

Health and Environmental Assessment of MTBE: The California Perspective

Arturo A. Keller
Bren School of Environmental Science and Management
University of California, Santa Barbara, CA 93106

Introduction

Methyl tert-Butyl Ether (MTBE) was first added to gasoline in Europe in 1973 to replace lead as an anti-knocking agent and as an octane enhancer (CAL-EPA, 1998). U.S. EPA approved it as a blending component in the U.S. in 1979, to eliminate the use of leaded gasoline. Typical MTBE levels used by refiners were around 2-3% by volume, blended in different proportions to achieve performance standards.

Oxygenated gasoline was introduced in some areas during the wintertime to reduce carbon monoxide (CO) concentrations. Oxygenates are gasoline additives which contain one or more oxygen atoms, to improve the combustion process. Denver, Colorado, was the first air basin to use oxygenated gasoline in the winter of 1988. In 1989, three domestic automakers and 14 oil companies established the Auto/Oil Air Quality Improvement Research Program (AQIRP), a six-year study to develop a database on the effects of different fuel compositions and vehicle fleet improvements on emission of pollutants into the atmosphere (AQIRP, 1997). The AQIRP study sought to evaluate the impact of different blends and additives on emissions, through a series of controlled tests.

The preliminary results of the AQIRP study were used to develop Section 211 of the 1990 Clean Air Act Amendments (CAAA), which set specific requirements in terms of fuel composition and performance, including a requirement that gasoline sold in specific air quality non-attainment areas be reformulated to contain at least 2.0 percent oxygen by weight, in the form of an oxygenated compound such as MTBE or ethanol leaving it up to the oil companies to decide how they would meet this requirement (42 U.S.C. Section 7409). This new gasoline formulation has been denominated Federal Reformulated Gasoline (RFG).

In 1991, the California Air Resources Board (CARB) staff proposed a set of regulations to reformulate gasoline sold in California to slightly different requirements than indicated in the Federal CAAA, based on an Agreement in Principle reached in August, 1991 (CARB, 1991). These regulations were adopted in 1996 (CCR, 1996), and the new gasoline was denominated California RFG Phase 2 (CaRFG2). The South Coast Air Basin, Ventura County and San Diego Air Basin were identified in 1990 as non-attainment areas based on their monitoring results from the late 1980s, and were thus required to begin selling CaRFG2 starting in January 1, 1995. State law required that all gasoline sold in California meet the CaRFG2 requirements as of June 1, 1996. A comparison of average properties for "conventional" gasolines sold in the U.S. with respect to the Federal RFG and CaRFG2 requirements are presented in Table 1.

Aromatics refers to hydrocarbons with one or more benzene rings (e.g. benzene, toluene), naturally present in crude oil. Although these compounds are desired from a combustion

perspective due to their higher octane rating, the results of the AQIRP study indicated that lowering aromatics can significantly reduce the emissions of hydrocarbons (HC) in newer vehicles (1989 and newer), both in exhaust emissions and evaporative losses throughout the fuel distribution system. Reducing aromatics also decreases carbon monoxide (CO) emissions. In addition, since aromatics are considered toxic substances, reducing the amount of aromatics has a significant effect on reducing the toxicity of the emissions (AQIRP, 1990, 1991a,b,c).

Table 1. Gasoline Properties for Conventional and Reformulated Gasolines

Property	Conventional	Federal RFG	CaRFG2 with MTBE
Aromatics, (vol. %)	32.0	max. 25	max. 25.0
Olefins, (vol. %)	9.2	N.S.*	max. 10.0
Benzene, (vol. %)	1.53	max. 1.0	max. 1.0
Oxygen content (%)	0	2.0-2.7	1.8-2.7
Sulfur (ppm by weight)	339	?	max. 40
Reid Vapor Pressure (psi)	8.7	max. 7.2	max. 7.0
T90, °F	330	N.S.	max. 300
T50, °F	218	N.S.	max. 210

*N.S. = not specified

Olefins refers to double bond hydrocarbons, also present in crude oil. Reducing olefin content in gasoline results in a modest decrease in HC emissions, little or no effect on CO or nitrogen oxides (NO_x) emissions, but significantly reduces the atmospheric reactivity of the emissions, which results in a decrease in ozone formation in urban environments (AQIRP, 1990, 1991a,b,c).

Benzene is specifically targeted in both the 1990 Federal CAAA and in the State of California regulations, given its known carcinogenicity (ATSDR, 1991). Although the AQIRP study did not specifically evaluate the effect of decreasing only benzene on air emissions, the effect is similar to the overall effect of reducing aromatics, and the expected result is a lowering of unburned benzene emissions.

