

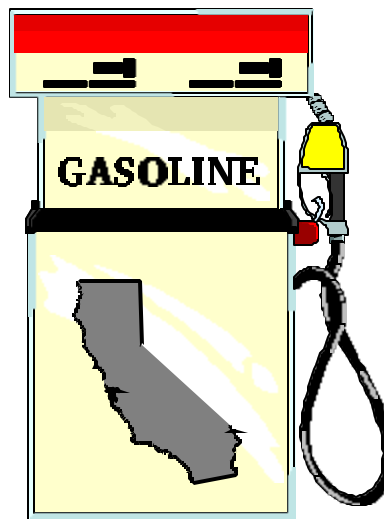
California Environmental Protection Agency



Air Resources Board

Staff Report

Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline



Release Date: November 18, 1999

**State of California
California Environmental Protection Agency
AIR RESOURCES BOARD
Planning and Technical Support Division**

Staff Report

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in California Reformulated Gasoline**

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Executive Summary

Governor Gray Davis issued Executive Order D-5-99 on March 25, 1999 calling for the removal of methyl *tertiary*-butyl ether (MTBE) from gasoline at the earliest possible date, but not later than December 31, 2002. Task 10 of the Executive Order states “the California Air Resources Board (ARB) and the State Water Resources Control Board (SWRCB) shall conduct an environmental fate and transport analysis of ethanol in air, surface water, and groundwater. The Office of Environmental Health Hazard Assessment (OEHHA) shall prepare an analysis of the health risks of ethanol in gasoline, the products of incomplete combustion of ethanol in gasoline, and any resulting secondary transformation products. These reports are to be peer reviewed and presented to the Environmental Policy Council by December 31, 1999 for its consideration.” To assist OEHHA in its health risk assessment, we conducted an analysis to estimate the changes in ambient air concentrations of potentially detrimental contaminants of exhaust and evaporative components and subsequent reaction products that would result from substituting ethanol-blended gasoline for gasoline blended with MTBE. We also included non-oxygenated gasoline in our analysis to provide a basis of comparison for the ethanol-containing gasolines. The California Energy Commission anticipates that alkylates will be used in non-oxygenated gasoline and some ethanol-containing gasolines in California to replace the octane normally provided by MTBE, so these compounds were also a focus of our analysis.

We conducted four types of analyses. First, we reviewed several recently published comprehensive assessments of the impact of oxygenated gasoline on the environment. The second type of analysis we conducted was a literature review of studies that measure the direct impact of the use of ethanol in gasoline. The third component of our study was to evaluate emission and air quality impacts from MTBE-free fuels in comparison to MTBE-containing fuel. The fourth component of our analysis is to close these data gaps as part of this study and on-going efforts that will not be complete until after the December 31, 1999 deadline in the Executive Order.

The major atmospheric loss processes for MTBE, ethanol, and alkylates are relatively slow. The major products are *tertiary*-butyl formate, formaldehyde, and methyl acetate from MTBE, acetaldehyde and PAN from ethanol, and alkyl nitrates, alcohols, and carbonyls from alkylates.

The studies of the impact of the use of ethanol-containing gasoline on air quality conducted in Denver, Albuquerque, and Brazil are not comprehensive but provide useful insight in how to design an ambient air monitoring program to directly measure the air quality impact of the MTBE phase-out. The impact on acetaldehyde concentrations is substantial only in Brazil, where the fuels contain either neat ethanol or 22 vol% ethanol. Due to the lack of RVP requirements for gasolines in Brazil, this acetaldehyde increase could be due to the addition of substantial evaporative emission, rather than strictly the result of an ethanol-for-MTBE substitution. Even with increased acetaldehyde concentrations, the observed increase in PAN concentrations was modest and well below historical levels observed in southern California.

It is possible that ethanol’s propensity to be tightly held by the activated carbon in conjunction with its hygroscopic nature may result in increased diurnal emissions. Data suggesting a reduced working capacity are somewhat conflicting in nature, which may be partially due to the difficulty in sampling ethanol. Additional research is needed in the area.

