the USEPA draft health advisory, the widespread use of MTBE, the past releases of gasoline from USTs and ASTs, and some instances of impact to drinking water wells, give reason for concern and provide the rationale for a comprehensive national assessment. The USEPA has completed similar assessments previously for other VOCs. Examples include the National Organics Reconnaissance Survey, 1975; the National Organics Monitoring Survey, 1976-77; the Community Water Supply Survey, 1978; the Rural Well Survey, 1978; and the Ground Water Supply Survey, 1981-82 (Pankow and Cherry, 1996). Additional MTBE monitoring data for drinking water are needed, from both the States which provided information for this preliminary assessment and from States that were unable to provide said information, before the significance of drinking water as a route of exposure can be assessed for the Nation.

Very little is known about the concentration of MTBE in surface water, except for the chemical's occurrence in urban storm water. As described previously, MTBE was detected at low concentrations in 40 percent of storm-water samples in the winter in three cities where MTBE was being used in oxygenated gasoline. MTBE was detected in storm water in five additional cities where the oxygenate was presumedly added as an octane enhancer. This illustrates that MTBE enters surface waters, at least during periods of overland runoff and storm-water discharge, and could be a pathway for MTBE to enter drinking-water supplies and ground water. The persistence of MTBE in surface water depends on the waters' velocity, depth, and temperature, and a wide range of half-lives may occur (see Tables 2.16 and 2.17). For deeper rivers, the predicted half-life of MTBE can be several days to three months (see the section on "Surface Waters and Storm Runoff"), which increases the exposure of MTBE to aquatic organisms and the potential for surface water with MTBE to infiltrate into aquifers. Because of the lack of adequate monitoring data and aquatic toxicity data, the significance of low levels of MTBE on drinking water provided from surface water and on aquatic life cannot be assessed.

ENVIRONMENTAL BEHAVIOR AND FATE OF FUEL OXYGENATES

This section relates the environmental behavior and fate of the fuel oxygenate compounds to their physical and chemical properties. It discusses: (1) the migration and partitioning characteristics of the fuel oxygenates; (2) their expected behavior in the ambient hydrologic cycle; (3) their biotic and abiotic degradation; and (4) their possible remediation at point-source release sites. Where appropriate, the properties of the oxygenates are contrasted with those of the BTEX compounds, because the latter are the most toxic compounds typically associated with conventional gasoline. Physical and chemical data for the compounds considered are presented in Tables 2.14 and 2.15. Information in these tables demonstrate that, relative to the BTEX compounds, the oxygenates are more water soluble and sorbed less strongly. Therefore, unless they undergo degradation, oxygenates will be transported with ground-water flow without significant retardation in the subsurface (Cline et al., 1991; Yeh and Novak, 1995). Multiple entries are given for some properties listed in Tables 2.14 and 2.15. This was done to illustrate the range of reported values, and to acknowledge that "best values" were not determined by the authors of this chapter.

Partitioning Between Environmental Compartments

The environment is comprised of a number of different compartments including water, soil, and air. The ways in which the different fuel oxygenate compounds behave in the environment is determined by how they distribute themselves among the different possible compartments. The behavior of an oxygenate compound in water is affected by its: (1) water solubility from gasoline; (2) partitioning between air and water, as occurs in the atmosphere during precipitation events and also in soil above the water table[3]; and (3) partitioning between water and soil materials. Each of these subjects is discussed below.

Solubility in Water from Gasoline. At a given temperature, the solubility of a pure organic liquid (e.g., benzene or MTBE) in water is a constant, represented here as c_s^0 (mg/L). The solubility of a compound from a mixture (i.e., gasoline) will be reduced from c_s^0 by the factor X_m, which is the fraction of the compound in the mixture on a mole-for-mole basis. An additional coefficient γ is needed when the chemical properties of the compound differ significantly from the properties of the mixture as a whole. The result is that the equilibrium water solubility of the compound from the mixture will be given by:

(1) $c_s(mg/L)=\gamma X_m c_s^0$ (all compounds)

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[3] Although it is not as important a process for the behavior of the fuel oxygenates in the water environment, vaporization from liquid gasoline to air can also affect the formation of vapor plumes in soil gas since vapor plumes can contaminate infiltrating water. It is therefore useful to point out that vaporization from gasoline is governed by relationships that are analogous with those presented here for solubility. For any compound of interest, these analogous relationships are obtained by substituting the partial pressure in the soil-gas phase and the pure compound vapor pressure for the solubility from the gasoline mixture and the pure compound solubility, respectively.

Table 2.14: *Reported chemical and physical properties of oxygenates and their degradation products.*

[Values are at 25°C unless otherwise stated. The ranges are from one reference and multiple listings are from multiple sources. Values in bold are values used in the narrative text. MeOH, methanol; EtOH, ethanol; TBA, *tert*-butyl alcohol; MTBE, methyl *tert*-butyl ether; ETBE, ethyl *tert*-butyl ether; TAME, *tert*-amyl methyl ether; DIPE, diisopropyl ether; TBF, *tert*-butyl formate. Sources: Budavari, 1989; Chiou *et al.*, 1979; Flick, 1991; Howard, 1990-93, 1991; Lide, 1994; Lyman *et al.*, 1990a, 1990b; Mackay *et al.*, 1991-93; McAuliffe, 1966; Montgomery and Welkom, 1990; Owen and Coley, 1990; Robbins *et al.*, 1993; Yeh, 1992]

Property	MeOH	EtOH	TBA	MTBE	ETBE	TAME	DIPE	TBF
Molecular weight (g/mole)	32.04	46.07	74.12	88.15	102.18	102.18	102.18	102.13
Specific gravity	0.796	0.794	0.791	0.744	0.73	0.77	0.736-0.7491	0.886
Boiling temp., °C	64.7	78-79	82.9	53.6-55.2	67	86	91 68-69	82
Water solubility, ($Cs_{(o)}$), mg/L	infinitely soluble	infinitely soluble	infinitely soluble	43,000-54,300 **50,000**	~26,000	~20,000	9,000 @ 20°C 2,039	~40,000
Vapor pressure @ 25°C, mm Hg	121.58	49-56.5	40-42	245-256	152	68.3	149-151@ 20°C	81@20°C
Log K_{ow}	-0.75	-0.16 -0.31	0.35	1.20	1.74		1.52	
Henry's Law constant, (H), (atm-m^3)/(g-mole)	4.42E-06	6.17E-6 5.13E-6 6.29E-6	1.175E-5 1.19E-5 1.04E-5 1.47E-5	5.87E-4 1.1E-3 1.4E-3 3E-3	2.66E-3	1.27E-3	9.97E-3 4.77E-3 5.87E-3	2.72E-4
Dimensionless Henry's Law constant (H/RT)	1.087E-4	2.522E-4 2.097E-4 2.571E-4	4.803E-4 4.864E-4 4.251E-4 5.927E-4 **4.8E-4**	2.399E-2 4.496E-2 5.722E-2 1.226E-1 2.6E-2 **0.018 @ 20°C**	1.087E-1	5.191E-2	4.075E-1 1.95E-1 2.399E-1	1.111E-2
Log Koc	0.921 0.44	1.21 0.20	1.57	1.091 1.035 1.049	2.2 0.95	2.2 1.27	1.82 1.46	1.11
CAS no.	67-56-1	64-17-5	75-65-0	1634-04-4	637-92-3	994-05-8	108-20-3	762-75-4

Table 2.15: *Reported chemical and physical properties of gasoline and BTEX compounds.*

[Values are at 25°C unless otherwise stated. The ranges are from one reference and multiple listings are from multiple sources. Values in bold are values used in the narrative text. Sources: Flick, 1991; Howard, 1990-93; Lide, 1994; Lyman *et al.*, 1990a, 1990b; Mackay *et al.*, 1991-93]

Property	Gasoline	Benzene	Toluene	Ethylbenzene	m-Xylene	o-Xylene	p-Xylene
Molecular weight (g/mole)	~100	78.11	92.13	106.16	106.16	106.16	106.17
Specific gravity	0.72-0.78	0.88 0.8765	0.8669	0.867	0.8842	0.8802	0.8611
Boiling temp., ˚C	27-225	80.1	110.6	136.25	139.3	144.4	137-138
Water solubility, ($C_{s(o)}$), mg/L	100-200	1,780	534.8	161	146	175	156
Vapor pressure @ 25˚C, mm Hg		76 95.19	28.4	9.53	8.3	6.6	8.7
Log K_{ow}		2.13 1.56-2.15	2.73 2.11-2.80	3.15	3.20	3.12 2.77-3.12	3.15 3.08-3.29
Henry's Law Constant, (H), (atm-m^3)/(g-mole)		5.43E-3	5.94E-3	8.44E-3	7.68E-3	5.1E-3	7.68E-3
Dimensionless Henry's Law Constant (H/RT)		2.219E-1 **0.22**	2.428E-1	3.45E-1	3.139E-1	2.084E-1	3.139E-1
Log K_{oc}		1.8-1.99 1.50-2.16 **$K_{oc} \cong 80$**	1.56-2.25	2.94 1.98-3.04	2.20 2.04-3.15 **$K_{oc} \cong 160$**	1.68-1.83	2.31 2.05-3.08
CAS no.		71-43-2	108-88-3	100-41-4	108-38-3	95-47-6	106-42-3

For a compound that has a molecular weight that is similar to the mean molecular weight of gasoline (~100 g/mol), X_m is closely approximated as the fraction of the compound on either a weight or volume basis. For example, for a gasoline that is 10 percent by weight MTBE, X_m for MTBE will be ~0.10. For the dissolution of low polarity compounds (like the BTEX group) from gasoline, γ will be close to 1 and equation 1 can then be approximated as:

(2) $c_s(mg/L)=X_m c_s^0$ (low polarity compounds)

The above equation assumes that dissolution is taking place into a water phase in which there are not large amounts of alcohols or other possible cosolvents that could increase the value of c_s^o. Since c_s^o values tend to decrease as the temperature decreases, predicted c_s values will also decrease as the temperature decreases.

Equilibrium solubility data obtained by Barker et al. (1991) indicate that equation 2 is also valid for the dissolution of the alkyl ether oxygenates from gasoline; for MTBE, their data indicate that $\gamma = 1.1$. For the alcohol oxygenates like TBA and EtOH, however, γ values will be significantly larger than one.

MTBE's high water solubility and its high concentration in an MTBE-oxygenated gasoline can result in high concentrations in water. For example, MTBE in a gasoline that is 10 percent (w/w) MTBE, has a solubility in water of approximately 5,000 mg/L at room temperature. By comparison, the total hydrocarbon water solubility for a non-oxygenated fuel is typically about 120 mg/L (Poulsen et al., 1992).

High concentrations of MTBE in ground water near gasoline-spill sites are consistent with experimental water-solubility data. Garrett et al. (1986) and Davidson (1995a) have observed MTBE concentrations as high as 200 mg/L. While these values are not as high (e.g. thousands of mg/L) as might be expected for water equilibrated with gasoline containing several percent MTBE, it is common for relatively uncontaminated water to dilute organic compounds to concentrations below what would be calculated with equation 2 (Feenstra et al., 1996). Also, lower levels in water can result because of depletion of MTBE in the gasoline by the dissolution process itself.

Cosolvent Effects. The high concentrations of fuel oxygenates that can occur in ground water at spill sites have raised the question as to whether or not they could enhance the subsurface transport velocities of the BTEX group through a "cosolvency effect." In fact, research has shown that cosolvency effects typically arise only when the cosolvent is present in water at 1 percent (10,000 mg/L) or more by volume (Pinal et al., 1990, 1991). Such concentrations are much higher than will typically be encountered in water in equilibrium with gasolines containing alkyl ether oxygenates. Gasoline that contains 15 percent MTBE by volume, when equilibrated with water, results in no more than 7,500 mg/L (~0.75% by volume) of MTBE in the water (Barker et al., 1991).

These conclusions regarding the potential for cosolvent effects are supported by laboratory research that employed gasoline to water ratios of 1:10 (v/v). No cosolvency effect was noted for gasolines containing any of the following: 15 percent MTBE, 10 percent EtOH, 10 percent TAME, and 10 percent isopropyl alcohol (Barker et al., 1991; Poulsen et al., 1992). In experiments with MeOH, no cosolvency effect was noted until the MeOH concentrations exceeded 8 percent by volume. As the aqueous concentration of MeOH increased from 8 to 50 percent, the aqueous BTEX solubility continued to increase as well (Barker et al., 1991; Horan and Brown, 1995; Poulsen et al., 1992).

Air/Water Partitioning. Air/water partitioning for a compound is described by its Henry's Law constant *H* which gives the ratio of the partial pressure of the compound in the gas phase to the concentration in the water that is at equilibrium with that partial pressure. Typical units for *H* are atm/(mol/m^3), or equivalently atm-m^3/mol.

When *H* is divided by the product of the gas constant *R* (8.2 x 10^{-5} atm-m^3/mol-K) and the temperature *T* (degrees K), the resulting *H/RT* value is referred to as the dimensionless Henry's Law constant. *H/RT* gives the ratio of the air to water concentrations at equilibrium, that is:

$$H/RT = \frac{\textit{concentration in air}}{\textit{concentration in water}} \tag{3}$$

A compound with a value of *H/RT* of 0.05 or larger will be very volatile from water. A compound with a low value of *H/RT* will tend to remain in the water phase, or viewed from another perspective, it will tend to partition strongly from the gas phase into the water phase if contaminated air is brought into contact with clean water.

At 25 °C, the *H/RT* values for MTBE and TBA are 0.026 and 0.00048, respectively. Other alkyl ether oxygenates exhibit *H/RT* values that are similar to that of MTBE. These values are the reason why the fuel oxygenates exhibit significant partitioning into water (e.g., into precipitation falling through the atmosphere, see the section on "*Air and Precipitation*"). These values also explain why MTBE and the other alkyl ether oxygenates are somewhat difficult to remove from water by aeration, and why TBA is exceedingly difficult to remove from water by aeration. In contrast, benzene exhibits an H/RT value of 0.22 at 25°C, making it rather volatile from water, as compared to the fuel oxygenates.

Water/Soil Partitioning. When a nonionic organic compound is dissolved in ground water and that ground water is moving in a porous subsurface medium, a primary factor determining the velocity of the compound relative to the ground-water velocity is the soil/water partition coefficient, K_d. The value of K_d gives the ratio of the concentration in/on the soil (in grams sorbed per gram of soil) to the concentration in water (in grams per mL).

The ratio of the water velocity to the velocity at which the compound is being transported is frequently referred to as the "retardation factor," *R*. A compound that is not retarded at all will move with the same velocity as the water, and so it exhibits an *R* value of 1. A compound that moves at one-half the velocity of the ground water exhibits an *R* value of 2. In porous media, *R* values can be calculated using the equation:

(4) $$R = 1 + \frac{\rho_b K_d}{n}$$

where ρ_b is the bulk density of the soil or aquifer material, and n is the porosity.

For nonionic compounds, K_d values are often estimated using the equation:

(5) $$K_d = f_{oc} K_{oc}$$

where f_{oc} is the weight fraction of the soil/aquifer material that is organic carbon, and K_{oc} is the organic-carbon-based partition coefficient. While the K_{oc} values of the BTEX compounds are not large enough to cause highly retarded transport (K_{oc} ~80 and ~160 for benzene and *m*-xylene, respectively), the K_{oc} values for the fuel oxygenates are even lower (K_{oc} ~11 and ~29 for MTBE and DIPE, respectively). Thus, under most circumstances, the fuel oxygenates will move at velocities that are similar to that of the local ground water (i.e., with R values fairly close to 1).

As an example, for a subsurface porous medium in which $f_{oc} = 0.005$ (0.5% by weight organic carbon), the predicted K_d values for benzene, *m*-xylene, MTBE, and DIPE will be 0.40, 0.80, 0.055, and 0.15, respectively. The corresponding R values will be about 2.9, 4.9, 1.3, and 1.7, respectively. Results exhibiting this pattern of relative mobilities have been observed in the field. In an injection study in the Borden aquifer conducted by Hubbard et al. (1994), benzene, ethylbenzene, and xylene were all slightly retarded (R = 1.1, 1.5, and 1.5, respectively). In contrast, MTBE movement was not retarded ($R = 1.0$). These results are in reasonable agreement with what would have been predicted based on the organic carbon content of the Borden aquifer ($f_{oc} \sim 0.0002$), namely R = 1.1, 1.8, and 1.2 for benzene, ethylbenzene, and the xylenes, respectively, and $R = 1.01$ for MTBE. Field data from actual spills have also demonstrated that MTBE migrates more rapidly than the BTEX compounds (Daniel, 1995; Davidson, 1995a).

Given the greater mobilities of the fuel oxygenates relative to the BTEX compounds, one can expect that the leading edge of a plume from an MTBE-oxygenated gasoline spill can contain significant levels of MTBE with very little or no BTEX contamination. This effect will be further amplified by the greater biodegradabilities of the BTEX compounds as compared to the alkyl ether oxygenates (see the section on “Biodegradation in the Environment”). In the ambient hydrologic cycle, for typical ground-water depths, the generally non-retarded movement of the alkyl ether oxygenates through the unsaturated zone can lead to the arrival at the water table of ambient levels of MTBE in precipitation within 5 to 10 years (see the section on “Ground Water”).

Behavior in the Ambient Hydrologic Cycle

Air and Precipitation. Similar to other VOCs in gasoline, the production, transport, and use of MTBE and other fuel oxygenates inevitably leads to the release of these compounds to the atmosphere. For example, releases to the atmosphere will occur due to vehicle refueling, evaporative emissions, and incomplete combustion. Once in the atmosphere, the compounds can be removed by chemical degradation and to a much lesser extent by precipitation.

Degradation in the Atmosphere. A limited amount of work has been conducted investigating the atmospheric lifetimes of selected fuel oxygenates. Wallington et al. (1988) and Tuazon et al. (1991) believe that it is reaction with hydroxyl radical (HO•) that is the main determining factor affecting the atmospheric fate of these compounds. For example, Wallington et al. (1988) point out that photolysis (Calvert and Pitts, 1966), reaction with ozone (Atkinson and Carter, 1984), and reaction with NO_3 radicals (Wallington et al., 1986, 1987) are all negligibly slow for ethers and alcohols like MTBE and TBA.

Wallington et al. (1988) studied the rate of reaction of both MTBE and TBA with HO• at 25 ° C. The main by-product of MTBE degradation is *tert* -butyl formate. Based on the values of the rate constants measured in that study and an average tropospheric HO• concentration of 10^6 radicals/cm^3, Wallington et al. (1988) predicted atmospheric lifetimes of about 4 and 11 days for MTBE and TBA, respectively[4]. These are much shorter lifetimes than result from partitioning to precipitation (see the section on "Partitioning to Precipitation"). The conclusions of Wallington et al. (1988) for MTBE were confirmed in a separate study by Smith et al. (1991). The lifetimes noted above apply to regional airsheds, in which the HO• concentration will approximate the 10^6 radicals/cm^3 value assumed by Wallington et al. (1988).

For DIPE, Wallington et al. (1993) found that the reactivity of this compound is higher than that of MTBE, ETBE, MeOH, and TBA. The primary by-products are isopropyl acetate and formaldehyde. If DIPE receives widespread use as a fuel oxygenate in the future, the implications of increased atmospheric levels of these two by-products in the atmosphere would need investigation.

Partitioning to Precipitation. Like other VOCs in the atmosphere, MTBE and other fuel oxygenates will tend to partition into atmospheric water, including precipitation. As discussed in "*Air/Water Partitioning*," the pertinent equilibrium constant for this partitioning is the Henry's Law constant H, or alternatively the dimensionless Henry's Law constant H/RT. Table 2.14 gives H and H/RT values for MTBE and other fuel oxygenates.

For the organic compounds of interest here, current knowledge indicates that partitioning equilibrium can be expected between precipitation arriving at ground surface and the concurrent atmospheric concentrations, also at ground surface (Slinn et al., 1978). A fall distance of only about 10 m (meters) is required to achieve partitioning equilibrium. This means that the assumption of a gas-phase concentration at the surface can be used to predict the corresponding concentration in the precipitation arriving at the surface. As a result, when concentrations immediately surrounding local sources are high when

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[4] Lifetime and half-life are not synonymous terms. Lifetime values can be converted to half-life values by multiplying the lifetime value by the natural logarithm of 2. For example, the atmospheric lifetime for MTBE of about 4 days is equivalent to a half-life of about 2.8 days.

averaged over timeframes of months to years, then rainfall passing through those concentrations may be expected to be similarly elevated. Conversely, a measured precipitation concentration can be used to calculate a corresponding atmospheric gas-phase concentration. For such calculations, the temperature dependence exhibited by H and H/RT for all compounds must be considered.

For an alkyl ether oxygenate like MTBE, falling precipitation will remove (i.e., wash out) only a negligible amount of the gas- phase compound. This may be shown as follows. Since H/RT is the air/water concentration ratio, the air/water mass ratio is obtained by multiplying H/RT by the air/water volume ratio:

$$(6) \qquad \frac{\textit{mass in air}}{\textit{mass in water}} = H/RT \times \frac{\textit{volume of air}}{\textit{volume of water}}$$

For a 1-m^2 (meter squared) area at ground surface and a tropospheric mixing height of 1,000 m, the air volume is 1,000 m^3 (cubic meter). For a precipitation event of 0.025 m (1 inch), the water volume is 0.025 m^3. At 20 °C, H/RT for MTBE is 0.018. Thus, the air/water mass ratio for the single event will be 0.018 x (1,000/0.025) = 720. Only one part in 720 (0.14%) will be removed by the precipitation event. Similar calculations can be made for the other fuel oxygenates.

Based on the above discussion, we conclude that even multiple precipitation events will not provide an important loss conduit for fuel oxygenates from the atmosphere. However, even when little net loss occurs from the atmosphere, it may nevertheless be important as a source since natural waters have not, of course, historically contained the fuel oxygenates. What concentrations are typical for the fuel oxygenates in airsheds and around local sources then becomes the most important issue determining the strength of the atmosphere as a source of these compounds to surface water and ground water.

Surface Waters and Storm Runoff. MTBE and other fuel oxygenates will enter surface waters when water (e.g., urban storm-water runoff or ground water) containing these compounds become surface water. Direct spills of gasoline and the pure oxygenates themselves to surface water are also possible. Concentrations of MTBE that have been found in storm-water runoff were described previously and are summarized in Tables 2.8 and 2.9.

Many variables will affect the occurrence and concentrations of fuel oxygenates in storm water, as well as those in streams and rivers. These variables include fuel-use patterns, weather, unpredicted spill events, and so forth. Comments can, nevertheless, be made concerning the length of time that would be required for fuel oxygenate compounds to be lost by volatilization from flowing surface water, be it a stream, river, or storm-water channel.

Volatilization from flowing water is affected by the rate of mass transport from the bulk water to the air/water interface, and by the rate of mass transport from the air/water interface up into the bulk air (Rathbun, 1990). The inherent volatility of the compound from water as measured by the dimensionless Henry's Law constant also plays a role, as does the temperature. High compound volatility tends to favor dominance of the volatilization process by the transport through the water phase and losses then occur readily at the air/water interface. This condition leads to: (1) rate-determining concentration gradients in the water phase; and (2) volatilization rates which do not depend on compound volatility (e.g., MTBE and benzene can volatilize to the atmosphere at essentially the same rate). Three factors affect the water-side transport process: the water velocity, the water depth, and the temperature. Two factors affect the air-side transport: the wind speed and the temperature.

Using methods outlined by Schwarzenbach et al. (1993), it is possible to carry out calculations yielding the half-life ($t_{1/2}$) values for MTBE, TBA, and benzene from flowing surface waters to a clean atmosphere as a function of water velocity and water depth. Biodegradation of the compounds is not included in the analysis, and the air to which volatilization is occurring is assumed to have negligible amounts of MTBE, TBA, and benzene. Table 2.16 gives results for MTBE at a winter temperature of 5 °C under calm air conditions[5]. For very deep, slow-moving rivers or lakes, the half-lives can be significant [e.g., $t_{1/2}$ = 52 days or 450 km (kilometers) of travel distance for a depth of 10 m and a velocity of 0.1 m/s (meter per second). MTBE entering a river under such conditions will largely remain in the water for months. Corresponding calculations for a summer temperature of 25 °C are given in Table 2-17. For any half-life of about 1 day or greater at 5 °C (Table 2.16), increasing to a summer temperature of 25 °C reduces the half-life as found in Table 2.17 by a factor of about 3. Somewhat greater reductions are predicted for very short half-life conditions as occur in fast-moving, shallow streams and urban-runoff channels. The alkyl ether oxygenates ETBE, TAME, and DIPE can be expected to behave very much like MTBE as described in these two tables. Calculations

Table 2.16: *Estimated half-life of MTBE in a stream or river under calm air conditions at 5 °C.*

[MTBE, methyl *tert*-butyl ether]

Water depth (meters)	Half-life (days) for the following water velocities, meters/second				
	0.032	0.1	0.32	1.0	3.2
0.1	0.17	0.14	0.12	0.11	0.10
0.32	0.72	0.54	0.43	0.37	0.34
1.0	3.3	2.3	1.7	1.4	1.2
3.2	16	11	7.2	5.4	4.3
10	85	52	35	23	17

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[5] The rate of volatilization of MTBE (and other alkyl ether oxygenates) described above and characterized in tables 2.16 and 2.17 will be reduced when the overlying atmosphere contains significant concentrations of the oxygenate. In contrast, biodegradation will reduce the half-life values, however, no information is known to exist on the biodegradation of MTBE in surface water.

for windy conditions yield results that are similar to the results for calm conditions. This is due to the dominance of the mass transport by liquid-side transport for all but the shallowest, fastest moving streams.

Predicted half-lives for benzene are very similar to those for MTBE, with the higher volatility of benzene from water causing the benzene $t_{1/2}$ values to be a little shorter than those for MTBE. For the alcohol TBA, the low H/RT value of this compound causes its half-lives to be increased by about 50 percent as compared to MTBE[6].

Table 2.17: *Estimated half-life of MTBE in a stream or river under calm air conditions at 25 °C.*

[MTBE, methyl *tert*-butyl ether]

Water depth (meters)	Half-life (days) for the following water velocities, meters/second				
	0.032	**0.1**	**0.32**	**1.0**	**3.2**
0.1	0.063	0.042	0.031	0.024	0.021
0.32	0.32	0.20	0.13	0.10	0.077
1.0	1.7	1.0	0.63	0.42	0.31
3.2	8.9	5.2	3.2	2.0	1.3
10	49	28	16	10	6.3

Ground Water. As noted previously, there are two source types for the entry of fuel oxygenates into the subsurface: point sources and non-point sources. For the latter, which are the focus here, one needs to consider the movement of fuel oxygenates from the atmosphere through the unsaturated zone[7] and into the ground-water zone by infiltration and diffusion.

Infiltration will be tied to the precipitation events in the area of interest; diffusion will occur independently of filtration. In order for there to be net downward transport of fuel oxygenates, these two processes require the existence of a concentration gradient between the atmosphere and the subsurface air. As a result, once the local ground water reaches equilibrium with the local ambient air concentration of MTBE at some mean temperature, then the ground-water concentration of MTBE will not build up further, although continued infiltration of the MTBE-containing water will cause the volume of the contaminated water to increase when shallow ground water moves laterally or deeper[8].

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[6] For MTBE half-lives of a day or longer.

[7] No scientific literature was identified as part of this assessment on root uptake of MTBE and other alkyl ether oxygenates. The significance of the process remains to be assessed.

[8] We note in this context that it is now well known that chlorofluorocarbon (CFC) compounds present in the atmosphere can also partition to ground water, and that analyses of ground water for the CFC compounds can even be used to distinguish recent from old ground water (Busenberg and Plummer, 1992; Plummer et al.,

Increases of MTBE in ambient air levels would, of course, cause an increase in the ground-water concentration. When the depth to the water table is around 5 m, modelling done for this assessment indicates that water which has equilibrated with the atmosphere, can occur at the water table in times as short as 5 to 10 years[9]. In some areas of the Nation, dry wells are used to recharge storm water directly to ground water. In such areas, MTBE and other fuel oxygenates are expected to occur in ground water much more rapidly.

Based on the data in Table 2.6, median concentrations of MTBE in urban air studied to date seem to be of the order of a part per billion by volume or less. For a mean winter temperature of 5°C, H for MTBE is 1 x 10^{-4} atm-m^3 /mol (Robbins *et al.*, 1993). Therefore, for an atmospheric concentration of 1 ppb-v, the equilibrium concentration of MTBE will be about 1 μg/L. Similarly, if a specific city had a high MTBE median concentration, say 3 ppb-v, then the equilibrium concentration in water will be about 3 μg/L. If the atmospheric concentrations are systematically much higher around certain source areas such as parking garages, gas stations, or roadways, then precipitation falling near those areas is predicted to have higher levels, which could lead to ground water near these sites having higher levels of MTBE. For example, if the ambient air concentration near a parking garage remained consistent at 30 ppb-v, then 30 μg/L could occur in ground water (and storm water) immediately around the parking garage.

Biodegradation in the Environment

This subsection briefly reviews the literature regarding the biodegradability of fuel oxygenates and their degradation products. Only a limited amount of work has been accomplished for most of the compounds. Moreover, the studies are difficult to compare because they have been performed under a wide variety of experimental conditions. Both aerobic and anaerobic experiments have been conducted. In general, the investigations have demonstrated that the alkyl ether oxygenates (MTBE, TAME, ETBE, DIPE) are difficult to biodegrade. In contrast, BTEX, EtOH and MeOH are readily biodegraded. The difficulty with which alkyl ether oxygenates (and TBA) degrade is due to the resistance to microbial attack of tertiary or quaternary carbon atoms (Suflita and Mormile, 1993; Yeh and Novak, 1994) and the very stable and chemically unreactive ether linkage (Harada and Nagashima, 1975; Salanitro *et al.*, 1994). This subsection also discusses the effects of fuel oxygenates on biodegradation of other gasoline components.

Fuel Oxygenates and By-Products.

Methyl *tert*-butyl ether. Most studies have demonstrated that MTBE is not biodegraded easily. For example, various workers have found MTBE biodegradation did not occur under conditions described as follows: anaerobic microcosms, denitrifying conditions, sulfate-reducing conditions, methanogenic conditions, and anaerobic conditions in landfill aquifer material, soils, and sludges (Fujiwara *et al.*,1984; Moller and Arvin, 1990; Mormile *et al.*, 1994; Salanitro *et al.*, 1994; Suflita and Mormile, 1993; Yeh, 1992; and Yeh and Novak, 1991, 1994, 1995). It has also been reported that there was no

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1993).

[9] The model used in this simulation is briefly described in Appendix 8.

degradation of MTBE in aerobic microcosms after more than 100 days of incubation (Yeh and Novak, 1995). In the only controlled release that has been reported, MTBE was "recalcitrant in the aquifer, exhibiting no mass loss over a sixteen month period" (Hubbard *et al.*, 1994).

In contrast to the preceding observations, degradation of MTBE has been recorded on occasion. In a recent study of an actual fuel spill, MTBE was observed to degrade (decay rate of 0.18 percent per day), but only near the source area (Daniel, 1995). In addition, laboratory studies performed as part of that project showed some degradation in aerobic microcosms prepared from soil collected at the spill's source. TBA was produced in the microcosms but degradation ceased when the concentration of MTBE reached 1 mg/L. Degradation has also been reported in oxygen-limited microcosms after 4 weeks of incubation (Thomas *et al.*, 1988) and in one of three microcosms similarly prepared with Ohio River sediment (Mormile *et al.*, 1994). In the latter experiment, the degradation product was TBA which was then persistent. Other laboratory studies have observed degradation under conditions described as anaerobic or methanogenic, but only within a limited pH range (near pH 5.5), and only when more easily degraded organic matter was not present (Yeh and Novak, 1991).

<u>Ethyl *tert*-butyl ether</u>. ETBE, while also fairly recalcitrant, is less resistant to biodegradation than MTBE. Similar to their work with MTBE, Mormile *et al.* (1994) studied the susceptibility of ETBE to anaerobic (sulfate and/or nitrate reducing conditions and methanogenic conditions) biodegradation. They observed no degradation when ETBE was incubated with various inocula, regardless of the electron acceptor status. Anaerobic degradation was observed, however, in one study after a lag period of approximately 120 days. TBA accumulated and degradation decreased rapidly as the pH was increased (Yeh and Novak, 1991). In more detailed subsequent studies, ETBE was observed to degrade at a slower rate under denitrifying conditions and TBA accumulation was not observed. Some enhancement of degradation was observed under methanogenic conditions, but there was not a direct relationship which suggests that other factors are involved. It was concluded that anaerobic degradation occurred only under limited conditions and when more easily degradable organic matter was not present (Yeh and Novak, 1995). In contrast, under aerobic conditions, after 30 days of incubation, ETBE was degraded rapidly (2.5 mg/L/d per gram of soil) and TBA accumulated.

<u>*tert*-Amyl methyl ether</u>. The susceptibility of TAME to anaerobic (sulfate and/or nitrate reducing conditions and/or methanogenic conditions) biodegradation has been evaluated. No degradation was observed when the microcosms were incubated with various inocula, regardless of the electron acceptor status (Mormile *et al.*, 1994). TAME (3 mg/L) was also not degraded in 60 days when incubated with aquifer material, soil, or activated sludges (Moller and Arvin, 1990).

<u>Diisopropyl ether</u>. Mormile *et al.* (1994) also studied the susceptibility of DIPE to anaerobic (sulfate and/or nitrate reducing conditions and/or methanogenic reducing conditions) biodegradation. No degradation was observed when the microcosms were incubated with various inocula, regardless of the electron acceptor status. Similar results

have been reported in other investigations (Fujiwara *et al.*, 1984; Suflita and Mormile, 1993).

<u>*tert*-Butyl alcohol</u>. Yeh and Novak (1995) reported that TBA persists in active microbial systems, even in microcosms where ETBE is undergoing rapid degradation. The resistance of TBA to biodegradation is consistent with reports by Hickman *et al.* (1989) and Suflita and Mormile (1993). When it does occur, anaerobic degradation of TBA is strongly dependent on the initial concentration, and the indigenous microbial activity (Hickman and Novak, 1989).

<u>*tert*-Butyl formate</u>. MTBE, the most commonly used oxygenate, is subject to photo-oxidation in the atmosphere. Several by-products are generated as a result of this process with a major product being *tert*-butyl formate (TBF). Other products are TBA, acetone, formaldehyde, methyl acetate, carbon dioxide, and water.

Because TBF is resistant to further photo-oxidation, and because its structure suggests resistance to biodegradation, it is a potential ground-water contaminant. No literature citations regarding its degradability have been located.

<u>Methanol</u>. In contrast to MTBE, which showed no mass loss for 16 months in a controlled release, rapid methanol utilization occurred following a three-and-a-half month lag period (Hubbard *et al.*, 1994). After 16 months, and only 45 m of travel, less than 1 percent of the original methanol remained. Insufficient oxygen was present in the plume to account for all of the removal, so methanol is believed to have biodegraded by first aerobic, then anaerobic mechanisms. In another study, methanol degraded rapidly after an acclimation period of only 5 days (Suflita and Mormile, 1993). The rapid degradability is not surprising, because there are at least eleven known species of methanogenic bacteria that can utilize methanol as a sole carbon source (Mormile *et al.*, 1994).

<u>Ethanol</u>. Simple alcohols, such as ethanol, as opposed to structurally complex compounds such as TBA, can be degraded by anaerobic respiration or, in the presence of sufficient oxygen, by aerobic processes (Chapelle, 1992). For example, the previous paragraph discussed the rapid degradability of methanol under anaerobic conditions. In the same experiment, ethanol was also degraded readily, but the acclimation period increased from 5 to 25 days (Suflita and Mormile, 1993). This information suggests that ethanol added to the environment as part of a gasoline spill would readily degrade, albeit slower than methanol.

Effects of Fuel Oxygenates on Biodegradation of Other Gasoline Components. Concern has been expressed that fuel oxygenates would have an inhibitory effect on the degradation of other fuel hydrocarbons such as BTEX. Consequently, several studies have evaluated this possibility. In the study by Hubbard *et al.* (1994), it was noted that the presence of MTBE had no measurable effect on the degradation of BTEX in an aquifer. Similarly, no effect on the BTEX respiration rate of sludge was observed for a hydrocarbon mixture that contained MTBE (Fujiwara *et al.*, 1984). In contrast, 200 mg/L of MTBE reportedly caused a weak inhibitory effect on the biodegradation of BTEX (Moller and Arvin, 1990) and 740 mg/L inhibited the mineralization of the fuel component hexadecane (Horan and Brown, 1995). An inhibitory effect of methanol on BTEX degradation also has been demonstrated (Hubbard *et al.*, 1994). Inhibition can occur because of the toxic effect of high methanol concentrations on microbial populations, oxygen depletion due to methanol biotransformation, and preferential microbial utilization of methanol as a substrate.

Abiotic Degradation in Natural Waters

Based on estimated physical-chemical properties or analogies to other structurally related aliphatic ethers, it has been reported that in water MTBE is not expected to significantly adsorb to bed sediments or suspended sediments, hydrolyze, directly photolyze, or photooxidize via reaction with photochemically produced hydroxyl radicals in the water (Prager, 1992). MTBE has been reported to be chemically unstable in acidic solutions (Budavari, 1989), however, hydrolosis is not expected to be significant in natural waters under normal conditions (pH 5-9) (Lyman *et al.*, 1990b). MTBE may be abiotically transformed via Fenton's reaction (see the section on "Remediation at Point-Source Release Sites"), however, conditions under which this reaction would occur rarely are seen in natural waters.

Remediation at Point-Source Release Sites

Point-source contributions of gasoline to ground water will continue to occur from releases at refineries, fuel distribution centers, during transportation and from refueling stations. Currently, the primary remedial technology for ground water contaminated with gasoline is removal by pumping followed by aboveground treatment. Another commonly used method, soil vapor extraction (SVE), often used in conjunction with pumping, relies on the high vapor pressure and biodegradability of gasoline. With SVE, a vacuum is used to remove the volatile hydrocarbons. The increased air flow resulting from the induced vacuum provides additional oxygen to enhance naturally occurring biodegradation. Consequently, the presence of fuel oxygenates, because of their greater water solubility and resistance to biodegradation, may complicate remedial activities.

There have been several evaluations of remedial technologies for fuel oxygenates, but these have typically indicated low efficiency and high costs. For example, Garrett *et al.* (1986) concluded that filtration through activated carbon is not cost effective: a 0.06-m^3 (cubic meter) bed lasts only a month or less on a household treatment system with an influent concentration of MTBE of only a few milligrams per liter. In more comprehensive studies, it was concluded that MTBE-contaminated water could be remediated and that air stripping, and air stripping with carbon adsorption had the lowest treatment costs (International Technology Corporation, 1991; Truong and Parmele, 1992). A recent survey of fifteen field air-stripping installations indicated that 56 to 99.9 percent of the MTBE was being removed with a median removal rate of 91 percent (API, 1990). Because of the relatively low efficiency of air stripping for MTBE, it may be cost effective to increase the Henry's Law constant (H) by heating the process water (Butillo *et al.*, 1994). Heating the air stripper influent stream to 80 °F over a 30-ft (foot) packed column was equivalent to using 50 °F water and a 60-ft packed column. When there can be no air emissions, use of oxidation with UV/peroxide/ozone is also a feasible treatment alternative. This latter approach, however, has high capital and operating costs.

Addition of hydrogen peroxide, provided initially as a source of oxygen to support microbial degradation, has been found to hydrolyze MTBE and ETBE with the immediate formation of TBA and some acetone (Yeh, 1992; Yeh and Novak, 1995). ETBE was oxidized faster than MTBE when hydrogen peroxide was added (Yeh and Novak, 1995), and the conversion of these two oxygenates was faster in organically rich soils, in comparison to organically poor soils (Yeh, 1992). The reaction only occurred when iron was added to act as a catalyst for the release of hydroxyl radicals from the hydrogen peroxide. The oxidation, therefore, occurs by means of Fenton's reaction. This reaction, however, does not have wide applicability because it is inefficient in aerobic or near-neutral (pH > 6.5) to alkaline environments.

An increasingly common method for managing gasoline spills is intrinsic bioremediation, also termed passive remediation. For this approach, protocols are being developed that demonstrate whether or not the activity of the indigenous microbial population is containing the spill. When such is the case, active remediation is not performed and the site is merely monitored to ensure that containment and natural removal continues. The presence of alkyl ether oxygenates will complicate use of this approach either by inhibiting degradation of the fuel components or because of their own resistance to degradation (Horan and Brown, 1995; Yeh and Novak, 1991). Although degradation in natural systems can be observed, slightly acidic conditions and very low levels of organic matter are required (Yeh and Novak, 1991). Those conditions are common in drinking-water aquifers, but such systems typically lack the nutrients that would be needed to sustain biodegradation.

Despite the resistance of MTBE to indigenous bacteria, it may be possible to develop biotreatment methods. Recent research has demonstrated that both mixed bacterial populations and certain pure bacterial strains, isolated from biotreater sludges and other sources, have the ability to utilize MTBE as a sole carbon source (Mo et al., 1995; Salanitro et al., 1994).

The preceding discussion has focused on the alkyl ethers but circumstances are much different for MeOH and EtOH. For both of these alcohols, biological treatment and intrinsic bioremediation are effective alternatives. However, high concentrations (>10%) may not be biodegradable (Brusseau, 1993) and lesser concentrations have an inhibitory effect on BTEX degradation (Butler et al., 1992).