The AQIRP study evaluated the addition of several oxygenates, which refers to organic chemicals that contain one or more oxygen atoms in their structure. Crude oil contains only trace amounts of these chemicals, so they must be added to refined gasoline to increase the oxygen content of gasoline. Some of the oxygenates come from renewable resources, such as ethanol from corn and other agricultural products, while other such as MTBE are synthetically produced from fossil fuels. In addition to improving the combustion process and thus reducing CO in tailpipe emissions, some oxygenates improve the octane rating of gasoline. For example, the octane rating of pure MTBE is 110, while the octane rating of pure ethanol is 115. These oxygenates can be blended with refined gasoline to produce a higher octane product, which results in better vehicle performance.

Adding MTBE to gasoline to meet the oxygen content requirement reduces both CO and HC emissions, slightly increases NO_x emissions and has a negligible effect on the emission of benzene, 1,3-butadiene, formaldehyde and acetaldehyde, which are toxic compounds typically

present as products of incomplete combustion of gasoline. It also has an insignificant effect on reducing peak ozone concentrations (AQIRP, 1990, 1991a,b,c,d, 1992a, 1995a). Addition of ethanol to gasoline at approximately 10% by volume produced similar results as MTBE addition (at 15% by volume) in terms of CO, exhaust HC, and NO_x. Ethanol addition increased the evaporative emission of HCs due to the higher volatility of the ethanol/gasoline mixture, and also resulted in higher formaldehyde and acetaldehyde emissions than unblended gasoline (AQIRP, 1991d). Ambient temperatures below 50 °F result in a decrease effectiveness of either MTBE or ethanol in reducing CO emissions (Most, 1989; Lax, 1994). Increasing altitude also has the effect of reducing the beneficial effect of oxygenates with respect to the reduction of CO (Most, 1989).

Field studies in Denver, Colorado using remote sensing devices evaluated the effect of using gasoline with different oxygen content on CO emissions (Bishop, 1989, 1990). The first study evaluated the use of gasoline with 1.5 wt % oxygen content, which resulted in a reduction of $6 \pm 2.5\%$ in CO emissions during hot, stable operating mode conditions, comparing the emissions during and after the wintertime oxygenated fuel program. The second study during the 1988-89 wintertime program in Denver, when 2.0 wt % gasoline was used, found a decrease of $16 \pm 3\%$ in CO emissions.

Sulfur is present in various organic and inorganic compounds that are naturally present in fossil fuels. When these compounds are oxidized in the combustion process, sulfur dioxide is formed, which is a precursor to acid rain. It is thus desirable to reduce sulfur from fossil fuels before the combustion process. In addition, sulfur compounds affect the activity of the catalytic converters used in vehicles to reduce CO and HC emissions, reducing the life of these control devices. Reducing the sulfur content of gasoline also reduces HC, CO, NO_x emissions, and it reduces the formation of ozone in urban environments (AQIRP, 1991e, 1992b, 1995b; Mayotte et al., 1994).

Reid Vapor Pressure (RVP) is a measure of the volatility of gasoline and is measured in pounds per square inch (psi). RVP is a strong function of temperature, increasing sharply as temperature increases. Thus, during hot summer days there is a higher volatilization rate for gasoline during fueling operations as well as from the fuel distribution systems. The AQIRP study showed that decreasing the RVP by 1 psi (from 9 to 8 psi) decreased fuel evaporative emissions by 4%. CO emissions were also reduced by reducing RVP, and the predicted ozone peak concentrations would also decrease under these conditions (AQIRP, 1991e). However, during cold days gasoline must have enough volatility to vaporize in the combustion chambers of the internal combustion engine, so gasoline manufacturers need to produce a gasoline with a minimum RVP to achieve adequate vehicle performance during cold starts.

The various hydrocarbons that compose a gasoline will evaporate from gasoline at different temperatures. At low temperatures the most volatile components are evaporated, while at high temperatures (e.g. greater than 300 °F) only the very heavy components remain. One way to characterize a gasoline is its distillation curve, which refers to the various fractions that remain at different temperatures. For example, T10 refers to the temperature at which 10% of the gasoline will have evaporated, T50 refers to the temperature at which 50% of the gasoline will have evaporated, and T90 refers to the temperature at which 90% of the gasoline has evaporated. The AQIRP results indicate that RVP and T10 are strongly correlated in their effects (AQIRP, 1991d). Reducing T50 or T90 reduces the overall HC emissions, but may result in slight increases in overall CO and NO_x emissions. Peak ozone concentrations should also decrease if T50 or T90 are decreased.

Given the preliminary results of the AQIRP studies outlined above, the CARB proposal for CaRFG2 was clearly a step in the right direction, limiting the levels of aromatics (and specifically benzene), olefins, sulfur, RVP, T50 and T90. Oxygen content also was justified by CARB based on the predicted beneficial effect of reducing CO emissions. CARB allowed some flexibility to gasoline manufacturers in terms of meeting the requirements for CaRFG2 using either a flat limit (shown in Table 1) or using an annual averaging formula, with specific maximum values for each property.