The ethanol evaporative emissions associated with a particular vehicle will depend on that vehicle's technology and the stringency of its emission standards. Flexible-fueled vehicles (FFV) in California will be controlled for their evaporative emissions of ethanol since they must be certified on the appropriate test fuel. For example, a FFV certified to gasoline/ethanol will be certified to E10 (10 vol% ethanol), which is a worst-case blend from the standpoint of evaporative emissions. Both early and late model-year vehicles other than FFVs are not controlled from the perspective of evaporative ethanol emissions, i.e., the certification test procedures for evaporative emissions do not take into account the use of commercially available ethanol-containing gasolines. Although more stringent evaporative emission standards were adopted in 1998 and applicable to the 2004 to 2006 model years, the procedures were pertinent only to the fuels in use at the time of adoption, and thus did not include ethanol blends. Revised certification test procedures to include ethanol-containing gasolines will need to be developed in order to control any incremental evaporative emissions resulting from these fuel blends. The U.S. EPA is currently considering such changes under their proposed Tier 2 emissions program.

Even small amounts of ethanol cause an RVP increase of about 1 psi when it is added to an ethanol-free base gasoline. The inadvertent commingling of ethanol-containing and ethanol-free gasolines in vehicle fuel tanks results in a combined gasoline with an RVP greater than 7.0 psi and increased evaporative VOC emissions. Prior studies used fuels with RVPs greater than the CaRFG2 limit of 7.0 psi, so clearly additional research is needed with CaRFG2-complying fuels. Current federal law requires all gasoline sold in southern California, Sacramento, and, shortly, the San Joaquin Valley, to contain an oxygenate. Under an MTBE ban, ethanol would be the only possible oxygenate. Thus, commingling would seldom happen in this large portion of California, representing 80% of the gasoline marketplace.

We used the best available information on the emission characteristics of fuels that will be available in 2003, and a comprehensive analysis of current air quality concentrations and a state-of-the-science photochemical model to estimate air quality in the future for the following four fuels:

- Current MTBE-based California Phase 2 Reformulated Gasoline (CaRFG2).
- Ethanol-based fully complying fuel (with oxygen content of 2.0 wt%).
- Ethanol-based fully complying fuel (with oxygen content of 3.5 wt%).
- Non-oxygenated fully complying fuel.

All pollutants of concern decrease from the 1997 MTBE baseline to the 2003 MTBE baseline due to reductions in overall emissions. The predicted decreases are especially pronounced for the toxic air contaminants, ranging from 13% for formaldehyde and acetaldehyde to 33% for benzene and 43% for 1,3-butadiene. The domain maximum one-hour-average ozone is predicted to decrease 6% between 1997 and 2003. The reductions from 1997 to 2003 for the three MTBE-free scenarios are similar to the 2003 MTBE baseline for all compounds but ethanol.

There are several changes in concentration between the 2003 MTBE baseline and the three 2003 MTBE-free fuel scenarios. Since fuel-related activities are the only inventoried source of MTBE, concentrations decrease 100%. Ethanol concentrations for the ethanol-blended gasoline increase by 48% (2.0 wt% oxygen) and 72% (3.5 wt% oxygen), but changes in secondary acetaldehyde from this ethanol increase are modest (0 to 2%), and total acetaldehyde is predicted to increase (4%) for only the ethanol-blended gasoline at 3.5 wt% oxygen. PAN concentrations are not predicted to increase for either ethanol-blended gasoline. Benzene concentrations increase slightly (1%) for the ethanol-blended

gasoline at 3.5 wt% oxygen, with decreases predicted for the other two gasolines. All three MTBE-free gasolines produce modest reductions in 1,3-butadiene (2%) and formaldehyde (2 to 4%) concentrations and essentially no change in ozone, NO₂, nitric acid, or PPN concentrations. As expected, the non-oxygenated gasoline results in higher predicted eight-hour-average CO concentrations (3%) and the 3.5 wt% oxygen ethanol-blend in lower CO values (-9%). It should be noted that these are summertime concentrations, a time period when violations of the standard do not occur. It is not clear if any of these impacts are statistically significant, due to uncertainties in the model inputs and the model itself. The 1997 and 2003 modeling results and observed air quality in 1997 were used to predict air quality in 2003. These results have been provided to OEHHA to determine the health risk.

Our analysis did not include the possibility of increased evaporative emissions due to reduced canister function or commingling. Additional analysis is required once the increased ethanol emissions have been quantified.