CONCLUSIONS

Conclusions are based on a review of the scientific literature, data, other agency information, and calculations summarized in this chapter. Except for MTBE, there are little to no monitoring data on fuel oxygenates in commercial use for ground water, surface water, and drinking water. As such, many of the conclusions are specific for MTBE. The following conclusions are made:

Sources and Releases

1. The sources of MTBE and other alkyl ether oxygenates to surface water and ground water are the same as those associated with the production, transport, storage, and use of conventional gasoline.
    - Examples of point sources include releases from refineries and gasoline storage tanks, spillage, and evaporative emissions during fuel handling.
    - Examples of non-point sources include precipitation, overland runoff, and vehicular mobile emissions.
2. The release of MTBE to the environment (water, land, and air) is almost entirely associated with the production, transport, storage, and use of this chemical as a fuel oxygenate.
    - Annual releases from vehicular emissions, evaporative losses from gasoline stations and vehicles, and storage tanks have not been reported in the scientific literature. However, such releases are perceived to be important sources for the entry of MTBE into the hydrologic cycle.
    - Petroleum storage tanks represent the largest population of potential point sources of alkyl ether oxygenates. Localized concentrations in ground water from these sources may be in the thousands of micrograms-per-liter range and some instances of impact to drinking-water wells have been reported. There are no current Federal or State summary data that characterize the frequency or scale of MTBE water-quality impacts from these sources.
    - Estimates of industrial releases reported via the TRI for 1993 totaled about 1.7 million kilograms:
        - About 84 percent of these known releases were from refineries.
        - About 97 percent of these releases were to the atmosphere.

Monitoring and Regulations

3. Comprehensive national monitoring to describe the occurrence of MTBE and other fuel oxygenates in all compartments of the hydrologic cycle and drinking water has not been completed to date.
    - USGS has measured MTBE in ground water in select areas of the Nation and in storm water in 16 large cities.
    - USEPA and others have measured MTBE in ambient air and in air near gas stations, parking lots and garages, roadways, and at or near blending and distribution facilities, as part of special studies.
4. Although information on MTBE monitoring is being compiled by the States and associated findings were sought as part of this assessment, only a few States were able or willing to compile and report their data within the allowable time frame.
    - Additional information is needed from the States and large water utilities to better

characterize monitoring of fuel oxygenates being done nationwide.

- At least eight States have monitored their public water-supply systems or a subset of systems for MTBE.
- Some States have monitored for MTBE in select private wells and public water-supply systems where contamination of ground water was known or suspected.

5. A Federal drinking-water standard or ground-water protection standard has not been established for MTBE or other fuel oxygenates, however, the USEPA has issued a draft drinking-water lifetime health advisory for MTBE of 20 to 200 µg/L.

- At least 11 States have established or are promulgating a drinking-water standard or health advisory/guideline for MTBE.
- At least 10 States have established action levels and/or clean-up levels for releases of gasoline containing MTBE to ground water.

Occurrence in Compartments of the Hydrologic Cycle

6. Available monitoring data show that the use of MTBE as a fuel oxygenate (or as an octane enhancer) can result in the introduction of MTBE to air, storm water, shallow ground water, and to a lesser extent to deeper ground water, in those cities or States where it is used.

- Low concentrations of MTBE have been measured in urban air in six special studies, typically at median levels at or below 1 ppb-v. Higher levels were found near gasoline stations, roadways, parking lots and garages, and blending and distribution facilities.
- MTBE was detected in about 7 percent of 592 storm water samples collected in 16 cities between 1991-1995.
  - When detected the concentration ranged between 0.2 to 8.7 µg/L, with a median of 1.5 µg/L.
  - A strong seasonal pattern of detection was evident; 83 percent of MTBE detections were found during the winter season.
  - MTBE was detected both in cities using oxygenated gasoline to abate carbon monoxide non-attainment, and in cities presumed to have used MTBE in gasoline for octane enhancement.
- MTBE was detected in about 5 percent of over 1,500 wells which were sampled as part of ground-water assessments, and at least one detection was found for 14 of 33 States surveyed to date.
  - Most of the detections occurred in shallow ground water in urban areas.
  - Less than 2 percent of the wells screened in deeper aquifers or deeper parts of shallow aquifers had MTBE, however, these data show that MTBE can reach deeper ground water. The mechanism for this deeper migration is not known.
  - Concentrations of MTBE in ground water greater than about 30 µg/L originate from point sources, whereas lower concentrations may originate from point sources, non-point sources, or both.

7. MTBE has been detected in public and private drinking-water supplies derived from ground water, however, data available for this initial assessment are inadequate to characterize MTBE occurrence in drinking water nationwide.

- MTBE was detected in 51 public drinking-water systems, and in 6 of 7 States that provided information. Nearly all the detections of MTBE in public water-supply systems were at concentrations less than 20 µg/L.

- MTBE has been detected in a few private wells in at least four States. Typically, high levels of MTBE (>200 µg/L) were evident in these wells, which were sampled because of known or suspected point-source contamination.
- Additional MTBE monitoring data for drinking water are needed before the significance of drinking water as a route of exposure can be assessed for the Nation.

Significance of Measured Concentrations to Drinking Water and Aquatic Life

8. Monitoring data indicate the presence of MTBE in some ground-water samples and, as such, drinking water derived from ground water represents a potential exposure route for humans to this chemical. Little information exists on MTBE in drinking water derived from surface water and, therefore, the potential for this exposure route remains to be shown by monitoring.
   - When detected, the concentration of MTBE in public drinking-water systems was nearly always below 20 µg/L, the lower limit of USEPA's current draft drinking-water lifetime health advisory. This indicates that the consumption of drinking water was not a major route of exposure for these systems.
   - With continued increased use, the occurrence and spatial distribution of MTBE in ground water may change from today's understanding, and alter the occurrence and possibly the concentration of this chemical in drinking water derived from ground water.
9. Taste and odor threshold values (for water) have been reported for MTBE, ETBE, and TAME, and the detection values for MTBE fall in the range of the USEPA's drinking-water lifetime health advisory for this chemical, 20 to 200 µg/L.
   - The taste detection thresholds for MTBE from two studies are 39 and 134 µg/L.
   - The odor detection thresholds for MTBE from two studies are 45 and 95 µg/L.
10. Inadequate information exists to assess the significance of MTBE and other alkyl ether oxygenates on aquatic life.
    - Water-quality criteria to protect aquatic life have not been established at the national level.
    - Chronic toxicity data are lacking, and limited information exists on acute toxicity to aquatic animals and plants.
    - Little monitoring data exist to determine the concentration of MTBE present in surface waters, to which aquatic life is exposed.

Environmental Behavior and Fate

11. Water that is equilibrated with an oxygenated fuel can contain a very high concentration of the oxygenate.
    - The water solubility of MTBE will be about 5,000 mg/L at room temperature for a gasoline that is 10 percent MTBE by weight. In contrast, the total hydrocarbon water solubility is typically about 120 mg/L for conventional gasoline.
    - Ground water MTBE concentrations as high as about 200 mg/L have been observed in wells near gasoline spills. The fact that these concentrations are typically lower than saturation levels for gasoline oxygenated with MTBE is likely due to either dilution by uncontaminated water as the contaminated water flows towards and into wells and/or a depletion of the MTBE levels in the gasoline by the dissolution process itself.
12. While gasoline containing alkyl ether oxygenates can lead to high concentrations of

fuel oxygenates in water, these concentrations are not typically high enough to increase either the water solubilities or the transport rates of the BTEX compounds in ground water.

- Gasolines containing very high percentages of EtOH and MeOH are capable of causing this effect, but such fuels are not in widespread use.

13. The fuel oxygenates sorb only weakly to soil and aquifer materials. Therefore, sorption to those materials will not retard their transport by ground water to any significant extent.

14. Relative to the BTEX compounds, MTBE and other alkyl ether oxygenates are significantly less degradable, while EtOH and MeOH are more easily degradable.

- MTBE, ETBE, TAME, and DIPE are not rapidly biodegraded.
- Except when present in concentrations high enough (>10%) to be toxic to microorganisms, EtOH and MeOH are readily degraded. Degradation of EtOH and MeOH may inhibit degradation of other gasoline components because they can be a preferred or competing substrate for indigenous microbes.
- For the limited conditions under which biodegradation has been observed, TBA, also difficult to degrade, is often formed from MTBE and ETBE.

15. MTBE and other alkyl ether oxygenates have lifetimes in the atmosphere that range from 4 days to 2 weeks. The main degradation pathway seems to be reaction with hydroxyl radicals.

16. Washout of gas-phase MTBE by precipitation will not by itself significantly alter the gas-phase concentration of this compound in the atmosphere. As such, washout by precipitation is not an important mechanism for the removal of this oxygenate from the atmosphere. Nevertheless, the partitioning of MTBE to water (precipitation) is strong enough to allow for measurable inputs of MTBE to surface water and ground water.

- For general atmospheric levels of MTBE in urban areas, based on limited available information, the concentration of MTBE in precipitation can range from sub micrograms per liter to about 3 µg/L.
- Near gasoline stations, roadways, and parking lots and garages, that experience consistently high sources of MTBE to the atmosphere, the concentration of MTBE in precipitation can be increased above the 3 µg/L level noted above.

17. The concentration of MTBE in ground water, that originates from atmospheric sources, is expected to change in response to increases or decreases in the concentration of MTBE in urban air. Several years or longer will be required before such changes are evident in ground water.

18. While MTBE is volatile from water, in large rivers and some streams this compound will not be lost quickly (e.g. half-lives >1 day) by volatilization, especially at low temperature. The rate of volatilization will frequently be controlled by mass-transport limitations in the water phase, and under such circumstances MTBE and other alkyl ether oxygenates will exhibit volatilization rates (half-lives) that are similar to those of the BTEX compounds.

19. Abiotic degradation processes, including hydrolysis, direct photolysis and indirect photolysis (e.g., reaction with hydroxyl radicals) are not expected to significantly alter the concentration of MTBE in natural waters.

Remediation

20. The presence of MTBE and other alkyl ether oxygenates does not prevent the application of conventional (active) remedial methods (air stripping, carbon adsorption,

and soil vapor extraction) for gasoline spills but it does raise the cost.

- Considering the equilibrium partitioning between air and water, the alkyl ether oxygenates are less volatile from water than the BTEX compounds.
- The alkyl ether oxygenates can be removed from water using aeration, but only with high air/water ratios.

21. The application of intrinsic (passive) bioremediation, an emerging, inexpensive approach to the management of gasoline spills, may be limited because of the difficulty with which alkyl ether oxygenates are biodegraded and the tendency of these compounds to migrate from release sites. For contaminant plumes containing EtOH or MeOH, however, intrinsic bioremediation, or enhancements to in-situ bioremediation will remain effective.

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REFERENCES

Allen, M., and D. Grande, 1995, Reformulated gasoline air monitoring study: Madison, Wis., State of Wisconsin Department of Natural Resources Bureau of Air Management, Publication No. AM-175-95.

Angle, C.R., 1991, If the tap water smells foul, think MTBE, letter to the editor: Journal of the American Medical Association, v. 226, no. 2, p. 2985-86.

American Chemical Society, 1996, Facts and figures for the chemical industry, 1. Production by the U.S. Chemical Industry: Chemical and Engineering News, June 24, 1996, p. 40-46.

American Petroleum Institute, 1989, Aboveground storage tank survey: Washington, D.C., American Petroleum Institute Health and Environment Affairs Department, Publication No. 301, 44 p.

American Petroleum Institute, 1990, A compilation of field-collected cost and treatment effectiveness data for the removal of dissolved gasoline components from groundwater: Washington, D.C., American Petroleum Institute, Publication No. 4525.

American Petroleum Institute, 1994a, A survey of API members' aboveground storage tank facilities: Washington, D.C., American Petroleum Institute Health and Environment Affairs Department, Publication No. 330, 65 p.

American Petroleum Institute, 1994b, Source control and treatment of contaminants found in petroleum product terminal tank bottoms: Washington, D.C., American Petroleum Institute, Publication No. 4606.

American Petroleum Institute, 1995a, Tertiary-amyl methyl ether (TAME): Washington, D.C., Toxicity to the freshwater alga, *Selenastrum capricorrutum*: Toxicology Report No. 402, CAIS Abstract No. 41-5415, 76 p.

American Petroleum Institute, 1995b, *Tert*-amyl methyl ether (TAME) - acute toxicity to daphnids (*Daphnia magna*) under flow-through conditions: Washington, D.C., TSCA Guideline 797.1300, Toxicology Report No. 406, CAIS Abstract No. 42-1519, 76 p.

American Petroleum Institute, 1995c, *Tert*-amyl methyl ether (TAME) - acute toxicity to mysid shrimp (*Mysidopsis bahia*) under static renewal conditions: Washington, D.C., TSCA Guideline 797.1930, Toxicology Report No. 407, CAIS No. 42-1520, 84 p.

American Petroleum Institute, 1995d, *Tert*-amyl methyl ether (TAME) - acute toxicity to rainbow trout (*Oncorhynchus mykiss*) under flow-through conditions: Washington, D.C., TSCA Guideline 797.1400, Toxicology Report No. 408, CAIS Abstract No. 42-1521, 80 p.

Anderson, P.D., Memorandum Dated September 22, 1986, State of Massachusetts, Executive Office of Environmental Affairs, Department of Environmental Quality Engineering, Office of Research and Standards.

Association for the Environmental Health of Soils - (AEHS), 1994, State cleanup standards for hydrocarbon contaminated soil and groundwater: Soils analysis, monitoring and remediation, December, p. 14-48.

Atkinson, R., and W.P.L. Carter, 1984, Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions: Chem. Rev., v. 84, p. 437-470.

Barker, J.F, R.W. Gillham, L. Lemon, C.I. Mayfield, M. Poulsen, and E.A. Sudicky, 1991, Chemical fate and impact of oxygenates in groundwater: Solubility of BTEX from Gasoline-Oxygenate Compounds: American Petroleum Institute Publication 4531, Washington, D.C., 90 p.

Barks, C.S., 1994, Verification and adjustment of regional regression models for urban storm-runoff quality using data collected in Little Rock, Arkansas: U.S. Geological Survey Water-Resources Investigations Report 94-4216, 12 p.

Bengtsson, E.B., and M. Tarkpea, 1983, The acute aquatic toxicity of some substances carried by ships: Mar Pollut. Bulletin 14(6), p. 213-214.

Benjamin, S., and D. Belluck, 1994, State groundwater regulation: Guide to laws, standards, and risk assessment: BNA Books, Bureau of National Affairs, Inc., Washington, D.C.

Boeri, R.L., P.L. Kowalski, and T.J. Ward, 1994a, Acute toxicity of ethyl tertiary butyl ether to the Sheepshead minnow, *Cyprinodon variegatus*: Marblehead, Mass.,T.R. Wilbury Laboratories, Inc., Study no. 425-AR, p. 1-17.

Boeri, R.L., P.L. Kowalski, and T.J. Ward, 1994b, Acute toxicity of ethyl tertiary butyl ether to the mysid, *Mysidopsis bahia*: Marblehead, Mass., T.R. Wilbury Laboratories, Inc., Study no. 426-AR, p. 1-21.

Bowman, M.C., W.L. Oller, T. Cairns, A.B. Gosnell, and K.H. Oliver, 1981, Stressed bioassay systems for rapid screening of pesticide residues. Part I: Evaluation of bioassay systems: Arch. Environ. Contam. Toxicol., v. 10, p. 9-24.

Bridie, A.L., C.J.M. Wolff, and M. Winter, 1979, The acute toxicity of some petrochemicals to goldfish: Water Res., v. 13, no. 7, p. 623-626.

Brusseau, M.L., 1993, Complex mixtures and groundwater quality: U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, EPA/600/S-93/004, Washington, D.C.

Budavari, S., ed., 1989, The merck index (11th ed): Rahway, New York.

Busenberg, E., and L.N. Plummer, 1992, Use of chlorofluorocarbons (CCL_3F and Ccl_2F_2) as hydrologic tracers and age-dating tools: The alluvium and terrace systems of central Oklahoma: Water Resources Research, v. 28, no. 9, p. 2257-2283.

Butillo, J.V., A.D. Pulido, N.M. Reese, and M.A. Lowe, 1994, Removal efficiency of MTBE in water: Confirmation of a predictive model through applied technology, Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Dublin, Ohio, National Ground Water Association, Prevention, Detection, and Remediation Conference, Houston, Texas, November 2-4, 1994, p. 91.

Butler, B.J., M. Vandergriendt, and J.F. Barker, 1992, Impact of methanol on the biodegradation activity of aquifer microorganisms: presented at SETAC, 13th Annual Meeting, November 8-12, 1992, Cincinnati, Ohio.

Calvert, J.G., J.B. Heywood, R.F. Sawyer, and J.H. Seinfeld, 1993, Achieving acceptable air quality: Some reflections on controlling vehicle emissions: Science, v. 261, p. 37-45.

Calvert, J., and J.N. Pitts, Jr., 1966, Photochemistry: New York, Wiley.

Chapelle, F.H., 1992, Ground-water microbiology and geochemistry: New York, Wiley and Sons.

Chemical Communication Subcommittee, 1990, Summary of State and Federal drinking water standards and guidelines: Federal-State Toxicology and Regulatory Alliance Committee (FSTRAC), February 1990.

Chiou, C.T., L.J. Peters, and V.H. Freed, 1979, A physical concept of soil-water equilibria for nonionic organic compounds: Science, v. 206, p. 831-832.

Cline, P.V., J.J. Delfino, and P.S.C. Rao, 1991, Partitioning of aromatic constituents into water from gasoline and other complex solvent mixtures: Environmental Science and Technology, v. 25, no. 5, p. 914-920.

Conrad, D.L., 1995, Facts of gasoline/oxygenate releases to the environment--A review of the literature: Port Arthur, Texas, Texaco Research and Development Department.

Cowgill, U.M., and D.P. Milazzo, 1991, The sensitivity of *Ceriodaphnia dubia* and *Daphnia magna* to seven chemicals utilizing the three-brood test: Arch. Environ. Contam. Toxicol., v. 20, no. 2, p. 211-217.

Daniel, R.A., 1995, Intrinsic bioremediation of BTEX and MTBE: Field, laboratory and computer modeling studies: Raleigh, North Carolina, North Carolina State University, Department of Engineering, Thesis.

Davidson, J.M., 1995a, Fate and transport of MTBE-the latest data: Proceedings of the 1995 Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Remediation Conference, November 1995, Houston, Texas, 17 p.

Davidson, J.M., 1995b, Groundwater health issues of MTBE: Sources: MTBE in precipitation, MTBE in ground water, fate and transport, MTBE in drinking water: Reformulated Gasoline Workshop, Oct. 12, 1995. Fort Collins, Colo., Alpine Environmental, Inc.

Davidson, J.M., R.A. Rykowski, D.J. Bott, and W.J. Piel, 1995, MTBE releases into the environment and their potential for occurrence in water supplies: Paper submitted in November for publication to Risk Analysis: An International Journal, 171 p.

Davidson, Naomi, Letter Dated September 17, 1987, State of Connecticut, Department of Health Services.

Dawson, G.W., A.L. Jennings, D. Drozdowski, and E. Rider, 1977, The acute toxicity of 47 industrial chemicals to fresh and saltwater fishes: Journal of Hazardous Materials, v. 1, no. 4, p. 303-318.

Delzer, G.C., J.S. Zogorski, T.J. Lopes, and R.L. Bosshart, 1996, Occurrence of the gasoline oxygenate MTBE and BTEX compounds in urban stormwater in the United States, 1991-95: U.S. Geological Survey Water-Resources Investigations Report 96-4145, 6 p.

Dey, J.C., R.A. Brown, and W.E. McFarland, 1991, Hazardous material control 4, p. 32-39, *as cited in* Suflita, J.M., and Mormile, M.R., 1993, Anaerobic biodegradation of known and potential gasoline oxygenates in the terrestrial subsurface: Environmental Science and Technology, v. 27, no. 5, p. 967-968.

De Zwart, D., and W. Slooff, 1987, Toxicity of mixtures of heavy metals and petrochemicals to *Xenopus laevis*: Bull. Environ. Contam. Toxicol. 38(2), p. 345-351.

Feenstra, S, J.A. Cherry, and B.L. Parker, 1996, Conceptual models for the behavior of dense non-aqueous phase liquids (DNAPLs) in the subsurface, *in* Pankow, J.F., and J.A. Cherry, eds., Dense chlorinated solvents and other DNAPLs in groundwater: Portland, Oregon, Waterloo Press, chap. 2, p. 53-88.

Flick, E.W., ed., 1991, Industrial solvents handbook (4th ed.): Park Ridge, New Jersey, Noyes Data Corporation.

Fujiwara, T., T. Kinoshita, H. Sato, and L. Kojima, 1984, Biodegradation and bioconcentration of alkylethers: Yukaguku, v. 33, p. 111-114.

Garrett , P., 1987, Oxygenates as ground water contaminants: Paper presented at 1987 Conference on Alcohols and Octane, April 1 and 2, San Antonio, Texas.

Garrett, P., M. Moreau, and J.D. Lowry, 1986, MTBE as a ground water contaminant: Paper presented at the 1986 NWWA/API Conference on Petroleum and Organic Chemicals in Ground Water, Houston, Texas, p. 227-238.

Geiger, D.L., D.J. Call, and L.T. Brooke, 1988, Acute toxicities of organic chemicals to fathead minnows (*Pimephales promelas*): Center for Lake Superior Environmental Studies, University of Wisconsin, Superior, Wisc., v. 1-5.

Gilliom, R.J., W.M. Alley, and M.E. Gurtz, 1995, Design of the National Water-Quality Assessment Program: Occurrence and Distribution of Water-Quality Conditions: U.S. Geological Survey Circular 1112, 33 p.

Harada, T., and Y. Nagashima, 1975, Utilization of alkylether compounds by soil bacteria: Journal of Ferment Technology, v. 53, p. 218-222.

Haslam, Bob, 1996, A moving story :MTBE at Summit Lodge-Killington, Vermont: LUST Line Bulletin 24, July 1996, p. 15.

Helsel, D.R., and R.M. Hirsch, 1992, Statistical methods in water resources: New York, Elsevier, 525 p.

Hickman, G.T., and J.T. Novak, 1989, Relationship between subsurface biodegradation rates and microbial density: Environmental Science and Technology, v. 23, p. 525-532.

Hickman, G.T., J.T. Novak, M.S. Morris, and M.J.J. Rebhun, 1989, Effects of site variations on subsurface biodegradation potential: Journal of Water Pollution Control Fed.: v. 61, p. 1564-1575.

Hoekman, S.K., 1992, Speciated measurements and calculated reactivities of vehicle exhaust emissions from conventional and reformulated gasolines: Environmental Science and Technology, v. 26, no. 6, p. 1206-1216.

Horan, C.M., and E.J. Brown, 1995, Biodegradation and inhibitory effects of methyl-tertiary-butyl ether (MTBE) added to microbial consortia-Proceedings of the 10th Annual Conference on Hazardous Waste Research, May 23-25, Manhatten, Kan., Great Plains/Rocky Mountain Hazardous Substance Research Center, p. 11-19.

Howard, P.H., 1990-93, Handbook of environmental fate and exposure data for organic chemicals, v. I-V: Chelsea, Mich., Lewis Publishers, Inc.

Howard, P.H., 1991, Handbook of environmental degradation rates: Chelsea, Michigan, Lewis Publishers, Inc.

Hubbard, C.E., J.F. Barker, S.F. O'Hannesin, M. Vandergriendt, and R.W. Gillham, 1994, Transport and fate of dissolved methanol, methyl-tertiary-butyl-ether, and monoaromatic hydrocarbons in a shallow sand aquifer: American Petroleum Institute Publication no. 4601: Appendix H, Institute for Groundwater Research, Waterloo, Ontario, Canada, University of Waterloo.

Illinois Environmental Protection Agency, 1994, Notice of health advisory for methyl tertiary-butyl ether (MTBE): Environmental Register, no. 484, July 1994, p. 18-25.

International Technology Corporation, 1991, Cost-effective, alternative treatment technologies for reducing the concentrations of methyl tertiary butyl ether and methanol in ground water: Washington, D.C., American Petroleum Institute Publication no. 4491.

James, F., 1995, Agribusiness keeps its clout in GOP's House: Chicago Tribune, Nov. 5, 1995.

Jaremn, Raymond, Letter Dated September 8, 1987, State of Connecticut, Department of Health Services.

Johnson, T., M. McCoy, and T. Wisbith, 1995, A study to characterize air concentrations of methyl tertiary butyl ether (MTBE) at service stations in the Northeast: Washington, D.C., American Petroleum Institute, Health and Environmental Sciences Department, API Publication no. 4619, 75 p.

Keller, A.E., 1993, Acute toxicity of several pesticides, organic compounds, and a wastewater effluent to the freshwater mussel, *Anodonta imbecillis*, *Ceriodaphnia dubia*, ...: Bull. Environ. Contam. Toxicol., v. 51, no. 5, p. 696-702.

Kelly, T.J., P.J. Callahan, J. Plell, and G.F. Evans, 1993, Method development and field measurements for polar volatile organic compounds in ambient air: Environmental Science and Technology, v. 27, no. 6, p.1146-1153.

Kirschner, E.M., 1995, Production of top 50 chemicals increased substantially in 1994: Chemical and Engineering News, April 10, 1995, p. 16-22.

Kirchstetter, T.W., B.C. Singer, R.A. Harley, G.R. Kendall, and Waymond Chan, 1996, Impact of oxygenated gasoline use on California light-duty vehicle emissions: Environmental Science and Technology, v. 30, no.2, p661-670.

Komex·H_2O Science, 1997, Draft Investigation Report: MTBE contamination, City of Santa Monica Charnock Well Field, Los Angeles, California: Huntington Beach, CA, March 21, 121 p.

Koterba, M.T., F.D. Wilde, and W.W. Lapham, 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program: Collection and documentation of water-quality samples and related data: U.S. Geological Survey Open-File Report 95-399, 113 p.

Kuhn, R., M. Pattard, K. Pernak, and A. Winder, 1989, Results of the harmful effects of selected water pollutants (anilines, phenols, aliphatic compounds) to *Daphnia magna*: Water Resources 23(4), p. 495-499.

Lagerspetz, K.Y.H., A. Tiiska, and K.E.O. Senius, 1993, Low sensitivity of ciliary activity in the gills of *Anodonta cygnea* to some ecotoxicals: Comp. Biochem. Physiol., v. 105C, no. 3, p. 393-395.

Lapham, W.W., F.D. Wilde, and M.T. Koterba, 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program -- selection, installation, and documentation of wells, and collection of related data: U.S. Geological Survey Open-File Report 95-398, 69 p.

Lide, D.R., editor-in-chief, 1994, CRC Handbook of Chemistry and Physics (75th ed,): Boca Raton, Fla., CRC Press.

Lopes, T.J., K.D. Fossum, J.V. Phillips, and J.E. Monical, 1995, Statistical summary of selected physical, chemical, and microbial characteristics and estimates of constituent loads in urban stormwater, Maricopa County, Arizona: U.S. Geological Survey Water-Resources Investigations Report 94-4240, 26 p.

Lund, L., 1995, Changes in UST and LUST: The Federal perspective: Lake Zurich, Ill., Tank Talk, Steel Tank Institute, v. 10, no. 2-3, p. 7.

Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt, 1990a, Handbook of chemical property estimation methods: Environmental behavior of organic chemicals: Washington, D.C., American Chemical Society.

Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt, 1990b, Handbook of organic chemical property estimation methods (2nd ed.): Environmental behavior of organic compounds: New York, McGraw Hill.

Mackay, D., G.W.Y. Shiu, and K.C. Ma, 1991-95, Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals: Chelsea, Mich., Lewis Publishers, v. I-IV.

Mason, A.S., Letter Dated September 14, 1987, State of Connecticut, Department of Health Services.

McAuliffe, C., 1966, Solubility in water of paraffin, cycloparaffin, olefin, acetylene, cycloolefin, and aromatic hydrocarbons: Journal of Physical Chemistry, v. 70, no. 4, p. 1267-1275.

McCoy, M., Jr., and T. Johnson, 1995, Petroleum industry data characterizing occupational exposures to methyl tertiary-butyl either (MTBE) 1983-1993: Washington, D.C., American Petroleum Institute, Publication no. 4622.

McKinnon, R.J., and J.E. Dyksen, 1984, Removing organics from groundwater through aeration plus GAC: Journal of American Water Works Association, May, p. 42-47.

McQuillan,Dennis, Letter Dated September 11, 1987, State of New Mexico, Health and Environment Department, Environment Improvement Division.

Mo, K., C.O. Lora, A. Wanken, and C.F. Kulpa, 1995, Biodegradation of methyl-t-butyl ether by pure bacterial cultures: American Society of Microbiology, 95th General Meeting, Washington, D.C., May 8-12.

Moller, H., and E. Arvin, 1990, Solubility and degradability of the gasoline additive MTBE, methyl-*tert*-butyl-ether and gasoline compounds in water, *in* Arendt, F., Hinsenveld, M., and van den Brink, W.J., eds, Contaminated Soil '90: Dordrecht, The Netherlands, Kluwer Academic Publishers, p. 445-448.

Montgomery, J.H., and L.M. Welkom, 1990, Ground water chemicals desk reference: Chelsea, Mich., Lewis Publishers.

Mormile, M.R., S. Liu, and J.M. Suflita, 1994, Anaerobic biodegradation of gasoline oxygenates: Extrapolation of information to multiple sites and redox conditions: Environmental Science and Technology, v. 28, no. 9, p.1727.

National Petroleum News, 1994, Supplement to December issue of National Petroleum News: Chicago, Ill., National Petroleum News, p. 3-4.

National Petroleum News, 1995, National Petroleum News 1995 Market Facts: Chicago, Ill., National Petroleum News, 198 p.

NATLSCO, 1995, Service station personnel exposures to oxygenated fuel components - 1994: Washington, D.C., American Petroleum Institute, Publication no. 4625.

New Jersey Drinking Water Quality Institute, 1994, Maximum contaminant level recommendations for hazardous contaminants in drinking water: September 26, 1994.

New York State Department of Health and U.S. Department of Health and Human Services, 1995, Draft health consultation, Silver Stream Village Mobile Home Park, Orange County, New Windsor, New York: Public Health Service, Agency for Toxic Substances and Disease Registry.

Oliver, T., P. Kostecki, and E. Calabrese, 1995, State summary of soil and groundwater cleanup standards: Soil and Groundwater Cleanup, November, p. 16-51.

Owen, K., and T. Coley, 1990, Automotive fuels handbook: Warrendale, Penn., Society of Automotive Engineers, Inc.

Pankow, J.F., and J.A. Cherry, 1996, Dense chlorinated solvents and other DNAPLs in ground water: Portland, Oregon, Waterloo Press, 522 p.

Pinal, R., P. Suresh, C. Rao, L.S. Lee, and P.V. Cline, 1990, Cosolvency of partially miscible organic solvents on the solubility of hydrophobic organic chemicals: Environmental Science and Technology, v. 24, no. 5, p. 639-647.

Pinal, R., L.S. Lee, and P.S.C. Rao, 1991, Prediction of the solubility of hydrophobic compounds in nonideal solvents: Chemosphere, v. 22, no. 9-10, p. 939-951.

Plummer, L.N., R.L. Michel, E.M. Thurman, and P.D. Glynn, 1993, Environmental tracers for age dating young ground water, *in* Alley, W.M. ed., Regional ground-water quality: New York, Van Nostrand Reinhold, chap. 11, p. 255-294.

Poirier, S.H., M.L. Knuth, C.D. Anderson-Buchou, L.T. Brooke, A.R. Lima, and P.J. Shubat, 1986, Comparative toxicity of methanol and n,n'-dimethylformamide to freshwater fish and invertebrates: Bull. Environ. Contam. Toxicol., v. 37, no. 4, p. 615-621.

Post, G., 1994, Methyl tertiary butyl ether, health-based maximum contaminant level support document: Division of Science and Research, New Jersey Department of Environmental Protection.

Poulsen, M., L. Lemon, and J.F. Barker, 1992, Dissolution of monoaromatic hydrocarbons into groundwater from gasoline-oxygenate mixtures: Environmental Science and Technology, v. 26, no. 12, p. 2483-2489.

Prager, J.C., ed., 1992, Methyl *tert*-butyl ether, *in* Dangerous properties of industrial materials report: v. 12, no. 3, p. 381-394.

Raese, J.W., D.L. Rose, and M.W. Sandstrom, 1995, U.S. Geological Survey Laboratory method for methyl *tert*-butyl ether and other fuel oxygenates: U.S. Geological Survey Fact Sheet FS-219-95, 4 p.

Rathbun, R.E., 1990, Prediction of stream volatilization coefficients: Journal of Environmental Engineering, American Society of Civil Engineering, v. 116, no. 3, p. 615-631.

Robbins, G., S. Wang, and J.D. Stuart, 1993, Using the static headspace method to determine Henry's Law constants: Analytical Chemistry, v. 65, no. 21, p. 3113-3118.

Rodriguez, Rey, 1997, MTBE in groundwater and the impact on the City of Santa Monica drinking water supply: ACWA Water Quality Workshop, March 13, 1997, Ontario, CA, City of Santa Monica, CA.

Roghair, C.J., A. Buijze, E.S.E. Yedma, and J.L.M. Hermens, 1994, QSAR for base-line toxicity to the midge *Chiromonus riparius*: Chemosphere 28(5), p. 989-997.

Salanitro, J.P., L.A. Diaz, M.P. Williams, and H.L. Wisniewski, 1994, Isolation of a bacterial culture that degrades methyl t-butyl ether: Applied and Environmental Microbiology, v. 60, no. 7, p. 2593-2596.

Schwarzenbach, R.P., P.M. Gschwend, and D.M. Imboden, 1993, Environmental Organic Chemistry: John Wiley and Sons, chap. 10, 681 p.

Scott, J.C., 1990, Computerized stratified random site-selection approaches for design of ground-water quality sampling networks: U.S. Geological Survey Water-Resources Investigations Report 90-4101, 109 p.

Slinn, W.G.N., L. Hasse, B.B. Hicks, A.W. Hogan, D. Lal, P.S. Liss, K.O. Munnich, G.A. Sehmel, and O. Vittori, 1978, Some aspects of the transfer of atmospheric trace constituents past the air-sea interface: Atmospheric Environment, v. 12, p. 2055-2087.

Smith, D.F., T.E. Kleindienst, E.E. Hudgens, C.D. McIver, and J.J. Buffalini, 1991, The photochemistry of methyl tertiary butyl ether: Int. Journal of Chemistry Kinetics, v. 23, p. 907-924.

Smith, J.S., Letter Dated September 18, 1987, State of New Hampshire, Department of Health and Human Services, Division of Public Health Services.

Squillace, P.J., D.A. Pope, and C.V. Price, 1995a, Occurrence of the gasoline additive MTBE in shallow ground water in urban and agricultural areas: U.S. Geological Survey Fact Sheet FS-114-95, 4 p.

Squillace, P.J., J.S. Zogorski, W.G. Wilber, and C.V. Price, 1995b, A preliminary assessment of the occurrence and possible sources of MTBE in ground water of the United States, 1993-94: U.S. Geological Survey Open-File Report 95-456, 29 p.

Squillace, P.J., J.S. Zogorski, W.G. Wilber, and C.V. Price, 1996, Preliminary assessment of the occurrence and possible sources of MTBE in groundwater in the United States, 1993-1994: Environmental Science and Technology, v. 30, no. 5, p. 1721-1730.

Stump, F.D., K.T. Knapp, and W.D. Ray, 1990, Seasonal impact of blending oxygenated organics with gasoline on motor vehicle tailpipe and evaporative emissions: Journal of Air and Waste Management Association, v. 40, no. 6, p. 872-880.

Suflita, J.M., and M.R. Mormile, 1993, Anaerobic biodegradation of known and potential gasoline oxygenates in the terrestrial subsurface: Environmental Science and Technology, v. 27, no. 5, p. 976.

Tangley, L., 1984, Groundwater contamination: Local problems become national issue: Bioscience, v. 34, p. 1421-148, *as cited in* Hartley, W.R., Englande, A.J., Jr., 1992, Health risk assessment of the migration of unleaded gasoline - A model for petroleum products: Water Science and Technology, v. 25, no. 3, p. 65-72.

Thomas, J.M., G.L. Clark, M.B. Tomson, P.B. Bedient, H.S. Rifai, and C.H. Ward, 1988, Environmental fate and attenuation of gasoline components in the subsurface: Washington, D.C., American Petroleum Institute, final report, p. 111.

TRC Environmental Corporation, 1994, Odor threshold studies performed with gasoline and gasoline combined with MTBE, ETBE, and TAME: Washington, D.C., American Petroleum Institute, Publication No. 4592.

Truong, K.N., and C.S. Parmele, 1992, Cost-effective alternative treatment technologies for reducing the concentrations of methyl tertiary butyl ether and methanol in groundwater: Hydrocarbon Contaminated Soils and Groundwater, v. 27, no. 2, p. 461-486.

Tuazon, E.C., W.P.L. Carter, S.M. Aschmann, and R. Atkinson, 1991, Products of the gas-phase reaction of methyl *tert*-butyl ether with the OH radical in the presence of NOx: International Journal of Chemical Kinetics, v. 23, p. 1003-1015.

U.S. Environmental Protection Agency, 1986, Nineteenth report of the Interagency Testing Committee to the Administrator, Receipt and request for comments regarding priority list of chemicals: Federal Register, November 14, 1986, v. 51, no. 220, p. 41417-41432.

U.S. Environmental Protection Agency, 1987a, Toxicological literature relevant to contamination of groundwater; methyl tertiary-butyl ether (1981) with cover letter dated 021287: OST-0513478.

U.S. Environmental Protection Agency, 1987b, Collection of individual reports and memos on the chemical analyses of well water from various states contaminated with MTBE.

U.S. Environmental Protection Agency, 1992, Methods for the determination of organic compounds in drinking water, Supplement II: Washington, D.C., Office of Research and Development, EPA/600/R-92/129, August, p. 5-50.

U.S. Environmental Protection Agency, 1993a, Toxic Chemical Release Inventory Reporting Form R and Instructions, revised 1993: Washington, D.C., United States Environmental Protection Agency, Office of Pollution Prevention and Toxics, EPA 745/K-94/001.

U.S. Environmental Protection Agency, 1993b, Toxic Release Inventory, 1987-1993: Office of Pollution Prevention and Toxics Environmental Assistance Division (7408), Washington, D.C. (digital data files).

U.S. Environmental Protection Agency, 1994, Health risk perspective on fuel oxygenates: Office of Research and Development, EPA 600/R-94/217, December, 11 p.

U.S. Environmental Protection Agency, 1995a, UST corrective action summary for 4th quarter FY 95, Quarterly statistical table, Oct. 30, 1995: Washington, D.C., Office of UST, U.S. Environmental Protection Agency, 3 p.

U.S. Environmental Protection Agency, 1995b, Drinking water regulations and health advisories: Office of Water, Washington, D.C.

U.S. Environmental Protection Agency, 1995c, 1993 Toxics release inventory: Public data release: Office of Pollution Prevention and Toxics (7408), EPA 745/R-95/010, March, p. 3-5.

Veith, G.D., D.J. Call, and L.T. Brooke, 1983a, Estimating the acute toxicity of narcotic industrial chemicals to fathead minnows, *in* Bishop, W.E., Cardwell, R.D., and Heidolph, B.B., eds., Aquatic toxicology and hazard assessment: Philadelphia, Pa., 6th Symposium, ASTM STP 802, p. 90.

Veith, G.D., D.J. Call, and L.T. Brooke, 1983b, Structure - Toxicity relationships for the Fathead Minnow, *Pimephales promelas*: narcotic industrial chemicals: Canadian Journal of Fish. and Aquatic Science, v. 40, no. 6, p. 743-748.

Vetrano, K.M., 1993a, Final report to ARCO Chemical Company on the odor and taste threshold studies performed with methyl tertiary-butyl ether (MTBE) and ethyl tertiary-butyl ether (ETBE): Windsor, Conn., TRC Environmental Corporation, TRC Project no. 13442-M31.

Vetrano, K., 1993b, Odor and taste threshold studies performed with tertiary-amyl methyl ether (TAME): Washington, D.C., American Petroleum Institute, Publication No. 4591.

Wallington, T.J., R. Atkinson, A.M. Winer, and J.N. Pitts, Jr., 1986, Absolute rate constants for the gas-phase reactions of the NO_3 radical with CH_3SH, CH_3SCH_3, CH_3SSCH_3, H_2S, SO_2, and CH_3OCH_3 over the temperature range 280 - 350 °K: Journal of Phys. Chemistry, v. 90, p. 5393-5396.

Wallington, T.J., R. Atkinson, A.M. Winer, and J.N. Pitts, Jr., 1987, A study of the reaction $NO_3 + NO_2 + M \rightarrow N_2O_5 + M(M=N_2 O_2)$, Intl. Journal of Chemistry Kinetics, v. 19, p. 243-249.

Wallington, T.J., P. Dagaut, R. Liu, and M.J. Kurylo, 1988, Gas-phase reactions of hydroxyl radicals with the fuel additives methyl *tert*-butyl ether and *tert*-butyl alcohol over the temperature range 240-440 K: Env. Science Technol., v. 22, p. 842-844.

Wallington, T.J., J.M. Andino, A.R. Potts, S.J. Rudy, W.O. Siegl, Z. Zhang, M.J. Kurylo, and R.E. Hule, 1993, Atmospheric chemistry of automotive fuel additives: Diisopropyl ether: Environmental Science and Technology, v. 27, no. 1, p. 98-104.

Yeh, C.K., and J.T. Novak, 1991, Anaerobic biodegradation of oxygenates in the subsurface-Proceedings of the 1991 Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration, November 20-22, 1991, Houston, Texas: Ground Water Management Book 8 of the Series.

Yeh, C.K., and J.T. Novak, 1994, Anaerobic biodegradation of gasoline oxygenates in soils: Water Environment Research, v. 66, no. 5, July/August, p. 744-752.

Yeh, C.K., and J.T. Novak, 1995, The effect of hydrogen peroxide on the degradation of methyl and ethyl *tert*-butyl ether in soils: Water Environment Research, v. 67, no. 5, p. 828.