Further work by the AQIRP after the preliminary results were published tested an additional formulation, denominated C1, which meets all the CaRFG2 requirements except that it does not contain any oxygenate (AQIRP, 1995a). The objective was to evaluate a gasoline formulation that could achieve the emissions requirements of CaRFG2, considering in addition the advances in motor vehicle technology, without the need to add MTBE or ethanol. Table 2 compares the properties of typical CaRFG2 using MTBE as the oxygenate, and C1.

Table 2. Gasoline Properties for Commercial CaRFG2 and C1¹

Property	CaRFG2 with MTBE	C1
Aromatics, (vol. %)	25	22.7
Olefins, (vol. %)	4.1	4.6
MTBE, (vol. %)	11.2	0
Benzene (vol. %)	0.93	0.94
Sulfur (ppm)	31	38
RVP (psi)	6.8	6.9
T10 (°F)	142	142
T50 (°F)	202	208
T90 (°F)	293	297
Net Heating Value (Btu/lb)	18,091	18,596

¹based on AQIRP study (1995a)

As indicated in the AQIRP report (1995a), the C1 formula resulted in essentially the same emissions reductions for HC, CO, NO_x and benzene as commercial CaRFG2 with MTBE. Similar reductions were obtained from C1, compared to CaRFG with MTBE, in the reactivity of the emissions that can contribute to ozone formation in urban environments, and a statistically significant reduction in the production of formaldehyde in the combustion engine. These results were tested for vehicles with different emissions control technologies from 1989 to 1995, with essentially no difference between the results of using C1 compared to using CaRFG2. There is a slight gain in fuel efficiency for C1 relative to commercial CaRFG2 with MTBE due to the higher net heating value of C1.

Estimating the air quality benefits of using CaRFG2, with or without MTBE, relative to conventional gasoline is complicated since the calculation depends on multiple factors, including but not limited to:

- combustion efficiency of the motor vehicle's engine
- fuel system technology (e.g. carburetor vs. fuel injection, type of catalytic converter)

- mechanical condition of the motor vehicle fleet
- driving patterns
- meteorological conditions (e.g. temperature, precipitation, wind, thermal inversions)
- differential sensitivity of various population groups to ambient air concentrations
- human activity patterns (e.g. indoor vs outdoor activities)

Based on the review of the air quality impacts of RFG by Koshland et al. (1998), any CaRFG2 formulation (with MTBE, ethanol or non-oxygenated) is expected to decrease the atmospheric concentrations of two criteria pollutants, ozone and carbon monoxide, as well as two air toxics, benzene and 1,3-butadiene. Of these four pollutants, benzene has the most direct impact on human health (ATSDR, 1991; IARC, 1985). Benzene can increase the incidence of leukemias and is classified as a group A carcinogen (known human carcinogen). Koshland et al. (1998) found that in comparison to conventional gasoline, RFGs show significant improvement on several measures of air quality. Emissions of carbon monoxide, volatile organic compounds, and nitrogen oxides are reduced with CaRFG2 as compared to conventional gasoline. Vehicle emission control technology, especially improvements in newer cars, also significantly reduce emissions of air pollutants and their precursors. MTBE and other oxygenates were found to have no significant effect on exhaust emissions from advanced technology vehicles. There is no statistically significant difference in the emissions reduction of benzene between oxygenated and non-oxygenated RFGs that meet all other CaRFG2 standards. Thus, there is no significant additional air quality benefit to the use of oxygenates such as MTBE in reformulated gasoline, relative to alternative CaRFG2 non-oxygenated formulations.

As a result of the 1990 Federal CAAA and the subsequent state laws to comply with the federal mandate, approximately 30% of gasolines currently used in the U.S. contain a percentage of oxygenates for air quality improvement programs (NSTC, 1997), with the East and West coasts using mostly MTBE and the Midwest using mostly ethanol to meet the oxygen content requirement in non-attainment areas. Most of the gasoline sold in California contains MTBE, at a level of 11% by volume (CAL-EPA, 1998). This has resulted in a major increase in MTBE consumption, rising from around 180 million gallons per year in 1980 to more than 4 billion gallons per year in 1997, and has become one of the highest volume production chemicals in the U.S. in 1997. MTBE production in the U.S. represents around 70% of the demand, with an additional 30% imported mainly from producers in the Middle East. California currently uses approximately 1.5 billion gallons of MTBE per year, with local production representing only about 12% of local demand. Around 80% of U.S. MTBE production is located in Texas (Wiley, 1998).

It is thus not surprising that we would find MTBE in the environment. Although there was some evaluation of the toxicology of MTBE prior to its large-scale introduction, there was apparently no major concern that a highly soluble, persistent chemical could threaten water supplies. The expected air quality benefits to be derived from the use of MTBE in CaRFG2 would soon cause major costs in water contamination and treatment.