Sensitivity calculations using an increase in VOC emissions to bracket the effect of a new motor vehicle emission resulted in increased population-weighted 24-hour-average acetaldehyde and PAN concentrations of 50% and 8%, respectively, from an ethanol-containing gasoline with 3.5 wt% oxygen in comparison to the non-oxygenated gasoline. These acetaldehyde and PAN impacts from the ethanol-containing gasoline represent an upper limit because the VOC emission increase we used is larger than expected from EMFAC2000 when it becomes final and the ozone episode modeled here is an high ozone event with high photochemical formation of acetaldehyde and PAN from ethanol. We plan to redo our analysis when EMFAC2000 becomes final.

Our predictions of future emissions and air quality provide only an initial estimate because of significant data gaps: 1) several uncertainties in how oil refiners will reformulate gasoline in response to California's proposed Phase 3 regulations, a possible summertime oxygenate waiver from the United States Congress, and market forces; 2) uncertainties in the inputs and mathematical formulation of the photochemical model; and 3) incomplete ambient measurements for some of the air contaminants. This analysis should be revisited as additional information is gained by our on-going efforts to address these data gaps.

1. Introduction

Governor Gray Davis issued Executive Order D-5-99 on March 25, 1999 calling for the removal of methyl *tertiary*-butyl ether (MTBE) from gasoline at the earliest possible date, but not later than December 31, 2002. Task 10 of the Executive Order states "the California Air Resources Board (ARB) and the State Water Resources Control Board (SWRCB) shall conduct an environmental fate and transport analysis of ethanol in air, surface water, and groundwater. The Office of Environmental Health Hazard Assessment (OEHHA) shall prepare an analysis of the health risks of ethanol in gasoline, the products of incomplete combustion of ethanol in gasoline, and any resulting secondary transformation products. These reports are to be peer reviewed and presented to the Environmental Policy Council by December 31, 1999 for its consideration."

1.1. Objective

This objective of this document is to meet the requirements of Executive Order D-5-99. To assist OEHHA in its health risk assessment, we conducted an analysis to estimate the changes in ambient air concentrations of potentially detrimental contaminants of exhaust and evaporative components and subsequent reaction products that would result from substituting ethanol-blended gasoline for gasoline blended with MTBE. We also included non-oxygenated gasoline in our analysis to provide a basis of comparison for the ethanol-containing gasolines. The California Energy Commission (CEC, 1999) anticipates that alkylates¹ will be used in non-oxygenated gasoline and some ethanol-containing gasolines in California to replace the octane² normally provided by MTBE, so these compounds were also a focus of our analysis.

OEHHA requested information on the following air contaminants:

- Criteria air pollutants [carbon monoxide (CO), nitrogen dioxide (NO₂), ozone, and particulate matter (PM₁₀, PM_{2.5})].
- Toxic air contaminants (acetaldehyde, benzene, 1,3-butadiene, and formaldehyde).
- Fuel oxygenates (ethanol and MTBE).
- Alkylates (C₆ to C₉ branched alkanes and cycloalkanes)
- Peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN).
- Nitric acid (HNO₃).
- Additional compounds of interest to OEHHA (*n*-hexane, isobutene, toluene, and xylene isomers).

1.2. Scope

Our analysis addressed ambient concentrations of air pollutants that the general public would be exposed to during outdoor activities. We estimated both maximum one-hour-average and annual-average exposures. We were not able to consider indoor and personal exposures since these are a complex function of indoor-outdoor air exchange rates, proximity to gasoline-related emission sources, and personal activity.

We also did not provide estimates of pollutant deposition onto land and water surfaces. While our analysis considers dry deposition, it is only for the purpose of treating the effect of this loss process on air quality concentrations. There was no need to consider rain and other precipitation events, as air quality is generally very good under these conditions. Wet and dry deposition is being considered by the SWRCB in their ethanol fate and transport analysis for surface water and groundwater.

¹ Alkylates are a gasoline blendstock produced by reacting isobutane with olefins. They consists of branched alkanes, have very low aromatic content, and no sulfur or olefins (NESCAUM, 1999).

² MTBE has 110 octane, ethanol has 115 octane, alkylates provide 91 to 99 octane, and aromatics have 100 octane (CEC, 1999).