Yeh, Kuei-Jyum, 1992, Degradation of gasoline oxygenates in the subsurface: Blacksburg, Va., Virginia Polytechnic Institute, dissertation.

Zibrua, Theresa, Letter Dated September 18, 1987, State of Massachusetts, Department of Health Services, Public Health Laboratory.

Appendix 1: *Estimated releases of MTBE for report year 1993.*

[Source: U.S. Environmental Protection Agency, 1995c]

Name	City	State	Reported releases (kilograms per year): Air	Under-ground	Land	Water
Bayway Chemical Plant Refining & Marketing Terminal	Linden	New Jersey	34,700	0	0	5
Amerada Hess Corp. Port Reading	Port Reading	New Jersey	14,224	0	0	2
Amerada Hess Corp. Second Reserve Terminal	Port Reading	New Jersey	5,126	0	0	0
Merck & Co. Inc.	Rahway	New Jersey	249	0	0	0
Shell Oil Co. Sewaren Plant	Sewaren	New Jersey	9,266	0	0	16
Ciba-Geigy Corp. Pharmaceuticals Div.	Summit	New Jersey	23	0	0	0
Sandoz Pharmaceuticals Corp.	East Hanover	New Jersey	1,709	0	0	0
Mobil Oil Paulsboro Refinery	Paulsboro	New Jersey	1,792	0	0	1,043
Coastal Eagle Point Oil Co.	Westville	New Jersey	1,089	0	0	0
Ford Motor Co. Edison Assembly Plant	Edison	New Jersey	160	0	0	0
GMC Chevrolet Pontiac Canada Group	North Tarrytown	New York	590	0	0	0
American Refining Group Inc.	Indianola	Pennsylvania	354	0	0	2
United Refining Co.	Warren	Pennsylvania	3,515	0	0	0
Witco Corp. Bradford Operations	Bradford	Pennsylvania	1,043	0	0	0
BP Exploration & Oil Inc. Marcus Hook Refinery	Trainer	Pennsylvania	1,369	0	0	0
Sun Refining & Marketing Co.	Marcus Hook	Pennsylvania	19,187	0	0	0
Chevron USA Products Co.	Philadelphia	Pennsylvania	6,318	0	0	0
Sun Refining & Marketing Co.	Philadelphia	Pennsylvania	4,427	0	0	0
Star Ent. Delaware City Refinery	Delaware City	Delaware	2,445	0	2	236
Primary Corp.	Richmond	Virginia	3,719	0	0	0
U.S. Doe Savannah River Site	Aiken	South Carolina	245	0	0	0
Citgo Asphalt Refining Co. Savannah Refinery	Savannah	Georgia	658	0	0	113
Petro Chemical Inc.	Jacksonville	Florida	780	0	0	0
Hunt Refining Co.	Tuscaloosa	Alabama	4,834	0	0	0
Wellborn Cabinet Inc.	Ashland	Alabama	2	0	0	0
Nissan Motor Mfg. Corp. USA Corp. USA	Smyrna	Tennessee	1,375	0	0	0
Saturn Corp.	Spring Hill	Tennessee	113	0	0	0
Tecumseh Prods. Co. Dunlap Ops.	Dunlap	Tennessee	113	0	0	0
Mapco Petroleum Inc.	Memphis	Tennessee	1,911	0	0	0
Chevron Products Co. Pascagoula Refinery	Pascagoula	Mississippi	28,894	0	0	0
Ashland Petroleum Co. Catlettsburg Refinery	Catlettsburg	Kentucky	6,858	0	0	504
GMC NAO Bowling Green Plant	Bowling Green	Kentucky	1,096	0	0	0
Honda of America Mfg. Inc.	Marysville	Ohio	2,320	0	0	0
Eli Lilly & Co. Lilly Industrial Center 1555	Indianapolis	Indiana	454	0	0	0
Rhone-Poulenc Basic Chemicals Co.	Hammond	Indiana	116	0	0	0

Appendix 1: *Estimated releases of MTBE for report year 1993.—Continued*

[Source: U.S. Environmental Protection Agency, 1995c]

			Reported releases (kilograms per year):			
Name	**City**	**State**	**Air**	**Under-ground**	**Land**	**Water**
Amoco Chemical Co.	Whiting	Indiana	1,163	0	0	0
Amoco Oil Co. Whiting Refinery	Whiting	Indiana	4,758	0	0	0
Subaru-Isuzu Automotive Inc.	Lafayette	Indiana	116	0	0	0
Eli Lilly & Co. Tippecanoe Labs.	Shadeland	Indiana	6,260	0	0	0
Saturn Corp.	Madison Heights	Michigan	113	0	0	0
Autoalliance Intl. Inc.	Flat Rock	Michigan	227	0	0	0
Marathon Oil Co.	Detroit	Michigan	2,011	0	0	0
Marathon Oil Co.	Detroit	Michigan	1,589	0	0	0
GMC Truck & Bus Group Flint Assembly	Flint	Michigan	1,383	0	0	0
GMC Lansing Automotive Plant 1	Lansing	Michigan	141	0	0	0
Upjohn Co. Production Facility	Portage	Michigan	22,339	0	0	0
Warner-Lambert Co. Parke-Davis Div.	Holland	Michigan	295	0	0	0
Baxter Diagnostics Inc. Burdick & Jackson Div.	Muskegon	Michigan	227	0	0	0
Sealed Power Div.	Muskegon Heights	Michigan	10	0	0	0
Tecumseh Prods. Co. Engine & Transmission Group	New Holstein	Wisconsin	116	0	0	0
Aldrich Chemical Co. Inc.	Sheboygan Falls	Wisconsin	454	0	0	0
Briggs & Stratton Corp.	Wauwatosa	Wisconsin	7,342	0	0	0
Aldrich Chemical Co. Inc.	Milwaukee	Wisconsin	454	0	0	0
Koch Refining Co.	Rosemount	Minnesota	1,170	0	0	0
Kraft General Foods Kraft USA	Melrose	Minnesota	113	0	0	0
Exxon Billings Refinery	Billings	Montana	2,994	0	0	0
U.S. Doe Argonne Natl. Lab	Argonne	Illinois	113	0	0	0
Shell Oil Co. Wood River Mfg. Complex	Roxana	Illinois	15,876	0	0	0
Marathon Oil Co.	Robinson	Illinois	1,021	0	0	0
BP Oil Co. Alliance Refinery	Belle Chasse	Louisiana	11,839	0	0	3
Evans Cooperage Co. Inc.	Harvey	Louisiana	84	0	0	0
Shell Norco Mfg. Complex E. Site	Norco	Louisiana	6,305	0	24	5
Mobil Oil Corp. Chalmette Refinery	Chalmette	Louisiana	7,303	0	0	0
Canal Refining Co.	Church Point	Louisiana	27	0	0	0
Citgo Petroleum Corp.	Lake Charles	Louisiana	16,057	0	0	0
Conoco Lake Charles Refinery	Westlake	Louisiana	9,163	0	0	0
Star Ent. Inc.	Union	Louisiana	30,890	0	0	23
Phibro Energy Usa Inc.	Krotz Springs	Louisiana	57,766	0	0	101
Ciba-Geigy Corp.	Saint Gabriel	Louisiana	469	0	0	0
Exxon Baton Rouge Refinery	Baton Rouge	Louisiana	140,160	0	40	14,969
Exxon Chemical Baton Rouge Chemical Plant	Baton Rouge	Louisiana	3,973	0	0	18

Appendix 1: *Estimated releases of MTBE for report year 1993.—Continued*

[Source: U.S. Environmental Protection Agency, 1995c]

			Reported releases (kilograms per year):			
Name	**City**	**State**	**Air**	**Under-ground**	**Land**	**Water**
Sinclair Oil Corp. Tulsa Refinery	Tulsa	Oklahoma	41	0	0	0
Conoco Ponca City Refinery	Ponca City	Oklahoma	6,394	0	0	21
La Gloria Oil & Gas Co.	Tyler	Texas	417	0	0	0
GMC Midsize Car Div.	Arlington	Texas	263	0	0	0
Texas Ind. Inc.	Midlothian	Texas	5	0	0	0
Phibro Energy USA Inc.	Houston	Texas	41,232	0	18	140
Lyondell-Citgo Refining Co. Ltd.	Houston	Texas	2,381	0	0	0
Texas Petrochemicals Corp.	Houston	Texas	20,263	0	0	39
Platzer Shipyard Inc.	Houston	Texas	50,698	0	0	0
Phillips 66 Co. Freeport Terminal I	Sweeny	Texas	10,827	0	0	0
Phillips 66 Co. Sweeny Complex	Old Ocean	Texas	29,897	0	0	0
Crown Central Petroleum Corp. Houston Refinery	Pasadena	Texas	9,869	0	0	0
Hoechst-Celanese Chemical Group Inc. Clear Lake Pl	Pasadena	Texas	816	0	0	0
Monsanto Co.	Alvin	Texas	68	0	0	0
Occidental Chemical Corp.	Alvin	Texas	7,044	0	0	0
Exxon Baytown Refinery	Baytown	Texas	48,277	0	0	0
Exxon Chemical Americas Baytown Chemical Plant	Baytown	Texas	13,608	0	0	0
Howell Hydrocarbons & Chemicals Inc.	Channelview	Texas	363	0	0	0
Lyondell Petrochemical Co.	Channelview	Texas	21,319	0	0	0
Arco Chemical Co.	Channelview	Texas	13,370	3,979	0	0
Global Octanes Corp.	Deer Park	Texas	1	0	0	0
Shell Oil Co. Deer Park Mfg. Complex	Deer Park	Texas	51,983	0	0	0
EGP Fuels Co.	La Porte	Texas	16,185	0	0	0
Amoco Oil Co. Texas City Refinery	Texas City	Texas	10,342	0	0	19,958
Phibro Energy USA Inc.	Texas City	Texas	12,322	0	0	267
Chevron USA Prods. Co. Port Arthur Refinery	Port Arthur	Texas	130,181	0	0	0
Texaco Chemical Co.	Port Neches	Texas	38,570	0	0	0
Mobil Oil Beaumont Refinery	Beaumont	Texas	57,198	0	0	0
Mobil Chemical Co. BCSP	Beaumont	Texas	16	0	0	0
Mobil Chemical Co. O/A	Beaumont	Texas	7	0	0	0
Coastal Refining & Marketing Inc.	Corpus Christi	Texas	253,070	0	0	0
Citgo Refining & Chemicals Inc.	Corpus Christi	Texas	3,019	0	0	0
Southwestern Refining Co. Inc.	Corpus Christi	Texas	13,372	0	51	1
Valero Refining Co.	Corpus Christi	Texas	11,193	0	0	0
Phillips 66 Co. Philtex/Ryton Complex	Borger	Texas	1,186	0	2	2
Diamond Shamrock Inc. Mckee Plants	Sunray	Texas	24,630	288	4	0

Appendix 1: *Estimated releases of MTBE for report year 1993.—Continued*

[Source: U.S. Environmental Protection Agency, 1995c]

Name	City	State	Reported releases (kilograms per year): Air	Under-ground	Land	Water
Pride Refining Inc.	Abilene	Texas	6,659	0	0	0
Fina Oil & Chemical Co.	Big Spring	Texas	123,831	0	0	0
El Paso Refinery L.P.	El Paso	Texas	816	0	0	0
Colorado Refining Co.	Commerce City	Colorado	5,474	0	0	15
Conoco Denver Refinery	Commerce City	Colorado	6,804	0	0	399
Frontier Refining Inc.	Cheyenne	Wyoming	166	0	0	0
Coastal Chem. Inc.	Cheyenne	Wyoming	13,406	0	0	0
Little America Refining Co.	Casper	Wyoming	2	0	0	0
Pennzoil Prods. Co. Roosevelt Refinery	Roosevelt	Utah	721	0	0	0
Amoco Oil Co.	Salt Lake City	Utah	683	0	0	0
Giant Refining Co. Ciniza	Jamestown	New Mexico	8,066	0	0	0
Bloomfield Refining Co.	Bloomfield	New Mexico	1,474	0	2	0
Chevron USA Prods. Co. El Segundo Refinery	El Segundo	California	19,051	0	37	3,992
Mobil Oil Torrance Refinery	Torrance	California	1,474	0	0	0
Paramount Petroleum Corp.	Paramount	California	1	0	0	0
Texaco Refining & Marketing Inc. Lap	Wilmington	California	7,575	0	0	0
Unocal Louisiana Refinery Wilmington Plant	Wilmington	California	2,627	0	0	0
Arco Prods. Co. Louisiana Refinery	Carson	California	6,849	0	0	0
U.S. Doe Naval Petroleum Reserves of California	Tupman	California	514	0	0	0
Texaco Refining & Marketing Inc.	Bakersfield	California	3,543	0	0	0
Exxon Co. USA Benicia Refinery	Benicia	California	9,616	0	0	0
Pacific Refining Co.	Hercules	California	113	0	0	0
Shell Oil Co. Martinez Mfg. Complex	Martinez	California	17,690	0	5	0
Tosco Refining Co.	Martinez	California	463	0	0	0
Unocal Corp. San Francisco Refinery	Rodeo	California	2,971	0	0	0
Chevron Research & Technology Co.	Richmond	California	26	0	0	0
Chevron USA Prods. Co. Richmond Refinery	Richmond	California	12,428	0	0	0
Arco Cherry Point Refinery	Ferndale	Washington	2,631	0	0	0
Mapco Alaska Petroleum Inc.	North Pole	Alaska	1,100	0	0	0

Appendix 2: *Statistical summary of the occurrence and concentration of MTBE in storm water from select USGS studies.*

[Oct. 1 - Mar. 31 is the most frequent time for oxygenated gasoline usage throughout the United States. The only detailed record of usage of oxygenated gasoline for this summarization of the USGS storm-water data are for Arizona (oxygenate use during Oct. 1 - Mar. 31) and Colorado (oxygenate use during Oct. 1 - Mar. 31). NA, not applicable; µg/L, micrograms per liter]

City/study period[1]	Sampling period	Reporting level (µg/L)[2]	Number of samples	Number of samples with detections	Percent occurrence	Detected concentrations (µg/L)		
						Minimum	Median	Maximum
Montgomery, Ala. (6/92 - 3/93)	Apr. 1 - Sept. 30	1.0	9	0	0	N/A	N/A	N/A
	Oct. 1 - Mar. 31	1.0	12	0	0	N/A	N/A	N/A
	Total		21	0	0	N/A	N/A	N/A
Birmingham, Ala. (2/92 - 3/93)	Apr. 1 - Sept. 30	1.0	10	0	0	N/A	N/A	N/A
	Oct. 1 - Mar. 31	1.0	9	1	11.1	2.0	2.0	2.0
	Total		19	1	5.3	2.0	2.0	2.0
Mobile, Ala. (2/93 - 4/95)	Apr. 1 - Sept. 30	0.2, 1.0	2	0	0	N/A	N/A	N/A
	Oct. 1 - Mar. 31	0.2, 1.0	4	0	0	N/A	N/A	N/A
	Total		6	0	0	N/A	N/A	N/A
Huntsville, Ala. (2/93 - 6/93)	Apr. 1 - Sept. 30	1.0	2	0	0	N/A	N/A	N/A
	Oct. 1 - Mar. 31	1.0	1	0	0	N/A	N/A	N/A
	Total		3	0	0	N/A	N/A	N/A
Little Rock, Ark. (6/92 - 1/94)	Apr. 1 - Sept. 30	1.0	12	0	0	N/A	N/A	N/A
	Oct. 1 - Mar. 31	1.0	10	0	0	N/A	N/A	N/A
	Total		22	0	0	N/A	N/A	N/A
Phoenix, Ariz. (Maricopa County) (10/91 - 9/94)	Apr. 1 - Sept. 30	0.2, 1.0	7	0	0	N/A	N/A	N/A
	Oct. 1 - Mar. 31	1.0	23	5	21.7	1.0	1.0	2.5
	Total		30	5	16.7	1.0	1.0	2.5
Denver-Lakewood, Colo. (3/92 - 8/92)	Apr. 1 - Sept. 30	1.0	20	0	0	N/A	N/A	N/A
	Oct. 1 - Mar. 31	1.0	2	1	50	1.5	1.5	1.5
	Total		22	1	4.5	1.5	1.5	1.5
Colorado Springs, Colo. (5/92 - 12/92)	Apr. 1 - Sept. 30	1.0	27	0	0	N/A	N/A	N/A
	Oct. 1 - Mar. 31	1.0	15	10	66.7	1.0	1.6	4.2
	Total		42	10	23.8	1.0	1.6	4.2

Appendix 2: *Statistical summary of the occurrence and concentration of MTBE in storm water from select USGS studies.—Continued*

[Oct. 1 - Mar. 31 is the most frequent time for oxygenated gasoline usage throughout the United States. The only detailed record of usage of oxygenated gasoline for this summarization of the USGS storm-water data are for Arizona (oxygenate use during Oct. 1 - Mar. 31) and Colorado (oxygenate use during Oct. 1 - Mar. 31). NA, not applicable; µg/L, micrograms per liter]

City/study period[1]	Sampling period	Reporting level (µg/L)[2]	Number of samples	Number of samples with detections	Percent occurrence	Detected concentrations (µg/L)		
						Minimum	Median	Maximum
Atlanta, Ga. (7/92 - 2/93)	Apr. 1 - Sept. 30	1.0	7	1	14.3	1.2	1.2	1.2
	Oct. 1 - Mar. 31	1.0	11	2	18.2	1.0	1.05	1.1
	Total		18	3	16.7	1.0	1.1	1.2
Boise, Idaho (10/93 - 10/94)	Apr. 1 - Sept. 30	0.2, 1.0	6	0	0	N/A	N/A	N/A
	Oct. 1 - Mar. 31	0.2, 1.0	9	0	0	N/A	N/A	N/A
	Total		15	0	0	N/A	N/A	N/A
Davenport, Iowa (7/92 - 11/94)	Apr. 1 - Sept. 30	0.2, 1.0	19	0	0	N/A	N/A	N/A
	Oct. 1 - Mar. 31	0.2, 1.0	8	0	0	N/A	N/A	N/A
	Total		27	0	0	N/A	N/A	N/A
Baton Rouge, La. (4/93 - 6/95)	Apr. 1 - Sept. 30	0.2, 1.0	20	1	5	0.4	0.4	0.4
	Oct. 1 - Mar. 31	0.2, 1.0	11	0	0	N/A	N/A	N/A
	Total		31	1	3.2	0.4	0.4	0.4
Independence, Mo. (no Rfg/oxy-fuels usage in State) (7/92 - 2/93)	Apr. 1 - Sept. 30	1.0	8	0	0	N/A	N/A	N/A
	Oct. 1 - Mar. 31	1.0	7	0	0	N/A	N/A	N/A
	Total		15	0	0	N/A	N/A	N/A
Omaha, Nebr. (no Rfg/oxy-fuels usage in State) (5/93 - 8/93)	Apr. 1 - Sept. 30	1.0	15	0	0	N/A	N/A	N/A
	Oct. 1 - Mar. 31	1.0	0	0	0	N/A	N/A	N/A
	Total		15	0	0	N/A	N/A	N/A
Dallas-Fort Worth, Tex. (2/92 - 6/93)	Apr. 1 - Sept. 30	1.0	71	4	5.6	1	2.7	3.4
	Oct. 1 - Mar. 31	1.0	108	9	8.3	1.4	3.4	8.7
	Total		179	13	7.3	1	3.3	8.7
San Antonio, Tex. (1/93 - 6/95)	Apr. 1 - Sept. 30	0.2, 1.0	70	1	1.4	1.8	1.8	1.8
	Oct. 1 - Mar. 31	0.2, 1.0	57	6	10.5	0.2	0.7	1.8
	Total		127	7	5.5	0.2	1.0	1.8

Appendix 2: *Statistical summary of the occurrence and concentration of MTBE in storm water from select USGS studies.—Continued*

[Oct. 1 - Mar. 31 is the most frequent time for oxygenated gasoline usage throughout the United States. The only detailed record of usage of oxygenated gasoline for this summarization of the USGS storm-water data are for Arizona (oxygenate use during Oct. 1 - Mar. 31) and Colorado (oxygenate use during Oct. 1 - Mar. 31). NA, not applicable; µg/L, micrograms per liter]

City/study period[1]	Sampling period	Reporting level (µg/L)[2]	Number of samples	Number of samples with detections	Percent occurrence	Detected concentrations (µg/L)		
						Minimum	Median	Maximum
Composite of all samples	Apr. 1 - Sept. 30	0.2, 1.0	305	7	2.3	0.4	1.8	3.4
	Oct. 1 - Mar. 31	0.2, 1.0	287	34	11.8	0.2	1.5	8.7
	Total		592	41	6.9	0.2	1.5	8.7

[1] Timeframe in which storm-water samples were collected and analyzed for MTBE.

[2] A change in the reporting level for MTBE occurred between Apr. 3, 1994 and Apr. 9, 1994. The reporting level changed from 1.0 µg/L to 0.2 µg/L.

Appendix 3: *Summary of general characteristics and results of programs that have analyzed for MTBE in ground water, by State and by program in each State.*

[Data were compiled by NAWQA VOC National Synthesis from the data sources indicated. SUS, Study-Unit Survey; LUS, Land-Use Study; Ag, Agricultural; Ur, Urban; SU, Study Unit; µg/L, micrograms per liter]

State	Data source	Program description[1]	Sampling year(s)	Reporting level, in µg/L	Number of detections of MTBE	Number of wells tested
Arkansas	nawqa.ozrksus	SUS: Ozark Plateau SU	1993	0.2	0	11
California	nawqa.sanj (1)	Ag LUS: San Joaquin-Tulare Basins SU	1993	0.2	0	20
California	nawqa.sanj (2)	Ag LUS: San Joaquin-Tulare Basins SU	1994	0.2	0	20
Colorado	nawqa.splt	Ag LUS: South Platte River Basin SU	1994	0.2	0	33
Colorado	nawqa.spltlusur	Ur LUS: South Platte River Basin SU	1993	0.2	23	29
Connecticut	nawqa.connlus31	Ur LUS: Connecticut, Housatonic, and Thames River Basins SU	1994	0.2	5	10
Connecticut	nawqa.connlus33	Ur LUS: Connecticut, Housatonic, and Thames River Basins SU	1994	0.2	1	3
Connecticut	nawqa.connlus34	Ur LUS: Connecticut, Housatonic, and Thames River Basins SU	1993-94	0.2	1	2
Connecticut	nawqa.connsus	SUS: Connecticut, Housatonic, and Thames Riuver Basin SU	1995	0.2	5	18
Florida	nawqg.gaflsus	SUS: Georgia-Florida Coastal Plain SU	1993	0.2	0	7
Georgia	nawqa.acfb	Ag LUS: Apalachicola-Chattahoochee-Flint River Basin SU	1993	0.2	0	32
Georgia	nawqa.gafl	Ag LUS: Georgia-Florida Coastal Plain SU	1994	0.2	0	23
Georgia	nawqa.gaflsus	SUS: Georgia-Florida Coastal Plain SU	1993	0.2	1	26
Georgia	nawqa.acfblusur1[2]	Ur LUS: Apalachicola-Chattahoochee-Flint River Basin SU	1994	0.2	2	23
Iowa	USGS.midcontinent	Quality of water (QW) in near-surface aquifers	1992	1.0	0	23
Iowa	USGS.midcontinent	QW in near-surface aquifers	1993	1.0	0	23
Idaho	nawqa.usnk (1)	Ag LUS: Upper Snake River Basin SU	1993	0.2	0	31
Idaho	nawqa.usnk (2)	Ag LUS: Upper Snake River Basin SU	1993	0.2	0	28
Idaho	nawqa.usnk (3)	Ag LUS: Upper Snake River Basin SU	1994	0.2	0	30
Idaho	nawqa.usnksus1	SUS: Upper Snake River Basin SU	1992-93	0.2	0	4
Illinois	USGS.midcontinent	QW in near-surface aquifers	1992	1.0	0	32
Illinois	USGS.midcontinent	QW in near-surface aquifers	1993	1.0	0	32
Indiana	USGS.midcontinent	QW in near-surface aquifers	1992	1.0	0	4
Indiana	USGS.midcontinent	QW in near-surface aquifers	1993	1.0	0	4
Kansas	nawqa.ozrksus	SUS: Ozark Plateaus SU	1993	0.2	0	1

Appendix 3: *Summary of general characteristics and results of programs that have analyzed for MTBE in ground water, by State and by program in each State.—Continued*

[Data were compiled by NAWQA VOC National Synthesis from the data sources indicated. SUS, Study-Unit Survey; LUS, Land-Use Study; Ag, Agricultural; Ur, Urban; SU, Study Unit; μg/L, micrograms per liter]

State	Data source	Program description[1]	Sampling year(s)	Reporting level, in μg/L	Number of detections of MTBE	Number of wells tested
Kansas	USGS.midcontinent	QW in near-surface aquifers	1992	1.0	0	1
Kansas	USGS.midcontinent	QW in near-surface aquifers	1993	1.0	0	1
Massachusetts	nawqa.conn	Ag LUS: Connecticut, Housatonic, and Thames River Basins SU	1993-94	0.2	2	23
Massachusetts	nawqa.connlus33	Ur LUS: Connecticut, Housatonic, and Thames River Basins SU	1994	0.2	1	6
Massachusetts	nawqa.connlus34	Ur LUS: Connecticut, Housatonic, and Thames River Basins SU	1994	0.2	4	7
Maryland	nawqa.poto	Ag LUS: Potomac River Basin SU	1993	0.2	0	16
Maryland	nawqa.lsussus2	SUS: Lower Susquehanna River Basin SU	1994	0.2	0	2
Michigan	USGS.midcontinent	QW in near-surface aquifers	1992	1.0	0	1
Michigan	USGS.midcontinent	QW in near-surface aquifers	1993	1.0	0	1
Minnesota	nawqa.rednsus2	SUS: Red River of the North SU	1993	0.2	0	26
Minnesota	nawqa.rednsus4	SUS: Red River of the North SU	1993	0.2	0	11
Minnesota	USGS.midcontinent	QW in near-surface aquifers	1992	1.0	0	16
Minnesota	USGS.midcontinent	QW in near-surface aquifers	1993	1.0	0	16
Missouri	nawqa.ozrksus	SUS: Ozark Plateaus SU	1993	0.2	0	32
Missouri	nawqa.ozrksus1	SUS: Ozark Plateaus SU	1993	0.2	0	9
Missouri	USGS.midcontinent	QW in near-surface aquifers	1992	1.0	0	9
Missouri	USGS.midcontinent	QW in near-surface aquifers	1992	1.0	0	9
North Carolina	nawqa.albe	Ag LUS: Albemarle-Pamlico Drainage SU	1994	0.2	0	20
North Carolina	nawqa.albesus1	SUS: Albemarle-Pamlico Drainage SU	1994	0.2	0	8
North Carolina	nawqa.albesus2	SUS: Albemarle-Pamlico Drainage SU	1994	0.2	0	10
North Carolina	nawqa.albesus4	SUS: Albemarle-Pamlico Drainage SU	1994	0.2	0	5
North Carolina	nawqa.albesus5	SUS: Albemarle-Pamlico Drainage SU	1994	0.2	0	2
North Dakota	nawqa.rednsus1	SUS: Red River of the North SU	1993	0.2	0	10
North Dakota	nawqa.rednsus3	SUS: Red River of the North SU	1993	0.2	0	3
North Dakota	USGS.midcontinent	QW in near-surface aquifers	1992	1.0	0	1
North Dakota	USGS.midcontinent	QW in near-surface aquifers	1993	1.0	0	1

Appendix 3: *Summary of general characteristics and results of programs that have analyzed for MTBE in ground water, by State and by program in each State.—Continued*

[Data were compiled by NAWQA VOC National Synthesis from the data sources indicated. SUS, Study-Unit Survey; LUS, Land-Use Study; Ag, Agricultural; Ur, Urban; SU, Study Unit; µg/L, micrograms per liter]

State	Data source	Program description[1]	Sampling year(s)	Reporting level, in µg/L	Number of detections of MTBE	Number of wells tested
Nebraska	USGS.midcontinent	QW in near-surface aquifers	1993	1.0	0	38
Nebraska	USGS.midcontinent	QW in near-surface aquifers	1993	1.0	0	38
New Jersey	nawqa.linj01 (1)	Various USGS projects and monitoring networks	1994	0.2	1	5
New Jersey	nawqa.linj01 (2)	Various USGS projects and monitoring networks	1995	0.2	0	1
New Jersey	nawqa.linj01 (3)	Various USGS projects and monitoring networks	1993	1.0	0	1
New Mexico	nawqa.riog (1)	Ag LUS: Rio Grande Valley SU	1994	0.2	0	20
New Mexico	nawqa.riog (2)	Ag LUS: Rio Grande Valley SU	1993	0.2	1	35
New Mexico	nawqa.rioglusur	Ur LUS: Rio Grande Valley SU	1993	0.2	1	24
Nevada	nawqa.nvbrlusur	Ur LUS: Nevada Basin and Range SU	1993	0.2	4	33
Nevada	nawqa.nvbr	Ur LUS: Nevada Basin and Range SU	1994	0.2	6	28
Nevada	nawqa.nvbrsus	SUS: Nevada Basin and Range SU	1995	0.2	1	14
New York	nawqa.hdsnlusur	Ur LUS: Hudson River Basin SU	1993	0.2	4	22
New York	nawqa.hdsnsus	SUS: Hudson River Basin SU	1994	0.2	1	46
New York	nawqa.linj01	Various USGS projects and monitoring networks	1992	5.0	1	15
Ohio	USGS.midcontinent	QW in near-surface aquifers	1992	1.0	0	1
Ohio	USGS.midcontinent	QW in near-surface aquifers	1992	1.0	0	1
Oklahoma	nawqa.ozrksus	SUS: Ozark Plateaus SU	1993	0.2	0	7
Oregon	nawqa.will (1)	Ag LUS: Willamette Basin SU	1993	0.2	0	15
Oregon	nawqa.will (2)	Ag LUS: Willamette Basin SU	1993	0.2	0	26
Oregon	nawqa.willsus	SUS: Willamette Basin SU	1993	0.2	0	64
Pennsylvania	nawqa.lsus	Ag LUS: Lower Susquehanna River Basin SU	1993	0.2	4	30
South Dakota	USGS.midcontinent	QW in near-surface aquifers	1992	1.0	0	3
South Dakota	USGS.midcontinent	QW in near-surface aquifers	1992	1.0	0	3
Texas	nawqa.trinlusur1	Ur LUS: Trinity River Basin SU	1993	0.2	3	17
Texas	nawqa.trinsus1	SUS: Trinity River Basin SU	1994	0.2	0	21
Texas	nawqa.trinsus2	SUS: Trinity River Basin SU	1994	0.2	0	13

Appendix 3: *Summary of general characteristics and results of programs that have analyzed for MTBE in ground water, by State and by program in each State.—Continued*

[Data were compiled by NAWQA VOC National Synthesis from the data sources indicated. SUS, Study-Unit Survey; LUS, Land-Use Study; Ag, Agricultural; Ur, Urban; SU, Study Unit; µg/L, micrograms per liter]

State	Data source	Program description[1]	Sampling year(s)	Reporting level, in µg/L	Number of detections of MTBE	Number of wells tested
Texas	nawqa.trinsus3	SUS: Trinity River Basin SU	1994	0.2	0	18
Virginia	nawqa.albesus1	SUS: Albemarle-Pamlico Drainage SU	1994	0.2	1	4
Virginia	nawqa.albesus2	SUS: Albemarle-Pamlico Drainage SU	1994	0.2	0	4
Virginia	nawqa.albesus4	SUS: Albemarle-Pamlico Drainage SU	1994	0.2	0	2
Vermont	nawqa.connlus32	Undeveloped LUS: Connecticut, Housatonic, and Thames River Basins SU	1994	0.2	1	7
Washington	nawqa.ccpt (1)	Ag LUS: Central Columbia Plateau SU	1993-94	0.2	0	43
Washington	nawqa.ccpt (2)	Ag LUS: Central Columbia Plateau SU	1993-94	0.2	0	21
Washington	nawqa.ccptsus	SUS: Central Columbia Plateau SU	1994	0.2	1	35
Wisconsin	nawqa.wmic (1)	Ag LUS: Western Lake Michigan Drainage SU	1993-94	0.2	0	28
Wisconsin	nawqa.wmic (2)	Ag LUS: Western Lake Michigan Drainage SU	1994	0.2	0	30
Wisconsin	USGS.midcontinent	QW in near-surface aquifers	1992	1.0	0	5
Wisconsin	USGS.midcontinent	QW in near-surface aquifers	1993	1.0	0	5
Wisconsin	nawqa.umis07	Ground-water quality monitoring network Wisconsin	1990-94	5.0	1	78

[1] For descriptions of ground-water studies designed for NAWQA, see Gillom and others (1995).

[2] Some springs were also sampled as part of this data.

Appendix 4: *Summary of general characteristics and results of State monitoring programs that have analyzed for MTBE in drinking water.*

[NK, not known; NA, not applicable; µg/L, micrograms per liter]

a. Drinking water derived from ground water – public water systems

State	Data source	Sampling year(s)	Reporting level (µg/L)	Number of detections	Number of systems with detections	Number of			Source of contamination	Reference	Remarks
						Wells sampled	Samples	Systems sampled			
New Jersey	cert labs	1994-95	NK	63	20	NK	1,269	NK	NK	Letter from New Jersey DEP, 24Jul95	--
New Jersey	NJ DOH	1992-94	NK	19	18	NK	31	NK	NK	Letter from New Jersey DEP, 24Jul95	Samples collected in response to consumer complaints.
Iowa	Alvord PWS	1994	NK	3	1	1	NK	NK	Believed to be leaking UST.	Memo from EPA Region 7, 26Jul95	--
Illinois	IL EPA	1990-95	NK	29	7	NK	NK	NK	UST or pipeline contamination from refinery or bulk terminal, source of Roanoke under investigation.	Letter from Illinois EPA, 09Jun95	Oakdale has abandoned its wells, water is piped in from nearby community. Island Lake uses the one-contaminated well minimally.
Wisconsin	WI DNR	1995	NK	0	0	NK	NK	3	NK	Letter from Wisconsin DNR, 14Jun95	Sampling conducted in April 1995 at 3 systems with ground-water source.
Texas	EPA Region VI	1988-93	NK	8	7	NK	15,352	NK	NK	Note from Texas State Water Program, 28Jul95	The 15,352 samples represent the total of PWS and private well samples, however, the majority are from PWS. Note that samples are not verified (i.e., systems with detections were not resampled for confirmation).
Rhode Island	RI DOH	1988-95	1	117	NK	NK	2,567	NK	NK	Letter from Rhode Island DOH, 18Oct95	2,567 samples includes an unknown number of surface-water samples, but number expected to be small.
Colorado	CO DOH&E	1995	0.2	1	1	NK	5	5	NK	EPA Region VIII, 24Oct95	--

b. Drinking water derived from ground water – private wells

Missouri	BHMGRP	1992-95	NK	133	4	4	161	NA	Massive failure of UST.	Letter from Missouri DNR, 19Jul95	Private wells located near active remediation site. Table 9 concentrations indicate levels prior to treatment.
Indiana	IN DEM	1991	NK	2	2	NK	NK	NA	NK	Letter from Indiana DEM, 21Jun95	Sampling conducted in response to consumer complaints.

Appendix 4: *Summary of general characteristics and results of State monitoring programs that have analyzed for MTBE in drinking water.—Continued*

[NK, not known; NA, not applicable; µg/L, micrograms per liter]

b. Drinking water derived from ground water – private wells—Continued

State	Data source	Sampling year(s)	Reporting level (µg/L)	Number of detections	Number of systems with detections	Number of			Source of contamination	Reference	Remarks
						Wells sampled	Samples	Systems sampled			
Texas	EPA Region VI	1988-93	NK	9	NK	NK	NK	NA	NK	Note from Texas State Water Program, 28Jul95	The number of samples from private wells in unknown, but thought to be a small subset of the 15,352 samples. Note that samples are not confirmed (i.e., wells with detections were not resampled for confirmation).
Rhode Island	RI DOH	1987-95	1	536	NK	NK	3,155	NA	NK	Letter from Rhode Island DOH, 18Oct95	--

c. Drinking water derived from surface water – public water systems

State	Data source	Sampling year(s)	Reporting level (µg/L)	Number of detects	Number of		Source	Reference	Remarks
					Samples	Systems sampled			
Wisconsin	WI DNR	1995	NK	0	NK	NK	NK	Letter from WI DNR, 14Jun95	Sampling conducted in April 1995 at two systems with surface-water source
Rhode Island	RI DOH	1988-95	1	1	NK	NK	NK	Letter from RI DOH, 180ct95	2,567 samples include an unknown number of surface-water samples, but number expected to be small.

Appendix 5: *Non-occurrence and occurrence of MTBE in ground water for those programs in which there was at least one detection of MTBE[1].*

[RL, reporting level; μg/L, micrograms per liter]

State	Data source	RL in μg/L	Type of well[2]																			
			Monitoring/Observation					Private supply					Public supply					Other/Not known				
			<RL	> = RL to <10 μg/L	> = 10 to <20 μg/L	> = 20 to < = 200 μg/L	>200 μg/L	<RL	> = RL to <10 μg/L	> = 10 to <20 μg/L	> = 20 to < = 200 μg/L	>200 μg/L	<RL	> = RL to <10 μg/L	> = 10 to <20 μg/L	> = 20 to < = 200 μg/L	>200 μg/L	<RL	> = RL to <10 μg/L	> = 10 to <20 μg/L	> = 20 to < = 200 μg/L	>200 μg/L
Colorado	nawqa.spltlusur	0.2	4	13		2	2		1									2	5			
Connecticut	nawqa.connlus31	0.2	5	5																		
Connecticut	nawqa.connlus33	0.2	2	1																		
Connecticut	nawqa.connlus34	0.2	1	1																		
Connecticut	nawqa.connsus	0.2						13	4										1			
Georgia	nawqa.gaflsus	0.2						12	1				13									
Georgia	nawqa.acfblusur1[2]	0.2	5					2										14	2			
Massachusetts	nawqa.conn	0.2																21	2			
Massachusetts	nawqa.connlus33	0.2	5	1																		
Massachusetts	nawqa.connlus34	0.2	3	4																		
New Jersey	nawqa.linj01 (1)	0.2	4	1																		
New Mexico	nawqa.riog	0.2																34	1			
New Mexico	nawqa.rioglus	0.2	23	1																		
Nevada	nawqa.nvbr	0.2																22	4		1	1
Nevada	nawqa.nvbrlusur	0.2	27	3														2		1		
Nevada	nawqa.nvbrsus	0.2						1					2	1				10				
New York	nawqa.hdsnlus1	0.2	12	2									3					3	2			
New York	nawqa.hdsnsus	0.2						41	1									4				
New York	nawqa.linj01	5.0	14	1																		
Pennsylvania	nawqa.lsus	0.2						25	4									1				
Texas	nawqa.trinlus1	0.2	14	3																		
Virginia	nawqa.albesus1	0.2	3	1																		
Vermont	nawqa.connlus32	0.2	6	1																		
Washington	nawqa.ccpt	0.2						1					5	1				28				
Wisconsin	nawqa.umis07	5/10																77	1			

[1] Numbers in this appendix denote either the number of wells in which MTBE was not detected (i.e., analysis was reported as less than the reporting level), or the number of wells in which MTBE was detected, in the specified concentration range.

[2] Some springs were also sampled as part of this study.