Cost and Extent of Water Contamination

There are significant risks and costs associated with water contamination due to the use of MTBE. MTBE is highly soluble in water and will transfer readily to groundwater from gasoline leaking from underground storage tanks, pipelines and other components of the gasoline distribution system. In addition, the use of gasoline containing MTBE in motor boats, in particular those using older 2-stroke engines, results in the contamination of surface water reservoirs. It is clear we are placing our limited water resources at risk by using MTBE. MTBE has been detected in several water supply systems, which have shut down the contaminated sources, resorting to alternative supplies or treatment. Since both groundwater wells and surface water reservoirs have been contaminated, alternative water supplies may not be an option for many water utilities. If MTBE continues to be used at current levels and more sources become contaminated, the potential for regional degradation of water resources especially groundwater basins, will increase.

Despite federal and state programs (CCR, 1994) to improve handling of gasoline and other fuels in pipelines, underground and above ground storage tanks and truck transport, gasoline spills still occur. In addition, uncombusted fuel is also spilled from boats and recreational equipment directly into surface waters which may be water supply reservoirs. The result is that MTBE is the second most frequently VOC detected in shallow groundwater (Squillace et al., 1996), based on the National Water Quality Assessment program of the USGS. A review by Lawrence Livermore National Laboratory (LLNL) researchers (Happel et al., 1998) found that out of 236 leaking underground fuel tank (LUFT) sites in their database, 78% reported detectable levels of MTBE and 74% had concentrations exceeding the 5 $\mu\text{g/L}$. A significant fraction (> 70%) had concentrations above 20 $\mu\text{g/L}$. Other studies have shown that out of 412 LUFT sites, 77% report the presence of MTBE (Buscheck et al., 1998).

In addition to detection of MTBE at LUFT sites, the California Department of Health Services (CAL-DHS) has implemented a monitoring and reporting program for public water utilities (CAL-DHS, 1998). Results to date indicate that out of 11,800 drinking water sources in California, 3,173 had sampled for MTBE as of July 6, 1998. Only 46 sources had detectable levels of MTBE. Twenty of the 46 water sources with MTBE were surface water reservoirs, with seven presenting concentrations greater than 5 $\mu\text{g/L}$. Of the 26 sources that are supplied from groundwater aquifers, ten had concentrations greater than 5 $\mu\text{g/L}$. Some communities, such as the City of Santa Monica, CA, have been forced to use alternative sources of drinking water due to the contamination of a significant fraction of their regular water supply (Rodriguez, 1998), effectively shutting down 70% of their groundwater sources.

MTBE has been detected in industrial stormwater (Butillo et al, 1993) at relatively high concentrations, requiring treatment. It has also been detected in urban stormwater (Lopes et al., 1996) at concentrations from 1.0 up to 4.2 $\mu\text{g/L}$, with a median of 1.5 $\mu\text{g/L}$ for 40 samples taken from cities and metropolitan areas which used MTBE in gasoline (NSTC, 1997). Uncombusted MTBE from auto exhaust emissions can disperse through the atmosphere and eventually transfer to rain and surface waters. Equilibrium partitioning between the atmospheric concentration and the concentration in precipitation occurs rapidly. Ambient concentrations of MTBE in areas which have introduced RFG with MTBE range from 0.3 to 28 ppbv, with median values ranging from 0.85 to 4.6 ppbv (Bishop et al., 1994). Concentrations within the perimeter of gas stations range from 1 to 140 ppbv, with a range in median values of 3 to 14 ppbv (Johnson et al., 1995).

Gasoline station customers and pump attendants may be exposed to concentrations as high as 780 ppbv even when Stage II vapor recovery systems are used, although for a short period of time. Atmospheric concentrations of MTBE in California, as monitored by CARB through the various air quality management districts (NSTC, 1997), are typically only up to 0.13 to 4.6 ppbv, which would result in an equilibrium concentration in water of less than 5 µg/L (Cohen et al., 1998; NSTC, 1997). Precipitation near the immediate vicinity of a gas station may have much higher concentrations, but it would probably be diluted before it reaches large surface water bodies or it infiltrates into the subsurface. Precipitation would take approximately 5-10 years to reach the water table in most regions of California (NSTC, 1997), although at concentrations of 5 µg/L or less. Mixing in the aquifer would dilute this concentration further. These estimates point to LUFTs as the primary source of MTBE in groundwater.

Given their high solubility, MTBE, ethanol and other oxygenates are quite mobile in the environment (Squillace et al., 1997; Landmeyer et al., 1998; Pankow et al., 1996). This presents significant issues when considering the fate and transport of these pollutants, as well as treatment options. These compounds move essentially at the same rate as groundwater flow, with practically no retardation due to sorption. Chemical transformation via hydrolysis is very slow and is not expected to be a major removal process for MTBE. Initial studies indicate that biodegradation of MTBE in the environment is slow (Borden et al., 1997; Mormile et al., 1994; Suflita et al., 1993; Steffan et al., 1997; Mo et al., 1997; Yeh and Novak, 1994), but these results may depend on soil and groundwater conditions. However, the relatively rapid detection of MTBE contamination at so many monitoring wells at LUFT sites since the wide spread introduction of MTBE indicates that it is relatively persistent under normal environmental conditions and natural biodegradation is unlikely to be a major removal process.