We also did not consider the possible mileage penalty from increasing the oxygen content of ethanol-containing gasoline to 3.5 wt%. Nor did we address global warming impacts, as this is being addressed under the proposed California Phase 3 Reformulated Gasoline Regulations (ARB, 1999a) and by the SWRCB.

1.3. Study Approach

We conducted four types of analyses. First, we reviewed several recently published comprehensive assessments of the impact of oxygenated gasoline on the environment. While the majority of these studies focused on the impact of MTBE-based gasoline, several contained information on alternative ethanol-containing and non-oxygenated gasolines. We found the prior assessments to be useful for identifying issues of concern related to air quality, but all lack a thorough review of ambient air studies in areas that introduced ethanol as a gasoline oxygenate. Thus, the second type of analysis we conducted was a literature review of studies that measure the direct impact of the use of ethanol in gasoline. Due to the already broad scope of the prior assessments, they did not conduct a comprehensive modeling and data analysis to estimate future air quality concentrations for MTBE-free fuel scenarios, although several suggested that such studies should be undertaken. In order to address this need, the third component of our study was to evaluate emission and air quality impacts for the following four fuels:

- Current MTBE-based California Phase 2 Reformulated Gasoline (CaRFG2).
- Ethanol-based fully complying fuel (with oxygen content of 2.0 wt%).
- Ethanol-based fully complying fuel (with oxygen content of 3.5 wt%).
- Non-oxygenated fully complying fuel.

This analysis was conducted with the best available information on the emission characteristics of fuels that will be available in 2003, and uses a comprehensive analysis of current air quality concentrations and a state-of-the-science photochemical model to estimate air quality in the future. Our predictions of future emissions and air quality provide only an initial estimate because of significant data gaps: 1) several uncertainties in how oil refiners will reformulate gasoline in response to California's proposed Phase 3 regulations (ARB, 1999a), a possible summertime oxygenate waiver from the United States Congress, and market forces; 2) uncertainties in the inputs and mathematical formulation of the photochemical model; and 3) incomplete ambient measurements for some of the air contaminants. The fourth component of our analysis is to close these data gaps as part of this study and on-going efforts that will not be complete until after the December 31, 1999 deadline in the Executive Order. We report here the results of a limited emission testing program with two commercial MTBE-free CaRFG2 gasolines that provide a reality check on the emission estimates, and progress in our long-term efforts to improve the photochemical model and collect ambient air quality data.

The following sections summarize our review of prior studies, describe emission issues related primarily to ethanol, present our predictions of future emissions and air quality, and discuss uncertainties and on-going studies to address them. Three appendices contain detailed technical information on our estimates of organic gas emission profiles and emission inventories, photochemical modeling of air quality impacts, and data analysis of baseline (1997) and future (2003) air quality concentrations. A fourth appendix contains our responses to a formal scientific peer review [to be added after the currently on-going peer review] by the University of California and comments on materials presented at public workshops on July 1, October 4, and November 10, 1999.

2. Review of Prior Studies

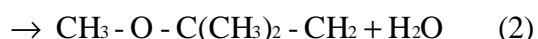
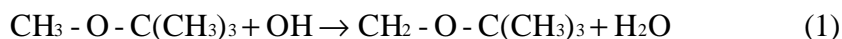
To provide a scientific foundation for our analysis, we reviewed the available literature on the atmospheric chemistry of MTBE, ethanol, and alkylates. We also reviewed seven major assessments of the impact of oxygenated gasoline on the environment that were conducted prior to our analysis. Ethanol has been used instead of MTBE as the primary gasoline oxygenate in several states in the United States. In Brazil, either neat (100%) ethanol or gasohol (a mixture of ethanol and gasoline) has been used as a fuel since 1979. We conducted a literature review of ambient air studies in these areas, which provide a direct measurement of the impact of the use of ethanol in gasoline.

2.1. Atmospheric Chemistry of MTBE, Ethanol, and Alkylates

The atmospheric chemistry of MTBE, ethanol, and alkylates have already undergone extensive reviews by others. These are briefly summarized below.