Appendix 6: *Concentration of MTBE measured at indicated well, by well type.*

[μg/L, micrograms per liter]

State	Data source	Well ID	Latitude	Longitude	Date of sample (MMDDYYYY)	Concentration of MTBE, in μg/L			
						Well type			
						Monitoring	Domestic supply	Public supply	Other/Not known
Colorado	nawqa.spltlusur	394234104595301	394234	1045953	08051993	800			
Colorado	nawqa.spltlusur	394326105003901	394326	1050039	08051993	0.6			
Colorado	nawqa.spltlusur	394507105004601	394507	1050046	07221993	3.2			
Colorado	nawqa.spltlusur	394830104564001	394830	1045640	08131993	33			
Colorado	nawqa.spltlusur	394833104572201	394833	1045722	07231993	9.6			
Colorado	nawqa.spltlusur	394858104591701	394858	1045917	07301993	0.5			
Colorado	nawqa.spltlusur	393736105004001	393736	1050040	07291993	5.1			
Colorado	nawqa.spltlusur	393843105005201	393843	1050052	08041993	1.2			
Colorado	nawqa.spltlusur	393922105031201	393922	1050312	08111993	0.5			
Colorado	nawqa.spltlusur	393944105000201	393944	1050002	07291993	0.6			
Colorado	nawqa.spltlusur	394044104533901	394044	1045339	08031993	3.5			
Colorado	nawqa.spltlusur	394648105072301	394648	1050723	07141993	23,000			
Colorado	nawqa.spltlusur	394654104584301	394655	1050115	07201993	83			
Colorado	nawqa.spltlusur	394728105045801	394728	1050458	07141993	0.7			
Colorado	nawqa.spltlusur	394811105023201	394811	1050232	07131993				0.3
Colorado	nawqa.spltlusur	393357105020201	393357	1050202	07151993	0.2			
Colorado	nawqa.spltlusur	394056104594801	394056	1045948	08191993				0.5
Colorado	nawqa.spltlusur	394156104550701	394156	1045507	08031993	0.3			
Colorado	nawqa.spltlusur	394314104575001	394314	1045750	08191993				1.3
Colorado	nawqa.spltlusur	394653105053601	394653	1050536	08121993				1.4
Colorado	nawqa.spltlusur	394655105030901	394655	1050309	07201993	0.7			
Colorado	nawqa.spltlusur	394824105065001	394824	1050650	08121993		0.4		
Colorado	nawqa.spltlusur	394835105053301	394835	1050533	09091993				0.2
Connecticut	nawqa.connlus31	415924072304401	415924	723044	06231994	0.7			
Connecticut	nawqa.connlus31	412722072495701	412722	724957	08051994	0.2			

Appendix 6: *Concentration of MTBE measured at indicated well, by well type.—Continued*

[µg/L, micrograms per liter]

State	Data source	Well ID	Latitude	Longitude	Date of sample (MMDDYYYY)	Concentration of MTBE, in µg/L			
						Well type			
						Monitoring	Domestic supply	Public supply	Other/Not known
Connecticut	nawqa.connlus31	413114072495401	413114	724954	07281994	0.2			
Connecticut	nawqa.connlus31	414926072300801	--	--	07261994	0.6			
Connecticut	nawqa.connlus31	415155072284601	415155	722846	07261994	0.5			
Connecticut	nawqa.connlus33	413434073245301	413434	732453	04051994	0.4			
Connecticut	nawqa.connlus34	411314073033501	411314	730335	02071994	0.3			
Connecticut	nawqa.connsus	BU126	414711	725607	06141995		2.2		
Connecticut	nawqa.connsus	ED6	415130	720441	06221995		0.3		
Connecticut	nawqa.connsus	NA46	412846	730119	05311995		1.5		
Connecticut	nawqa.connsus	RX28	413336	731839	06131995				2.1
Connecticut	nawqa.connsus	WHV449	411652	725828	06201995		0.8		
Georgia	nawqa.gaflsus	322513082051401	322513	820514	08171993		0.9		
Georgia	nawqa.acfbsprur1	335519084230001	--	--	10051994				8.7
Georgia	nawqa.acfbsprur1	335734084250101	335734	842501	12071994				0.2
Massachusetts	nawqa.conn	415542072273601	415542	722736	05051994				0.3
Massachusetts	nawqa.conn	415837072305501	415837	723055	05051994				0.2
Massachusetts	nawqa.connlus33	422633073155501	422633	731555	08251994	1.1			
Massachusetts	nawqa.connlus34	420637072451401	420637	724514	06281994	0.3			
Massachusetts	nawqa.connlus34	420744072451001	420744	724510	06281994	0.4			
Massachusetts	nawqa.connlus34	420347071521801	420347	715218	08021994	0.4			
Massachusetts	nawqa.connlus34	420558072185301	420558	721853	08241994	0.5			
New Jersey	nawqa.linj01 (1)	403524074485001	403524	744850	08311994	0.5			
New Mexico	nawqa.riog	373849106074301	373849	1060743	09071993				0.6
New Mexico	nawqa.rioglus	350653106400601	350653	1064006	08151993	7.9			
Nevada	nawqa.nvbr	393022119444301	393022	1194443	08031994				140
Nevada	nawqa.nvbr	393032119473501	393032	1194735	07261994				0.8
Nevada	nawqa.nvbr	393054119445501	393054	1194455	05241994				1.4

Appendix 6: *Concentration of MTBE measured at indicated well, by well type.—Continued*

[µg/L, micrograms per liter]

State	Data source	Well ID	Latitude	Longitude	Date of sample (MMDDYYYY)	Concentration of MTBE, in µg/L			
						Well type			
						Monitoring	Domestic supply	Public supply	Other/Not known
Nevada	nawqa.nvbr	393132119422801	393132	1194228	06011994				6.2
Nevada	nawqa.nvbr	393132119485801	393132	1194858	08151994				0.3
Nevada	nawqa.nvbr	393139119493401	393139	1194934	06211994				220
Nevada	nawqa.nvbrlusur	360617115063802	360617	1150638	08171993	0.4			
Nevada	nawqa.nvbrlusur	360648115084901	360648	1150849	08231993	0.4			
Nevada	nawqa.nvbrlusur	360821115025001	360821	1150250	08241993	0.7			
Nevada	nawqa.nvbrlusur	360854115060901	--	--	08201993				13
Nevada	nawqa.nvbrsus	360719115095903	360719	1150959	02151995			0.3	
New York	nawqa.hdsnlus1	424418073485601	424418	734856	07131993	0.2			
New York	nawqa.hdsnlus1	424744073592301	424744	735923	07211993	0.6			
New York	nawqa.hdsnlus1	424942073474401	--	--	08231994				0.4
New York	nawqa.hdsnlus1	425048073472501	--	--	08231994				0.3
New York	nawqa.hdsnsus	411938073595201	411938	735952	11301994		0.2		
New York	nawqa.linj01	404631073543901	404631	735439	09161992	7.9			
Pennsylvania	nawqa.lsus	395346076502901	395346	765029	07121993		1.3		
Pennsylvania	nawqa.lsus	400229076020301	400229	760203	07151993		0.5		
Pennsylvania	nawqa.lsus	400629076365201	400629	763652	07201993		0.5		
Pennsylvania	nawqa.lsus	400724075593201	400724	755932	07191993		0.3		
Texas	nawqa.trinlusur1	324243097105001	324243	971050	09021993	1.4			
Texas	nawqa.trinlusur1	325144097040201	325144	970402	07281993	0.2			
Texas	nawqa.trinlusur1	325225097045901	325225	970459	08201993	0.7			
Virginia	nawqa.albesus1	364101076544803	364101	765448	08171994	1			
Vermont	nawqa.connlus32	430746072263701	430746	722637	08121994	2.4			
Washington	nawqa.ccptsus	470904119190401	470858	1191905	08011994			1.8	
Wisconsin	nawqa.umis07	BG392	450006	923849	06091994				0.8

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
New Jersey	cert labs	61223	distribution	01251994		1.4
New Jersey	cert labs	61223	distribution	03221994		3.3
New Jersey	cert labs	61223	distribution	04261994		33.6
New Jersey	cert labs	61223	distribution	08091994		9.5
New Jersey	cert labs	61223	distribution	11091994		3.9
New Jersey	cert labs	13001	distribution	06151994		0.7
New Jersey	cert labs	13001	distribution	06151994		2.2
New Jersey	cert labs	13001	distribution	09071994		2.3
New Jersey	cert labs	13001	distribution	09281994		0.7
New Jersey	cert labs	18202	distribution	03281994		0.7
New Jersey	cert labs	18202	distribution	04041994		0.5
New Jersey	cert labs	18202	distribution	04041994		0.8
New Jersey	cert labs	18202	distribution	04041994		1.8
New Jersey	cert labs	18202	distribution	04041994		0.8
New Jersey	cert labs	18202	distribution	04041994		0.5
New Jersey	cert labs	18202	distribution	09121994		3.1
New Jersey	cert labs	18202	distribution	12191994		0.6
New Jersey	cert labs	18202	distribution	12271994		1.1
New Jersey	cert labs	26733	distribution	05181994		0.34
New Jersey	cert labs	26733	distribution	05181994		0.39
New Jersey	cert labs	20011	distribution	03211994		1.2
New Jersey	cert labs	13026	distribution	01061994		0.8
New Jersey	cert labs	51597	distribution	01211994		0.5
New Jersey	cert labs	22908	distribution	12211994		0.8
New Jersey	cert labs	26113	distribution	02091994		3.4
New Jersey	cert labs	26113	distribution	05231994		3.8
New Jersey	cert labs	26113	distribution	08191994		4.1
New Jersey	cert labs	26113	distribution	11181994		1.9
New Jersey	cert labs	42800	distribution	08171994		1.3
New Jersey	cert labs	58008	distribution	02011994		2.8
New Jersey	cert labs	58008	distribution	03011994		3
New Jersey	cert labs	58008	distribution	04051994		3.6
New Jersey	cert labs	58008	distribution	07051994		4.2
New Jersey	cert labs	58008	distribution	08021994		0.8
New Jersey	cert labs	58008	distribution	08021994		4.8
New Jersey	cert labs	58008	distribution	08171994		1.3
New Jersey	cert labs	58008	distribution	09061994		7
New Jersey	cert labs	58008	distribution	10041994		6.8
New Jersey	cert labs	58008	distribution	10041994		5.5
New Jersey	cert labs	58008	distribution	11011994		6.9

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
New Jersey	cert labs	15205	distribution	06131994		1.34
New Jersey	cert labs	13293	distribution	05261994		1.9
New Jersey	cert labs	13293	distribution	07201994		4.3
New Jersey	cert labs	13293	distribution	12281994		1.5
New Jersey	cert labs	13293	distribution	12311994		1.5
New Jersey	cert labs	13293	distribution	02011995		0.8
New Jersey	cert labs	13293	distribution	02011995		1.5
New Jersey	cert labs	14144	distribution	03071994		11
New Jersey	cert labs	14144	distribution	06071994		4.8
New Jersey	cert labs	14144	distribution	09011994		6.1
New Jersey	cert labs	16616	distribution	12271994		1.1
New Jersey	cert labs	18293	distribution	03251994		0.58
New Jersey	cert labs	18293	distribution	03251994		16.4
New Jersey	cert labs	16121	distribution	01101994		0.9
New Jersey	cert labs	16121	distribution	04051994		0.5
New Jersey	cert labs	16121	distribution	06071994		0.7
New Jersey	cert labs	16121	distribution	07071994		0.6
New Jersey	cert labs	16121	distribution	10041994		0.8
New Jersey	cert labs	31160	distribution	06071994		2.4
New Jersey	cert labs	19203	distribution	03281994		0.8
New Jersey	cert labs	19203	distribution	07121994		0.7
New Jersey	cert labs	19203	distribution	07121994		1.5
New Jersey	cert labs	19319	distribution	03151994		0.8
New Jersey	New Jersey DOH	32159	distribution	12071992		0.7
New Jersey	New Jersey DOH	77000	distribution	12221992		1
New Jersey	New Jersey DOH	60011	distribution	08171994		0.4
New Jersey	New Jersey DOH	60011	distribution	08171995		0.4
New Jersey	New Jersey DOH	80865	distribution	05061992		0.2
New Jersey	New Jersey DOH	38904	distribution	05051992		0.1
New Jersey	New Jersey DOH	42800	distribution	01201994		0.6
New Jersey	New Jersey DOH	45480	distribution	02071994		0.4
New Jersey	New Jersey DOH	58008	distribution	02021994		2
New Jersey	New Jersey DOH	13126	distribution	01281993		2
New Jersey	New Jersey DOH	86452	distribution	05121992		0.8
New Jersey	New Jersey DOH	16678	distribution	02081993		0.4
New Jersey	New Jersey DOH	33226	distribution	05111992		0.5
New Jersey	New Jersey DOH	66270	distribution	02231992		0.9
New Jersey	New Jersey DOH	16121	distribution	09281994		0.5
New Jersey	New Jersey DOH	13227	distribution	09221994		1

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
New Jersey	New Jersey DOH	26434	distribution	06111992		0.3
New Jersey	New Jersey DOH	52856	distribution	03181992		0.7
New Jersey	New Jersey DOH	10566	distribution	05061992		0.8
Iowa	Alvord PWS	21130	well	01121994		63
Iowa	Alvord PWS	21130	well	08031994		15
Iowa	Alvord PWS	21130	well	10171994		17
Missouri	BHMGRP	private well #1	well prior to filters	09021992	3,300	
Missouri	BHMGRP	private well #1	well prior to filters	09221992	4,700	
Missouri	BHMGRP	private well #1	well prior to filters	09301992	7,000	
Missouri	BHMGRP	private well #1	well prior to filters	10061992	3,100	
Missouri	BHMGRP	private well #1	well prior to filters	10201992	4,400	
Missouri	BHMGRP	private well #1	well prior to filters	12291992	2,900	
Missouri	BHMGRP	private well #1	well prior to filters	11031992	6,000	
Missouri	BHMGRP	private well #1	well prior to filters	11171992	1,200	
Missouri	BHMGRP	private well #1	well prior to filters	12031992	3,000	
Missouri	BHMGRP	private well #1	well prior to filters	12181992	1,300	
Missouri	BHMGRP	private well #1	well prior to filters	01141993	4,500	
Missouri	BHMGRP	private well #1	well prior to filters	01291993	3,000	
Missouri	BHMGRP	private well #1	well prior to filters	02091993	2,800	
Missouri	BHMGRP	private well #1	well prior to filters	02231993	6,900	
Missouri	BHMGRP	private well #1	well prior to filters	03181993	9,000	
Missouri	BHMGRP	private well #1	well prior to filters	03301993	9,300	
Missouri	BHMGRP	private well #1	well prior to filters	04131993	11,000	
Missouri	BHMGRP	private well #1	well prior to filters	04271993	4,500	
Missouri	BHMGRP	private well #1	well prior to filters	05261993	14,000	
Missouri	BHMGRP	private well #1	well prior to filters	06081993	11,000	
Missouri	BHMGRP	private well #1	well prior to filters	06231993	3,400	
Missouri	BHMGRP	private well #1	well prior to filters	07191993	4,000	
Missouri	BHMGRP	private well #1	well prior to filters	09161993	1,800	
Missouri	BHMGRP	private well #1	well prior to filters	10071993	880	
Missouri	BHMGRP	private well #1	well prior to filters	10221993	4,400	
Missouri	BHMGRP	private well #1	well prior to filters	11051993	1,800	
Missouri	BHMGRP	private well #1	well prior to filters	11231993	1,400	
Missouri	BHMGRP	private well #1	well prior to filters	12081993	1,500	
Missouri	BHMGRP	private well #1	well prior to filters	12211993	2,000	
Missouri	BHMGRP	private well #1	well prior to filters	01061994	2,000	
Missouri	BHMGRP	private well #1	well prior to filters	02021994	3,300	
Missouri	BHMGRP	private well #1	well prior to filters	02161994	4,040	
Missouri	BHMGRP	private well #1	well prior to filters	03171994	3,902	

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Missouri	BHMGRP	private well #1	well prior to filters	04271994	2,400	
Missouri	BHMGRP	private well #1	well prior to filters	07071994	1,200	
Missouri	BHMGRP	private well #1	well prior to filters	07211994	1,200	
Missouri	BHMGRP	private well #1	well prior to filters	08041994	1,900	
Missouri	BHMGRP	private well #1	well prior to filters	08181994	1,300	
Missouri	BHMGRP	private well #1	well prior to filters	08311994	700	
Missouri	BHMGRP	private well #1	well prior to filters	09121994	780	
Missouri	BHMGRP	private well #1	well prior to filters	09261994	920	
Missouri	BHMGRP	private well #1	well prior to filters	10131994	2,600	
Missouri	BHMGRP	private well #1	well prior to filters	10271994	1,400	
Missouri	BHMGRP	private well #1	well prior to filters	11031994	1,400	
Missouri	BHMGRP	private well #1	well prior to filters	11091994	1,600	
Missouri	BHMGRP	private well #1	well prior to filters	01111995	1,900	
Missouri	BHMGRP	private well #2	well prior to filters	09021992	3,000	
Missouri	BHMGRP	private well #2	well prior to filters	09151992	2,100	
Missouri	BHMGRP	private well #2	well prior to filters	09221992	3,400	
Missouri	BHMGRP	private well #2	well prior to filters	09301992	3,600	
Missouri	BHMGRP	private well #2	well prior to filters	10061992	1,700	
Missouri	BHMGRP	private well #2	well prior to filters	04131993	7,100	
Missouri	BHMGRP	private well #2	well prior to filters	04271993	1,800	
Missouri	BHMGRP	private well #2	well prior to filters	05141993	3,800	
Missouri	BHMGRP	private well #2	well prior to filters	05261993	17,000	
Missouri	BHMGRP	private well #2	well prior to filters	06081993	14,000	
Missouri	BHMGRP	private well #2	well prior to filters	06231993	5,000	
Missouri	BHMGRP	private well #2	well prior to filters	07191993	8,200	
Missouri	BHMGRP	private well #2	well prior to filters	09161993	2,300	
Missouri	BHMGRP	private well #2	well prior to filters	10071993	1,500	
Missouri	BHMGRP	private well #2	well prior to filters	10221993	4,100	
Missouri	BHMGRP	private well #2	well prior to filters	11051993	5,900	
Missouri	BHMGRP	private well #2	well prior to filters	11231993	2,200	
Missouri	BHMGRP	private well #2	well prior to filters	12211993	2,600	
Missouri	BHMGRP	private well #2	well prior to filters	03031994	3,060	
Missouri	BHMGRP	private well #2	well prior to filters	03171994	2,903	
Missouri	BHMGRP	private well #2	well prior to filters	04191994	3,600	
Missouri	BHMGRP	private well #2	well prior to filters	04271994	2,300	
Missouri	BHMGRP	private well #2	well prior to filters	07071994	1,700	
Missouri	BHMGRP	private well #2	well prior to filters	07211994	2,200	
Missouri	BHMGRP	private well #2	well prior to filters	08041994	2,200	
Missouri	BHMGRP	private well #2	well prior to filters	08181994	1,600	

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Missouri	BHMGRP	private well #2	well prior to filters	08311994	850	
Missouri	BHMGRP	private well #2	well prior to filters	09121994	670	
Missouri	BHMGRP	private well #2	well prior to filters	09261994	940	
Missouri	BHMGRP	private well #2	well prior to filters	10131994	1,300	
Missouri	BHMGRP	private well #2	well prior to filters	11091994	510	
Missouri	BHMGRP	private well #2	well prior to filters	01111995	1,100	
Missouri	BHMGRP	private well #3	well prior to filters	09021992	690	
Missouri	BHMGRP	private well #3	well prior to filters	09081992	990	
Missouri	BHMGRP	private well #3	well prior to filters	09151992	790	
Missouri	BHMGRP	private well #3	well prior to filters	09221992	160	
Missouri	BHMGRP	private well #3	well prior to filters	09301992	2,200	
Missouri	BHMGRP	private well #3	well prior to filters	10061992	1,100	
Missouri	BHMGRP	private well #3	well prior to filters	10201992	1,700	
Missouri	BHMGRP	private well #3	well prior to filters	11031992	1,100	
Missouri	BHMGRP	private well #3	well prior to filters	12031992	1,100	
Missouri	BHMGRP	private well #3	well prior to filters	12181992	610	
Missouri	BHMGRP	private well #3	well prior to filters	01141993	910	
Missouri	BHMGRP	private well #3	well prior to filters	01291993	530	
Missouri	BHMGRP	private well #3	well prior to filters	02091993	1,300	
Missouri	BHMGRP	private well #3	well prior to filters	02231993	250	
Missouri	BHMGRP	private well #3	well prior to filters	03181993	720	
Missouri	BHMGRP	private well #3	well prior to filters	03301993	450	
Missouri	BHMGRP	private well #3	well prior to filters	04131993	1,300	
Missouri	BHMGRP	private well #3	well prior to filters	04271993	2,600	
Missouri	BHMGRP	private well #3	well prior to filters	05141993	540	
Missouri	BHMGRP	private well #3	well prior to filters	05261993	1,000	
Missouri	BHMGRP	private well #3	well prior to filters	06081993	1,600	
Missouri	BHMGRP	private well #3	well prior to filters	06231993	140	
Missouri	BHMGRP	private well #3	well prior to filters	07191993	1,400	
Missouri	BHMGRP	private well #3	well prior to filters	09161993	210	
Missouri	BHMGRP	private well #3	well prior to filters	10071993	230	
Missouri	BHMGRP	private well #3	well prior to filters	10221993	740	
Missouri	BHMGRP	private well #3	well prior to filters	11101993	72	
Missouri	BHMGRP	private well #3	well prior to filters	11231993	620	
Missouri	BHMGRP	private well #3	well prior to filters	12081993	1,100	
Missouri	BHMGRP	private well #3	well prior to filters	12211993	960	
Missouri	BHMGRP	private well #3	well prior to filters	01061994	730	
Missouri	BHMGRP	private well #3	well prior to filters	02021994	1,500	
Missouri	BHMGRP	private well #3	well prior to filters	02161994	738	

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Missouri	BHMGRP	private well #3	well prior to filters	03031994	525	
Missouri	BHMGRP	private well #3	well prior to filters	03171994	981	
Missouri	BHMGRP	private well #3	well prior to filters	03291994	794	
Missouri	BHMGRP	private well #3	well prior to filters	04141994	100	
Missouri	BHMGRP	private well #3	well prior to filters	04191994	340	
Missouri	BHMGRP	private well #3	well prior to filters	04271994	110	
Missouri	BHMGRP	private well #3	well prior to filters	05121994	76	
Missouri	BHMGRP	private well #3	well prior to filters	05251994	400	
Missouri	BHMGRP	private well #3	well prior to filters	06011994	46	
Missouri	BHMGRP	private well #3	well prior to filters	07071994	280	
Missouri	BHMGRP	private well #3	well prior to filters	07211994	490	
Missouri	BHMGRP	private well #3	well prior to filters	08041994	50	
Missouri	BHMGRP	private well #3	well prior to filters	08181994	99	
Missouri	BHMGRP	private well #3	well prior to filters	08311994	14	
Missouri	BHMGRP	private well #3	well prior to filters	09121994	13	
Missouri	BHMGRP	private well #3	well prior to filters	10131994	380	
Missouri	BHMGRP	private well #3	well prior to filters	10271994	340	
Missouri	BHMGRP	private well #3	well prior to filters	11031994	430	
Missouri	BHMGRP	private well #3	well prior to filters	11091994	370	
Missouri	BHMGRP	private well #3	well prior to filters	01111995	780	
Missouri	BHMGRP	private well #4	well prior to filters	09161993	8.8	
Missouri	BHMGRP	private well #4	well prior to filters	07071994	1,500	
Illinois	IL EPA	73081	distribution	08041993		770
Illinois	IL EPA	73081	distribution	09291993		270
Illinois	IL EPA	73081	distribution	12281993		620
Illinois	IL EPA	73081	distribution	02151994		400
Illinois	IL EPA	73081	distribution	02151994		400
Illinois	IL EPA	73081	well	02241994		580
Illinois	IL EPA	73081	well	02241994		350
Illinois	IL EPA	32018	distribution	12091993		50
Illinois	IL EPA	32018	distribution	01261994		37
Illinois	IL EPA	32018	distribution	02151994		50
Illinois	IL EPA	32018	distribution	05251994		20
Illinois	IL EPA	47420	distribution	03061995		4
Illinois	IL EPA	76547	distribution	03211994		24
Illinois	IL EPA	76547	distribution	06081994		11
Illinois	IL EPA	76547	distribution	08211994		24

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Illinois	IL EPA	76547	distribution	04111995		15
Illinois	IL EPA	76547	distribution	04111995		15
Illinois	IL EPA	76547	distribution	04111995		15
Illinois	IL EPA	76547	distribution	09141994		10
Illinois	IL EPA	76547	distribution	11281994		19
Illinois	IL EPA	36973	well	07091990		1.8
Illinois	IL EPA	36973	well	07091990		1.2
Illinois	IL EPA	42786	well	07091990		0.9
Illinois	IL EPA	42786	well	07091990		1.1
Illinois	IL EPA	42786	well	07231990		0.8
Illinois	IL EPA	42786	distribution	07231990		0.4
Illinois	IL EPA	66369	distribution	06291993		85
Illinois	IL EPA	66369	distribution	08301993		14
Illinois	IL EPA	66369	distribution	11221993		24
Indiana	IN DEM	private well 1	well	00001991	5,400	
Indiana	IN DEM	private well 2	well	00001991	40	
Texas	EPA Region VI	2020013	distribution	03181993		6.3
Texas	EPA Region VI	2050011	distribution	06071993		4.3
Texas	EPA Region VI	1011467	distribution	06151993		8
Texas	EPA Region VI	0840063	distribution	06151993		10.4
Texas	EPA Region VI	1011033	distribution	06151993		8.2
Texas	EPA Region VI	1012202	distribution	06151993		4.7
Texas	EPA Region VI	1012722	distribution	06151993		3.6
Texas	EPA Region VI	2020013	distribution	06231993		42
Texas	EPA Region VI	private well	well	02061990	5	
Texas	EPA Region VI	private well	well	04201990	2	
Texas	EPA Region VI	private well	well	11281990	12	
Texas	EPA Region VI	private well	well	04221991	2	
Texas	EPA Region VI	private well	well	05201991	3,360	
Texas	EPA Region VI	private well	well	09101991	20	
Texas	EPA Region VI	private well	well	12041991	2	
Texas	EPA Region VI	private well	well	03181992	8	
Texas	EPA Region VI	private well	well	12041992	2.8	
Rhode Island	RI DOH	public water system	distribution	01261988		2
Rhode Island	RI DOH	public water system	distribution	10181988		53
Rhode Island	RI DOH	public water system	distribution	09261988		61
Rhode Island	RI DOH	public water system	distribution	11211988		1
Rhode Island	RI DOH	public water system	distribution	02161989		33
Rhode Island	RI DOH	public water system	distribution	06081989		48

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Rhode Island	RI DOH	public water system	distribution	07121989		3
Rhode Island	RI DOH	public water system	distribution	09061989		32
Rhode Island	RI DOH	public water system	distribution	09261989		17
Rhode Island	RI DOH	public water system	distribution	10121989		28
Rhode Island	RI DOH	public water system	distribution	11091989		21
Rhode Island	RI DOH	public water system	distribution	11101989		9
Rhode Island	RI DOH	public water system	distribution	11271989		4
Rhode Island	RI DOH	public water system	well	01101990		5
Rhode Island	RI DOH	public water system	distribution	01241990		8
Rhode Island	RI DOH	public water system	well	03081990		10
Rhode Island	RI DOH	public water system	distribution	03121990		1
Rhode Island	RI DOH	public water system	distribution	03161990		5
Rhode Island	RI DOH	public water system	distribution	04131990		5
Rhode Island	RI DOH	public water system	distribution	05091990		3
Rhode Island	RI DOH	public water system	distribution	05101990		4
Rhode Island	RI DOH	public water system	distribution	05101990		9
Rhode Island	RI DOH	public water system	distribution	05161990		12
Rhode Island	RI DOH	public water system	distribution	06061990		5
Rhode Island	RI DOH	public water system	well	06191990		5
Rhode Island	RI DOH	public water system	distribution	06201990		5
Rhode Island	RI DOH	public water system	distribution	07061990		3
Rhode Island	RI DOH	public water system	distribution	07241990		1
Rhode Island	RI DOH	public water system	distribution	07311990		5
Rhode Island	RI DOH	public water system	distribution	08161990		4
Rhode Island	RI DOH	public water system	distribution	08171990		39
Rhode Island	RI DOH	public water system	well	08171990		4
Rhode Island	RI DOH	public water system	distribution	08171990		4
Rhode Island	RI DOH	public water system	distribution	09171990		1
Rhode Island	RI DOH	public water system	distribution	09171990		2
Rhode Island	RI DOH	public water system	distribution	09171990		9
Rhode Island	RI DOH	public water system	well	01051990		17,800
Rhode Island	RI DOH	public water system	distribution	10251990		2
Rhode Island	RI DOH	public water system	well	10251990		9
Rhode Island	RI DOH	public water system	distribution	10291990		1
Rhode Island	RI DOH	public water system	well	11071990		1
Rhode Island	RI DOH	public water system	well	11191990		5
Rhode Island	RI DOH	public water system	well	11201990		8
Rhode Island	RI DOH	public water system	well	12051990		7
Rhode Island	RI DOH	public water system	well	12191990		4

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Rhode Island	RI DOH	public water system	well	01161991		2
Rhode Island	RI DOH	public water system	well	02121991		2
Rhode Island	RI DOH	public water system	well	02131991		2
Rhode Island	RI DOH	public water system	distribution	02131991		1
Rhode Island	RI DOH	public water system	well	02211991		8
Rhode Island	RI DOH	public water system	distribution	03121991		4
Rhode Island	RI DOH	public water system	distribution	03121991		5
Rhode Island	RI DOH	public water system	well	04121991		1
Rhode Island	RI DOH	public water system	well	04181991		2
Rhode Island	RI DOH	public water system	well	04181991		6
Rhode Island	RI DOH	public water system	well	05091991		1
Rhode Island	RI DOH	public water system	distribution	05151991		2
Rhode Island	RI DOH	public water system	well	05171991		1
Rhode Island	RI DOH	public water system	well	05171991		2
Rhode Island	RI DOH	public water system	well	05171991		3
Rhode Island	RI DOH	public water system	well	05171991		4
Rhode Island	RI DOH	public water system	well	06041991		1
Rhode Island	RI DOH	public water system	well	06051991		2
Rhode Island	RI DOH	public water system	distribution	07251991		1
Rhode Island	RI DOH	public water system	well	07251991		1
Rhode Island	RI DOH	public water system	well	07291991		2
Rhode Island	RI DOH	public water system	well	08141991		1
Rhode Island	RI DOH	public water system	well	09171991		5
Rhode Island	RI DOH	public water system	well	09251991		2
Rhode Island	RI DOH	public water system	distribution	10071991		1
Rhode Island	RI DOH	public water system	distribution	10071991		1
Rhode Island	RI DOH	public water system	well	10151991		2
Rhode Island	RI DOH	public water system	distribution	10301991		1
Rhode Island	RI DOH	public water system	well	10301991		1
Rhode Island	RI DOH	public water system	well	11141991		2
Rhode Island	RI DOH	public water system	distribution	11181991		1
Rhode Island	RI DOH	public water system	well	11191991		3
Rhode Island	RI DOH	public water system	well	11221991		3
Rhode Island	RI DOH	public water system	well	11221991		3
Rhode Island	RI DOH	public water system	well	11221991		3
Rhode Island	RI DOH	public water system	well	01071992		1
Rhode Island	RI DOH	public water system	well	01281992		1
Rhode Island	RI DOH	public water system	distribution	03051992		7
Rhode Island	RI DOH	public water system	distribution	08191992		1

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Rhode Island	RI DOH	public water system	well	01051993		2
Rhode Island	RI DOH	public water system	well	01111990		7
Rhode Island	RI DOH	public water system	distribution	02021993		2
Rhode Island	RI DOH	public water system	well	11181993		6
Rhode Island	RI DOH	public water system	well	12231993		1
Rhode Island	RI DOH	public water system	well	12231993		5
Rhode Island	RI DOH	public water system	well	12231993		4
Rhode Island	RI DOH	public water system	surface water	01251994		1
Rhode Island	RI DOH	public water system	distribution	02031994		8
Rhode Island	RI DOH	public water system	distribution	03091994		5
Rhode Island	RI DOH	public water system	well	03291994		1
Rhode Island	RI DOH	public water system	well	04141994		6
Rhode Island	RI DOH	public water system	distribution	04291994		6
Rhode Island	RI DOH	public water system	distribution	05191994		7
Rhode Island	RI DOH	public water system	distribution	06071994		6
Rhode Island	RI DOH	public water system	well	06291994		5
Rhode Island	RI DOH	public water system	distribution	07061994		6
Rhode Island	RI DOH	public water system	distribution	08111994		7
Rhode Island	RI DOH	public water system	distribution	08251994		6
Rhode Island	RI DOH	public water system	well	09061994		1
Rhode Island	RI DOH	public water system	well	09061994		3
Rhode Island	RI DOH	public water system	distribution	09261994		5
Rhode Island	RI DOH	public water system	distribution	10211994		6
Rhode Island	RI DOH	public water system	distribution	12291994		12
Rhode Island	RI DOH	public water system	well	02231995		14
Rhode Island	RI DOH	public water system	well	04051995		10
Rhode Island	RI DOH	public water system	well	05251995		22
Rhode Island	RI DOH	public water system	distribution	07101995		10
Rhode Island	RI DOH	public water system	well	07101995		3
Rhode Island	RI DOH	public water system	distribution	04181995		9.6
Rhode Island	RI DOH	public water system	well	06301995		2.2
Rhode Island	RI DOH	public water system	distribution	05241995		9
Rhode Island	RI DOH	public water system	distribution	07171995		15
Rhode Island	RI DOH	public water system	distribution	06291995		10
Rhode Island	RI DOH	private well	well	10201987	5	
Rhode Island	RI DOH	private well	well	10271987	213	
Rhode Island	RI DOH	private well	well	10301987	25	
Rhode Island	RI DOH	private well	well	11041987	130	
Rhode Island	RI DOH	private well	well	11041987	150	

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Rhode Island	RI DOH	private well	well	11091987	4	
Rhode Island	RI DOH	private well	well	11161987	1	
Rhode Island	RI DOH	private well	well	11231987	1	
Rhode Island	RI DOH	private well	well	12101987	16	
Rhode Island	RI DOH	private well	well	12141987	35	
Rhode Island	RI DOH	private well	well	12171987	80	
Rhode Island	RI DOH	private well	well	01071988	40	
Rhode Island	RI DOH	private well	well	01201988	290	
Rhode Island	RI DOH	private well	well	01191988	47	
Rhode Island	RI DOH	private well	well	01211988	27	
Rhode Island	RI DOH	private well	well	02011988	35	
Rhode Island	RI DOH	private well	well	02011988	170	
Rhode Island	RI DOH	private well	well	03281988	73	
Rhode Island	RI DOH	private well	well	03291988	12	
Rhode Island	RI DOH	private well	well	04041988	300	
Rhode Island	RI DOH	private well	well	04111988	90	
Rhode Island	RI DOH	private well	well	04111988	100	
Rhode Island	RI DOH	private well	well	04111988	120	
Rhode Island	RI DOH	private well	well	04251988	20	
Rhode Island	RI DOH	private well	well	05231988	13	
Rhode Island	RI DOH	private well	well	05231988	2	
Rhode Island	RI DOH	private well	well	05231988	170	
Rhode Island	RI DOH	private well	well	05231988	1,300	
Rhode Island	RI DOH	private well	well	05231988	4	
Rhode Island	RI DOH	private well	well	05231988	1,000	
Rhode Island	RI DOH	private well	well	05251988	60	
Rhode Island	RI DOH	private well	well	05251988	4	
Rhode Island	RI DOH	private well	well	05311988	85	
Rhode Island	RI DOH	private well	well	06061988	43	
Rhode Island	RI DOH	private well	well	06061988	1	
Rhode Island	RI DOH	private well	well	06071988	1,800	
Rhode Island	RI DOH	private well	well	06071988	11	
Rhode Island	RI DOH	private well	well	06241988	53	
Rhode Island	RI DOH	private well	well	06301988	2	
Rhode Island	RI DOH	private well	well	07121988	2	
Rhode Island	RI DOH	private well	well	07121988	10	
Rhode Island	RI DOH	private well	well	07121988	3	
Rhode Island	RI DOH	private well	well	07121988	7	
Rhode Island	RI DOH	private well	well	07121988	2	

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Rhode Island	RI DOH	private well	well	07121988	250	
Rhode Island	RI DOH	private well	well	07121988	40	
Rhode Island	RI DOH	private well	well	07181988	2	
Rhode Island	RI DOH	private well	well	07151988	22	
Rhode Island	RI DOH	private well	well	08221988	3	
Rhode Island	RI DOH	private well	well	09011988	26	
Rhode Island	RI DOH	private well	well	08221988	2	
Rhode Island	RI DOH	private well	well	09201988	2	
Rhode Island	RI DOH	private well	well	09191988	5	
Rhode Island	RI DOH	private well	well	10191988	11	
Rhode Island	RI DOH	private well	well	05031989	1	
Rhode Island	RI DOH	private well	well	09191988	9	
Rhode Island	RI DOH	private well	well	11141988	3	
Rhode Island	RI DOH	private well	well	12121988	35	
Rhode Island	RI DOH	private well	well	01051989	12	
Rhode Island	RI DOH	private well	well	01231989	120	
Rhode Island	RI DOH	private well	well	01241989	35	
Rhode Island	RI DOH	private well	well	01311989	30	
Rhode Island	RI DOH	private well	well	01311989	40	
Rhode Island	RI DOH	private well	well	01301989	140	
Rhode Island	RI DOH	private well	well	02011989	35	
Rhode Island	RI DOH	private well	well	03071989	4	
Rhode Island	RI DOH	private well	well	04041989	36	
Rhode Island	RI DOH	private well	well	04041989	5	
Rhode Island	RI DOH	private well	well	04251989	1	
Rhode Island	RI DOH	private well	well	05221989	230	
Rhode Island	RI DOH	private well	well	06191989	8	
Rhode Island	RI DOH	private well	well	06191989	120	
Rhode Island	RI DOH	private well	well	07131989	9	
Rhode Island	RI DOH	private well	well	04281989	150	
Rhode Island	RI DOH	private well	well	05021989	125	
Rhode Island	RI DOH	private well	well	08201989	50	
Rhode Island	RI DOH	private well	well	08101989	13	
Rhode Island	RI DOH	private well	well	08101989	8	
Rhode Island	RI DOH	private well	well	08101989	12	
Rhode Island	RI DOH	private well	well	07261989	94	
Rhode Island	RI DOH	private well	well	09191989	25	
Rhode Island	RI DOH	private well	well	09191989	37	
Rhode Island	RI DOH	private well	well	09191989	6	

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Rhode Island	RI DOH	private well	well	09201989	56	
Rhode Island	RI DOH	private well	well	10051989	2	
Rhode Island	RI DOH	private well	well	10021989	1	
Rhode Island	RI DOH	private well	well	10171989	28	
Rhode Island	RI DOH	private well	well	10171989	45	
Rhode Island	RI DOH	private well	well	10211989	12	
Rhode Island	RI DOH	private well	well	10211989	139	
Rhode Island	RI DOH	private well	well	10251989	2	
Rhode Island	RI DOH	private well	well	11111989	30	
Rhode Island	RI DOH	private well	well	11111989	7	
Rhode Island	RI DOH	private well	well	11031989	23	
Rhode Island	RI DOH	private well	well	11071989	33	
Rhode Island	RI DOH	private well	well	11071989	49	
Rhode Island	RI DOH	private well	well	11071989	41	
Rhode Island	RI DOH	private well	well	11071989	18	
Rhode Island	RI DOH	private well	well	11171989	4	
Rhode Island	RI DOH	private well	well	11201989	79	
Rhode Island	RI DOH	private well	well	11241989	5	
Rhode Island	RI DOH	private well	well	12061989	34	
Rhode Island	RI DOH	private well	well	12051989	70	
Rhode Island	RI DOH	private well	well	12141989	10	
Rhode Island	RI DOH	private well	well	12191989	5	
Rhode Island	RI DOH	private well	well	01111990	31	
Rhode Island	RI DOH	private well	well	01111990	1	
Rhode Island	RI DOH	private well	well	01051990	90	
Rhode Island	RI DOH	private well	well	01161990	4	
Rhode Island	RI DOH	private well	well	01251990	6	
Rhode Island	RI DOH	private well	well	01221990	92	
Rhode Island	RI DOH	private well	well	01221990	27	
Rhode Island	RI DOH	private well	well	01221990	85	
Rhode Island	RI DOH	private well	well	01221990	147	
Rhode Island	RI DOH	private well	well	01221990	716	
Rhode Island	RI DOH	private well	well	02011990	116	
Rhode Island	RI DOH	private well	well	02011990	27	
Rhode Island	RI DOH	private well	well	01191990	320	
Rhode Island	RI DOH	private well	well	01191990	35	
Rhode Island	RI DOH	private well	well	01191990	2	
Rhode Island	RI DOH	private well	well	01221990	46	
Rhode Island	RI DOH	private well	well	01221990	59	

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Rhode Island	RI DOH	private well	well	01221990	77	
Rhode Island	RI DOH	private well	well	01191990	5	
Rhode Island	RI DOH	private well	well	01191990	3	
Rhode Island	RI DOH	private well	well	02121990	39	
Rhode Island	RI DOH	private well	well	02121990	20	
Rhode Island	RI DOH	private well	well	02121990	3	
Rhode Island	RI DOH	private well	well	02121990	33	
Rhode Island	RI DOH	private well	well	02051990	5	
Rhode Island	RI DOH	private well	well	02051990	6	
Rhode Island	RI DOH	private well	well	02151990	53	
Rhode Island	RI DOH	private well	well	02051990	177	
Rhode Island	RI DOH	private well	well	02151990	30	
Rhode Island	RI DOH	private well	well	11211989	3	
Rhode Island	RI DOH	private well	well	02021990	100	
Rhode Island	RI DOH	private well	well	02191990	1	
Rhode Island	RI DOH	private well	well	02211990	1	
Rhode Island	RI DOH	private well	well	02231990	29	
Rhode Island	RI DOH	private well	well	02261990	4	
Rhode Island	RI DOH	private well	well	02011990	274	
Rhode Island	RI DOH	private well	well	02011990	1	
Rhode Island	RI DOH	private well	well	02221990	4	
Rhode Island	RI DOH	private well	well	02221990	16	
Rhode Island	RI DOH	private well	well	03071990	40	
Rhode Island	RI DOH	private well	well	03071990	15	
Rhode Island	RI DOH	private well	well	03081990	39	
Rhode Island	RI DOH	private well	well	03081990	5	
Rhode Island	RI DOH	private well	well	03021990	15	
Rhode Island	RI DOH	private well	well	03021990	1,439	
Rhode Island	RI DOH	private well	well	03111990	5	
Rhode Island	RI DOH	private well	well	03111990	28	
Rhode Island	RI DOH	private well	well	03201990	478	
Rhode Island	RI DOH	private well	well	03201990	77	
Rhode Island	RI DOH	private well	well	03201990	6	
Rhode Island	RI DOH	private well	well	03201990	102	
Rhode Island	RI DOH	private well	well	03201990	18	
Rhode Island	RI DOH	private well	well	03201990	24	
Rhode Island	RI DOH	private well	well	03201990	40	
Rhode Island	RI DOH	private well	well	03201990	49	
Rhode Island	RI DOH	private well	well	03201990	22	