There are several health concerns regarding MTBE (Froines et al., 1998). CAL-EPA has recently proposed a Public Health Goal (PHG) for MTBE of 14 ppb (CAL-EPA, 1998), based on a review of the available data on carcinogenicity of MTBE in animals. Given the necessary extrapolation from high-dose animal studies to low-dose human response, the PHG has an uncertainly factor of 1000, to ensure the protection of human health. This means that if the data from the available studies was directly extrapolated, one would need to drink water at a concentration of 14,000 µg/L for 70 years to increase the probability of cancer by one in a million, which is generally considered an "acceptable" risk (USEPA, 1996; CAL-DHS, 1985). However, taste and odor studies, have shown that a few individuals can detect MTBE in water at levels as low as 2 µg/L. This has prompted CAL-DHS to propose a secondary drinking water standard, based on taste and odor, of 5 µg/L (CAL-DHS, 1997).

The annualized cost of treating MTBE-contaminated surface and ground waters in California is estimated to be on the order of \$340 to \$1,480 million, relative to the cost that would have incurred if conventional gasoline had been used (Keller et al., 1998a). The major treatment cost is the clean-up of Underground Storage Tank (UST) leaks, which is expected to cost from \$330 to \$1,400 million above the cost that would have been incurred if conventional gasoline without MTBE had been used. The groundwater remediation cost includes the legacy of older leaking USTs that stored gasoline with MTBE, which will cost from \$320 to \$1,030 million per year to remediate, relative to conventional gasoline leaks. The projected cost of future leaks of MTBE from upgraded USTs is between \$7 million and \$370 million, relative to conventional gasoline. Treatment costs are based on a thorough review and experimental work on treatment technologies (Keller et al., 1998b).

Based on the information from Fogg et al. (1998), there are an estimated 350 active UST sites in California that have not been upgraded and are likely to have MTBE at levels which will impact groundwater. There are an estimated 3,270 groundwater sites with detectable levels of MTBE, that have not yet been remediated, and it is likely that 2,100 of these sites (64%) will have MTBE concentrations greater than 100 ug/L. These sites represent the remediation backlog of the use of MTBE and the older UST technology that must be remediated in the next few years.

In addition, there are approximately 54,500 active tanks used for petroleum products (including gasoline, diesel, jet fuel, fuel oil, solvents, etc.), and an estimated 75-80% of these contain gasoline, or 41,000 to 44,000 tanks (EPA Office of Underground Storage Tanks, 1998). The annual failure rate for older tanks is around 2.7%, but the failure rate for upgraded tanks is estimated to be lower (Couch and Young, 1998), in the range from 0.07 to 2% per year, resulting in 30 to 880 new UST failures per year. The large uncertainty in this estimate reflects the unknown performance of upgraded USTs. If the technological improvements in leak prevention, detection and monitoring prove successful, the future number and size of gasoline leaks, leaks from these systems could result in very low annual costs, reducing the cost of using MTBE; the high estimate is based on current failure rates of underground tanks.

Exposure Risk

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

Cost-Benefit Analysis

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

gasoline would result in much lower risk to water supplies, lower water treatment costs in the event of a spill of either of these alternative RFG formulations, and lower monitoring costs.

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

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

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

Policy Recommendations

During the transition phase, a number of policies are suggested to reduce the cost of using MTBE while protecting water supplies (Keller et al., 1998c). These policies are:

1. Restrict the use of CaRFG2 with MTBE to ozone non-attainment areas during the summer months. It is recommended that CARB review the length of the ozone summer season for those air basins in non-attainment, to limit as much as possible the use of CaRFG2 with oxygenates.
2. Obtain a waiver of the Federal requirement that RFG sold in California have an oxygen content, via the passage of HR Bill 630 and Senate Bill 1576. This will allow the sale of non-oxygenated CaRFG2 in all areas.