2.1.1. MTBE

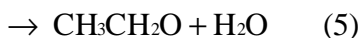
Kinetic and mechanistic studies of the atmospheric chemistry of MTBE have been summarized by Koshland *et al.* (1998). The only significant atmospheric reaction for MTBE is with hydroxyl (OH) radicals. Two possible initial reactions are:



Several researchers have measured the rate constant for this reaction and the preferred value by the International Union of Pure and Applied Chemistry (IUPAC) is $2.94 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature (298 K) (Atkinson *et al.*, 1999a). Photoreactor studies showed that the major products formed in the presence of NO_x were *tertiary*-butyl formate (59 to 76% molar yield), formaldehyde (37 to 48%), methyl acetate (14 to 17%), and acetone (2.1 to 2.6%). Other species identified included 2-methoxy-2-methylpropanal, methanol, and isobutene (Koshland *et al.*, 1998).

2.1.2. Ethanol

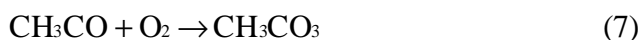
Grosjean (1997) has summarized the few studies of the atmospheric chemistry of alcohols. The only significant atmospheric reaction for ethanol is with OH radicals. Three possible initial reactions are:



The major reaction pathway of ethanol is Reaction 4 which involves H-atom abstraction from the weakest C-H bond. The reaction pathway that involves H-atom abstraction from the O-H bond (Reaction 5) is negligible under atmospheric conditions, and Reaction 3 is a minor pathway. The preferred IUPAC value for the reaction with the OH radical above is $3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson *et al.*, 1999a). Product studies showed that the major product from the reaction of

ethanol with OH radicals is acetaldehyde with a formation yield of about 80%. The other possible minor products include formaldehyde and methyl nitrate (Grosjean, 1997).

Once formed from the atmospheric reaction of ethanol with OH radicals, acetaldehyde is rapidly consumed by photolysis and by reaction with OH radicals. Photolysis leads to formation of CO and formaldehyde while reaction with the OH radical leads to PAN by the following process:



The acetyl (CH_3CO_3) radical also reacts with NO to form CH_3CO_2 and NO_2 . In addition, PAN decomposes back to CH_3CO_3 and NO_2 in a reaction that increases at higher temperatures. Ambient concentrations of PAN are a function of ambient temperature, the NO_2 -to-NO ratio, and the concentration of the acetyl radical precursor.

2.1.3. Alkylates

Alkylates consist of branched alkanes and cycloalkanes, mostly with six to nine carbons such as iso-octane (2,2,4-trimethylpentane) and methylcyclopentane. The atmospheric chemistry of alkanes has been reviewed by Atkinson (1994). Under atmospheric conditions, the potential reaction pathways for alkylates include gas-phase reactions with OH and nitrate (NO_3) radicals. The gas-phase reaction of alkylates with ozone is of negligible importance.

Kinetic studies (Atkinson, 1994 and references therein) have been carried out for several alkylates and the rate constants with OH radicals range from 1 to $13 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. Aschmann and Atkinson (1995) reported that the measured rate constants of selected alkanes with NO_3 radicals range from 0.8 to $2.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. Product studies (Atkinson, 1999b) for alkylates with OH and NO_3 radicals showed that the possible products include alkyl nitrates, alcohols, and carbonyls.

2.1.4. Atmospheric Lifetime and Ozone Formation Potential

Table 2.1 lists the calculated atmospheric lifetimes of MTBE, ethanol, and alkylates due to gas-phase reaction with OH radicals. The calculation was based on the IUPAC-recommended OH rate constants and an ambient OH radical concentration of $1.6 \times 10^6 \text{ molecule/cm}^3$, representative of moderately polluted conditions. Maximum incremental reactivities (MIRs) -- measures of ozone formation potential -- were obtained from a recent assessment of reactivity (Carter, 1999). For comparison purposes, the composite MIR for gasoline exhaust is 3 to 4 g ozone/g VOC

Table 2.1. Calculated Atmospheric Lifetimes Due to Gas-Phase Reaction with OH Radicals and MIRs for MTBE, Ethanol, and Alkylates

Compound	Atmospheric Lifetime ^a (daylight hours)	Maximum Incremental Reactivity ^b (g ozone/g VOC)
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MTBE	59	0.88
Ethanol	53	1.88
Alkylates	11-214	1.0-2.3

^aFor a 12-hour daytime-average OH radical concentration of 1.6×10^6 molecule/cm³.

^bFrom Carter (1999), using the techniques described in Carter (1994).