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Rhode Island	RI DOH	private well	well	03201990	9	
Rhode Island	RI DOH	private well	well	03151990	41	
Rhode Island	RI DOH	private well	well	03151990	164	
Rhode Island	RI DOH	private well	well	03091990	4	
Rhode Island	RI DOH	private well	well	03091990	5	
Rhode Island	RI DOH	private well	well	03091990	18	
Rhode Island	RI DOH	private well	well	03091990	65	
Rhode Island	RI DOH	private well	well	02221990	15	
Rhode Island	RI DOH	private well	well	02221990	19	
Rhode Island	RI DOH	private well	well	03281990	4	
Rhode Island	RI DOH	private well	well	03211990	19	
Rhode Island	RI DOH	private well	well	04051990	37	
Rhode Island	RI DOH	private well	well	04051990	9	
Rhode Island	RI DOH	private well	well	04051990	3	
Rhode Island	RI DOH	private well	well	04031990	12	
Rhode Island	RI DOH	private well	well	04031990	1,500	
Rhode Island	RI DOH	private well	well	04251990	9	
Rhode Island	RI DOH	private well	well	04251990	38	
Rhode Island	RI DOH	private well	well	04251990	29	
Rhode Island	RI DOH	private well	well	04241990	9	
Rhode Island	RI DOH	private well	well	04251990	4	
Rhode Island	RI DOH	private well	well	04261990	4	
Rhode Island	RI DOH	private well	well	04301990	3	
Rhode Island	RI DOH	private well	well	04301990	2	
Rhode Island	RI DOH	private well	well	05011990	34	
Rhode Island	RI DOH	private well	well	05011990	32	
Rhode Island	RI DOH	private well	well	05011990	16	
Rhode Island	RI DOH	private well	well	05011990	28	
Rhode Island	RI DOH	private well	well	05021990	19	
Rhode Island	RI DOH	private well	well	05021990	9	
Rhode Island	RI DOH	private well	well	05021990	98	
Rhode Island	RI DOH	private well	well	05021990	14	
Rhode Island	RI DOH	private well	well	05021990	61	
Rhode Island	RI DOH	private well	well	05021990	8	
Rhode Island	RI DOH	private well	well	05021990	28	
Rhode Island	RI DOH	private well	well	05071990	140	
Rhode Island	RI DOH	private well	well	05031990	1	
Rhode Island	RI DOH	private well	well	05101990	4	
Rhode Island	RI DOH	private well	well	05101990	32	

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Rhode Island	RI DOH	private well	well	05101990	4	
Rhode Island	RI DOH	private well	well	05101990	2	
Rhode Island	RI DOH	private well	well	05171990	35	
Rhode Island	RI DOH	private well	well	05171990	3	
Rhode Island	RI DOH	private well	well	05161990	41	
Rhode Island	RI DOH	private well	well	05161990	157	
Rhode Island	RI DOH	private well	well	05161990	4	
Rhode Island	RI DOH	private well	well	05161990	28	
Rhode Island	RI DOH	private well	well	05231990	1,353	
Rhode Island	RI DOH	private well	well	05231990	9	
Rhode Island	RI DOH	private well	well	05241990	23	
Rhode Island	RI DOH	private well	well	05241990	127	
Rhode Island	RI DOH	private well	well	05241990	94	
Rhode Island	RI DOH	private well	well	05241990	5	
Rhode Island	RI DOH	private well	well	05241990	6	
Rhode Island	RI DOH	private well	well	05171990	2	
Rhode Island	RI DOH	private well	well	05241990	52	
Rhode Island	RI DOH	private well	well	05241990	748	
Rhode Island	RI DOH	private well	well	05241990	28	
Rhode Island	RI DOH	private well	well	05241990	38	
Rhode Island	RI DOH	private well	well	06041990	40	
Rhode Island	RI DOH	private well	well	05311990	17	
Rhode Island	RI DOH	private well	well	06041990	4	
Rhode Island	RI DOH	private well	well	06141990	24	
Rhode Island	RI DOH	private well	well	06241990	5	
Rhode Island	RI DOH	private well	well	06241990	97	
Rhode Island	RI DOH	private well	well	06211990	31	
Rhode Island	RI DOH	private well	well	06271990	2	
Rhode Island	RI DOH	private well	well	06271990	9	
Rhode Island	RI DOH	private well	well	07021990	11	
Rhode Island	RI DOH	private well	well	07021990	23	
Rhode Island	RI DOH	private well	well	07051990	3	
Rhode Island	RI DOH	private well	well	07051990	2	
Rhode Island	RI DOH	private well	well	07051990	33	
Rhode Island	RI DOH	private well	well	07051990	5	
Rhode Island	RI DOH	private well	well	07061990	1	
Rhode Island	RI DOH	private well	well	07181990	2	
Rhode Island	RI DOH	private well	well	07171990	20	
Rhode Island	RI DOH	private well	well	07171990	15	

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Rhode Island	RI DOH	private well	well	07251990	4	
Rhode Island	RI DOH	private well	well	07251990	1	
Rhode Island	RI DOH	private well	well	07261990	23	
Rhode Island	RI DOH	private well	well	07251990	74	
Rhode Island	RI DOH	private well	well	07251990	8	
Rhode Island	RI DOH	private well	well	07251990	6	
Rhode Island	RI DOH	private well	well	07251990	6	
Rhode Island	RI DOH	private well	well	07251990	6	
Rhode Island	RI DOH	private well	well	07261990	3	
Rhode Island	RI DOH	private well	well	07261990	157	
Rhode Island	RI DOH	private well	well	07261990	86	
Rhode Island	RI DOH	private well	well	07261990	15	
Rhode Island	RI DOH	private well	well	07261990	24	
Rhode Island	RI DOH	private well	well	07261990	33	
Rhode Island	RI DOH	private well	well	07271990	1	
Rhode Island	RI DOH	private well	well	08091990	1,040	
Rhode Island	RI DOH	private well	well	08091990	16	
Rhode Island	RI DOH	private well	well	08201990	24	
Rhode Island	RI DOH	private well	well	08221990	14	
Rhode Island	RI DOH	private well	well	08271990	2	
Rhode Island	RI DOH	private well	well	08271990	29	
Rhode Island	RI DOH	private well	well	08271990	23	
Rhode Island	RI DOH	private well	well	08271990	29	
Rhode Island	RI DOH	private well	well	08271990	123	
Rhode Island	RI DOH	private well	well	08271990	64	
Rhode Island	RI DOH	private well	well	08271990	13	
Rhode Island	RI DOH	private well	well	08271990	17	
Rhode Island	RI DOH	private well	well	08301990	63	
Rhode Island	RI DOH	private well	well	08301990	8	
Rhode Island	RI DOH	private well	well	08301990	46	
Rhode Island	RI DOH	private well	well	08301990	18	
Rhode Island	RI DOH	private well	well	08301990	6	
Rhode Island	RI DOH	private well	well	08301990	800	
Rhode Island	RI DOH	private well	well	08301990	9	
Rhode Island	RI DOH	private well	well	08301990	21	
Rhode Island	RI DOH	private well	well	09051990	2	
Rhode Island	RI DOH	private well	well	09051990	11	
Rhode Island	RI DOH	private well	well	09121990	2	
Rhode Island	RI DOH	private well	well	09101990	11	

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Rhode Island	RI DOH	private well	well	09101990	3	
Rhode Island	RI DOH	private well	well	09101990	30	
Rhode Island	RI DOH	private well	well	09101990	45	
Rhode Island	RI DOH	private well	well	09101990	8	
Rhode Island	RI DOH	private well	well	09101990	20	
Rhode Island	RI DOH	private well	well	09101990	50	
Rhode Island	RI DOH	private well	well	09181990	86	
Rhode Island	RI DOH	private well	well	09201990	6	
Rhode Island	RI DOH	private well	well	09171990	1,484	
Rhode Island	RI DOH	private well	well	09171990	28	
Rhode Island	RI DOH	private well	well	09171990	22	
Rhode Island	RI DOH	private well	well	09171990	98	
Rhode Island	RI DOH	private well	well	09171990	23	
Rhode Island	RI DOH	private well	well	09171990	17	
Rhode Island	RI DOH	private well	well	09171990	103	
Rhode Island	RI DOH	private well	well	09171990	47	
Rhode Island	RI DOH	private well	well	09171990	16	
Rhode Island	RI DOH	private well	well	10021990	104	
Rhode Island	RI DOH	private well	well	10101990	31	
Rhode Island	RI DOH	private well	well	10151990	2	
Rhode Island	RI DOH	private well	well	10111990	1	
Rhode Island	RI DOH	private well	well	10111990	3	
Rhode Island	RI DOH	private well	well	10161990	2	
Rhode Island	RI DOH	private well	well	10221990	60	
Rhode Island	RI DOH	private well	well	10221990	83	
Rhode Island	RI DOH	private well	well	10221990	78	
Rhode Island	RI DOH	private well	well	10221990	97	
Rhode Island	RI DOH	private well	well	10221990	37	
Rhode Island	RI DOH	private well	well	10221990	25	
Rhode Island	RI DOH	private well	well	10221990	11	
Rhode Island	RI DOH	private well	well	10251990	2	
Rhode Island	RI DOH	private well	well	10311990	9	
Rhode Island	RI DOH	private well	well	10311990	11	
Rhode Island	RI DOH	private well	well	10311990	47	
Rhode Island	RI DOH	private well	well	10311990	31	
Rhode Island	RI DOH	private well	well	10311990	24	
Rhode Island	RI DOH	private well	well	10311990	21	
Rhode Island	RI DOH	private well	well	10301990	12	
Rhode Island	RI DOH	private well	well	10301990	5	

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Rhode Island	RI DOH	private well	well	11141990	3	
Rhode Island	RI DOH	private well	well	11271990	17	
Rhode Island	RI DOH	private well	well	11271990	80	
Rhode Island	RI DOH	private well	well	11271990	15	
Rhode Island	RI DOH	private well	well	11271990	17	
Rhode Island	RI DOH	private well	well	11271990	5	
Rhode Island	RI DOH	private well	well	11271990	22	
Rhode Island	RI DOH	private well	well	11281990	37	
Rhode Island	RI DOH	private well	well	11281990	22	
Rhode Island	RI DOH	private well	well	11281990	80	
Rhode Island	RI DOH	private well	well	11281990	2	
Rhode Island	RI DOH	private well	well	11271990	45	
Rhode Island	RI DOH	private well	well	12061990	2	
Rhode Island	RI DOH	private well	well	12061990	29	
Rhode Island	RI DOH	private well	well	12191990	210	
Rhode Island	RI DOH	private well	well	12191990	9	
Rhode Island	RI DOH	private well	well	12191990	27	
Rhode Island	RI DOH	private well	well	12191990	67	
Rhode Island	RI DOH	private well	well	12191990	7	
Rhode Island	RI DOH	private well	well	12191990	49	
Rhode Island	RI DOH	private well	well	12191990	18	
Rhode Island	RI DOH	private well	well	12191990	26	
Rhode Island	RI DOH	private well	well	12201990	29	
Rhode Island	RI DOH	private well	well	12201990	11	
Rhode Island	RI DOH	private well	well	12201990	14	
Rhode Island	RI DOH	private well	well	12201990	3	
Rhode Island	RI DOH	private well	well	12201990	4	
Rhode Island	RI DOH	private well	well	12201990	17	
Rhode Island	RI DOH	private well	well	12201990	3	
Rhode Island	RI DOH	private well	well	12201990	16	
Rhode Island	RI DOH	private well	well	01171991	2	
Rhode Island	RI DOH	private well	well	01221991	1	
Rhode Island	RI DOH	private well	well	02111991	3,000	
Rhode Island	RI DOH	private well	well	02141991	52	
Rhode Island	RI DOH	private well	well	02251991	2	
Rhode Island	RI DOH	private well	well	02251991	5	
Rhode Island	RI DOH	private well	well	02271991	5	
Rhode Island	RI DOH	private well	well	01281991	1	
Rhode Island	RI DOH	private well	well	02261991	3	

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Rhode Island	RI DOH	private well	well	03051991	2	
Rhode Island	RI DOH	private well	well	03051991	2	
Rhode Island	RI DOH	private well	well	03061991	14	
Rhode Island	RI DOH	private well	well	03211991	305	
Rhode Island	RI DOH	private well	well	03211991	5	
Rhode Island	RI DOH	private well	well	03211991	2	
Rhode Island	RI DOH	private well	well	03071991	2	
Rhode Island	RI DOH	private well	well	04021991	1	
Rhode Island	RI DOH	private well	well	03261991	3	
Rhode Island	RI DOH	private well	well	04021991	3	
Rhode Island	RI DOH	private well	well	04101991	1	
Rhode Island	RI DOH	private well	well	04101991	5	
Rhode Island	RI DOH	private well	well	04051991	7	
Rhode Island	RI DOH	private well	well	04051991	8	
Rhode Island	RI DOH	private well	well	05071991	21	
Rhode Island	RI DOH	private well	well	05071991	22	
Rhode Island	RI DOH	private well	well	05071991	190	
Rhode Island	RI DOH	private well	well	05071991	1	
Rhode Island	RI DOH	private well	well	05131991	277	
Rhode Island	RI DOH	private well	well	05131991	21	
Rhode Island	RI DOH	private well	well	05161991	5	
Rhode Island	RI DOH	private well	well	05221991	1	
Rhode Island	RI DOH	private well	well	06021991	7	
Rhode Island	RI DOH	private well	well	06131991	59	
Rhode Island	RI DOH	private well	well	06131991	6	
Rhode Island	RI DOH	private well	well	06181991	155	
Rhode Island	RI DOH	private well	well	07031991	2	
Rhode Island	RI DOH	private well	well	07171991	2	
Rhode Island	RI DOH	private well	well	06211991	209	
Rhode Island	RI DOH	private well	well	08211991	1	
Rhode Island	RI DOH	private well	well	08131991	9	
Rhode Island	RI DOH	private well	well	08261991	87	
Rhode Island	RI DOH	private well	well	08271991	7	
Rhode Island	RI DOH	private well	well	08271991	31	
Rhode Island	RI DOH	private well	well	08271991	18	
Rhode Island	RI DOH	private well	well	09051991	4	
Rhode Island	RI DOH	private well	well	09111991	14	
Rhode Island	RI DOH	private well	well	10031991	2	
Rhode Island	RI DOH	private well	well	10041991	2	

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Rhode Island	RI DOH	private well	well	10041991	103	
Rhode Island	RI DOH	private well	well	10041991	73	
Rhode Island	RI DOH	private well	well	10081991	55	
Rhode Island	RI DOH	private well	well	10081991	1	
Rhode Island	RI DOH	private well	well	10081991	5	
Rhode Island	RI DOH	private well	well	10081991	12	
Rhode Island	RI DOH	private well	well	10171991	2	
Rhode Island	RI DOH	private well	well	10231991	6	
Rhode Island	RI DOH	private well	well	10231991	7	
Rhode Island	RI DOH	private well	well	10231991	2	
Rhode Island	RI DOH	private well	well	10291991	2	
Rhode Island	RI DOH	private well	well	10311991	1	
Rhode Island	RI DOH	private well	well	11081991	5	
Rhode Island	RI DOH	private well	well	11121991	8	
Rhode Island	RI DOH	private well	well	12031991	2	
Rhode Island	RI DOH	private well	well	12171991	3	
Rhode Island	RI DOH	private well	well	11131991	2	
Rhode Island	RI DOH	private well	well	09101991	1	
Rhode Island	RI DOH	private well	well	09101991	1	
Rhode Island	RI DOH	private well	well	07171991	1	
Rhode Island	RI DOH	private well	well	07171991	4	
Rhode Island	RI DOH	private well	well	08191992	30	
Rhode Island	RI DOH	private well	well	08201992	130	
Rhode Island	RI DOH	private well	well	08201992	3	
Rhode Island	RI DOH	private well	well	08201992	2	
Rhode Island	RI DOH	private well	well	09281992	2	
Rhode Island	RI DOH	private well	well	11051992	1.5	
Rhode Island	RI DOH	private well	well	11061992	2	
Rhode Island	RI DOH	private well	well	12021992	3	
Rhode Island	RI DOH	private well	well	12021992	2	
Rhode Island	RI DOH	private well	well	12021992	45	
Rhode Island	RI DOH	private well	well	12181992	2	
Rhode Island	RI DOH	private well	well	01281993	2	
Rhode Island	RI DOH	private well	well	03091993	1	
Rhode Island	RI DOH	private well	well	03161993	11	
Rhode Island	RI DOH	private well	well	04061993	3	
Rhode Island	RI DOH	private well	well	04061993	2	
Rhode Island	RI DOH	private well	well	03251993	1	
Rhode Island	RI DOH	private well	well	04151993	7	

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Rhode Island	RI DOH	private well	well	04201993	7	
Rhode Island	RI DOH	private well	well	04221993	1	
Rhode Island	RI DOH	private well	well	04221993	3	
Rhode Island	RI DOH	private well	well	04221993	4	
Rhode Island	RI DOH	private well	well	04221993	23	
Rhode Island	RI DOH	private well	well	04151993	111	
Rhode Island	RI DOH	private well	well	04151993	65	
Rhode Island	RI DOH	private well	well	04151993	35	
Rhode Island	RI DOH	private well	well	04221993	2	
Rhode Island	RI DOH	private well	well	04221993	3	
Rhode Island	RI DOH	private well	well	06101993	1	
Rhode Island	RI DOH	private well	well	06221993	3	
Rhode Island	RI DOH	private well	well	06301993	25	
Rhode Island	RI DOH	private well	well	06301993	9	
Rhode Island	RI DOH	private well	well	07271993	2	
Rhode Island	RI DOH	private well	well	07301993	17	
Rhode Island	RI DOH	private well	well	07301993	3	
Rhode Island	RI DOH	private well	well	07301993	3	
Rhode Island	RI DOH	private well	well	07271993	2	
Rhode Island	RI DOH	private well	well	07301993	13	
Rhode Island	RI DOH	private well	well	08261993	8	
Rhode Island	RI DOH	private well	well	08251993	1	
Rhode Island	RI DOH	private well	well	08261993	17	
Rhode Island	RI DOH	private well	well	09021993	4	
Rhode Island	RI DOH	private well	well	09021993	31	
Rhode Island	RI DOH	private well	well	09171993	55	
Rhode Island	RI DOH	private well	well	09171993	885	
Rhode Island	RI DOH	private well	well	09171993	280	
Rhode Island	RI DOH	private well	well	09171993	5	
Rhode Island	RI DOH	private well	well	09171993	65	
Rhode Island	RI DOH	private well	well	09171993	185	
Rhode Island	RI DOH	private well	well	09171993	15	
Rhode Island	RI DOH	private well	well	09231993	1	
Rhode Island	RI DOH	private well	well	09231993	1	
Rhode Island	RI DOH	private well	well	09211993	3	
Rhode Island	RI DOH	private well	well	09211993	1	
Rhode Island	RI DOH	private well	well	09211993	5	
Rhode Island	RI DOH	private well	well	09241993	77	
Rhode Island	RI DOH	private well	well	09241993	2	

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Rhode Island	RI DOH	private well	well	09241993	1	
Rhode Island	RI DOH	private well	well	09241993	2	
Rhode Island	RI DOH	private well	well	09241993	2	
Rhode Island	RI DOH	private well	well	09241993	2	
Rhode Island	RI DOH	private well	well	09291993	1	
Rhode Island	RI DOH	private well	well	09291993	1	
Rhode Island	RI DOH	private well	well	09291993	2	
Rhode Island	RI DOH	private well	well	10081993	14	
Rhode Island	RI DOH	private well	well	10071993	3	
Rhode Island	RI DOH	private well	well	10071993	87	
Rhode Island	RI DOH	private well	well	10071993	237	
Rhode Island	RI DOH	private well	well	11091993	2	
Rhode Island	RI DOH	private well	well	11301993	6	
Rhode Island	RI DOH	private well	well	12011993	44	
Rhode Island	RI DOH	private well	well	12091993	5	
Rhode Island	RI DOH	private well	well	01061994	1	
Rhode Island	RI DOH	private well	well	01111994	2,500	
Rhode Island	RI DOH	private well	well	01211994	42	
Rhode Island	RI DOH	private well	well	01211994	40	
Rhode Island	RI DOH	private well	well	01211994	115	
Rhode Island	RI DOH	private well	well	01211994	20	
Rhode Island	RI DOH	private well	well	02011994	35	
Rhode Island	RI DOH	private well	well	02011994	67	
Rhode Island	RI DOH	private well	well	02011994	27	
Rhode Island	RI DOH	private well	well	02031994	10	
Rhode Island	RI DOH	private well	well	02101994	126	
Rhode Island	RI DOH	private well	well	02101994	235	
Rhode Island	RI DOH	private well	well	02221994	54	
Rhode Island	RI DOH	private well	well	02221994	120	
Rhode Island	RI DOH	private well	well	02221994	21	
Rhode Island	RI DOH	private well	well	02221994	23	
Rhode Island	RI DOH	private well	well	02221994	23	
Rhode Island	RI DOH	private well	well	02221994	16	
Rhode Island	RI DOH	private well	well	02221994	10	
Rhode Island	RI DOH	private well	well	02241994	11	
Rhode Island	RI DOH	private well	well	02241994	1	
Rhode Island	RI DOH	private well	well	03291994	1,150	
Rhode Island	RI DOH	private well	well	07221994	70	
Rhode Island	RI DOH	private well	well	07221994	170	

Appendix 7: *Concentration of MTBE measured at indicated sampling point, by type of drinking-water supply.—Continued*

[µg/L, micrograms per liter]

State	Data source	System number	Sampling point description[1]	Date of sample	Private (µg/L)	Public (µg/L)
Rhode Island	RI DOH	private well	well	07221994	530	
Rhode Island	RI DOH	private well	well	07221994	780	
Rhode Island	RI DOH	private well	well	07221994	1,050	
Rhode Island	RI DOH	private well	well	07221994	490	
Rhode Island	RI DOH	private well	well	08041994	1	
Rhode Island	RI DOH	private well	well	08171994	12	
Rhode Island	RI DOH	private well	well	08171994	21	
Rhode Island	RI DOH	private well	well	09161994	55	
Rhode Island	RI DOH	private well	well	09161994	91	
Rhode Island	RI DOH	private well	well	09161994	375	
Rhode Island	RI DOH	private well	well	09161994	1,390	
Rhode Island	RI DOH	private well	well	09161994	730	
Rhode Island	RI DOH	private well	well	09161994	235	
Rhode Island	RI DOH	private well	well	10261994	4	
Rhode Island	RI DOH	private well	well	12081994	31	
Rhode Island	RI DOH	private well	well	06201995	15	
Rhode Island	RI DOH	private well	well	06201995	170	
Rhode Island	RI DOH	private well	well	06151995	8	
Rhode Island	RI DOH	private well	well	06151995	37	
Rhode Island	RI DOH	private well	well	06151995	49	
Rhode Island	RI DOH	private well	well	06151995	17	
Rhode Island	RI DOH	private well	well	06281995	2	
Rhode Island	RI DOH	private well	well	06281995	110	
Rhode Island	RI DOH	private well	well	06281995	3	
Colorado	CO DOH&E	13419	distribution	09271995		0.29

[1] Refers to samples collected from the public water distribution network. Samples may be of treated or untreated water. Well refers to samples of untreated water collected at a well or wellhead.

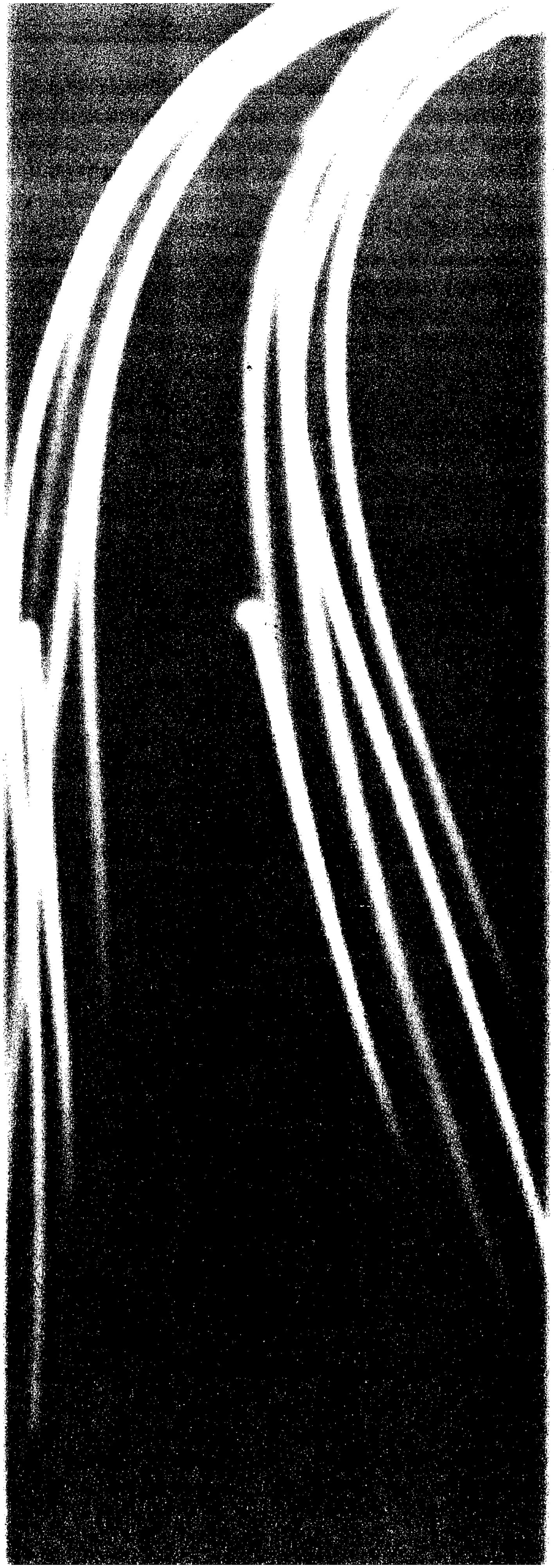
Appendix 8: *Brief description of the modelling done to simulate the transport of atmospheric MTBE to shallow ground water.*

MTBE transport was simulated using a numerical two-phase flow and transport model. This model allows tracking of a single component in either phase in three spatial dimensions. Both fluid components were considered active, hence capillary, gravitational, and viscous forces were all allowed to act on both phases. Transport in the gaseous or aqueous phases included the processes of: advection, diffusion, dispersion, equilibrium gas/water transfer, and equilibrium sorption.

A control volume numerical formulation approach was used to approximate the governing equations. A sequential approach was used to simulate the flow and transport components within the model. The resulting set of highly non-linear equations were solved using a full Jacobian iterative approach in conjunction with pre-conditioned orthomim solver at each time step.

All of the MTBE simulations used a one-dimensional model domain. The boundary conditions for water flow at the lower boundary was prescribed at 2 meters below the initial equilibrium water-table location. The upper boundary flow condition was a prescribed flux during infiltration events. When there was no precipitation, the boundary was either "no flow" or a specified evapotranspiration rate. The gas-phase boundary condition at the upper boundary was constant atmospheric pressure.

The initial conditions for transport were zero for MTBE concentrations throughout the subsurface domain. The transport boundary condition for the upper boundary for the gas phase was either a constant concentration condition (during periods when MTBE was present in the atmosphere) or diffusion through a stagnant boundary layer when the atmospheric MTBE concentration was zero. For the aqueous phase, the MTBE flux at the upper boundary was controlled by rainfall when MTBE was present in the atmosphere. At the lower boundary, mass was allowed to leave the model domain by advective transport only.



Fuel Economy and Engine Performance Issues

3

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CONTENTS

EXECUTIVE SUMMARY

- Oxygenates have been used in gasoline since the 1970s as fuel extenders or octane enhancers. During the 1980s, oxygenates came into wider use as some states implemented oxygenated gasoline programs for the control of carbon monoxide (CO) pollution. Denver, Colorado, implemented the first oxygenated gasoline program in 1988.

- The 1990 Clean Air Act Amendments required oxygenated gasoline programs in several areas of the country that failed to attain the National Ambient Air Quality Standards (NAAQS) for CO. Many new oxygenated gasoline programs were first implemented during the winter months of 1992–1993.

- Consumers in some areas of the country expressed concerns that oxygenated gasoline has led to large reductions in fuel economy or poor engine performance. This chapter examines existing studies and literature related to fuel economy and engine performance. Large fuel economy losses (as high as 20%) have been claimed by some consumers.

- With regard to fuel economy, the theoretical change in fuel economy as a result of the addition of oxygenates to gasoline is in the range of a 2% to 3% reduction in fuel economy. Existing research indicates that "real world" fuel economy changes correspond to changes in energy content. A 2% to 3% reduction in fuel economy equates to a less than 1 mile per gallon change in fuel economy for a car that averages 27 miles per gallon.

- Engine performance problems due solely to the presence of allowable levels of oxygenates in gasoline are not expected. Although engine performance problems may be linked to poor gasoline quality, the manufacturing and handling actions that cause poor quality can occur with either oxygenated or nonoxygenated gasoline. Many engine performance problems are due to factors other than gasoline and may be corrected by relatively simple consumer actions.

SCOPE OF THE CHAPTER

Consumers in some areas of the country have expressed concern that the use of oxygenated gasoline has led to large reductions in fuel economy or poor engine performance. The purpose of this chapter is to assess the effects of oxygenated gasoline on fuel economy and engine performance issues and to summarize all relevant literature.

This chapter discusses nonoxygenated and oxygenated gasoline from the standpoint of fuel economy and engine performance. The focus is on winter oxygenated gasoline (i.e., gasoline designed to meet the requirements of CO reduction programs). Issues that are not likely to be encountered during the winter months, such as summer volatility issues, are not discussed.

The following fuel-related sources of potential engine performance problems are discussed: enleanment, fuel quality, antiknock quality, fuel handling and storage practices, water absorption/phase separation, materials compatibility, and fuel mixtures. All of the fuel-related potential engine performance problems can occur with either oxygenated or nonoxygenated gasoline.

Engine performance problems due solely to the presence of oxygenates in gasoline are not expected because oxygenated gasoline and nonoxygenated gasolines are blended to conform to the same American Society for Testing and Materials (ASTM) standard. Many engine performance problems are linked to factors such as operating conditions, normal vehicle wear, deterioration due to aging, or poor maintenance practices.

With regard to fuel economy, the theoretical change in fuel energy as a result of the addition of oxygenates to gasoline is in the range of a 2–3% reduction when compared to nonoxygenated gasoline. This corresponds to less than 1 mile per gallon (i.e., approximately 0.5 to 0.8 miles per gallon) for a car that averages 27 miles per gallon. As discussed in greater detail below, the large body of research indicates that actual measurements of changes in fuel economy agree with the theoretical changes in fuel energy. However, some older vehicles experience slightly improved fuel economy with oxygenated gasoline because of the resulting enleanment of the air-fuel mixture. Any fuel economy loss actually experienced is the result of the slight decrease in energy content of the fuel.

The primary reference for this chapter is EPA's "Technical Overview of the Effects of Reformulated Gasoline on Automotive and Non-Automotive Engine Performance."[1]

FUEL ECONOMY

Since the introduction of the oxygenated gasoline (CO) and RFG (ozone) programs, the EPA has received questions from the public regarding various aspects of the programs.

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[1] EPA420-R-95-001 (April 1995).

The majority of the questions have been related to reduced vehicle performance and fuel economy. Some motorists indicated large fuel economy losses in excess of 20%. Such complaints were not consistent with the experiences of most motorists in regions of the country using similar oxygenated gasoline formulations. The complaints were also inconsistent with the results of many automotive testing programs which indicate that oxygenated gasoline does not negatively impact vehicle driveability and will not produce more than a slight reduction in fuel economy.

Measurement Variability

A large amount of variability is inherent in fuel economy measurements. Sources of this variability include differences in personal driving habits, weather conditions (temperature, wind effects and precipitation), traffic patterns (e.g., rush hour versus midday or weekends and highway driving versus city driving), the temperature effect on fuel volumes when fueling, and changes in tire pressure.

Ambient Temperature Effects

Wintertime driving results in large decreases in fuel economy when compared to other times of the year. These large decreases are due to increased stop and go driving, more friction between vehicle mechanical parts, idling to heat up the vehicle prior to a trip, increased rolling resistance due to poor road conditions, a greater power load on the engine, and longer periods spent in cold engine operating modes at richer fuel/air mixtures. A combination of these variables can produce a profound effect on mileage. For example, the difference between city versus highway driving, excluding the wintertime temperature effects of increased wind resistance and tire rolling resistance, can cause a variation in fuel economy in the range of 5 to 10 miles per gallon. These cumulative effects can account for as much as a 35 to 40% difference in expected fuel economy and far outweigh the effect of the small change in gasoline energy density that is described below.

Seasonal Fuel Composition

Wintertime gasoline has a lower density and therefore less energy per gallon than summertime gasoline, regardless of whether it is oxygenated. Lower energy results in lower fuel economy.

One of the most important characteristics of gasoline is its rate of evaporation. The property of a liquid that defines its evaporation characteristics is called “volatility.” A gasoline with low volatility will evaporate comparatively slowly and will cause engine start up and warm up problems. These problems are caused by either insufficient fuel reaching the combustion chamber or insufficient mixing of the air-fuel charge. Evaporation that is too rapid (high volatility) will cause warm engine operating problems, primarily because the liquid gasoline turns to a gas prior to reaching the carburetor or fuel injectors, thereby blocking fuel flow. Such a condition is called “vapor lock.” Fuel manufacturers vary the proportions of gasoline components to produce volatilities within appropriate ranges. The wintertime mixture is made up of less dense, lower molecular weight hydrocarbons in order to provide higher volatility for cold weather engine operation.

Historic data on geographic and seasonal variations in temperature are used by manufacturers to produce fuels with volatilities that are appropriate for the temperatures in their marketing area. The ASTM specifications for gasoline include a schedule for volatility classes based on climate and region.

Theoretical Basis for Fuel Economy Changes Due to Oxygenates

Fuel economy theoretically decreases when oxygenates are used due to the lower energy content of the oxygenate which is added. The energy content of MTBE is approximately 93,500 British Thermal Units per gallon[2] (Btu/gal) while that of gasoline is approximately 109,000 Btu/gal.[3] Therefore, for equal amounts of MTBE and gasoline, MTBE contains approximately 14 percent less energy than gasoline.[4] The following table indicates the theoretical loss in energy for the addition of various oxygenates at levels required for the RFG program (2.0 weight percent oxygen), the oxygenated gasoline program (2.7 weight percent oxygen), and, in the case of ethanol, for levels (3.5 weight percent oxygen) traditionally used in both regulated and non-regulated areas.

As can be seen in Table 3-1, the theoretically expected decrease in fuel energy as a result of oxygenate use is in the 2% to 3% range when compared to gasoline. This corresponds to 0.5 to 0.8 miles per gallon for a car that averages 27 miles per gallon. As can be seen from the works cited below, research in this area indicates that any fuel economy loss experienced as a result of oxygenate use agrees with the theoretical prediction for fuel energy loss. Thus, it is reasonable to conclude that any fuel economy loss experienced with oxygenate use is solely a function of the change in fuel composition and the resulting slight decrease in energy content of the fuel.

Table 3-1. Theoretically expected effect of oxygenates on fuel energy.

Oxy-genate	Weight percent oxygen	Volume percent oxygenate	Volume percent gasoline	Energy content of oxygenate Btu/gal	Energy from oxygenate Btu/gal	Energy from Gasoline Btu/gal	Energy of 1 gal of Blend Btu/gal	%Reduction Compared to Gasoline
MTBE	2.0	11.0	89.0	93,500	10,285	97,010	107,295	1.6
Ethanol	2.0	5.7	94.3	76,000	4,332	102,787	107,119	1.7
ETBE	2.0	12.6	87.4	97,700	12,310	95,266	107,576	1.3
MTBE	2.7	15.0	85.0	93,500	14,025	92,650	106,675	2.1
Ethanol	2.7	7.7	92.3	76,000	5,852	100,607	106,459	2.3
ETBE	2.7	17.0	83.0	97,700	16,609	90,470	107,079	1.8
Ethanol	3.5	10.0	90.0	76,000	7,600	98,100	105,700	3.0

Studies Related to Fuel Economy Effects

The EPA, industry, and the scientific community have conducted numerous studies examining the effects of oxygenates on motor vehicles. Listed below are some of the fuel economy test results from the many known test programs. The name of each study, which appears in *italics*, is followed by a summary of the findings.

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[2] "Alcohols and Ethers," American Petroleum Institute, API Publication 4261, 1988, p.2.

[3] Starkman, E.S., H.K. Newhall, and R.D. Sutton, "Comparative Performance of Alcohol and Hydrocarbon Fuels," Society of Automotive Engineers Paper Number SP-254, p. 5.

[4] The precise energy content of any gasoline blend varies somewhat. These calculations are for a typical blend.

"On-Road Study of the Effects of Reformulated Gasoline on Motor Vehicle Fuel Economy in Southeastern Wisconsin " U.S. Environmental Protection Agency and the Wisconsin Department of Natural Resources, March 31, 1995. The Wisconsin Department of Natural Resources and the U.S. Environmental Protection Agency conducted an on-road study of the fuel economy effects of RFG in March, 1995. The intent of the study was to respond to consumer concerns that RFG was responsible for large reductions in motor vehicle fuel economy–much larger than the 2% to 3% reduction predicted by previous studies or by the theoretical energy content of the fuel formulations. In this study, fuel economy was measured from a group of Milwaukee area vehicles representing various model years and fuel delivery systems, and using four types of gasolines, one conventional gasoline and three oxygenated RFGs (MTBE, ETBE, and ethanol). Eight vehicles were driven over a fixed, 100-mile route with urban, suburban and rural segments. Their fuel usage was determined by weighing the fuel at the beginning and end of the route. The study utilized vehicles with highly variable technologies and included carbureted vehicles, port fuel-injected vehicles, and throttle body fuel-injected vehicles. The study vehicles included older and newer technology vehicles as well as a pickup truck in order to represent as large an array of on-road vehicles as possible.

In general, the results of this practical on-the-road study were consistent with the predictions (based on both laboratory and on-road studies, as well as the energy content of the fuels tested) that were set out in the RFG regulations. The average change in fuel economy when RFG was compared to conventional gasoline was a 2.8% reduction in miles per gallon when using RFG.

40 CFR Part 80 Regulation of Fuels and Fuel Additives: Standards for Reformulated and Conventional Gasolines, February 16, 1994. EPA combined the results of 19 studies with over 4000 vehicle/fuel tests. The analysis confirmed that fuel economy impacts are solely a function of fuel energy content. The analysis concluded that fuel economy is reduced by 2% to 3% during the winter season and 1% to 2% during the summer season.

"Fuel Composition Effects on Automotive Fuel Economy - Auto/Oil Air Quality Improvement Research Program." Albert M. Hochhauser et al., AQIRP, SAE Paper #930138. Excerpt: "The Auto/Oil Air Quality Improvement Research Program (AQIRP) is a cooperative research program initiated by three domestic automobile companies and 14 petroleum companies. This paper discusses the fuel economy measurements from two fleets of vehicles running on fuels whose composition varied in a number of parameters. The vehicle fleets used in this study are identified as the "Current Fleet" (20 vehicles, 1989 model year) and the "Older Fleet" (14 vehicles, model years 1983 to 1985)."

Summary of findings on fuel economy: "Reducing aromatics from 45% to 20% lowered fuel economy by 2.8% in the Current Fleet and by 3.2% in the Older Fleet."

"Adding 2.7 wt% oxygen lowered fuel economy by 2.3% in the Current Fleet and by 1.6% in the Older Fleet."

"Reducing T_{90} from 360 °F to 280 °F lowered fuel economy by about 1.5% in both fleets."

"Reducing olefins from 20% to 5% lowered fuel economy by 0.2% in the Current Fleet and by 0.6% in the Older Fleet."

"Performance Features of 15% MTBE/Gasoline Blends," Walter H. Douthit, et al., Sun Refining and Marketing Company, SAE Paper #881667. An average 1.8% to 3.4% loss in fuel economy was observed in a nine-vehicle test program comparing a 15 wt% MTBE blend to a nonoxygenated fuel.

"Are the Reductions in Vehicle Carbon Monoxide Exhaust Emissions Proportional to the Fuel Oxygen Content?" J.A. Gething, et al., Chevron Research Company, SAE Paper #890216. An average 1.8% decrease in fuel economy was observed in an 18-vehicle test program testing a nonoxygenated fuel and comparing it to a 2.0 wt% MTBE fuel and a 3.5 wt% ethanol fuel.

"Fuel Economy Effects -- Controlled Fleet Study," Memo from Frank Gerry, BP Oil Company, to Jim Williams, American Petroleum Institute, February 24, 1995." British Petroleum Company conducted an extensive on-road fuel economy test program testing eight 1992 model cars on nonoxygenated fuel and a 10% ethanol blended fuel. Each car accumulated 20,000 miles of test data. The results of this study show a fuel economy loss due to the use of the ethanol blend of 3.3% for the summer season, 2.4% for the winter season, and 2.8% overall.

"The Effect of Gasoline Composition and Characteristics on Fuel Economy," Downstream Alternatives, Inc. Information Document #930901, September 1993. This paper is a summary of current studies and an overview of the many factors that may affect fuel economy. The factors discussed are engine design, consumer practices, climate, and fuel composition. The paper emphasizes the effects of oxygenates on fuel economy. The paper cites theoretical calculations and observed fuel economy results from several sources. The conclusion is that a 2.7 wt% oxygen level fuel will cause, on average, a 1.6% to 2.3% decrease in fuel economy.

"Vehicle Fuel Economy -- The CleanFleet Alternative Fuels Project," John E. Orban, Michael J. Murphy, M. Claire Matthews, Battelle, SAE Paper #950396. Dynamometer tests were conducted on 36 vehicles comparing California Phase 2 reformulated gasoline to industry average unleaded gasoline (RF-A). Tests results revealed a 2.7% decrease to a 0.9% increase in fuel economy.

"Evaporative and Exhaust Emissions from Cars Fueled with Gasoline Containing Ethanol or Methyl Tert-Butyl Ether," R.L. Furey and J.B. King, SAE Paper #800261. Motor vehicle test fuels using 10 volume percent ethanol or 15 volume percent MTBE experienced a decrease in fuel economy ranging from 0.9% to 3.7%. These results were consistent with the generally lower energy content of oxygenated fuels. The ethanol test fuel had a 3.4% lower energy content and the MTBE test fuel had a 2.8% lower energy content than the nonoxygenated base fuel.