3. Recommend that CARB facilitate promotion of the production and distribution of non-oxygenated CaRFG2 in all attainment areas as well as during the non-summer season in non-attainment areas.
4. Promote the accelerated removal of older, high emitting motor vehicles through the use of industrial emissions off-sets or a fund created by an appropriate tax. This program would be significantly more cost-effective than mandating the use of oxygenates in fuels in reducing air pollutant emissions. An aggressive program aimed at gross CO polluters would be a cheaper and less risky option than using oxygenates.
5. Maintain the Underground Storage Cleanup Fund Program, possibly beyond the year 2005 to cover the costs of MTBE cleanup, with a review in 3 years to determine the effectiveness of upgraded underground storage tank systems in reducing the rate of failures, and thus the potential to reduce the annual fees.
6. Where contamination of groundwater by MTBE is known or suspected, evaluation of plume extent and potential threats to drinking-water supply wells should be carried out immediately. Plume containment, remediation, or other corrective actions should then proceed soon as possible to reduce risk and costs.
7. Require the adoption of Best Management Practices for surface water reservoirs, following the lead of the Santa Clara Valley Water District.
8. Establish specific emissions requirements for motor boat engines, in particular with respect to emissions of unburned fuel. Promote legislation with incentives to phase out motor boat engines that do not meet emissions requirements.
9. Assess the environmental impacts of using other oxygenates such as ethanol. It must be stressed, however, that there are potential adverse health effects associated with incomplete combustion products of ethanol, and further study of combustion byproducts and potential health effects of such products is required before substitution of ethanol for MTBE on a large scale can be recommended. If ethanol is found to both improve air quality, provide a net energy savings, and have minimal environmental impacts, then increase the availability of ethanol as a potential oxygenate by increasing the use of agricultural wastes such as rice straw for ethanol production. This also would reduce the emissions from burning the rice straw. The increase in this program could cost \$22 million per year, which can be funded through reductions in the cost of monitoring and enforcing the ban of rice straw burning.
10. The State should invest in a long-term research program, using the enormous base of expertise available in California's universities and professional organizations, to determine the toxicological effects of untested industrial products that will be used in large amounts. Such research should, for example, examine effective alternatives for motor vehicle fuels, and develop more cost-effective remediation and treatment technologies. The current structure of State Agencies, which focus on specific media

(land, air, water), leads to fragmented and incomplete environmental impact assessments. Any new large-scale programs in California should be preceded by an independent Environmental Impact Assessment, rather than an *a posteriori* evaluation of the consequences.

The full report of the UC Toxic Substances Research and Teaching Program study mandated by the California Legislature under Senate Bill 521 can be obtained from www.tsrtp.ucdavis.edu/mtberpt. The author wishes to acknowledge the contribution of many individuals to the various sections comprised in the full report, as well as the funding of this project by the UC Toxic Substances Research and Teaching Program at UC Davis.

References

- Anderson, L.G., Wolfe, P., Lanning, J.A., 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, Falls Church, VA, July 26-28, *U.S. Environmental Protection Agency Technical Report*, EPA/600/R-95/134.
- AQIRP, 1990. Technical Bulletin No.1. Initial Mass Exhaust Emissions Results from Reformulated Gasolines, *Auto/Oil Air Quality Improvement Research Program*. December 1990.
- AQIRP, 1991a. Technical Bulletin No. 3. Air Quality Modeling Results for Reformulated Gasolines in Year 2005/2010, *Auto/Oil Air Quality Improvement Research Program*. May 1991.
- AQIRP, 1991b. Technical Bulletin No. 4. Mass Exhaust Emissions Results from Reformulated Gasolines in "Older" Vehicles, *Auto/Oil Air Quality Improvement Research Program*. May 1991.
- AQIRP, 1991c. Technical Bulletin No. 5. Exhaust Emissions of Toxic Air Pollutants Using Reformulated Gasolines, *Auto/Oil Air Quality Improvement Research Program*. June 1991.
- AQIRP, 1991d. Technical Bulletin No. 6. Emissions Results of Oxygenated Gasolines and Changes in RVP, *Auto/Oil Air Quality Improvement Research Program*. September 1991.
- AQIRP, 1991e. Technical Bulletin No. 2. Effects of Fuel Sulfur Levels on Mass Exhaust Emissions, *Auto/Oil Air Quality Improvement Research Program*. February 1991.
- AQIRP, 1992a. 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*. April 1992.
- AQIRP, 1992b. Technical Bulletin No. 8. . Effects of Fuel Sulfur Levels on Mass Exhaust Emissions, Air Toxics and Reactivity, *Auto/Oil Air Quality Improvement Research Program*. February 1992.