2.1.5. Conclusions of Review of Atmospheric Chemistry

The major atmospheric loss process for MTBE, ethanol, and alkylates is reaction with OH radicals, which is relatively slow. Photolysis and reactions of these compounds with ozone and NO₃ radicals are slow and of negligible importance. Several product studies showed that the major products are *tertiary*-butyl formate, formaldehyde, and methyl acetate from MTBE, acetaldehyde and PAN from ethanol, and alkyl nitrates, alcohols, and carbonyls from alkylates.

2.2. Recent Assessments of the Impact of Oxygenated Gasoline on the Environment

We reviewed seven major assessments of the impact of oxygenated gasoline on the environment that were conducted prior to our analysis. We focused our review on air quality issues and do not report conclusions on health, water quality, fuel supply, political, and other topics that were not the subject of our analysis. The reports are summarized below in order of their applicability to the scope of our analysis.

2.2.1. University of California MTBE Report

As required by California Senate Bill 521, the University of California conducted a comprehensive assessment of the current health and environmental impacts of MTBE use in California (Keller *et al.*, 1998). Their findings formed the basis for Executive Order D-5-99 issued by Governor Gray Davis that precipitated our ethanol fate and transport analysis. The University of California associated decreased automotive CO emissions and increased emissions of formaldehyde, isobutene, and unburned MTBE with MTBE-based CaRFG2. (Koshland *et al.*, 1998). The MTBE atmospheric reaction product *tertiary*-butyl formate (see Section 2.1.1) is not formed as a combustion byproduct.

The University of California review of emission studies for ethanol-containing gasoline (Koshland *et al.*, 1998) concluded that 10 vol% ethanol (3.7 wt% oxygen) results in statistically significant changes in exhaust emissions of CO (13% reduction), VOC (6% reduction), NO_x (5% increase), acetaldehyde (159% increase), and benzene (11% reduction), as well as increases in evaporative emissions. However, these findings are not applicable to fully complying CaRFG2 fuels that have the same Reid vapor pressure (RVP)³ requirement and are constrained by the ARB Predictive Model (ARB, 1995) to meet the same limits on exhaust emissions of VOC, NO_x, and cancer

³ Reid vapor pressure is a measure of the gas pressure a liquid/gas system will exert to a closed system when heated to 100 F, measured in pounds per square inch (psi). Gasolines with a higher RVP are more volatile than those with a lower RVP, and thus have a greater propensity to evaporate.

risk-weighted toxic air contaminants. For these fully complying gasolines, Koshland *et al.* (1998) concluded that MTBE and other oxygenates have no significant effect on exhaust emissions from advanced technology vehicles, nor is there a statistically significant difference in the emission reduction of benzene from oxygenated and non-oxygenated CaRFG2 fuels. Keller *et al.* (1998) expressed concerns about increased ethanol emissions, and recommended modeling studies to predict the air quality concentration increases of acetaldehyde and PAN that would be expected to result from the large-scale substitution of ethanol for MTBE. This recommendation is addressed in Section 4.2.

2.2.2. U.S. EPA Blue Ribbon Panel on Oxygenates in Gasoline

United States Environmental Protection Agency (U.S. EPA) Administrator Carol Browner appointed a Blue Ribbon Panel in November 1998 to investigate the air quality benefits and water quality concerns associated with oxygenates in gasoline, and to provide independent advice and recommendations on ways to maintain air quality while protecting water quality (U.S. EPA, 1999). Similar to the requirement in the Executive Order, the Blue Ribbon Panel concluded that the U.S. EPA should conduct a full, multi-media assessment (on air, soil, and water) of any major new additive to gasoline prior to its introduction. They also recommended the establishment of routine and statistically valid methods for assessing the actual composition of reformulated gasoline and its air quality benefits, including the development of field monitoring and emissions characterization techniques to assess “real world” effects of different blends on emissions. These types of studies were already conducted in California during the implementation of CaRFG2 in 1996 (Kirchstetter and Harley, 1999ab; Gertler *et al.*, 1999; Larsen, 1999), and we describe a similar program for Phase 3 reformulated gasoline in Section 5.3. The Blue Ribbon Panel also presented information on increased evaporative emissions from commingling of ethanol-containing and non-ethanol gasolines. This issue will be discussed in Section 3.2.5.