"Exhaust and Evaporative Emissions from Alcohol and Ether Fuel Blends," T.M. Naman and J.R. Allsup, U.S. DOE, SAE Paper #800858. Steady-state tests were conducted on a chassis dynamometer at 35- and 45-mph on 7 volume percent MTBE and 10 volume percent ethanol blends using a fleet of eight 1978 model-year automobiles. The fuel economy results ranged from a 3.3% decrease to a 0.2% increase. An on-road study using a 1978 Oldsmobile Delta 88 was also conducted on the same 10 volume percent ethanol blend resulting in an average 2.7% decrease in fuel economy.

"Assessment of Unregulated Emissions from Gasoline Oxygenated Blends," Craig Harvey, U.S. EPA, SAE Paper #902131. Five vehicles of various technology types were tested on four fuels. The general conclusion is that fuel economy is lower when oxygenates are present in gasoline. No fuel economy specifics were cited.

"Effects of MTBE on Gasoline Engine Cold Weather Operation," J. Viljanen, J. Kokko, and M. Lundberg, Neste Oy Finland, SAE Paper #890052 Eight vehicles were tested in cold weather conditions. The average fuel consumption of these test vehicles was 0.8% higher on gasoline using 8 volume percent MTBE than on a nonoxygenated base fuel.

"Alcohols and Ethers: A Technical Assessment of Their Application as Fuels and Fuel Components," API Publication 4261, second edition, July 1988. This is a comprehensive survey of the effects of oxygenates on fuel economy, measured volumetrically, for 256 test vehicles ranging from model year 1973 to 1980. Overall, fuel economy was reduced by 1.7%. As a group, the forty-one 1973 and 1974 model year vehicles showed a 3.7% to 4.1% lower fuel economy due to the use of oxygenates. One hundred ninety-seven vehicles of model years 1975 to 1979 showed a 0.6% to 1.7% fuel economy loss.

"Air Pollution Control Division Report to the Colorado Air Quality Control Commission," August 1995. A report on the eighth year of operation of the Colorado Oxygenated Gasoline Program, a wintertime CO control program in the Denver area. Fuel economy measurements from mass emissions testing were used to determine the fuel economy effects from gasoline oxygenated with MTBE and ethanol. Taking the market share of MTBE and ethanol blended gasoline into account, and the breakdown of the motor vehicle fleet by vehicle technology group, average fuel economy was reduced by approximately 1.0%.

ENGINE PERFORMANCE ISSUES

Fuel-related sources of engine performance problems include excessively high or low volatility, water absorption, improper storage and handling, enleanment, reduced motor octane, and materials compatibility. Performance problems can occur for a variety of reasons, and tracing performance problems to a specific cause is difficult, and often impossible. Potential engine performance problems resulting from fuel-related sources include rough engine operation, overheating, damaged pistons, vapor lock, starting difficulty, plugged fuel filters, fouled spark plugs, fuel leaks, hesitation during acceleration, flooding, stalling, and engine fires.

Most engine performance problems are, however, the result of non-fuel factors related to vehicle age or mileage, operating conditions, or maintenance history. In general, the normal changes in engine tune up parameters that occur over time, the wear caused by hard use, severe weather conditions, and improper maintenance, are much more significant than the contribution of an oxygenated fuel, if any, to the occurrence of performance problems. Most performance problems can be mitigated by operator preventative or corrective actions.

Oxygenated gasolines are very similar to many nonoxygenated gasolines in terms of composition and physical and chemical properties. In those cases where performance problems are related to fuel characteristics, no performance problems have been found that happen solely with oxygenated fuels and not with nonoxygenated (conventional) fuels. Certain small engine manufacturers have found that problems can occur if oxygenate blends are not blended to appropriate ASTM specifications, especially for volatility characteristics. The information available from automotive and non-automotive engine manufacturers suggests that performance problems directly attributable to oxygenate use are unlikely when ASTM gasoline standards are complied with.

All automobile manufacturers allow or recommend oxygenated gasolines up to the legally allowed oxygenate limits[5]. Most non-automotive engine manufacturers' owner's manuals also include oxygenated fuels in their list of acceptable or recommended fuels and will not void their warranties if gasolines containing oxygenates within the allowed limits are used. However, some manufacturers acknowledge that because only limited testing with oxygenated gasolines on non-automotive engines has been completed, they are not completely certain of the effects, if any, of oxygenated gasolines on their engine components or performance.

Mixtures of gasolines containing different oxygenates and mixtures of oxygenated and nonoxygenated gasolines are likely to occur in consumers' fuel tanks. However, such mixtures should not impact engine performance any differently than nonoxygenated fuels or mixtures of fuels containing the same oxygenate. Overblends, that is, gasolines containing oxygenates at greater than the legally allowed limits, could adversely affect engine performance, depending on the volume of oxygenate used. However, for a number of technical and economic reasons, such blends are unlikely to be encountered in the marketplace.

Enleanment

Nonoxygenated gasolines are mixtures of many hydrocarbon compounds that consist solely of hydrogen and carbon. Oxygenates consist of hydrogen, carbon and oxygen. The addition of oxygen to a hydrocarbon-only fuel results in a change in the proportion of fuel to air that is required to provide complete combustion of the fuel to water and carbon dioxide. The exact air-to-fuel ratio needed for complete combustion of gasoline is called its “stoichiometric air-fuel ratio,” and is about 14.7 pounds of air to one pound of fuel (14.7:1) for nonoxygenated gasoline. For oxygenated gasolines, less air is required because oxygen is contained in the fuel and because some of the hydrocarbons have been displaced. For example, oxygenated gasolines containing the 2.7 weight percent oxygen, required in CO nonattainment areas in the wintertime, require 14.2 to 14.3 pounds of air per pound of fuel. The effect of this type of fuel change on an engine is called “enleanment.”

The air-fuel ratio requirement is an important factor in the design of engines and fuel metering controls. Most automobiles made after 1981 use some form of “closed loop” fuel system that continuously monitors and adjusts the amount of fuel delivered to the engine to maintain the stoichiometric air-fuel ratio. These vehicles have adjustment ranges that accommodate oxygenated fuels and, when operating in the “closed loop” mode, do not experience any effects from the oxygenated fuel. During cold start and at full throttle, these systems operate in an “open loop” mode that provides a rich fuel mixture that is

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[5] Although EPA regulations allow methanol blend gasoline, and most vehicle manufacturers allow its use within specified limits, it is not currently in the marketplace. Another oxygenate, MTBE, is sometimes confused with methanol.

necessary for those conditions. In the rich mixture, "open loop" mode, vehicles do experience enleanment effects from the oxygenated fuel.

Automobile driveability characteristics are not normally affected by switching between oxygenated and nonoxygenated gasolines, whether or not a vehicle is using a "closed loop" fuel control system. In a situation where a vehicle is not properly adjusted and is operating in a "too lean" condition, switching to a fuel with increased oxygen would increase the risk of a driveability problem. The symptom most likely to appear in this situation is a hesitation during acceleration. Vehicles that are in an adequate state of tune should not experience such problems.

In older vehicles (built before 1981) and in small engines like those used in lawnmowers, snowmobiles, and marine applications, "open loop" fuel metering systems are used, which do not automatically compensate for changes in fuel oxygen content. They provide the same ratio of air to fuel for both oxygenated and nonoxygenated gasolines. As a result, the air-fuel mixture is slightly enleaned when oxygenated fuel is used and some change in engine operation is possible. In general, the dynamic operating range of most engine air-fuel ratios is large relative to the small change caused by enleanment and the change should be imperceptible to the operator.

Many engines, particularly small air-cooled engines such as those used in snowmobiles and in other high performance or high load applications, use fuel-rich mixtures to cool the engine under some operating conditions. Heat is absorbed by the additional fuel as it evaporates, thus cooling the engine combustion chamber and valves. In these engines, particularly if they are "open loop," the enleanment effect of oxygenates can increase engine operating temperatures.

In small engines, temperature increase is the primary fuel-related performance effect due to enleanment. The enleanment effect due to oxygenates, in engines with "open loop" systems, is similar in magnitude to the enleanment effect due to operating the engine at low ambient temperatures where the higher air density enleans the air-fuel mixture. Some small engine manufacturers recommend enriching the air-fuel mixture when using oxygenated gasolines, just as they recommend enriching the mixture to compensate for the enleanment effect of low temperatures. The adjustment needed to offset the enleanment effect due to oxygenates is roughly comparable to the enrichment needed to offset a 5 to 15 °F drop in ambient temperature[6].

Fuel Quality

Rough engine operation includes stalling, stumbling, rough idle, engine misfire, or engine knocking. It can occur for a variety of reasons, many of which are not fuel-related. Substandard fuel can, however, contribute to rough engine operation. The fuel characteristics responsible for such problems include excessively high or low volatility, insufficient octane, contaminants, and gum formation.

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[6] Any adjustments for enleanment should be performed carefully; overcompensating for enleanment can create additional engine performance problems and increase emissions. Consumers should consult the manufacturer or a qualified service technician to obtain further information about engine adjustments.

Volatility. Gasoline volatility is controlled during refining to meet the requirements for the climate and region where it is sold. If its volatility is not appropriate, may cause either cold engine or warm engine start up problems.

Octane. As with any gasoline, insufficient fuel octane can result in knock or dieseling. Such problems may be corrected by switching to a higher-octane fuel. Continued rough operation on premium fuel may be an indicator of mechanical or other problems with the engine.

Contaminants. Plugged fuel filters occur when contaminants block the filter surface, reducing fuel flow through the filter. Some gasoline constituents, such as ethanol, behave like solvents and remove or dissolve components built up in the fuel tank or fuel lines. Once these components are loosened, they are transported to the fuel filter and if excessive, may cause filter plugging. Gasoline may also pick up contaminants from storage tanks and delivery trucks. For automobiles, this type of fuel filter plugging is expected to be a concern only in older cars (pre-1975 vintage). The lacquer build-up in the fuel systems of those cars is probably caused by gasoline with poor oxidation stability. The amount of build-up is related to vehicle age. Newer non-automotive equipment may experience fuel filter plugging though this is related more to extended storage periods where gasoline can deteriorate and lead to more deposits. The only remedy to a plugged fuel filter is replacement. Both automobile manufacturers and non-automotive equipment manufacturers usually offer a prescribed service schedule which includes periodic replacement of the filter.

Gum formation. Stored gasolines will oxidize over time and produce gums. The rate of gum formation varies with the types of hydrocarbons, the amount of oxidation inhibitor present, and time. Gum formation from poor quality gasoline can plug fuel filters and form engine deposits. In addition to poor gasoline quality, gum formation can occur due to adverse storage conditions, as discussed later in this report.

Antiknock Quality

The octane value posted on retail gasoline pumps is the average of the "Research" (RON or R) and "Motor" (MON or M) octane numbers, or "(R+M)/2". In the past, oxygenates have been used to increase gasoline octane, since oxygenates have higher octanes than many gasoline components. Oxygenates boost research octane to a greater extent than motor octane, however, and as a result, it is possible for an oxygenated fuel, with the same posted octane rating as a nonoxygenated fuel, to have a slightly lower motor octane level. Some engines respond more strongly to motor octane than research octane. At high speeds or under heavy load conditions, for instance when pulling a trailer up a hill, motor octane is the best indicator of antiknock performance. For these engines, a small reduction in motor octane could result in a slightly higher incidence of engine performance problems, such as engine knock, dieseling, or increased temperature. Over time, severe engine knock can lead to damaged pistons or other engine damage.

Although ASTM does not specify a minimum standard, it recommends that gasolines with a (R+M)/2 octane of 87 have a minimum motor octane of 82. Some refiners have their own internal minimum value which their gasoline must meet. Switching to a higher octane fuel will usually reduce or eliminate the symptoms caused by insufficient octane. If the symptoms persist, the engine is most likely suffering from problems unrelated to the fuel and should be examined by a qualified repair technician.

Improper Fuel Handling and Storage Practices

Improper fuel handling and storage practices can create a number of operational problems and can occur at all levels: fuel distributors, retailers, consumers. Gum formation and phase separation are two fuel-related phenomena that can be caused by improper handling and storage procedures and that can lead to operational problems.

Any gasoline stored for long periods of time or at high temperatures can deteriorate, contributing to gum formation, which can lead to plugged fuel filters and engine deposits, and the formation of deposits in engines and fuel systems. If gasoline is not to be used for long periods of time (greater than 1-2 months), it should be drained from the fuel tank or stabilized with a fuel stabilizer.

Ethanol-blended gasolines are particularly sensitive to poor handling and storage practices because of the possibility of phase separation. Basic precautions must be followed when introducing ethanol-containing fuels in a fuel distribution system for the first time. Water must be removed from fuel tanks and fuel lines to prevent water absorption and possible subsequent phase separation. Anytime a new fuel ingredient is introduced, its compatibility with the storage and delivery system materials must be verified to prevent deterioration of system components. Filters and screens must be in place to ensure that any foreign material is removed before it reaches consumers' fuel tanks. Failure to do so can result in fuel contamination with fuel system component materials or deposits, which can in turn impair vehicle performance by clogging fuel filters. Both the American Petroleum Institute and the Renewable Fuels Association have guidelines for station operators to follow to prevent problems related to fuel handling and contamination.

Water Absorption/Phase Separation

Separation of a single phase gasoline into a "gasoline phase" and a "water phase" can occur when too much water is introduced into the fuel tank. The actual occurrence of phase separation is rare. However, the water absorption that can eventually lead to phase separation is less rare and is most commonly caused by improper fuel storage practices at the fuel distribution or retail level, or due to the accidental introduction of water during vehicle refueling. Water has a higher density than gasoline, so if the water separates, it will form a layer below the gasoline. Because water does not burn, and because most engines obtain their fuel from at, or near, the bottom of their fuel tank, most engines will not run once the phases separate. Some small engines, however, that require that oil be mixed with the gasoline, may create a special situation. In such cases, if phase separation occurs, the alcohol/water phase may separate with the oil, thus removing the oil from the gasoline. If the engine is able to run on the remaining gasoline, damage could result from insufficient lubrication. Again, because the engine draws fuel from the bottom of the tank, it is unlikely to run on the alcohol/water mixture.

Nonoxygenated gasolines can absorb only very small amounts of water before phase separation occurs. Gasolines containing ethers such as MTBE or ETBE can absorb slightly more water before phase separation occurs. In such circumstances, the ethers remain mostly blended into the gasoline. The situation is more complicated for ethanol-containing fuels, however. Such fuels can absorb significantly more water without phase separation occurring than either nonoxygenated or ether-containing gasolines. Ethanol-containing fuels can actually dry out fuel tanks by absorbing the water and allowing it to be drawn harmlessly into the engine with the gasoline. If, however, too much water is introduced into an ethanol-containing gasoline, the water and most of the ethanol (typically 60-70%) will separate from the gasoline and the remaining ethanol. The amount of water that can be absorbed by ethanol-blended gasolines without phase separation, varies from 0.3 to 0.5 volume percent, depending on temperature, aromatics and ethanol content[7]. If phase separation does occur, the ethanol/water mixture would be drawn into the engine. In general, no gasoline engine can run on this mixture (except those also designed to run on high ethanol content blends).

Some manufacturers have expressed concern that ethanol-blended gasolines might absorb water vapor from the atmosphere, leading to phase separation. Such problems are of greatest concern for engines with open-vented fuel tanks that are operated in humid environments, such as marine engines. However, evidence for this phenomenon occurring is limited at best. States with extensive ethanol programs, such as Minnesota, have not reported problems with phase separation due to absorption of water from the atmosphere. Limited testing with ethanol blends suggests that the rate of water absorption from the atmosphere is very slow; it requires several months for open-vented marine fuel tanks to accumulate sufficient water to make phase separation possible, and another source of water is needed before separation will actually occur. Of far greater concern is the accidental introduction of water, by splash or spray, during fueling or the presence of water in the fuel tank prior to the addition of ethanol-blended gasolines.

Ether-blended gasolines are no more susceptible to phase separation than nonoxygenated gasolines. Consumers storing equipment for extended periods can select an ether blend if they are concerned about phase separation. Consumers can prevent phase separation by maintaining full fuel tanks when not in use and by purging the fuel tank of water condensation prior to introducing fuels, particularly ethanol-containing fuels. If phase separation does occur, the separated fuel should be removed from the tank and disposed of properly, in accordance with federal, state, or local requirements.

Materials Compatibility

Some materials used in fuel systems tend to degrade over time, such as the elastomeric materials used to make hoses and valves. Other fuel system components are made of metals and plastics and must also be compatible with the wide range of fuels. Elastomer degradation can occur for many reasons, such as repeated heating and cooling cycles, normal oxidation by the atmosphere, and corrosion by road salt and other substances. Fuel composition can also affect deterioration rates. For example, aromatics (a natural component of gasoline) can cause some parts to swell. In addition, degradation of some older elastomeric fuel distribution components may be accelerated by exposure to oxygenates, particularly methanol and ethanol.[8]

There are two distinct types of materials compatibility problems. <u>Acute failures</u> occur when a substance causes a part to fail within a very short period of time. <u>Accelerated deterioration</u> occurs when a substance causes a part to fail noticeably faster than would have been the case had the part not been exposed to that substance. Accelerated

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[7] Fuel Ethanol Technical Bulletin: Archer Daniels Midland, September 1993.

[8] Of the alcohols, methanol blends may have the largest effect on elastomeric deterioration but methanol blends are not utilized to any significant degree in gasoline markets today.

deterioration can result from corrosion, chemical reactions between the fuel and the affected material, or permeation of the fuel through the material.

New elastomers called fluoroelastomers have been used in automotive and non-automotive engines since the mid-1980s. These newer materials are specifically designed to handle all modern gasolines, including high-aromatic, ethanol-containing, and ether-containing gasolines within these substances' legally permissible levels, without experiencing either of the materials compatibility concerns described above. Fluoroelastomers are far more resistant to permeation and corrosion than were earlier elastomers.[9]

Except for the oxygenates, the components found in oxygenated gasoline are normal constituents of gasoline that have been thoroughly tested for materials compatibility. The oxygenates used in gasoline have also been tested for materials compatibility, and no acute failures have been noted. Engine and elastomer manufacturers have indicated that even in older vehicles, any materials compatibility or deterioration problems that may be encountered would not result in immediate, acute failures of elastomeric components but rather would result in an increase in deterioration rates in-use. However, areas covered by the Oxygenated Gasoline program have not reported higher rates of materials degradation or failure than areas receiving conventional gasolines. Furthermore, gasolines with high levels of aromatics accelerate material degradation to a similar degree as oxygenated fuels. However, no increase in the rate of materials failures has been reported over the past several decades despite substantial increases in aromatics levels in order to maintain desired octane levels.

Permeation of fuel through elastomers can accelerate deterioration. In general, ethanol blends have higher permeation rates through elastomers than ether blends, which have slightly higher permeation rates than nonoxygenated gasoline. The higher permeation rates of oxygenate-containing gasolines are well within safety limits and are not expected to create performance, deterioration, or safety problems. No such problems have arisen during the 15 to 20 years of oxygenate use in the U.S. Furthermore, engines built since the mid-1980's generally use fluoroelastomers, which have far lower permeation and deterioration rates than earlier materials regardless of the oxygenate type and concentration found in the fuel (within legally permitted limits).

As part of normal vehicle maintenance, engine owners should inspect their engine and fuel distribution system for leaks and replace older or leaking components. Owners of pre-1986 engines (both automotive or non-automotive) with degraded elastomers and other engine parts should consider installing modern replacement parts, which are engineered to assure compatibility with all modern gasolines, including oxygenated gasolines.

Ether-based oxygenated gasolines are generally believed to be compatible with the fuel system materials. One automobile manufacturer has investigated the cause of fuel leaks in some of its 1984 - 1989 models and believes that exposure to gasolines containing MTBE was a factor in the deterioration of a plastic (nylon 6,6) component in the fuel injectors of those vehicles. The manufacturer is conducting a voluntary service campaign to replace fuel injectors and fuel hoses. The replacement plastic fuel injector components

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[9] Manufacturers' data suggest that fluoroelastomers and Viton are the preferred materials for use with alcohols, ethers, and high concentrations of aromatics. "Changes in Gasoline II," Downstream Alternatives, Inc., July 1992.

are made from another formulation of nylon 6,6. Other manufacturers using similar plastics have not reported similar problems.

Ethanol-based oxygenated gasolines also generally present no significant difficulty for fuel systems in vehicles manufactured after the early 1980's, again because of the use of fluoroelastomeric components. Ethanol blends could present some problems in older fuel systems and some small engine fuel systems, however, blends of up to 10% ethanol should not present significant materials compatibility problems. Because these oxygenates have been in use throughout the country for years, most older vehicles have been using them and will not experience an abrupt change in fuel composition.

Some concerns have been raised about the effect of oxygenated fuels on vehicle external surfaces such as paint and metals. Auto manufacturers' materials testing results have not indicated adverse affects on automobile non-engine external or cosmetic parts such as highly polished aluminum and painted surfaces.

Fuel Mixtures

EPA is not aware of, and does not expect, performance or driveability problems in vehicles that are operating on mixtures of gasolines that contain different oxygenates. Consumers have operated with mixtures of different oxygenates over the past fifteen years, the result of refueling at different service stations, without experiencing performance or other problems.

The adverse engine performance effects discussed earlier were either a function solely of the oxygen content of the fuel (as in the case of enleanment) or related to the specific types of oxygenates (as in the case of materials deterioration, water absorption/phase separation, and motor octane levels). None of these effects has any impact on whether mixtures of multiple oxygenates will produce any effects.

Nonoxygenated gasoline may not be sold in areas covered by an oxygenated gasoline program. Consumers, however, are not limited to purchasing gasoline only where they live. They can and do purchase gasoline in both covered and non-covered areas, thereby commingling the fuels. No unique problems have been observed from mixtures of oxygenated gasoline and nonoxygenated gasoline.

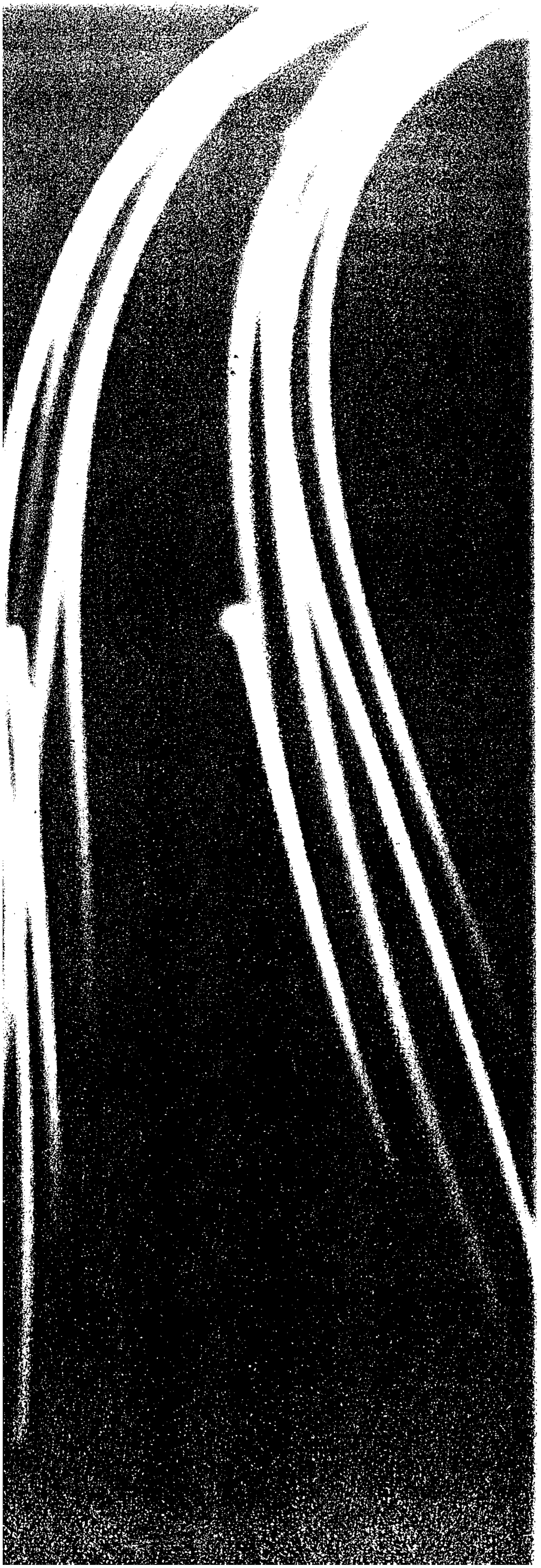
Gasoline containing higher levels of oxygenates than legally allowed (over blends) could cause or contribute to vehicle performance problems. While gasoline containing more than 15% MTBE or 10% ethanol (the upper limits currently permitted in gasoline) could cause or contribute to the problems discussed here or to other problems, it is highly unlikely that overblending will occur. First, and foremost, gasoline containing oxygenate in excess of the waivered limits are illegal and should not be available in the marketplace. EPA and the states have a range of enforcement programs designed to ensure that gasolines sold commercially meet the legal requirements, and private industry also monitors fuel quality nationwide. Second, oxygenates tend to be more expensive than gasoline, so it would not be economically sound for a fuel producer to overblend. Finally, blending processes at either the refinery or at the terminal have become far more sophisticated and less susceptible to error over the past decade, thereby minimizing overblending (although the risk of accidental overblending can never be eliminated completely).

CONCLUSIONS

Oxygenates have been used in gasoline for many years. Since the 1970s, ethanol has been added to gasoline. During the 1980s, other oxygenates, primarily MTBE, came into widespread use. Oxygenated gasoline blends are manufactured to meet the same ASTM specifications as nonoxygenated gasolines and are therefore very similar in composition. The fuel parameters of oxygenated gasoline are well within the parameters of gasolines that have been in widespread use.

Engine performance problems due solely to the presence of oxygenates in gasoline are not expected because of the chemical similarity of oxygenated and nonoxygenated gasolines and because of the demonstrated ability of in-use engines to accommodate the relatively minor differences.

Consumer concerns about large reductions in fuel economy are not supported by numerous laboratory and on-road studies. Existing research indicates that the largest fuel economy loss that could be attributed to the presence of oxygenates is 3%. Consumer estimates frequently fail to account for several critical factors that would explain their calculation error or provide the reason for lower fuel economy.



Potential Health Effects of Oxygenated Gasoline

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SCOPE OF THE CHAPTER

Soon after the oxygenated gasoline program was introduced nationally in the winter of 1992-1993, anecdotal reports of acute health symptoms were received by health authorities in various areas of the country. Such health symptoms had not been anticipated but have subsequently focused attention on possible health risks associated with using oxygenated gasoline. Potential health effects of oxygenated gasoline were evaluated in two separate reports, one prepared by an interagency group of health scientists under the auspices of the Interagency Oxygenated Fuels Assessment and Steering Committee of the National Science and Technology Council (NSTC, 1996) and the second by the Health Effects Institute (HEI) and a panel of experts (HEI, 1996). Both of these reports underwent extensive external peer review and were then reviewed by the National Research Council (NRC, 1996). This chapter summarizes the information on the health effects of oxygenated gasoline that was presented in the NSTC and HEI reports, with particular attention given to comments from the NRC review. The HEI report provides an extensive review on health effects caused by ingestion of moderate to large quantities of ethanol and concludes that these effects would not likely occur at the low ambient air levels associated with the use of ethanol in oxygenated fuels.

HUMAN EXPOSURE (NONOCCUPATIONAL)

The exposure of human populations to emissions related to the use of oxygenated gasoline is a critical component of any attempt to assess the potential human health risks or benefits associated with oxygenated fuels. At issue is not just how much oxygenate exposure occurs in connection with using oxygenated fuels but the change in exposure, if any, to the array of chemicals constituting the evaporative and combustive vehicle emissions and photochemically transformed products resulting from the use of oxygenated gasoline versus the use of conventional gasoline.

The objective of the winter oxygenated fuels program is to reduce human exposure to CO, but empirical data to illuminate whether, or how much, CO exposure is actually reduced with use of oxygenates are quite limited. Vehicle emissions and ambient air quality data provide at best only a rough indication of the direction in which human population exposure levels would be expected to change, but they are not currently adequate to gauge accurately either acute or long-duration exposures of human populations. Uncertainties increase progressively as one moves from emissions characterization to environmental (i.e., air, soil, or water) quality characterization to exposure characterization, in large part because the number of variables that come into play increases progressively at each stage. For example, emissions are a function not only of the type of fuel, but also of operating conditions and other factors (type and condition of vehicle, temperature, altitude, etc.). Air quality in turn is a function not only of emissions, but also of meteorological and topographical variations in different locales, as well as the characteristics of the vehicle fleet (e.g., the age and condition of vehicles in an area). Exposure is a function not only of air (as well as other media) concentrations at different times of the day and year, but also of human activity patterns that may bring individuals into contact with a pollutant at various times and for various durations. In short, assuming that CO emissions are reduced from vehicles using oxygenated fuels, indefinite is the extent to which human exposures to CO are reduced. At present, one cannot simply extrapolate directly from emissions data or even air quality data to estimate quantitative changes in population exposure levels associated with using oxygenated fuels.

To support a meaningful quantitative comparative assessment of oxygenated and conventional gasolines, it would be necessary to have sufficient data collected on random samples of human populations to estimate accurately the distribution of exposure levels to key oxygenated fuel and conventional fuel emissions and by-products. Such information would not only provide a basis for estimating an average or typical exposure, but it would also enhance scientific confidence that upper-tail exposures had been reasonably well determined. In lieu of adequate distributional data, a rough estimate of instantaneous exposures in the upper tail of the distribution may possibly be obtained from measurements taken in selected microenvironments where certain activities or scenarios typically occur (e.g., around gasoline stations during refueling, in vehicles during transit). However, it is not possible at present to estimate "average" or "typical" exposures because of the lack of adequate distributional data. Even if adequate concentration data existed for certain microenvironmental acute exposure scenarios, exposure assessment, particularly assessment of chronic exposures, requires adequate data on the range, duration, and frequency of activities that bring people into contact with the pollutants of interest.

As described in the Interagency Health Assessment (NSTC, 1996) and the HEI Report (HEI, 1996), a limited number of studies have been conducted to measure MTBE exposure in various occupational and nonoccupational settings. These studies have focused primarily on exposures around gasoline stations, particularly during refueling and are especially relevant to those in the general population who refuel their own vehicles ("self-service" customers) as well as to workers whose job involves refueling of multiple vehicles. No single study has attempted to evaluate meteorological variations; indeed, relatively few measurements have been obtained under conditions of direct relevance to the oxygenated fuels program, that is, during winter months with 2.7% oxygenated gasoline. Nevertheless, as far as available data on acute exposures to the general population are concerned, refueling appears to pose the highest potential for acute inhalation exposures to oxygenates. Various studies that have collected personal breathing zone samples of MTBE during gasoline refueling suggest that such exposures, which typically amount to 2-5 minutes in duration, may range as high as 2 to 32 ppm MTBE; however, most of the data for exposure during refueling are below 10 ppm for 1 to 20 minute sampling periods.

To estimate longer term average exposures (e.g., daily or annual), one must have empirical data and/or make assumptions about the concentrations and durations of exposures during the course of daily activities. Based on limited empirical data and various explicitly conservative provisions (e.g., rounding up of average concentrations to the next higher half order of magnitude, assuming a person lives in a house with an attached garage where a fuel spill occurred with the door closed, assuming outdoor activities are in the vicinity of a gasoline station or a heavily traveled highway), the Interagency Health Assessment offered estimates of time-weighted average exposure levels of 0.018 and 0.035 ppm MTBE for two different presumed "worst-case" exposure scenarios during an oxygenated fuels season (NSTC, 1996); estimated annual exposures based on either a 6-month or 4-month oxygenated fuels season for these two scenarios were on the order of about 0.01 to 0.02 ppm MTBE. The HEI Report made no attempt to derive such an estimate but did present data from various studies in tabular and graphical forms (see Fig. 2 in HEI, 1996). The NRC Review concluded that "HEI could have performed a quantitative risk assessment using the exposure data represented by ... maximum (approximately 0.01 ppm) daily MTBE exposures as estimates of exposure" (NRC, 1996, p. 71). The difference between the NRC and Interagency high-end estimates is almost certainly not as great as the uncertainty bounds or confidence limits that would surround these numbers. Indeed, it is not even possible to quantify these confidence limits in a meaningful manner, given that they are based on qualitative assumptions about the various exposure scenarios. Thus, any attempt to characterize chronic health risks based on such estimates should explicitly note the inherent uncertainty of the resulting risk estimates.

It should also be noted that, owing to the lack of data, no oxygenated fuel exposure analysis conducted thus far has attempted or been able to include dermal or oral exposures to MTBE in estimating presumed worst-case or upper bound exposures. Skin contact and ingestion exposure are different from the routine types of inhalation exposures that occur during operation or refueling of a vehicle. For the general population, dermal contact with fuel would probably constitute an infrequent acute exposure. Ingestion of oxygenates might occur either acutely or chronically but would probably be of greatest relevance to general population exposures in terms of possible long-term, low-level ingestion of contaminated drinking water (see Chapter 2 on Water Quality). Nevertheless, true worst-case or upper-bound exposures might well reflect contacts through these other two routes. Thus, additional caution, apart from the uncertainties resulting from a lack of empirical distributional data, may be in order when referring to or otherwise attempting to use presumed worst-case or upper-bound exposure estimates that are based solely on inhalation exposure.

In summary, it is possible to generate estimates of high-end exposure levels to MTBE, and such estimates may be usable in preliminary risk characterizations, particularly if the estimates are coupled with toxicity potency or reference values. In the case of oxygenated fuels, however, such estimates involve significant assumptions and consequently are highly uncertain. Moreover, even this type of exercise would not address the critical question of the comparative risks and benefits of using oxygenated fuels in relation to conventional fuels. A meaningful answer to this key question will require more than just data on human exposures to oxygenates; it will also need quantitative evaluations on how exposures to CO, benzene, 1,3-butadiene, aldehydes, and numerous other toxic compounds in fuels and their combustion and transformation products are altered with use of oxygenated gasoline versus conventional gasoline.

HUMAN EXPOSURE (OCCUPATIONAL)

As discussed in the reports by the Health Effects Institute (HEI, 1996) and the Interagency Health Assessment (NSTC, 1996), the predominant occupation with potential exposure to MTBE as an oxygenate is that of service station attendant. Extent-of-exposure studies by government and industry indicate time-weighted average exposures to MTBE while dispensing fuel are typically at or below 1 ppm, with maximum averages of less than 6 ppm. Although HEI gives no overall range or average for this occupational category, its presentation of median values from specific studies is within this range. Both reports note that several microenvironmental conditions, including climate, amount of fuel dispensed, and amount of oxygenate in the fuel, affect the extent of exposure.

Automotive mechanics comprise another important occupational category with potential exposure to MTBE. Evaluations of these exposures, again conducted by government and industry, are summarized in the NSTC and HEI reports. Time-weighted average exposures range up to approximately 12 ppm, averaging approximately 0.1 ppm.

Other occupations with available MTBE exposure information are those associated with automobile traffic (i.e., service station managers, parking attendants, taxicab drivers, etc.) and those involved in manufacturing and distributing MTBE. Of 14 samples collected among the former group in support of an epidemiologic evaluation, only one had detectable levels, reported at 0.10 ppm (NSTC, 1996). Among the latter group, time-weighted average exposures reported by American Petroleum Institute (API) member companies range up to approximately 700 ppm (6-9 h exposure samples collected during transport of pure MTBE). The geometric mean of more than 300 long-term samples from all operations was 0.3 ppm; the highest mean for any category was 1.7 ppm (API, 1995).

In summary, the available environmental data suggest that among employees exposed to MTBE from its use as an oxygenate in gasoline (primarily service station attendants and mechanics), time-weighted average exposures may range up to approximately 12 ppm and average below 1 ppm. Employees involved with manufacturing or transporting MTBE may be exposed up to 700 ppm, with average exposures less than 1 ppm.

METABOLISM, DISPOSITION, AND TOXICOKINETICS OF MTBE IN ANIMALS

Although very limited information is available on the toxicokinetics of ETBE, TAME, and other gasoline oxygenates, more data were reported on the metabolism, disposition, and elimination of MTBE.

MTBE is rapidly absorbed into the circulation of rats after oral, intraperitoneal, intravenous, or inhalation exposure (Bio-Research Laboratories, 1990a; 1990b; 1990c; 1990d). However, dermal absorption of MTBE is somewhat limited and slower than absorption by other routes. The relative bioavailability of dermally applied MTBE is low (20-40%), and it is likely that dermal absorption of MTBE may be limited by its high volatility (Bio-Research Laboratories, 1990b). Peak blood concentrations of MTBE are rapidly attained; however, the time to achieve these levels varied as a function of the route of exposure and the dose administered. The time to achieve peak blood levels varied from 5-10 min after intravenous or oral exposure to 2-4 h after dermal or inhalation exposure. Once in the blood, MTBE is distributed to all major rat tissues. Distribution studies suggested that neither MTBE nor any of its metabolites has the potential for bioaccumulation in animals. The reported half life of MTBE ranged from less than 1h after oral, i.v., and inhalation exposures to 1-2 h after dermal application. On the other hand, the half life of TBA was longer than MTBE and ranged from 1-3 h after all routes of administration (Bio-Research Laboratories, 1990a; 1990b; 1990c; 1990d).

Metabolism and elimination of MTBE and its metabolites also proceed rapidly regardless of the route of administration. From the available experimental evidence, it is established that MTBE undergoes hepatic oxidative demethylation via the cytochrome P450 enzymes to yield TBA and formaldehyde (Bio-Research Laboratories, 1990b; Brady *et al.*, 1990). TBA may be eliminated unchanged in the expired air or may undergo secondary metabolism, resulting in the formation of 2-methyl-1,2-propanediol and α-hydroxyisobutyric acid; both metabolites are eliminated in the urine. In vitro evidence also suggested that TBA may undergo oxidative demethylation to produce formaldehyde and acetone (Cederbaum and Cohen, 1980). Identification of $^{14}CO_2$ in the expired air of ^{14}C-MTBE-treated rats indicates that a portion of the administered MTBE dose undergoes complete oxidation. It is likely that complete oxidation of MTBE to CO_2 may proceed via the formaldehyde intermediate. Differences in the disposition and toxicokinetic parameters of MTBE in rats after various doses suggest that there is a potential for saturation of MTBE metabolizing enzymes at high exposure levels and after bolus administration of MTBE.

Although human studies showed that exposure to MTBE, similar to exposure in animal studies, leads to the appearance of TBA in blood, no reports of MTBE metabolism to formaldehyde in humans are available. However, there is no evidence showing that humans would metabolize MTBE differently than animals. Further, because MTBE metabolism is catalyzed by the cytochrome P450 enzymes, coexposure to environmental chemicals may alter MTBE metabolism and its potential toxicity.

Elimination of MTBE and its metabolites occurs primarily via the lungs and the kidneys. Exhaled organic compounds are mostly MTBE and TBA and the ratio of the two components is dose- and route-dependent. Clearance of unchanged MTBE via the lungs is thought to be a function of the blood/air partition coefficient (11.5) (Borghoff *et al.*, 1996) and appears to be directly proportional to the peak blood levels of MTBE. A small percentage of the administered MTBE dose to rats is eliminated as CO_2 (0.1-1.1% of dose after oral, i.v., and inhalation exposure), and a negligible portion is eliminated in the feces (0.1-1.3% of dose) after similar exposures (Bio-Research Laboratories, 1990a; 1990b; 1990c; 1990d).

Urinary elimination of MTBE-derived radioactivity is also dose- and route-dependent and two urinary metabolites, 2-methyl-1,2-propanediol and α-hydroxyisobutyric acid, were identified in the urine of rats that received ^{14}C-MTBE. These two metabolites are most likely formed via the secondary metabolism of TBA. The metabolism of MTBE to formaldehyde has been demonstrated in vitro. However, metabolism of MTBE to formaldehyde in vivo requires additional investigation.

In order to assess the contribution of MTBE metabolites to MTBE's overall toxicity, the qualitative and quantitative behavior of MTBE in both humans and animals must be fully investigated. Determining the rates of metabolism as well as the internal dose of MTBE and its main metabolites (TBA and formaldehyde) will be critical for understanding the mechanisms of MTBE-induced toxicity. Further, these data will be essential for extrapolating effects observed in animals to humans and for more accurately assessing the potential human health risks resulting from exposure to MTBE.

METABOLISM AND TOXICOKINETICS IN HUMANS

To date, only a limited number of studies on the metabolism and toxicokinetics of MTBE in humans has been performed. These studies (Buckley *et al.*, 1995; Cain *et al.*, 1996; Johanson *et al.*, 1995; Prah *et al.*, 1994) evaluated levels of MTBE or TBA in blood or breath following short-term exposure to MTBE in chambers. One study involved significantly higher exposure concentrations, but all were consistent in their primary findings.

When human subjects are exposed to air containing MTBE, levels of the oxygenate in their blood and breath show a rapid increase but do not reach a steady-state level even after 1 h. Upon removal of the subjects from the chamber, the blood MTBE levels drop rapidly but show a multiexponential decrease leading to blood levels that are higher than pre-exposure levels, even after 8 h postexposure ($t_{1/2}$ values were 2-5 min, 15-60 min, and >190 min). The multiexponential character of the MTBE excretion indicates that this compound is distributed into tissue or is bound to some blood component. The slower decrease in blood MTBE levels after 60-90 min postexposure to MTBE was not seen in rats (Borghoff *et al.*, 1996). Except for total body weight, the fraction of body weight that is fat is the most dissimilar physiological parameter between rats and humans that may account for this difference. The lack of a large fat fraction in young rats may account for the failure to detect a secondary, longer half-life phase of MTBE in this species. TBA levels in human blood also rise quickly after the exposure begins, but the plateau period is much longer than for MTBE.