- AQIRP, 1995a. Technical Bulletin No. 17. Gasoline Reformulation and Vehicle Technology Effects on Exhaust Emissions, *Auto/Oil Air Quality Improvement Research Program*. August 1995.
- AQIRP, 1995b. Technical Bulletin No. 18. Effects of Gasoline T50, T90 and Sulfur on Exhaust Emissions of Current and Future Vehicles, *Auto/Oil Air Quality Improvement Research Program*. August 1995.
- AQIRP, 1997. Program Final Report, *Auto/Oil Air Quality Improvement Research Program*. January 1997.
- ATSDR, 1991. Toxicological Profile for Benzene. *Agency for Toxic Substances and Disease Registry*, U.S. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA.
- Barker, J.R., Herstrom, A.A., Tingey, D.T., 1996. Formaldehyde: Environmental partitioning and vegetation exposed, *Water, Air and Soil Pollution*, 86:71-91.
- Bishop, G.A., Stedman, D.H., 1989. Oxygenated fuels, a remote sensing evaluation, *SAE Technical Paper Series* No. 891116.
- Bishop, G.A., Stedman, D.H., 1990. On-road carbon monoxide emission measurement comparisons for the 1988-1989 Colorado oxy-fuels program, *Enviro. Sci. and Technol.*, 24:843-847
- Bishop, G.A., Zhang, Y., McLaren, S.E., Guenther, P.L., Beaton, S.P., Peterson, J.E., Stedman, D.H., Pierson, W.R., Knapp, K.T., Zweidinger, R.B., Duncan, J.W., McArver, A.Q., Groblicki, P.J., Day, J.F., 1994. Enhancements of remote sensing for vehicle emissions in tunnels. *J. Air, Waste Management Association*, 44[2]:169-175.
- Borden, R.C., Daniels, R.A., LeBrun, L.E. IV, Davis, C.W., 1997. Intrinsic biodegradation of MTBE and BTEX in a gasoline-contaminated aquifer, *Water Resources Research*, 33[5]:1105-1115
- Buscheck, T.E., Gallagher, D. J., Kuehne, D.L., Zuspan, C.R., 1998. Chevron Research and Technology Company, presented at the *National Groundwater Association*, Southwest Focused Conference, June 3-4, 1998.
- Butillo, J.V., Pulido, A.D., Reese, N.M., Lowe, M.A., 1993. Removal efficiency of MTBE in water: Confirmation of a predictive model through applied technology.
- CAL-DHS, 1985. Guidelines for chemical carcinogen risk assessments and their scientific rationale. California Department of Health Services, Sacramento, California
- CAL-DHS, 1997. Proposed Regulation for a Revision to the Secondary MCL List and Revisions to Unregulated Chemical Monitoring List and Associated Requirements for Drinking Water. California Department of Health Services, Sacramento, California.
- CAL-DHS, 1998. Summary of sampling of public drinking water systems for methyl tertiary butyl ether (MTBE): covers data through June 18, 1998. Prevention Services, Division of Drinking Water and Environmental Management, *California Department of Health Services*. (<http://www.dhs.cahwnet.gov/ps/ddwem/chemicals/MTBE/mtbesummary.html>), June 1998.

- CAL-EPA, 1998. Public Health Goal for Methyl Tertiary Butyl Ether (MTBE) in Drinking Water, Pesticide and Toxicology Section, Office of Environmental Health Hazard Assessment, *California Environmental Protection Agency*. June 1998.
- CAL-EPA, 1998. MTBE (methyl tertiary butyl ether) briefing paper by the California Environmental Protection Agency. *California Environmental Protection Agency*, Sacramento, California. March 30, 1998.
- CARB, 1991. California Phase 2 Reformulated Gasoline Specifications, vol. 1. Staff Report, *California Air Resources Board*, October 1991.
- CCR, 1994. Underground Storage Tank Regulations, California Code of Regulations, Title 23, Sections 2610-2728, Effective May 5, 1994.
- CCR, 1996. The California Reformulated Gasoline Regulations, Title 13, California Code of Regulations, Sections 2250-2272. Last amended in July 2, 1996.
- Cohen, Y., Yaffe, D., Winer, A. M., Fruin, S. A., 1998. Multimedia distribution of oxygenate fuel additives, presented at the MTBE Workshop, Center for Environmental Risk Reduction, UC Los Angeles, Feb. 28.
- Couch, A., Young, T., 1998. Failure rate of Underground Storage Tanks, in *Health and environmental assessment of MTBE*, vol. 3. UC Toxics Research and Teaching Program, UC Davis.
- Dolislager, L.J., 1996. The effect of California's wintertime Oxygenated Fuels Program on ambient carbon monoxide concentrations, *J. Air, Waste Management Assoc.* 47[7]:775-783
- 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, Nov. 7-10
- Fogg, G.E., Meays, M.E., Trask, J.C., Green, C.T., LaBolle, E.M., Shenk, T.W., Rolston, D.E., 1998. Impacts of MTBE on California groundwater, in *Health and environmental assessment of MTBE*, vol. 3. UC Toxics Research and Teaching Program, UC Davis.
- Froines et al., 1998. In *Health and environmental assessment of MTBE*, vol. 2. UC Toxics Research and Teaching Program, UC Davis.
- Happel, A.M., Beckenbach, E.H., Halden, R.U., 1998. An evaluation of MTBE impacts to California groundwater resources, Report UCRL-AR-130897, *Lawrence Livermore National Laboratory*, Livermore, California. June 11, 1998.
- Johnson, T., McCoy, M., Wisbith, T., 1995. A study to characterize the air concentrations of Methyl tert-Butyl Ether (MTBE) at service stations in the Northeast. *American Petroleum Institute, Health and Environmental Sciences Dept.*, API Publication No. 4619, 75p.
- Keller, A.A., L.F. Fernandez, S. Hitz, H. Kun, A. Peterson, B. Smith, M. Yoshioka, 1998a. An Integral Cost-Benefit Analysis of Gasoline Formulations Meeting California Phase II Reformulated Gasoline Requirements, in *Health and environmental assessment of MTBE*, vol. 5. UC Toxics Research and Teaching Program, UC Davis.
- Keller, A.A., Sandall, O.C., Rinker, R.G., Mitani, M.M., Bierwagen, B.G., Michael, M.J., 1998b. Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated

- Water, in *Health and environmental assessment of MTBE, vol. 4*. UC Toxics Research and Teaching Program, UC Davis.
- Keller, A.A., J. Froines, C. Koshland, J. Reuter, I. Suffet, J. Last, 1998b. Health & Environmental Assessment of MTBE, Summary and Recommendations, in *Health and environmental assessment of MTBE, vol. 1*. UC Toxics Research and Teaching Program, UC Davis.
- Koshland, C.P., Sawyer, R.F., Lucas, D., Franklin, P., 1998. Evaluation of Automotive MTBE Combustion Byproducts, in *Health and environmental assessment of MTBE, vol. 2*. UC Toxics Research and Teaching Program, UC Davis.
- Landmeyer, J.E., Chapelle, F.H., Bradley, P.M., Pankow, J.F., Church, C.D. and Tratnyek, P.G., 1998. Fate of MTBE relative to Benzene in a Gasoline-contaminated Aquifer [1993-98]. *Ground Water Monitoring, Remediation*, in print.
- 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.
- Lopes, T.J., Delzer, G.C., Zogorski, J.S., 1996. Occurrence of the gasoline additive MTBE and BTEX compounds in urban stormwater in the United States, 1991-95. in Abstracts of the 1996 Fall Meeting of the *American Geophysical Union*, San Francisco, CA (USA), 15-19 Dec 1996.
- Mayotte, S.C., Lindhjem, C.E., Rao, V., Sklar, M.S., 1994. Reformulated gasoline effects on exhaust emissions: Phase I. Initial investigation of oxygenate, volatility, distillation and sulfur effects, *SAE Technical Paper Series No. 941973*.
- Mo, K., Lora, C.O., Wanken, A.E., Javanmardian, M., Yang, X., Kulpa, C.F., 1997. Biodegradation of methyl t-butyl ether by pure bacterial cultures, *Appl. Microbiol. Biotechnol.* 47:69-72.
- Mormile, M.R., Liu, S., Sufflita, J.W., 1994. Anaerobic degradation of gasoline oxygenates: extrapolation of information to multiple sites and redox conditions, *Environ. Science, Technol.*, 28[9]:1727-1732.
- Most, W.J., 1989. Coordinating research Council study of winter exhaust emissions with gasoline/oxygenate blends, *SAE Technical Paper Series No. 892091*.
- NSTC, 1997. Interagency Assessment of Oxygenated Fuels, *National Science and Technology Council*, June 1997.
- Pankow, J.F., Rathburn, R.E., Zogorski, J.S., 1996. Calculated volatilization rates of fuel oxygenate compounds and other gasoline-related compounds from rivers and streams. *Chemosphere*, 33[5]:921-937.
- Rodriguez, R., 1997. MTBE in Groundwater and the impact on the City of Santa Monica drinking water supply, in *Technical Papers of the 13th Annual Environmental Management and Technology Conference West*, Nov. 4-6.
- Squillace, P.J., Pankow, J.F., Korte, N.E., Zogorski, J.S., 1997. Review of the environmental behavior and fate of MTBE. *Journal of Environmental Toxicology and Chemistry*, 16[9]:1836-1844.

- Squillace, P.J., Zogorski, J.S., Wilber, W.G., Price, C.V., 1996. Preliminary assessment of the occurrence and possible sources of MTBE in groundwater in the United States, 1993-1994. *Environ. Science, Technol.*, 30[5]:1721-1730
- Steffan, R.J., McClay, K., Vainberg, S., Condee, C.W., Zhang, D., 1997. Biodegradation of the gasoline oxygenates methyl tert-butyl ether, ethyl tert-butyl ether and tert-amyl methyl ether by propane oxidizing bacteria. *Applied and Environmental Microbiology*, 63[11]:4216-4222.
- Suflita, J.M., Mormile, M.R., 1993. Anaerobic degradation of known and potential gasoline oxygenates in the terrestrial subsurface. *Environ. Science, Technol.*, 27[5]:976-978.
- U.S. EPA, 1996. Proposed guidelines for carcinogenic risk assessment. United States Environmental Protection Agency, Washington D.C., Federal Register 61[79]:17959-18011, April 23, 1996.
- USEPA, 1991. Handbook: Control technologies for hazardous air pollutants. United States Environmental Protection Agency Report EPA/625/6-91/014, Cincinnati, Ohio.
- Wiley, 1998. Clean air versus clean water: Does California need MTBE? California Senate position paper on MTBE, *California Senate Office of Research, Sacramento, California*. February 1998.
- Yeh, C.K., Novak, J.T., 1994. Anaerobic biodegradation of gasoline oxygenates in soils. *Water Environment Research*, 66[5]:744-752.