To date, toxicokinetic experiments in humans have involved short-term, single exposures of healthy individuals to undiluted MTBE; however, most environmental and occupational exposures are repeated events and usually involve a mixture of MTBE with other gasoline components. The frequency and time of exposure depends on many factors, including job activities and frequency of gasoline refueling. Internal dose levels of MTBE also may be compounded by lower level exposures during commuting or other activities. It is unclear whether repeated exposures of individuals, as occurs during commuting, will result in elevated background internal dose levels of MTBE or if excretion rates are fast enough to prevent accumulation in these types of exposures. Studies are needed to evaluate the toxicokinetics of MTBE when it is included as a component of gasoline and when repeated exposures occur.

ACUTE HUMAN HEALTH EFFECTS

Nature of the Available Data

A relatively small number of epidemiologic investigations and surveys have been conducted to examine the occurrence of acute health symptoms among people who were exposed to fuels containing oxygenates, primarily during the 1992-93 oxygenated-fuel season. These studies were prompted by anecdotal reports of acute complaints of symptoms after the introduction of oxygenated gasoline in some areas and focused primarily on the set of symptoms (headache, eye irritation, burning of the nose or throat, cough, nausea or vomiting, dizziness, and a sensation of spaciness or disorientation) that had been reported most frequently by community residents in Fairbanks, AK, at the start of the 1992-93 oxygenated fuel season. These symptoms are not specific to exposure to oxygenated gasoline and can be caused or triggered by a variety of other environmental and occupational exposures, including exposure to conventional gasoline.

Most of the studies conducted to date were designed to be screening or exploratory in nature and were not formal studies designed to test specific hypotheses. All of these studies were highly responsive to public concerns and displayed creativity in coping with serious limitations in time and resources. The same limitations apply to many of these studies: inadequate sample size, potential bias in sample selection, inadequate exposure information, and reliance on highly subjective measures of effect. Ideally, larger and more carefully planned epidemiologic studies would have followed to test some of the hypotheses generated by anecdotal reports and these initial investigations. Although such studies have been recommended (USEPA, 1995), they have not been conducted to date, and no new epidemiologic studies are expected to be completed in the near future.

In their review, the NRC Committee concluded that "the available data consistently indicate that exposures to gasoline containing MTBE in occupational settings are associated with an increased rate of acute symptoms" (NRC, 1996, p. 10) and noted that both the report of the HEI Oxygenates Evaluation Committee (HEI, 1996) and that of the Interagency Working Group (NSTC, 1996) had "failed to acknowledge" this consistency (NRC, 1996, p.90). In light of these comments, we re-examined the results from the available field studies, controlled exposure studies, and anecdotal reports of acute symptoms for any consistencies in findings or evidence of dose-related effects.

Acute Health Effects at Higher Exposure Levels

The highest potential exposures to MTBE occur in the workplace, and although exposures within any one job category can vary by orders of magnitude, the highest occupational exposures to MTBE have been measured during the transport of MTBE and MTBE-containing fuel. Three controlled human exposure studies of the sensory, symptomatic, cellular, and eye responses of healthy human subjects exposed to MTBE in air have been conducted, in which short-term (1 or 2 h) exposures to MTBE at concentrations similar to those that have been measured in some MTBE manufacturing and transportation operations (from 1.4 ppm up to 50 ppm) (Prah *et al.*, 1994; Cain *et al.*, 1996; Johanson *et al.*, 1995). In two studies (Prah *et al.*, 1994; Cain *et al.*, 1996), subjects were exposed only once for 1-h to MTBE, and in the third study (Johanson *et al.*, 1995), subjects were exposed for three successive 2-h periods to progressively higher concentrations of MTBE. These controlled human exposure studies tested pure MTBE compound, not a mixture of MTBE and gasoline, and included only healthy volunteers. Taken together, these three studies consistently showed that controlled exposure to pure MTBE in air under laboratory conditions (around 24 °C) did not cause increased symptoms or any notable adverse effects (e.g., irritation, behavioral changes) among healthy adult subjects.

Little information is available about the occurrence of acute health symptoms among workers involved in either the manufacture or distribution of MTBE or MTBE-containing fuels. The American Petroleum Institute canvassed 18 member companies to collect information about health complaints that had been passively received from workers and consumers from 1984 to 1994 (McCoy *et al.*, 1995). Given the unstated but presumed large total workforce of these 18 companies, this passive reporting system picked up few complaints (complaints had been received from 71 workers over this period). The most common health complaints were headache, dizziness, nausea, and respiratory tract irritation, and the complaints were most frequent during the 1992-93 oxygenated fuel season. A greater number of complaints came from workers involved in MTBE distribution than in MTBE refueling or MTBE production. It is not possible to make any conclusions about the relative likelihood of complaints in one job category compared with another because this reporting process had obviously low and perhaps variable sensitivity, and no information was available on the total number of workers in each job category. Mehlman (1995) collected information about the acute health symptoms that were being reported among refinery workers who were members of the Oil, Chemical, and Atomic Workers Union and exposed to MTBE. The most common complaints were headaches, sinus problems, fatigue, and shortness of breath. However, given the limited nature of this survey, it is not possible to estimate the prevalence of specific symptoms among refinery workers or to examine dose-response relationships in complaints among refinery workers with different exposures.

Gasoline station attendants and automotive mechanics also can experience higher exposures to MTBE-containing gasoline, although at levels substantially lower than those of some workers involved in manufacturing or transporting of oxygenated gasoline. In Fairbanks, AK, complaints of health symptoms (such as headache, eye irritation, burning of the nose and throat, and dizziness), were fairly common among a nonrandom, convenient sample of 18 workers (10 of whom were mechanics, service station attendants, or workers at car dealerships) while oxygenated gasoline containing MTBE was in use (Moolenaar *et al.*, 1994). The four workers with the highest blood levels of MTBE all reported one or more key symptoms, whereas 9 of the remaining 14 workers reported one or more of these symptoms (this difference was not statistically significant). These complaints essentially disappeared after the oxygenated gasoline program was suspended. In two small-scale field studies primarily of mechanics that were conducted in the spring of 1993 in Stamford, CT, (CDC, 1993a; White *et al.*, 1995), and in New Jersey (Mohr *et al.*, 1994), most workers reported no adverse health effects related to oxygenated gasoline. In Stamford, all of the gasoline sold at the time of the investigation was oxygenated, and thus it was not possible to identify a comparison group of workers who were exposed to only conventional gasoline. Qualitatively, the prevalence of the most common symptoms occurring over the last month, such as headache and cough, were not appreciably higher among men who worked around cars and gasoline stations in Stamford than that reported in a similar investigation about one month later in Albany, NY, where exposure to MTBE was generally much lower because no oxygenated gasoline program was in place (CDC, 1993b). Personal breathing-zone air monitoring and biological monitoring of MTBE levels in blood, however, clearly demonstrated that exposures to MTBE can be highly variable among mechanics, even among workers in the same garage. The availability of blood MTBE measurements among a subsample of 30 workers permitted a more precise classification of these workers by exposure level. Workers with the highest blood MTBE levels (>3.8 µg/L) were significantly more likely to report one or more of the key symptoms on the day of testing than were other workers. Workers with the highest exposures to MTBE in gasoline, however, were also more highly exposed to other components of gasoline.

In New Jersey, researchers interviewed state garage workers in two parts of the state: 115 workers in northern New Jersey, where oxygenated fuel was still in use, and 122 workers in the southern New Jersey, where use of oxygenated fuels had been discontinued 10 weeks earlier (Mohr *et al.*, 1994). This investigation did not report major differences in symptom reporting between these two groups of workers in New Jersey who presumably had different levels of exposure to MTBE. Because some of the highest exposures to gasoline were likely to occur during vehicle refueling, comparisons were made between a small subset of 11 workers in the north who pumped gasoline more than 5 h per day, and 11 workers in the south matched by age, sex, and education for whom some air-monitoring data indicated that exposures to MTBE were likely to be low. At the beginning of the workshift, a composite "MTBE-symptom" score was similar between both groups, but by the end of the workshift, the gasoline pumpers in the north were reporting more symptoms, whereas the comparison workers were reporting fewer symptoms. This difference was not statistically significant but the study had low statistical power because of the small number of workers in each group.

Acute Health Effects at Lower Exposure Levels

In November 1992, public concern and media attention over oxygenated fuels in Fairbanks, AK, began almost immediately after the start of the oxygenated fuel program. In both Fairbanks and Anchorage, the only oxygenate added to gasoline that winter was MTBE. In December 1992, the Alaska Department of Health and Social Services conducted surveys of taxicab drivers, health care workers, and university students at different locations in Fairbanks and Anchorage, AK (Beller and Middaugh, 1992; Chandler and Middaugh, 1992). This survey documented that people in both cities were reporting a perceived increase in certain symptoms after the introduction of oxygenated fuels but provided little information to judge the true prevalence of such symptoms in the broader population or whether such symptoms were actually caused by oxygenated gasoline.

During the winter of 1994-95, the Alaska Department of Health conducted a weekly random telephone survey of 100 adult residents in Anchorage for 16 consecutive weeks to identify possible health problems related to using ethanol as an oxygenate in fuels (Egeland and Ingle, 1995). The results indicated a much lower prevalence of symptoms than had been reported 2 yrs earlier when MTBE was used in gasoline, and the reported prevalence of symptoms remained fairly similar during periods when ethanol-containing gasoline was either not in use, was in use, or was being phased in or phased out.

Considerable media coverage and public concern about oxygenated fuel containing MTBE also occurred in Missoula, MT, during the 1992-93 winter season; the symptoms reported included many of the same acute effects that had been reported in Alaska, as well as others, including an exacerbation of symptoms among people with asthma. The next winter, the oxygenate used was ethanol rather than MTBE, and public concern over this issue essentially disappeared (E. Leahy, Missoula City-County Health Department, personal communication, 1995).

Several other state health departments have also received some health complaints related to oxygenated gasoline from citizens that are similar to those received in Alaska. State health departments, however, do not routinely conduct surveillance for complaints related to gasoline or other environmental exposures. In addition, citizens would not necessarily report health complaints of a nonspecific and noninfectious nature, such as a headache, to the health department, even if they believed symptoms were caused by gasoline or some other environmental agent. Although information on the number and nature of complaints received by different health departments has been collected, analyses of this data are difficult to interpret (Livo, 1995; McCoy *et al.*, 1995)

Motorists who had no occupational exposures to gasoline had also been included among the people interviewed in both the investigations in Stamford, CT, where oxygenated gasoline was in use (CDC, 1993a), and in Albany, NY, where oxygenated gasoline was not in use (CDC, 1993b). Because both investigations relied on convenience samples rather than on random samples of motorists, the people interviewed may not have been representative of the larger population in either city. In both cities, the most common symptoms were headaches and cough, and the reported prevalence of these and other symptoms was fairly similar among motorists in both cities.

In response to public concern over reformulated gasoline (some of which contained MTBE, but at lower concentrations than is used in oxygenated gasoline), the Department of Health in Wisconsin conducted, during the winter of 1994-95, a random telephone survey of symptoms among approximately 500 residents in Milwaukee, WI, Chicago, IL, (which also used reformulated fuels but had not experienced the same intense media coverage of the issue), and areas in Wisconsin that did not use reformulated fuels (Anderson *et al.*, 1995). Overall, the survey found that people in Milwaukee reported a higher prevalence of unusual symptoms than did residents of other areas of the state or of Chicago. Several other findings are of relevance in evaluating this increase. First, every symptom was elevated in Milwaukee, not just symptoms that had previously been associated with gasoline or chemical solvents. Second, the symptom prevalence figures were not elevated in Chicago compared with such figures in areas of Wisconsin where reformulated gasoline was not used, although Chicago was also using reformulated gasoline. Third, although people were asked to report unusual symptoms, the symptoms reported in Milwaukee were more likely to be associated with having had a cold or the flu, smoking cigarettes, or being aware of reformulated gasoline than were symptoms reported by people in Chicago or the rest of Wisconsin. This survey had limitations, including lower participation rates than desired (especially in Chicago), imprecise classification of exposure to reformulated fuels based on questionnaire responses, and potential problems with the respondents' characterization of symptoms as unusual.

Summary of Findings and Conclusions

The Interagency Health Assessment had concluded that, "taken together, these studies suggest that most people do not experience adverse health effects from MTBE in gasoline, but the studies cannot rule out the possibility that some people do experience more acute symptoms from exposure to oxygenated gasoline than to conventional gasoline. Many basic questions, such as the relative importance of individual characteristics, exposure situations, and factors other than oxygenates for the occurrence of various health symptoms remain" (NSTC, 1996, p. 34). After a re-examination of the available data, we agree with the thrust of the NRC committee's findings that greater attention should be given to the potential health risks from oxygenated gasoline among occupationally exposed workers. Exposure to high concentrations of conventional gasoline can cause headaches and other acute health effects, but some evidence suggests that higher blood concentrations of MTBE were associated with a greater likelihood of acute health symptoms among persons exposed to oxygenated gasoline. However, we believe that the NRC committee's conclusion that "there is enough consistency among various studies to suggest that the levels of exposure to gasoline containing MTBE in certain occupational settings are associated with increased rates of symptom reporting" overstates the strength and quality of the available data, which we found to be quite limited.

The Interagency Health Assessment also concluded that "a causal association between acute health effects and exposure to MTBE or other oxygenates in gasoline in a relatively smaller proportion of persons has not been demonstrated but cannot be ruled out on the basis of the limited epidemiologic studies that have been conducted to date" (NSTC, 1996, p. 34). The largely anecdotal reports of acute health symptoms among some individuals at sometimes fairly low levels of exposure to oxygenated fuel cannot be adequately explained, but also cannot be dismissed. Several factors could have a role in contributing to these reported symptoms. The HEI Oxygenates Evaluation Committee discussed the potential contribution of odor in the development of symptoms (HEI, 1996). It also has been suggested that many of the acute health symptoms that have been reported in areas using oxygenated gasoline may have been caused by the by-products of the atmospheric chemistry of MTBE (Joseph, 1995). Heightened public awareness resulting from intense media attention may also contribute to increased symptom reporting (Anderson *et al.*, 1995). Another hypothesis put forth in both the Interagency Health Assessment (NSTC, 1996) and the report of the HEI Oxygenates Evaluation Committee (HEI, 1996) was that certain people may be more sensitive to the effects of evaporative or combustion emissions of oxygenated gasoline containing MTBE. This suggestion was not intended to imply that effects would be confined to "sensitive" individuals or that everyone who experienced acute symptoms suffered from some unique condition comparable to multiple chemical sensitivity. The NRC committee agreed that "some people may indeed have greater sensitivity than others to MTBE" (NRC, 1996, p. 105), and commented that the development of objective criteria for determining sensitivity "would not seem out of place" (NRC, 1996, p. 106). The NRC committee also suggested that demographic or medical characteristics, such as sex, allergies, and history of exposure, could be studied as predisposing factors. We agree that an examination of possible predisposing factors might be useful to better understand the occurrence of various symptoms in the general population following exposure to MTBE-containing gasoline.

NEUROTOXIC POTENTIAL OF MTBE

In experimental animal models, the characteristic response of the nervous system to MTBE at high levels is sedation with a domination of anesthetic effects seen at very high levels of exposure. The sedative effects, which manifest as alterations in activity and reactivity levels, are transient and usually dissipate within an hour following cessation of exposure. While MTBE displays neuroactive properties at sufficiently high concentrations in animals, there is no conclusive evidence that exposure to MTBE at air concentrations from 100 ppm to 3000 ppm will produce neurotoxicity (for reviews: Burbacher, 1993; Costantini, 1993).

The effects of acute exposure to MTBE on the nervous system have been studied in rats following a single 6-h exposure by inhalation to 0, 800, 4000, and 8000 ppm MTBE (Gill, 1989). Labored respiration and lacrimation occurred during exposure to 8000 ppm MTBE. Using a systematic neurological assessment, the Functional Observational Battery (FOB), a mild level of ataxia was evident in 20% of the animals at 4000 ppm and 50% at 8000 ppm immediately following cessation of exposure. Measurements of fore- or hindlimb grip strength and righting reflex were not altered at any exposure level nor was treadmill performance altered at levels of 4000 ppm or below. No effect was seen at the 6-h post-exposure evaluation period. In animals exposed to 8000 ppm, there was an initial decrease in automated measurements of motor activity during the first 10 min immediately following exposure. This was followed by a brief period of increased motor activity. Animals exposed to 800 or 4000 ppm showed increased activity levels during the first 10 min following cessation of exposure, reflecting either a low-dose stimulant effect or an exaggerated recovery from anesthetic effects.

Following 13 days of repeated exposure, a decreased level of activity and mild ataxia were observed in both rats and mice during the 6-h exposure session at levels of either 4000 or 8000 ppm (Dodd and Kintigh, 1989). Immediately following the 13th day of exposure, motor activity was observed to be decreased in 20% of the animals exposed to 8000 ppm. In this same exposure group, 70% showed signs of mild (30%) or moderate (40%) ataxia. Both effects dissipated within the first hour following cessation of exposure. In animals exposed to 2000 or 4000 ppm, no exposure related behavioral alterations were observed following cessation of exposure. In a 13-week exposure paradigm, Dodd and Kintigh (1989) imposed a time delay between exposure and testing in order to minimize the influence of sedation associated with acute exposure. Male rats exposed to 8000 ppm showed decreased activity levels at 8 weeks, which dissipated by 13 weeks. In addition, female rats exposed to lower concentrations showed an increase in activity levels at 8 weeks with no effect seen at 13 weeks. Other measurements of motor function, such as gait, hindlimb splay, hindlimb grip strength, or performance on a treadmill were not altered by exposure to MTBE. Given the limited accuracy of brain parameter measurements and the relationship to body weight, it is unlikely that the reported changes of less than 5% actual brain weight or 2% brain length were a significant alteration attributable to MTBE at exposures as high as 8000 ppm (Dodd and Kintigh, 1989) and exposure times as long as 24 months (Chun *et al.*, 1992). Histological evaluation of various brain regions and peripheral nerves failed to indicate evidence of morphological alterations in nervous system tissue following 13 weeks of exposure (Dodd and Kintigh, 1989).

Examination of the original data sets from each of these studies (Gill, 1989; Dodd and Kintigh, 1989) found extremely high levels of motor activity and high variability in both controls and exposed animals, suggesting that the specific apparatus used to record activity was not solely measuring ambulatory locomotor activity. Furthermore, although multiple statistical comparisons were conducted for the activity measurements, the FOB measurements, and the brain parameters, the original statistical analysis contained no correction for the number of comparisons performed within each data set. This would increase the likelihood of type 1 statistical errors and inflate the level of significance. Thus, caution is required in drawing conclusions from isolated points in these data sets prior to an appropriate statistical re-analysis.

Based upon altered motor activity levels in experimental animals as reported in two relatively short-term exposure studies (Gill, 1989; Dodd and Kintigh, 1989), the HEI review concluded that MTBE has neurotoxic potential (HEI, 1996). The Interagency report (NSTC, 1996) evaluated data from these same acute exposure studies, and from longer exposure studies of 13 weeks (Dodd and Kintigh, 1989; Robinson *et al.*, 1990) and 24 months (Chun *et al.*, 1992). This report concluded that the transient effect of MTBE on activity and reactivity were evidence of the neuropharmacological properties of MTBE at high levels of exposure rather than overt neurotoxicity. Any effects seen occurred only during exposure and within the first few minutes following cessation of exposure. In addition, during longer exposure periods, animals appeared to adapt to the neuropharmacological actions of MTBE and sedation was no longer evident. Although exposure to neat MTBE vapor did not produce toxicologically significant neurobehavioral changes in these animal studies, task oriented performance could be hindered due to sedation during actual exposure to sufficiently high levels of MTBE. While measurements of motor activity and evaluations by the FOB do not assess more complex behaviors such as learning and memory or subtle alterations in sensory functioning, the experimental animal data currently available do not suggest the need for additional animal testing of neat MTBE vapors at lower doses.

The HEI report identified the need for additional short-term animal studies on MTBE to determine blood levels and correlate levels with altered CNS function. In contrast, given the transient neuropharmacological effect of MTBE, the NSTC report did not identify additional testing for CNS effects at low levels of exposure as a critical research need. Occurrence of sedation during actual MTBE exposure was reported in standard clinical observations. It is likely that existing pharmacokinetic studies may include clinical observations for sedation and ataxia and provide information concerning blood levels and sedation. The adaptation to sedation with continued exposure, however, would suggest that any such correlation would be limited to acute exposure.

GENETIC TOXICITY

Oxygenated Fuel Additives

MTBE has been extensively tested for genetic toxicity (NSTC, 1996; HEI, 1996). In vitro, MTBE was not toxic or mutagenic in the *Salmonella* mutation (Ames) test, and did not produce gene conversion in yeast, or chromosome aberrations (ABS) or sister chromatid exchanges (SCE) in Chinese hamster ovary cells. MTBE was not mutagenic in cultured Chinese hamster V79 cells, but was mutagenic in mouse lymphoma L5178Y cells with, but not without, exogenous metabolic activation. This positive response was presumed to be the result of the production of formaldehyde during the in vitro metabolism of MTBE. MTBE did not damage DNA in primary rat hepatocytes in culture.

Inhalation of MTBE at 800, 3000, or 8000 ppm did not produce ABS in bone marrow cells of rats exposed 6 h/day for 5 days or micronuclei in the bone marrow cells of mice exposed to 400, 3000, or 8000 ppm, 6 h/day for 2 days. Intraperitoneal injections of up to 0.4 mL MTBE/kg body weight given to rats in single acute doses or in five consecutive doses did not produce an increase in ABS in bone marrow cells. Oral administration of MTBE to male and female mice for 3 weeks at doses of 1, 10, 100, or 1000 mg/kg did not produce mutations at the *hprt* locus in lymphocytes. MTBE did not induce sex-linked recessive lethal mutations in the fruit fly, *Drosophila melanogaster*.

ETBE was neither mutagenic nor toxic in *Salmonella*; and TAME was not mutagenic or toxic in *Salmonella* and did not induce micronuclei in bone marrow cells of mice that had received intraperitoneal injections.

Ethanol has been extensively tested for genetic toxicity in vitro and in vivo (NSTC, 1996; HEI, 1996). With one exception, which may be the result of the generation of oxygen radicals, ethanol was not mutagenic in *Salmonella*. Ethanol induced genetic crossing over and aneuploidy in fungi, mutations in yeast without an exogenous metabolic activation system, and ABS and SCE in cultured mammalian cells in the presence, but not the absence, of exogenous metabolic activation. These positive results are likely due to the presence of the metabolite, acetaldehyde, that can be formed from the in vitro metabolic activation system. With few exceptions, there was no induction of ABS or SCE in cultured human lymphocytes when tested without an exogenous metabolic activation system; ethanol was not tested with metabolic activation. Ethanol produced cell transformation in a mouse cell line, but not in a Syrian hamster cell line.

In vivo studies in rodents showed mixed results for the induction of SCE, and there was no induction of ABS or micronuclei in bone marrow cells of mice. There are conflicting studies of the induction of micronuclei in rats. Ethanol was active in the mouse dominant lethal test and it induced aneuploidy in vivo.

Metabolites and Photoxidation Products

TBA was not toxic or mutagenic in *Salmonella* or in L5178Y mouse lymphoma mutagenicity tests. No increase in ABS or SCE was seen in Chinese hamster ovary cells in culture.

Formaldehyde has been extensively tested for genetic toxicity, with generally positive results. It produced DNA strand breaks and mutations in bacteria, yeast, fungi, and human and rodent cells, ABS and SCE in cultured human and rodent cells, and sex-linked recessive lethal mutations and reciprocal translocations in *Drosophila*.

Formaldehyde produced DNA damage in monkey and rat cells treated in vivo. Mutations were detected in the *p53* gene isolated from nasal tumors of rats after inhalation exposure to 15 ppm formaldehyde for 2 years. Mixed results were obtained in other genetic tests in rodents and humans. ABS, SCE, and micronuclei were induced in rat and mouse cells treated in vivo in some studies but not in others. Increases in ABS were seen in pulmonary macrophages but not in bone marrow cells of rats exposed by inhalation to 0.5, 3, or 15 ppm formaldehyde for 6 h/day, 5 days/week, for 1 or 8 weeks. In rats treated by inhalation for 6 h/day for 5 days, no increase in ABS or SCE was seen in peripheral blood lymphocytes. Similarly, ABS, SCE, and micronuclei were found in humans exposed to formaldehyde in work environments in some studies but not in others. Many of these differences could be the result of different exposure regimens and test protocols or of differences in the performance of the test laboratories. Formaldehyde produced sperm morphology changes in rats but not in mice or humans.

Acetaldehyde has been extensively tested in vitro. With few exceptions, acetaldehyde was not mutagenic in *Salmonella*. It produced ABS, SCE, micronuclei, and DNA damage in cultured mammalian cells and in cultured human lymphocytes. There was induction of SCE in rodent bone marrow cells after in vivo exposure.

Summary of Genetic Toxicity Data

MTBE has been extensively tested for genetic toxicity with generally negative results. The only positive result was in an in vitro test. This effect was attributed to the mutagenicity of the putative metabolite, formaldehyde. Although TAME was tested only in *Salmonella* and for micronuclei in mouse bone marrow cells, these two tests are generally considered sufficient to define a nongenotoxic chemical. There are insufficient data from which to evaluate the genetic toxicity of ETBE. Ethanol has been extensively tested in vitro and in vivo in rodents. It appears to be genotoxic in mammalian cells in vitro through its metabolite, acetaldehyde. The in vivo test results are mixed, but ethanol is clearly mutagenic in some endpoints.

Among the metabolites, formaldehyde has been studied extensively and was mutagenic in a wide range of in vitro and in vivo test systems. Acetaldehyde has been studied extensively in vitro. It is generally mutagenic, with the exception of *Salmonella*; there are insufficient data from in vivo studies. There are insufficient data for TBA, and no test data for *tertiary*-butyl formate (TBF).

REPRODUCTIVE AND DEVELOPMENTAL TOXICITY

There are only two published studies on the reproductive effects of MTBE and one unpublished study on TBA, all three in rats, and two published studies on the developmental effects of MTBE, one involving rats and mice and a second involving mice and rabbits. There are no reproductive or developmental toxicity studies on ETBE or TAME.

Neeper-Bradley *et al.* (1991) conducted a two-generation rat reproductive study using 6 h/day, 5 days/week inhalation exposures of males and females, at vapor-target concentrations of 400, 3000 and 8000 ppm. Adult toxicity in the form of a slight increase in relative liver weights was observed at 3000 ppm, along with slight reductions in P_0 adult weight gain and in pup weight gain postnatally for both the F_0 and F_1 generations. At 8000 ppm, toxicities were more severe for both the adults and pups, including a four-fold increase in pup deaths between birth and postnatal day four. There was no significant histological change noted in any generation. In a single-generation rat inhalation study, Biles *et al.* (1987) reported no biologically significant changes in body weight or effects in any reproductive or fertility endpoint measured following MTBE exposures of 300, 1300 and 3400 ppm, 6 h/day, 5 day/week. Thus, MTBE appears to be a reproductive toxicant only at concentrations that also reduce adult weight gain and increase relative liver weight.

Neeper-Bradley *et al.* (1989; 1990) conducted developmental toxicity studies in pregnant female CD1 mice and New Zealand white rabbits, exposed to MTBE on gestation days (Gd) 6-15 and 6-18 respectively, at vapor-target concentrations of 1000, 4000 and 8000 ppm. Maternal toxicity was reported for mice and rabbits in the 4000 and 8000 ppm exposure groups. Fetuses of the CD1 mice in these two exposure groups exhibited weight reductions and skeletal variations which were attributed to this maternal toxicity. The number of viable implants of CD1 mice was also decreased in the 8000 ppm exposure group. For the rabbits, however, there was no significant decrease in the number of corpora lutea, implants or dead and live fetuses, or increases in malformations or resorptions in any exposure group. Based upon these results, no-observed-adverse-effect levels (NOAELs) were reported as 1000 ppm for developmental and maternal toxicities in mice and maternal toxicity in rabbits, and 8000 ppm for developmental toxicity in rabbits. In addition, Conaway *et al.* (1985) reported no maternal toxicity and no significant change in fetal weights or frequency of fetal malformations following MTBE inhalation exposures of pregnant female CD1 mice and Sprague-Dawley rats on Gd 6-15 at vapor-target concentrations of 250, 1000 and 2500 ppm.

Tertiary-butyl alcohol (TBA) was assessed in the Sperm Morphology and Vaginal Cytology Evaluation by the National Toxicology Program (NTP, 1995). F344 male and female rats and B6C3F$_1$ male and female mice were exposed to TBA in drinking water for 90 days at concentrations of 2.5, 5.0, 10, 20, or 40 mg/mL. There was no change in caudal, epididymal or testis weights, sperm motility, sperm density, or percent abnormal sperm of male rats or mice, and there was no change in estrual cyclicity or average estrous length in female rats or mice. Determinations of reproductive function were not made. Nelson *et al.* (1985) exposed pregnant rats to ethanol vapors of 10,000, 16,000, or 20,000 ppm for 7 h per day on Gd 1-19. In the highest exposure group, where dams were severely narcotized and food consumption was reduced, mean fetal weights were reduced by about 8%. There was no increase in skeletal or soft tissue malformations at any exposure level.

In summary, MTBE caused reproductive and developmental toxicity in rodents only at exposures that produce significant liver effects or body weight reduction in the exposed adult. Considering the magnitude and duration of exposures used, MTBE is not expected to pose a reproductive or developmental health hazard under the intermittent, low-level exposures experienced by humans. There were no reproductive or developmental toxicity data on TBA, ETBE or TAME.

CARCINOGENICITY

Although there are no published studies on the carcinogenicity of MTBE in humans, there are multiple carcinogenicity studies in animals. Experimental studies show that MTBE is carcinogenic in rats and mice by the inhalation route of exposure and carcinogenic in rats by the oral (gavage) route, with tumor responses seen at multiple organ sites. TBA and formaldehyde, the primary metabolites of MTBE, also show evidence of carcinogenic activity in animals exposed directly to these substances. Several papers related to the health effects of MTBE were published subsequent to the preparation of this report. These are listed following the references cited in this chapter.

Ingestion of ethanol in relatively large quantities increases the risks for several forms of human cancer. In animals, ingestion of ethanol enhances the carcinogenic effects of other agents. No studies have been reported on the carcinogenicity of ETBE, TAME, or TBF. Unresolved at this time is whether the cancer risk of oxygenated gasoline is different from that of nonoxygenated gasoline.

Carcinogenicity of MTBE

Inhalation exposure of F344 rats to 0, 400, 3000, or 8000 ppm MTBE (6 h/day, 5 days/week, for up to 2 years) produced increased incidences of renal tubular adenomas and carcinomas and of interstitial cell adenomas (Leydig cell tumors) of the testes in male rats (Chun *et al.,* 1992). Whereas kidney tumors are uncommon in control rats, testicular tumors occur at a high spontaneous rate in this strain. The severity of chronic nephropathy was increased in exposed male and female rats, although no carcinogenic response was observed in females. Excessive mortality of male rats in the 3000 and 8000 ppm dose groups was due mainly to chronic progressive nephropathy and these dose groups had an early sacrifice. CD-1 mice were exposed to the same concentrations of MTBE as were rats, but for only 18 months. Exposure to 8000 ppm MTBE produced increased incidences of hepatocellular carcinomas in male mice and hepatocellular adenomas and carcinomas in female mice (Burleigh-Flayer *et al.,* 1992). The high-dose male mice had decreased survival. Because of the shortened duration of this study, it is not possible to determine whether MTBE induces late developing tumors in the low or mid-exposure groups in mice or whether more hepatocellular adenomas would have progressed to carcinomas. The tumor data from the rat and mouse inhalation studies were not analyzed using statistical methods that adjust for differences in survival between the control and exposed groups. These studies were conducted under an EPA TSCA Section 4 Test Rule Consent Agreement with the fuel industry and are documented by detailed technical reports submitted to EPA.

Administration of MTBE by gavage in olive oil to Sprague-Dawley rats, four times per week for 104 weeks, at doses of 0, 250, or 1000 mg/kg body weight produced a dose-related increase in lymphohematopoietic tumors (lymphomas and leukemia) in female rats, but not in male rats, and an increased incidence of interstitial cell tumors of the testes in the high-dose group of males (Belpoggi *et al.,* 1995). The animals were allowed to live out their normal lives, rather than being sacrificed at 104 weeks. Dysplastic proliferation of lymphoreticular tissue was also increased in treated female rats; no other toxicity was reported. The authors used statistical methods that adjust the tumor incidence for intercurrent mortality. A detailed technical report for this bioassay is not available.

Carcinogenicity of MTBE Metabolites

Administration of TBA in drinking water to F344 rats for 2 years produced increased incidences of renal tubular hyperplasias and renal tubular adenomas or carcinomas in male rats but not in female rats. As with MTBE by inhalation, TBA increased the severity of nephropathy in both male and female rats. Exposure of $B6C3F_1$ mice to TBA in drinking water for 2 years produced increased incidences of follicular cell hyperplasias and follicular cell adenomas or carcinomas of the thyroid gland (Cirvello *et al.,* 1995; NTP, 1995). NTP concluded that the responses in male rats and female mice constitute “some” evidence of carcinogenicity while the responses in male mice constituted “equivocal” evidence.

Inhalation exposure of F344 rats and $B6C3F_1$ mice to formaldehyde (a genotoxic metabolite of MTBE) for 2 years at concentrations up to 14.3 ppm induced squamous cell carcinomas of the nasal cavity in rats (at concentrations greater than 5.6 ppm), but not in mice (Kerns *et al.,* 1983). A dose-related increase in incidence of leukemia was observed in a lifetime drinking water study of formaldehyde in Sprague-Dawley rats (Soffritti *et al.,* 1989), however, a 2-year drinking water study using Wistar rats (Til *et al.,* 1989) at doses ranging up to 82 mg/kg/d in males and 109 mg/kg/d in females showed no evidence of carcinogenicity. Both EPA and IARC view formaldehyde as a “probable” human carcinogen.

Relevance of the Rat Kidney Tumor Response for Human Risk Assessment

When male and not female rat kidney tumors are seen in bioassays and the presence of the α2u-globulin protein is also observed in the kidney, it is EPA’s practice to determine whether that tumor occurrence will or will not be used as an indicator of potential human hazard.

The Interagency report (NSTC, 1996) concluded that the available data do not support the view that the male kidney tumor response was due solely to accumulation of α2u-globulin. The HEI report (HEI, 1996) indicated that the mechanisms are not understood; it was possible that other proteins related to α2u-globulin, or having similar characteristics, might be involved. They stated, "although it appears that the hyaline droplet nephropathy in the male F344 rats may be rightfully implicated as a potential factor in the pathogenesis of the renal tumor response, other factors may also be involved", and "it is conceivable that the MTBE and TBA induced renal tumor response may involve similar pathogenic mechanisms, however, not all findings are consistent with this interpretation". During 1996, research conducted at Chemical Industry Institute of Toxicology (CIIT) on MTBE and α2u-globulin (i.e., Prescott-Mathews *et a.l*, 1996; Poet *et al.*, 1996) became available in abstract or poster form. The NRC panel took the position of relying on these, and concluded that the research conducted at CIIT appears to have "fulfilled the EPA criteria for causation" with respect to α2u-globulin and that "the data for MTBE induced kidney tumors in male rats should not be used for human risk assessment until the recently reported data on mechanism of action are reviewed and evaluated. If the new data support the view that α2u-globulin nephropathy is involved in the response, as this committee now believes, then this endpoint should be discounted for human risk assessment". The NRC report did not discuss how the available data matched with the EPA criteria.

EPA (USEPA, 1991) established risk assessment criteria for examining male rat kidney α2u-globulin evidence. The three criteria are: (1) increased number and size of hyaline droplets in renal proximal tubule cells of treated male rats; (2) accumulating protein in the hyaline droplets is α2u-globulin; and (3) additional aspects of the pathological sequence of lesions associated with α2u-globulin nephropathy are present; if the response is mild all of the typical lesions may not be observed, however, some elements consistent with the pathological sequence must be demonstrated to be present. EPA specifies that if experimental data do not meet the criteria in any one of these three categories, then the α2u-globulin process alone is not considered to be responsible and the kidney tumor response may be used for both hazard identification and quantitative risk estimation. If experimental data reasonably fulfill the criteria yet some tumors are attributable to other carcinogenic processes, then EPA's cancer risk assessment policy is to include the tumor response for hazard identification but to only engage in quantitative risk estimation if the non α2u potency can be estimated. If the tumor response is solely attributable to α2u nephropathy, then EPA does not use that response in human hazard identification or quantitative risk estimation.

Based on a review of the NRC report and of all currently available data, including the newer abstract and poster information, we conclude that, of the three EPA criteria for causation of an α2u-globulin effect, the first criterion has been satisfied but not the second and third. The discussion in the following paragraphs supports this judgment. The evaluation of the MTBE inhalation kidney tumor response is difficult because the evidence is showing mild α2u-globulin accumulation and symptomatic nephropathy, with some of the nephropathy being intermingled with a background of non α2u rat nephropathy in both males and females.

Previously cited immunohistochemical studies for α2u-globulin in kidney sections from male rats exposed to MTBE for 13 weeks did not show an exposure-related increase in staining of this protein (Swenberg and Dietrich, 1991). Because staining was equivalent after exposure to 400, 3000, or 8000 ppm MTBE, yet only the two higher concentrations produced kidney tumors, a clear relationship between α2u-globulin accumulation and kidney carcinogenesis could not be established. Furthermore, proteinaceous casts localized at the junction of the proximal tubules and the thin loop of Henle did not stain positively for α2u-globulin. Thus, classical effects of α2u-globulin nephropathy-inducing agents are not evident in rats exposed to MTBE (Swenberg and Dietrich, 1991), suggesting that other factors are involved in MTBE-induced nephropathy and renal carcinogenicity in male rats.

Unpublished data from CIIT indicate that 10-day exposures to MTBE (at 0, 400, 1500, or 3000 ppm) produce exposure-related increases in protein droplet accumulation and in renal epithelial cell proliferation in proximal tubules of male F344 rats but not in female rats (Prescott-Mathews *et al.,* 1996). Unlike other chemicals that induce α2u-globulin nephropathy, only a mild increase in the concentration of α2u-globulin was observed in the kidney of male rats exposed to 3000 ppm MTBE, as measured by an enzyme-linked immunosorbent assay. The authors concluded, in their abstract, that the mild α2u-globulin increase in male rats exposed to MTBE was not totally responsible for the increase in protein droplet accumulation. A comparison between the renal effects of unleaded gasoline and MTBE further illustrates this point. In a previously published study from this same laboratory (Borghoff *et al.,* 1992), treating male F344 rats with unleaded gasoline for 10 days produced dose-related increases in protein droplets, α2u-globulin accumulation, and renal epithelial cell proliferation. At exposures to unleaded gasoline and MTBE that produced comparable increases in protein droplets and cell proliferation, male rats treated with unleaded gasoline had much greater increases in α2u-globulin (300%) than those treated with MTBE (40%). Further, the slope of plots of cell proliferation rate versus concentration of α2u-globulin in the male rat kidney is much steeper for MTBE than it is for unleaded gasoline. The disconnect between increases in protein droplets or cell proliferation after exposure to MTBE and α2u-globulin accumulation suggests that the second EPA criterion has not been met and that other factors contribute to the protein droplet and cell proliferation responses in rats exposed to MTBE. In addition, a 10-day cell proliferation study is not of sufficient duration to demonstrate a sustained response.

Poet et al. (1996) found that the interaction between kidney proteins and MTBE did not withstand dialysis in buffer or anion exchange chromatography and suggested that binding between MTBE and kidney proteins was either very weak or nonspecific. For other chemicals that induce α2u-globulin accumulation in the male rat kidney, approximately 20-40% of the ligand remains bound after dialysis in buffer. This finding is true even for chemicals such as 1,4-dichlorobenzene and its metabolite 2,5-dichlorophenol (Charbonneau *et al.,* 1989), which have weak binding affinities for α2u-globulin (Borghoff *et al.,* 1991). Thus, interactions between MTBE and α2u-globulin appear to be different from those of other chemicals that induce the accumulation of this protein. A binding constant for MTBE with a α2u-globulin had not been reported. Other than necrosis in short-term studies and hyaline droplet accumulation, the typical sequence of pathological lesions associated with α2u-globulin nephropathy have not been observed after 10-day or 13-week inhalation exposures to this chemical. Renal tubular necrosis and accumulation of hyaline droplets containing small amounts of α2u-globulin can occur by mechanisms that do not necessarily involve binding to this protein (Melnick *et al.,* 1996).

Finally, EPA 1993 notes that a nephrotoxic response in the female rat suggests the possibility of other processes leading to or influencing the kidney tumor response.

Nephropathy was increased in female rats exposed for 13 weeks to TBA, a metabolite of MTBE, which is also carcinogenic to the male rat kidney; and exposure of female rats to MTBE in the 2-year inhalation study increased the severity of chronic nephropathy. We conclude that currently available information does not support the NRC's contention that the kidney tumor response in male rats exposed to MTBE has met the EPA criteria of causation due to α2u-globulin accumulation. Because the NRC did not specify how they arrived at their conclusion, we cannot determine where the difference in judgment lies.

Depending on the judgments involved in using the EPA decision criteria, the evidence for an α2u-globulin role in the rat kidney tumor response may be considered to be borderline or lacking, but as yet it does not reasonably fulfill the criteria in our judgment. Based on available experimental data, it is reasonable to believe that other modes-of-action are operating. Because evidence of an actual influence of α2u-globulin on the rat kidney tumor response is not established, the prudent public health approach is to use this tumor response for both hazard identification and quantitative estimation of cancer risk, yet we acknowledge that other views have been expressed on this subject. Users of this risk information should be cautious to recognize that the cancer potency value based on male rat kidney tumors shown later in this assessment could be substantially lower in magnitude if α2u-globulin is having a meaningful influence.

Several key issues need to be resolved to better understand the possible involvement of α2u-globulin in the male rat kidney response; these include: (1) the basis for accumulation of moderate to large protein droplets in proximal tubular epithelial cells of male rats exposed to MTBE when there is only a mild increase in kidney α2u-globulin concentration, (2) a determination of whether the weak interaction between MTBE and α2u-globulin is sufficient to account for the hyaline droplet nephropathy observed in male rats exposed to MTBE, (3) characterization of the role of TBA in MTBE-induced kidney nephropathy, and (4) an evaluation of the impact of non α2u-globulin nephropathy in the kidney of male and female rats exposed to MTBE or TBA.

Risk Assessment Relevance of Lymphoma/Leukemia Response in Female Rats and Testicular Tumors in Male Rats in the Oral-Gavage Study

Belpoggi *et al.,* (1995) using olive oil gavage, reported a dose-related increase in lymphoma-leukemia in female rats as well as increased dysplastic proliferation of the lymphoreticular tissue; there was no corresponding response in males. High dose male rats showed an increase in interstitial cell tumors of the testes. The Belpoggi study is the only lifetime oral exposure bioassay for MTBE and it is the first report of a lymphoma/leukemia response with this chemical. The reported increase in testicular tumors, is the second such report for this tumor response, as the rat inhalation study also showed increases in benign testicular tumors with a positive trend across dose groups. The high-dose testicular tumors in the Belpoggi study are of some interest for determining human hazard potential but may be less useful for low-dose risk characterization compared to other tumor types that show increased incidence at lower doses. An oil gavage bioassay such as this one provides a perspective on ingestion risks, is a study by another route of exposure, and contributes to the overall evidence for human hazard potential. However, this type of exposure introduces uncertainties for drinking water risk assessment because of dose-rate and vehicle issues.

The Belpoggi *et al.* study was published in the peer reviewed literature. However, no detailed technical report of the bioassay is available. Lacking a detailed report about the bioassay, the NRC panel (NRC, 1996) identified a number of issues and questions which reflect upon the risk assessment use of these data. The NRC noted that the morphological criteria used to classify histopathological findings for both the lymphoma-leukemia and interstitial cell tumor responses were not adequately described and that the study did not adequately address the impact on tumor outcomes of differences in survival between controls and dosed groups. NRC went on to say that "because of the importance of this study for eventual use in risk assessment, the superficial reporting of the data and the nature of the observed lesions, the committee felt strongly that an independent in-depth review of the data, especially the pathology (microscopic slides) of the critical lesions is warranted (as was done with the inhalation studies) before the data are used for risk assessment". While the NRC raised questions about survival differences and the tumor outcome, it should be noted that Belpoggi *et al.* included statistical analyses that adjusted for intercurrent mortality. Several attempts by the Interagency Oxygenated Fuels Assessment Steering Committee to arrange for a pathology review of the Belpoggi *et al.* study have not been successful, hence, the underlying concerns raised by the NRC review cannot yet be resolved.

The lack of a detailed technical report of the Belpoggi *et al.* study, including data on the individual animals, is a limitation of this study, as is the lack of an independent peer review of the histopathology. The model for carcinogenesis study conduct and reporting is the NTP Carcinogenesis Bioassay Program. However, independent peer review of pathological findings are not routinely performed in many carcinogenesis studies used by the risk assessing community and EPA. Such a review was not conducted for the MTBE inhalation studies, though NRC (1996) indicated such. Even in the absence of the Belpoggi *et al.* study, MTBE would be considered to pose a potential risk from oral exposure pathways due to the fact that pharmacokinetic data and neoplastic effects from the inhalation study indicate systemic exposure in both rats and mice.

Questions about the combining of the lymphoma-leukemia incidence, as done by Belpoggi *et al.,* were discussed by HEI (1996) and by NSTC (1996). HEI noted that a panel of pathologists assembled by the National Toxicology Program recommended that lymphomas and leukemias in F344 rates be analyzed separately. If the neoplastic lesions in the Belpoggi *et al.* study were composed of similar cell types (e.g., mononuclear cells) and the lymphomas were interpreted as extravascular invasions of leukemic cells, (i.e., as is commonly observed in F344 rats with mononuclear cell leukemia), then combining the lymphomas and leukemias may be an appropriate approach (HEI 1996). While not verifiable at this time, the combining of the tumor incidences in the Belpoggi *et al.* study may be defensible but should be reevaluated as further information on the study pathology becomes available. The lack of a full technical report or the lack of an independent pathology review should not be an *a priori* condition for excluding the results in a hazard characterization. The use of the data to generate risk estimates is a choice that depends on judgments about the value of estimating potency as part of risk characterization compared to the limitations and uncertainties of such estimates. Regulatory agencies have historically used data from reports like that of Belpoggi *et al.* in performing risk assessments and will continue to consider such data in order to characterize the full body of available information, recognizing that the added influence should be viewed cautiously.

Consistency of Findings

Consistency of findings across studies contributes to the weight-of-evidence in evaluating carcinogenicity data. Thus, the increased incidence of interstitial cell tumors of the testis in high-dose Sprague-Dawley rats that were administered MTBE by gavage, supports the finding of an exposure-related increase in F344 rats that were exposed to MTBE by inhalation, even though the latter strain exhibits a high spontaneous rate of these benign tumors. The lack of a tumor response in the testes of rats that were given TBA in their drinking water suggests that exposure to the parent compound, rather than to this metabolite, may be the cause of this effect. The finding of kidney tumors in male F344 rats exposed to MTBE by inhalation is supported by a similar response in male F344 rats treated with TBA. The lack of a kidney tumor response in Sprague-Dawley rats treated with MTBE by olive oil gavage at doses that were lower than those used in the inhalation study may be due to differences in target organ dosimetry of the causal agent. Pharmacokinetic studies may help explain this difference in response.

The reported increase in lymphomas and leukemia in female rats given MTBE by gavage is supported by the increase in these tumors in Sprague-Dawley rats administered formaldehyde via their drinking water and suggests a possible involvement of this metabolite in the leukemogenic effect of MTBE. In addition to the reported positive response in Sprague-Dawley rats, there is also a negative drinking water study of formaldehyde in Wistar rats. It should be noted that the contribution of formaldehyde, produced metabolically from MTBE, may be different than a drinking water study of formaldehyde in terms of target organ dosimetry. The lack of a lymphoma-leukemia response in F344 rats exposed to MTBE by inhalation may be clouded by the high spontaneous rate of mononuclear cell leukemia in this strain of rat and early mortality in males.

Weight-of-Evidence for Human Hazard

Although there are no published human carcinogenicity studies for MTBE, there are multiple animal studies showing carcinogenic activity and there is supporting animal carcinogenicity data for the MTBE metabolites. With the multiplicity of MTBE tumor responses in two animal species, and by two routes of exposure, one can conclude there is sufficient evidence that MTBE is an animal carcinogen. HEI (1996) concluded “the possibility that ambient levels of MTBE may pose some risk of carcinogenic effects in human populations cannot be excluded”. NRC (1996) considered the animal evidence to be positive but “weak” for the purpose of assessing human hazard. Different parties can support more than one conclusion about weight-of-evidence depending on how information about metabolites, pharmacokinetics, mode-of-action hypotheses and the lack of background information for the oral MTBE bioassay is incorporated. We believe the weight-of-evidence supports regarding MTBE as having a carcinogenic hazard potential for humans. The risk assessing community should monitor the ongoing research to see what evolves regarding new studies and modes-of-action research and what these indicate about the likelihood of a human hazard.

Cancer Potency

Once a hazard potential has been established the follow-on task is frequently to characterize the possible impact of exposure on humans. For animal evidence this is done through a dose-response-extrapolation analysis to produce an estimate of possible human risk (i.e., potency) using assumptions and procedures which are not likely to understate the risk. The presentation of estimated cancer potency values in this section provides a crude estimate of possible risk. The act of performing the calculations does not add more certainty to the original hazard weight-of-evidence position or debate. Risk managers must be very cautious about using the estimates for regulatory decision-making purposes and must consider the uncertainties in determining the appropriate use of these potency estimates.

Based on carcinogenicity data from the inhalation and oral studies of MTBE in rats or mice, upper-bound unit cancer risk estimates for lifetime human exposure to MTBE were calculated using the linearized multistage model (NSTC, 1996). These estimates are based on the assumptions that dose-response relationships are linear and that the mechanisms of tumor induction by MTBE in rats and mice can also occur in humans. In the absence of compelling scientific information showing otherwise, these assumptions are made as a policy choice for ensuring the protection of public health. Estimates were also made of the human cancer ED_{10} benchmark dose (i.e., the estimated dose associated with an increased cancer risk of 10% converted to a human equivalent dose) for comparison with other carcinogenic agents (see Table 4.1).

Table 4-1. Cancer potency estimates for MTBE based on rat and mouse tumor data using linear multistage extrapolation[a]

Species, sex	Tumor site	Exposure route	Upper bound unit cancer risk	ED_{10}
mouse, female	liver	inhalation	$3x10^{-4}$ per ppm[b]	480 ppm[b] 500 mg/kg/d[b]
rat, male	kidney	inhalation	$6x10^{-4}$ per ppm[b]	330 ppm[b] 350 mg/kg/d[b]
rat, female	lymphoma/ leukemia	oral (gavage)	$4x10^{-3}$ per mg/kg/d[b,c]	38 mg/kg/d[b,c]

[a] In the absence of appropriate human data or definitive information on the mode-of-action of carcinogenicity findings in animals, public health conservative risk estimation techniques are used. These techniques yield estimates which are not likely to underestimate risk for the general population. True risk for most individuals in the population is likely to be lower and for some may even be nearly zero. The ability to calculate such an estimate does not imply greater confidence in potential cancer hazard. There are uncertainties inherent in these values and they should be used cautiously.

[b] Additional understanding of the mode-of action of this response could substantially alter these estimates or possibly make them irrelevant for characterizing potential human risk. See text for additional comment about limitations and cautions regarding their use.

[c] The use of oil-gavage (i.e. bolus dosing) as a surrogate for inhalation or drinking water exposure has inherent limitations due to differences in dose-rate and possible vehicle effects. In addition, the lack of a detailed report for the oral study in rats, including morphological criteria used to classify the histopathology findings and the lack of individual animal data, limit the use of the findings for estimating risk. The NRC panel, for example, raised strong cautions about using the oral female rat tumor incidence in risk estimation until these questions can be answered.

In terms of quantitative risk estimation (i.e. potency), the oral Belpoggi *et al.* study has no direct influence on inhalation risk estimation, unless route extrapolation is contemplated for comparison with the inhalation based estimates. In the absence of a chronic drinking water study, the use of an oil gavage (bolus dose) tumor dose-response as a surrogate for a drinking water exposure carries inherent limitations because of dose-rate and possible vehicle influences on the tumor response. Likewise, extrapolating from an inhalation dose-response as a surrogate for a drinking water exposure has limitations. This report provides, for informational purposes only, an oral risk estimate (potency-unit risk as well as ED_{10}) based on the Belpoggi lymphoma-leukemia incidence, using identified assumptions and noted caveats.

The inhalation upper-bound cancer unit risks for MTBE are six to seven times lower than those of fully vaporized conventional gasoline (2×10^{-3} per ppm based on induction of liver tumors in mice and 4×10^{-3} per ppm based on induction of kidney tumors in rats, using the linearized multistage model). For comparison, cancer ED_{10} benchmarks for 80 other Clean Air Act hazardous air pollutants range from 0.0000015 mg/kg/d (most potent) to 80 mg/kg/d (least potent). Estimates for MTBE ED_{10} fall at the low end of the range.

Limitations in Estimating Human Cancer Risk

Estimations of human cancer risks using animal study data are influenced by the exposure estimates, extrapolation models, and estimates of cancer potency. Ideally, human exposures to MTBE would be estimated from measurements of MTBE in ambient air, measurements of MTBE concentrations in specific micro environments (e.g., inside automobiles), and estimates of the distribution of time spent in each environment. At this time, estimates of low-dose human cancer risk associated with lifetime exposure to MTBE are complicated by several scientific uncertainties, including (1) the adequacy of the exposure characterizations (especially with respect to the distribution of exposures in the environment and the workplace), (2) potential differences in sensitivity between laboratory animals and humans, (3) the assumption that the mechanisms that caused tumors in rodents under the bioassay conditions operate in humans at ambient exposures, (4) the adequacy of the models that were used to perform low-dose extrapolations and estimate cancer potency, and (5) inter-individual differences in sensitivity among the exposed human population. The use of tumor data from the gavage study of MTBE to estimate cancer risk for inhalation exposure involves additional assumptions (e.g., that equivalent total exposures by inhalation and gavage administration result in similar internal doses of MTBE and that differences in dose rate and metabolism from gavage and inhalation exposures do not affect the tumor response). An oil gavage bioassay provides a perspective on potential oral risks, however, it may introduce important uncertainties for use in drinking water risk assessment because of dose-rate and vehicle issues. Further research in this area should help to clarify these issues.

Overall Evaluation

Inhalation exposure to MTBE produced increased incidences of kidney and testicular tumors in male rats and liver tumors in mice. Oral administration of MTBE produced an increased incidence of leukemia and lymphomas in female rats and testicular tumors in male rats. Two metabolites of MTBE, TBA and formaldehyde, show carcinogenic activity in animals, with some responses paralleling those seen with MTBE (rat kidney and perhaps leukemia) and some responses being at different sites (thyroid gland and nasal cavity). Epidemiological studies suggest a causal relationship between exposure to formaldehyde and nasopharyngeal cancer (IARC, 1995). The mechanisms by which MTBE causes cancer in rodents are not understood, nor is the relative role of the parent compound and its metabolites known. Consequently, the possibility of a low-dose hazard cannot be excluded. It is unlikely that carcinogenic effects of ethanol would result from inhalation exposure to ambient air concentrations associated with use of ethanol in gasoline.

Based on the weight-of-evidence on MTBE carcinogenicity (positive in two species, by two routes of exposure, and at multiple organ sites), other supporting factors (e.g., one metabolite is a "probable" human carcinogen and the other also induces male rat kidney tumors), and considering various uncertainties, it is reasonable to regard this alkyl ether oxygenate as posing a potential carcinogenic hazard and risk to humans. At the same time, it should be recognized that 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 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. More important is whether the cancer risk from using oxygenated gasoline containing MTBE is significantly different than the cancer risk attributed to using 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 concentrations and personal exposure to the air toxicants that are present in both the evaporative and exhaust emissions from both types of fuels. Exposure to mobile-source air toxicants may be affected by the composition of the gasoline, the engine, the emissions control technology, and atmospheric conditions.

Comparing Potential Cancer Risks of Conventional Gasoline and Oxygenated Gasoline

The NRC concurred with the Interagency view that the interpretation of any cancer risks related to the addition of MTBE to gasoline requires a comparison to the cancer risks associated with the use of conventional gasoline (NRC, 1996). The NRC also agreed with the opinion of the Interagency assessment (NSTC, 1996) and the HEI report (HEI, 1996) that large data gaps on exposures and health effects of the mixture of compounds to which people are exposed through the use of oxygenated and nonoxygenated fuels prevent the development of a definitive comparative risk assessment. However, the NRC believes that sufficient data are available to bound a quantitative assessment of the cancer risks associated with use of oxygenated gasoline and nonoxygenated gasoline, and recommended the development of a framework for conducting a comparative risk assessment of these two types of fuels. The NRC claims that even an assessment with uncertain data is justified as long as uncertainties are specified and thoroughly characterized. EPA had previously developed a research strategy and framework for conducting comparative risk assessments on conventional and alternative fuels (USEPA, 1992).

A comprehensive comparative risk assessment on oxygenated and nonoxygenated fuels requires information on the level and distribution of human exposure to toxic compounds in each of these fuels and those present in evaporative and combustion emissions, as well as atmospheric transformation products. Assessments of potential health risks should account for multipathway exposures (including drinking water and inhalation) and potential interactive effects among this complex mixture of compounds. However, because there are no data that address the mixture issue, because information on general population exposures via drinking water are very sparse, and because it is likely that not all toxic compounds have been identified, a narrower assessment of relative cancer risk from inhalation exposure performed at this time would have to be limited to additive effects of MTBE and the small number of confirmed carcinogenic air pollutants that have been identified in fuels and/or in combustion emissions (e.g., benzene, 1,3-butadiene, formaldehyde, acetaldehyde). For the latter compounds, reliable estimates of cancer potency are available. However, even with this highly restricted approach, the human exposure assessment still presents an enormous challenge. Emission studies on test vehicles found that fuel oxygenates decrease the emissions of benzene and 1,3-butadiene and increase the emissions of aldehydes (formaldehyde from use of MTBE and acetaldehyde from use of ethanol or ETBE). The effects of low temperatures on toxic emissions are not well characterized. It is not certain whether results from emission studies are directly applicable to the ambient air effects of the on-road fleet (see Air Quality chapter of this report). Quantifying vehicle emissions and exposures that occur during refueling and when operating motor vehicles fueled with oxygenated or nonoxygenated gasoline must account for actual changes in fuel composition beyond the addition of the oxygenate (e.g., differences in levels of aromatics and olefinic hydrocarbons in the fuel), fleet composition with respect to the type of emission control system, vehicle maintenance condition, vehicle operation, meteorology (including effects of ambient temperature), and altitude of different geographical sites. Information on emissions from vehicles operating on oxygenated fuels under varied conditions is very fragmentary. However, even if suitable emissions data were available, translation of quantitative evaluations of differences in emissions resulting from use of oxygenated versus nonoxygenated gasoline to realistic estimates of ambient air and microenvironment concentrations of these toxic air pollutants are needed. The ambient and microenvironment estimates should be compared to the limited data on actual concentrations. Assessments of human exposure and health risks also need to account for effects of meteorology (e.g., wind, temperature, and precipitation during the oxygenated fuels season) and differences in human activity patterns, since these factors can have a substantial effect on individual and population exposures. Inconsistent accounting of the numerous variables that impact on exposure could result in a mistaken differential effect of the two fuels.

EPA and other agencies are analyzing available data, collecting new data, and developing better models to reduce uncertainties in the exposure and health effects assessments. The Interagency Oxygenated Fuels Assessment Steering Committee shares the desire of the NRC to assess the health risks and benefits associated with the use of oxygenated gasoline compared to those resulting from use of nonoxygenated gasoline; however, the Steering Committee believes that a quantitative comparative risk assessment would not be useful at this time because large data gaps in human exposure could result in considerable overestimation or underestimation of the actual risks associated with use of either or both of these types of fuels. Information on cancer risks associated with evaporative and combustion emissions from use of nonoxygenated gasoline are not adequate to serve as a baseline against which changes in risk associated with use of oxygenated fuels could be measured. Excessive reliance on hypotheses and assumptions would not likely yield a useful health assessment. The feasibility of preparing a quantitative comparative risk assessment will be reexamined periodically, particularly after EPA has conducted an inventory of existing data and models for their usefulness in producing meaningful evaluations. This step should be reached even before new data become available that will more definitively fill some of the critical information gaps. EPA is taking steps to obtain data that would allow a comprehensive comparative risk assessment. Existing health effects testing requirements for fuels and fuel additives, promulgated under section 211(b) of the Clean Air Act, have led to discussions between EPA and representatives of a consortium of fuel and additive manufacturers that are expected to result in the performance of bioassay and exposure studies and will help fill some of the critical information gaps.

CONCLUSIONS

Exposures to MTBE in various occupational and nonoccupational settings have been examined in a limited number of studies. Available data indicate that the highest potential for acute inhalation exposure to oxygenates for the general population occurs during refueling at gasoline stations. Based on several qualitative assumptions about various exposure scenarios, high-end, time-weighted annual average exposure to MTBE in the general population was estimated to be on the order of about 0.01 to 0.02 ppm. The exposure data were too limited to make quantitative estimates of the range and distribution of MTBE exposure. Less information is available on exposures to other oxygenates.

MTBE is rapidly absorbed by humans or rats after inhalation exposure. Studies in rats also show rapid absorption after oral exposure. Metabolism and elimination of MTBE and its metabolites proceed rapidly regardless of the route of exposure. Studies in rats indicate that MTBE is metabolized by cytochrome P450 enzymes to TBA and formaldehyde. Measurements of blood levels of TBA in humans exposed to MTBE show a rapid rise after exposure begins and a slow elimination rate.

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. At the lower concentrations that are experienced by the general population, 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.

The assessment found that chronic non-cancer health effects, including neurotoxic, developmental, or reproductive effects, 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.

MTBE has been tested for genotoxicity with generally negative results, whereas its metabolite formaldehyde is genotoxic in a variety of experimental systems. Experimental studies indicate that MTBE is carcinogenic in rats and mice at multiple organ sites after oral or inhalation exposure. The mechanisms by which MTBE causes cancer in animals are not well understood. *Tertiary*-butyl alcohol and formaldehyde, the primary metabolites of MTBE biotransformation, are also carcinogenic in animals. While there are no studies on the carcinogenicity of MTBE in humans, there is sufficient evidence to indicate that MTBE is an animal carcinogen and to regard MTBE as having a human hazard potential. However, estimates of human risk from MTBE contain large uncertainties in both human exposure and cancer potency.

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 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 acute or chronic health risks associated with the addition of MTBE to gasoline requires a comparison to the health risks associated with conventional gasoline. Meaningful predictions of human cancer risk from the wintertime use of oxygenated gasoline versus nonoxygenated gasoline require much more knowledge on human exposures to oxygenates, as well as quantitative evaluations on how exposures to the toxic compounds in both evaporative and exhaust emissions of fuels are altered with use of oxygenated gasoline.

REFERENCES

American Petroleum Industry (API), 1995, Petroleum industry data characterizing occupational exposures to MTBE 1983-1993. Washington, DC: API #4622.

Anderson, H.A., Hanrahan, L., Goldring, J., and Delaney, B., 1995, An investigation of health concerns attributed to reformulated gasoline use in southeasternWisconsin: final report. Madison, WI: Wisconsin Department of Health and Social Services, Bureau of Public Health; May 30.

Beller, M. and Middaugh, J., 1992, Potential illness due to exposure to oxygenated fuels, Fairbanks, Alaska. Anchorage, Alaska: State of Alaska Department of Health and Social Services, December 11.

Belpoggi, F., Soffritti M., and Maltoni, C., 1995, Methyl-tertiary-butyl ether (MTBE)—a gasoline additive—causes testicular and haematopoietic cancers in rats. Toxicol. Ind. Health 11:119-149.

Biles, R.W., Schroeder, R.E., and Holdsworth, C.E., 1987, Methyl tertiary butyl ether inhalation in rats: a single generation reproduction study. Toxicol. Ind. Health 3:519-534.

Bio-Research Laboratories, 1990a, Pharmacokinetics of methyl tert-butyl ether (MTBE) and tert-butyl alcohol (TBA) in male and female Fischer-344 rats after administration of ^{14}C-MTBE by intravenous, oral, and dermal routes. Bio-Research Laboratories Report #38842, Senneville, Quebec, Canada.

Bio-Research Laboratories, 1990b, Mass balance of radioactivity and metabolism of methyl tert-butyl ether (MTBE) in male and female Fischer-344 rats after administration of ^{14}C-MTBE by intravenous, oral, and dermal routes. Bio-Research Laboratories Report #38843, Senneville, Quebec, Canada.

Bio-Research Laboratories, 1990c, Pharmacokinetics of methyl tert-butyl ether (MTBE) and tert-butyl alcohol (TBA) in male and female Fischer-344 rats after single and repeat inhalation nose-only exposure to ^{14}C-MTBE. Bio-Research Laboratories Report #38844, Senneville, Quebec, Canada.

Bio-Research Laboratories, 1990d, Disposition of radioactivity and metabolism of methyl tert-butyl ether (MTBE) in male and female Fischer-344 rats after nose-only inhalation exposure to ^{14}C-MTBE. Bio-Research Laboratories Report #38845, Senneville, Quebec, Canada.

Borghoff, S.J., Miller, A.B., Bowen, J.P., and Swenberg, J.A., 1991, Characteristics of binding to α2u-globulin in vitro–evaluating structure-activity relationships. Toxicol. Appl. Pharmacol. 107:228-238.

Borghoff, S.J., Youtsey, N.L., and Swenberg, J.A., 1992, A comparison of European high test gasoline and PS-6 unleaded gasoline in their abilities to induce α2u-globulin nephropathy and renal cell proliferation. Toxicol. Lett. 63:21-33.

Borghoff, S.J, Murphy, J.E., and Medinsky, M.A., 1996, Development of a physiologically based pharmacokinetic model for methyl tertiary-butyl ether and tertiary-butanol in male Fischer-344 rats. Fundam. Appl. Toxicol. 30:264-275.

Brady, J.F., Xiao, F., Ning, S.M., and Yang, C.S., 1990, Metabolism of methyl tertiary-butyl ether by rat hepatic microsomes. Arch. Toxicol. 64:157-160.

Burbacher, T.M., 1993, Neurotoxic effects of gasoline and gasoline constituents. Environ. Health Perspect. 101(Suppl. 6):133-141.

Buckley, T.J., Wallace, L.A., Prah, J.D., Ashley, D., and Zweidinger, R.A., 1995, Breath and urine measurements to assess environmental inhalation exposure to methyl tertiary butyl ether (MTBE) - draft, U.S. Environmental Protection Agency, National Exposure Research Laboratory, Research Triangle Park, NC.

Burleigh-Flayer, H.D., Chun, J.S., and Kintigh, W.J., 1992, Methyl tertiary butyl ether: vapor inhalation oncogenicity study in CD-1 mice. Export, PA: Bushy Run Research Center; OPTS-42098.

Cain, W.S., Leaderer, B.P., Ginsberg, G.L., Andrews, L.S., Cometto-Muniz, J.E., Gent, J.F., Buck, M., Berglund, L.G., Mohsenin, V., Monahan, E., and Kjaergaard, S. , 1996, Acute exposure to low-level methyl tertiary-butyl ether (MTBE): human reactions and pharmacokinetic responses. Inhal. Toxicol. 8:21-48.

Cederbaum, A.I. and Cohen, G., 1980, Oxidative demethylation of tertiary-butyl alcohol by rat liver microsomes. Biochem. Biophys. Res. Comm. 97:730-736.

Centers for Disease Control and Prevention (CDC), 1993a, An investigation of exposure to methyl tertiary butyl ether among motorists and exposed workers in Stamford, Connecticut. Atlanta, GA: U.S. Department of Health and Human Services, National Center for Environmental Health; September 14.

Centers for Disease Control and Prevention (CDC), 1993b, An investigation of exposure to MTBE and gasoline among motorists and exposed workers in Albany, New York [draft]. Atlanta, GA: U.S. Department of Health and Human Services, National Center for Environmental Health; August 4.

Chandler, B. and Middaugh, J., 1992, Potential illness due to exposure to oxygenated fuels, Anchorage, Alaska. Anchorage, AK: State of Alaska Department of Health and Social Services, December 23.

Charbonneau, M., Strasser, J., Lock, E.A., Turner, M.J., and Swenberg, J.A., 1989, Involvement of reversible binding to α2u-globulin in 1,4-dichlorobenzene-induced nephropathy. Toxicol. Appl. Phamacol. 99:122-132.

Chun, J.S., Burleigh-Flayer, H.D., and Kintigh, W.J., 1992, Methyl tertiary butyl ether: vapor inhalation oncogenicity study in Fischer 344 rats. Export, PA: Bushy Run Research Center; Report 91N0013B.

Cirvello, J.D., Radovsky A., Heath, J.E., Farnell, D.R., and Lindamood, C., 1995, Toxicity and carcinogenicity of t-butyl alcohol in rats and mice following chronic exposure in drinking water. Toxicol. Ind. Health 11:151-165.

Conaway, C.C., Schroeder, R.E., and Snyder, N.K., 1985, Teratology evaluation of methyl tertiary butyl ether in rats and mice. J. Toxicol. Environ. Health 16:797-809.

Costantini, M.G., 1993, Health effects of oxygenated fuels. Environ. Health Perspect. 101 (Suppl. 6):151-160.

Dodd, E.E. and Kintigh, W.J., 1989, Methyl tertiary butyl ether (MTBE): repeated (13-week) vapor inhalation study in rats with neurotoxicity evaluation. Export, PA: Bushy Run Research Center; Report 52-507.

Egeland, G.M. and Ingle, D., 1995, Ethanol-blended fuel in Anchorage, 1994-1995: residents may smell the difference but have no health complaints. Anchorage, AK: Alaska Department of Health and Social Services, State of Alaska Epidemiology Bulletin, August 17, 1995.

Gill, M.W., 1989, Methyl tertiary butyl alcohol: single exposure vapor inhalation neurotoxicity study. Export, PA: Bushy Run Research Center; Report no. 52-533.

Health Effects Institute (HEI), 1996, The potential health effects of oxygenates added to gasoline. A review of the current literature. Health Effects Institute, Cambridge, MA.

International Agency for Research on Cancer (IARC), 1995, Formaldehyde. In: IARC monographs on the evaluation of carcinogenic risks to humans: wood dust and formaldehyde. Lyon, France: IARC 62:217-362.

Johanson, G., Nihlen, A., and Lof, A., 1995, Toxicokinetics and acute effects of inhaled MTBE and ETBE in male volunteers. Toxicol. Lett. 82-83:713-718.

Joseph, P., 1995, Letter to the Editor. Arch. Environ. Health 50:395-396.

Kerns, K.D., Pavkov, K.L., Donofrio, D.J., Gralla, E.J., and Swenberg. J.A., 1983, Carcinogenicity of formaldehyde in rats and mice after long-term inhalation exposure. Cancer Res. 43:4382-4392.

Livo, K.B., 1995, Overview of public's perspective of health effects from oxygenated gasolines in Colorado. Presented at the HEI Workshop on Acute Health Effects on Oxygenates and Oxygenated Gasolines, Chicago, July 27.

McCoy, M. Jr, Abernethy, J., and Johnson, T., 1995, Anecdotal health-related complaint data pertaining to possible exposures to methyl tertiary butyl ether (MTBE): 1993 and 1994 follow-up surveys (1984-1994). American Petroleum Institute; Publication No. 4623. Washington, DC.

Mehlman, M.A., 1995, Dangerous and cancer-causing propoerties of products and chemicals in the oil refining and petrochemical industry, Part XV, Health hazards and health risks from oxygenated automotive fuels (MTBE): Lessons not heeded. Int. J. Occup. Med. Toxicol. 4:1-16.

Melnick, R.L., Kohn, M.C., and Portier, C.J., 1996, Implications for risk assessment of suggested nongenotoxic mechanisms of chemical carcinogenesis. Environ. Health Perspect.104 (Suppl. 1):123-134.

Mohr, S.N., Fiedler, N., Weisel, C., and Kelly-McNeil, K., 1994, Health effects of MTBE among New Jersey garage workers. Inhal. Toxicol. 6:553-562.

Moolenaar, R.L., Hefflin, B.J., Ashley, D.L., and Etzel, R.A., 1994, Methyl tertiary butyl ether in human blood after exposure to oxygenated fuels in Fairbanks, Alaska. Arch. Environ. Health 49:402-409.

National Research Council (NRC), 1996, Toxicological and performance aspects of oxygenated motor vehicle fuels. National Academy Press, Washington, DC.

National Science and Technology Council (NSTC), 1996, Interagency assessment of potential health risks associated with oxygenated gasoline. NSTC, Washington, DC.

National Toxicology Program (NTP), 1995, Toxicology and carcinogenesis studies of t-butyl alcohol (CAS No. 76-65-0) in F344/N rats and B6C3F1 mice (drinking water studies). Research Triangle Park, NC: National Institutes of Health; Technical Report Series No. 436, NIH Publication No. 94-3167.

Neeper-Bradley, T.L., Tyl, R.W., Fisher, L.C., Tarasi, D.J., Fait, D.L., Dodd, D.E., Pritts, I.M., Panson, R.S., and Ridlon, S.A., 1990/1989, Developmental toxicity study of inhaled methyl tertiary butyl ether (MTBE) in New Zealand White rabbits and CD-1 mice [abstract] Society of Toxicology, 1990; and Bushy Run Research Center Project Reports 51-628 and 52-526,1989.

Neeper-Bradley, T.L., 1991, Final report: Two-generation reproduction study of inhaled methyl tert-butyl ether in Sprague-Dawley rats. Bushy Run Research Center, Export, PA.

Nelson, B.K., Brightwell, W.S. MacKenzie, D.R., Khan, A., Burg, J.R., Weigel, W.W., and Goad, P.T., 1985, Teratological assessment of methanol and ethanol at high inhalation levels in rats. Fundam. Appl. Toxicol. 5:727-736.

Poet, T.S., Murphy, J.E., and Borghoff, S.J., 1996, In vitro uptake of methyl t-butyl ether (MTBE) in male and female rat kidney homogenate: solubility and protein interactions. Toxicologist 30:305 (abstract).

Prah, J., Goldstein, G., Devlin, R., Otto, D., Ashley, D., House, D., Cohen, K., and Gerrity, T., 1994, Sensory, symptomatic, inflammatory and ocular responses to and the metabolism of methyl tertiary butyl ether in a controlled human exposure experiment. Inhal. Toxicol. 6:521-538.

Prescott-Mathews, J.S., Wolf, D.C., Wong, B.A., and Borghoff, S.J., 1996, Methyl tert-butyl ether (MTBE)-induced protein droplet nephropathy and cell proliferation in male F-344 rats. Toxicologist 30:304 (abstract).

Robinson, M., Bruner, R.H., and Olson, G.R., 1990, Fourteen- and ninety-day oral toxicity studies of methyl tertiary-butyl ether in Sprague-Dawley rats. J. Am. College Toxicol. 9:525-540.

Soffritti, M., Maltoni, C., Maffei, F., and Biagi, R., 1989, Formaldehyde: an experimental multipotential carcinogen. Toxicol. Ind. Health 5:699-730.

Swenberg, J.A. and Dietrich, D.R., 1991, Immunohistochemical localization of α2u-globulin in kidneys of treated and control rats of a 13-week vapor inhalation study undertaken with methyl tertiary butyl ether (MTBE). Report to the MTBE Health Effects Testing Task Force.

Til, H.P., Woutersen, R.A, Feron, V.J., Hollanders, V.H.M., Falke, H.E., 1989, Two-year drinking water study of formaldehyde in rats. Food Chem. Toxicol. 27:77-87.

U.S. Environmental Protection Agency (USEPA),1991, Alpha 2u-globulin: association with chemically induced renal toxicity and neoplasia in the male rat. Risk Assessment Forum. EPA/625/3-91/019F. USEPA, Washington, DC.

U.S. Environmental Protection Agency (USEPA), 1992, Alternative fuels research strategy. Office of Research and Development. EPA/600/AP-92/002. USEPA, Washington, DC.

U.S. Environmental Protection Agency (USEPA), 1995, Workshop panel report on developing guidelines on the feasibility and design of epidemiologic studies among populations exposed to MTBE. Research Traingle Park, NC: National Health and Environmental Effects Research Laboratory; December 1995.

White, M.C., Johnson, C.A., Ashley, D.L., Buchta, T.M., and Pelletier, D.J., 1995, Exposure to methyl tertiary butyl ether from oxygenated gasoline in Stamford, Connecticut. Arch. Environ. Health 50:183-189.

SUPPLEMENTAL REFERENCES

(The following papers related to the health effects of MTBE were published subsequent to the preparation of this report and may be of interest to the reader.)

Bird, M.G., Burleigh-Flayer, H.D., Chun, J.S., Douglas, J.F., Kneiss, J.J., Andrews, L.S., April, 1997, Oncogenicity studies of inhaled methyl tertiary-butyl ether (MTBE) in CD-1 mice and F-344 rats, J. Appl. Toxicol. 17(S1): S45-S55.

Casanova, M., Laethem, C., d'A Heck, H., 1997, Lack of evidence for the involvement of formaldehyde in the hepatocarcinogenicity of methyl-t-butyl ether (MTBE), Fund. Appl. Toxicol., 36:339 (abstract).

Hutcheon, D.E., Arnold, J.D., ten Hove, W., Boyle, J. 3rd, 1996, Disposition, metabolism, and toxicity of methyl tertiary-butyl ether, an oxygenate for reformulated gasoline, J. Toxicol. Environ. Health 47:453-464.

Mackerer, C.R., Angelosanto, F.A., Blackburn, G.R., Schreiner, C.A., 1996, Identification of formaldehyde as the metabolite responsible for the mutagenicity of methyl tertiary-butyl ether in the activated mouse lymphoma assay. Proc. Soc. Exp. Biol. Med. 212:338-341.

Moser, G.J., Wong, B.A., Wolf, D.C., Fransson-Steen, R.L., Goldsworthy, T.L., 1996, Methyl tertiary butyl ether lacks tumor promoting activity in N-Nitrosodiethylamine-initiated B6C3F1 female mouse liver. Carcinogenesis 17:2753-2761.

Prescott-Mathews, J.S., Wolf, D.C., Wong, B.A., Borghoff, S.J., 1997, Methyl tert-butyl ether causes α2u-globulin nephropathy and enhanced renal cell proliferation in male Fisher-344 rats. Toxicol. Appl. Pharmacol. 143:301-314.

Abbreviations and Terms

ABBREVIATIONS AND TERMS

ABS	chromosome aberrations
A/F	air/fuel
AK	Alaska
API	American Petroleum Institute
AQIRP	Air Quality Improvement Research Program
AST	aboveground storage tank
ASTM	American Society for Testing and Materials. An independent organization with members from industry, government and academia, as well as private citizens.
Auto/Oil AQIRP	Auto/Oil Air Quality Improvement Research Program
BTEX	benzene, toluene, ethylbenzene, and xylenes
Btu	British thermal unit
CAA	Clean Air Act
CARB	carbureted
CARB	The California Air Resources Board
CFR	Code of Federal Regulations
CIIT	Chemical Industry Institute of Toxicology
CL	closed loop
CNS	central nervous system
CO	carbon monoxide
CO_2	carbon dioxide
Complex Model	EPA model developed for use by vehicle manufacturers and petroleum refiners to predict the effects of fuel formulations on primarily 1990 technology vehicle emissions
CT	Connecticut
CWA	Clean Water Act
DIPE	diisopropyl ether
DNA	deoxyribonucleic acid
EC_{50}	median effective concentration
Emission level	FTP measure of mass emission in grams per mile (g/mi)
EPA	The U. S. Environmental Protection Agency
ETBE	ethyl *tertiary*-butyl ether, a fuel oxygenate
EtOH	ethanol
exceedance	jargon, meaning an air pollution event in which the ambient concentration of a pollutant exceeds the EPA NAAQS
FOB	Functional Observational Battery
FTP	Federal Test Procedure, a standard procedure for measuring vehicle exhaust emissions at 75 °F
gal	gallon
gasoline	Fuel sold for use in spark ignition, internal combustion engines (including motor vehicles). It is a volatile mixture of liquid hydrocarbons that may or may not contain "oxygenates" and very small amounts of additives that are designed to preserve fuel quality and prevent engine deposits.

GC/MS	gas chromatography/mass spectrometry
Gd	gestation days
GM	General Motors
g/mi	grams of pollutant per vehicle mile
h	hour
HC	hydrocarbon
HEI	Health Effects Institute
IL	Illinois
I/M	Inspection and Maintenance
i.v.	intravenous
kg	kilogram
L	liter
LC_{50}	median lethal concentration
MeOH	methanol
μg	microgram
mg	milligram
mi	mile
min	minute
mL	milliliter
mph	miles per hour
MOBILE Model	EPA model developed for use by states for predicting vehicle emission inventories and the effects of emission control programs
MPFI	multi-port fuel injection
MT	Montana
MTBE	methyl *tertiary*-butyl ether, a fuel oxygenate
MY	model year (of vehicle)
NAWQA	National Water Quality Assessment
NY	New York
NAAQS	National Ambient Air Quality Standard
NO	nitric oxide
NPDES	National Pollution Discharge Elimination System
nonoxygenated gasoline	Gasoline that contains no measurable oxygenates or oxygenates at very low levels due to commingling during distribution and storage.
NO_x	nitrogen oxides (NO and NO_2)
NRC	National Research Council
NSTC	National Science and Technology Council
NTP	National Toxicology Program
OC	oxidation catalysts
OL	open loop
oxygenated gasoline	Gasoline that contains oxygenates. For oxygenated gasoline programs to reduce carbon monoxide (CO) pollution, the minimum oxygen content is typically 2.7 weight percent.

oxygenates	Compounds containing oxygen (alcohols and ethers) that are added to fuels to increase its oxygen content. Lawful use of these substances as components of gasoline requires that they either be “substantially similar” under section 211(f)(1) of the Clean Air Act or approved under a waiver granted under section 211(f)(4) of the Clean Air Act. Methyl tertiary butyl ether (MTBE) and ethanol are the most common oxygenates currently used, although there are a number of other possible oxygenates.
ppbv	parts per billion by volume
ppm	parts per million
ppmv	parts per million by volume
psi	pounds per square inch, pressure
RFG	Reformulated gasoline. Specially formulated fuels developed to minimize vehicle emissions of ozone-forming and toxic air pollutants and improve air quality. RFG contains, on average, a minimum of 2.0 weight percent oxygen.
rpm	revolutions per minute.
RVP	Reid vapor pressure, fuel vapor pressure (Psi) at 100 °F
SCE	sister chromatid exchange
TA	*tertiary*-butyl alcohol
TAEE	*tertiary*-amyl ethyl ether, a fuel oxygenate
TAME	*tertiary*-amyl methyl ether, a fuel oxygenate
TAP	toxic air pollutants (benzene, 1,3-butadiene, formaldehyde, acetaldehyde, and polycyclic organic matter)
TBA	*tertiary*-butyl alcohol
TBF	*tertiary*-butyl formate
TBI	throttle body fuel injection
TRI	Toxics Release Inventory
TWO	three-way catalysts
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
UST	underground storage tank
VOC	volatile organic compound
WI	Wisconsin
wt	weight
yr	year

For additional copies or information contact:

Additional copies of the "Interagency Assessment of Oxygenated Fuels" can be requested through GCRIO User Services:

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