2.2.3. Northeast States for Coordinated Air Use Management

In response to a request from the New England Governor’s Conference, the Northeast States for Coordinated Air Use Management (NESCAUM) investigated the air quality, fuel supply, and cost impacts of MTBE and its alternatives (NESCAUM, 1999). They identified ethanol, aromatics, and alkylates as the likely replacements for MTBE. NESCAUM reported that combustion of ethanol-blended gasoline results in a 70% increase of acetaldehyde emissions, although the basis for this statement is not referenced. Concerns were also expressed for substantially increased toxic emissions if aromatics were used to replace MTBE. Although NESCAUM identified alkylates as an MTBE substitute that would not increase toxic emissions, they recommended that a rigorous evaluation of combustion byproducts and environmental fate and transport should be conducted before increasing its use in gasoline. They also presented information on increased evaporative emissions from commingling of ethanol-containing and non-ethanol gasolines. This will be discussed further in Section 3.2.5.

2.2.4. National Research Council

At the urging of some members of the United States Congress, the U.S. EPA arranged for the National Research Council (NRC) to conduct a comparison of the ozone formation potential of MTBE and ethanol as gasoline oxygenates (NRC, 1999). The NRC found that the ozone formation potential (as measured with the California MIR scale) of exhaust emissions from motor vehicles operating on ethanol-blended gasoline were lower -- but not significantly lower -- than from motor vehicles using

MTBE-blended gasoline. The NRC also concluded that the mass and ozone formation potential (per mile) of evaporative emissions from motor vehicles fueled with ethanol-blended gasoline were significantly higher, and that this increase would be detrimental to air quality in terms of ozone. This latter finding was attributed to an RVP increase of 1 psi from splash blending the ethanol-containing gasoline, and is consistent with the conclusions of an earlier ARB (1998b) analysis using the same vehicle test data. However, these findings are not applicable to the fully-complying ethanol-blended gasolines that need to meet the same RVP requirements as MTBE-blended gasolines that are under study in the current analysis.

2.2.5. National Research Council of Canada

The National Research Council of Canada estimated the relative impacts of an industry-average gasoline and a gasoline containing 10 vol% ethanol and having about a 1 psi greater RVP (Singleton *et al.*, 1997). They used a photochemical box model to project air quality in 1995 with model scenarios based on the ozone episode of August 1 to 4, 1988 in southern Ontario. The ethanol-blended fuel results in an overall change of emissions for VOC (9% increase) and CO (15% decrease), with no change in NO_x. This leads to increases in concentrations of ozone (0.4 to 1.6%), formaldehyde (1.0 to 1.5%), acetaldehyde (about 2.7%), and PAN (2.9 to 4.5%), and an approximate 15% reduction in CO concentrations (Singleton *et al.*, 1997). The light-duty gasoline vehicle contribution to the 24-hour-average secondary formaldehyde and acetaldehyde concentrations was 10 to 18% and 28 to 36% greater, respectively, for the ethanol blend. The light-duty gasoline vehicle contribution to PAN was 12 to 18% greater for the E10 gasoline than that for industry-average gasoline. As with the NRC study, these results for non-complying gasolines are not germane to our analysis.

2.2.6. American Methanol Institute

The American Methanol Institute funded Malcolm Pirnie, Inc. (1998) to evaluate the fate and transport of ethanol in the environment. The primary focus of the report was on soil and groundwater impacts, and the air quality analysis consisted entirely of a literature review. Based primarily on the ARB (1998b) analysis of a non-complying ethanol-containing gasoline with a 1 psi RVP increase, they concluded that ethanol will lead to reduced CO emissions and increased VOC, NO_x, and acetaldehyde emissions with overall detrimental results on ozone and PAN concentrations.

2.2.7. Governors' Ethanol Coalition

A recent ethanol fate and transport study funded by the 22-state Governors' Ethanol Coalition (Ulrich, 1999) focused primarily on the impact on subsurface and surface water quality and placed only cursory attention on air quality issues. The report recommended that additional information on air quality issues should be considered, including whether PAN concentrations increased with ethanol-blended gasolines.

2.2.8. Conclusions of Review of Recent Assessments

The majority of these studies focused on the impact of MTBE-based gasoline, but several discussed issues related to ethanol-containing and non-oxygenated gasolines as an alternative to MTBE. We found the prior assessments to be useful for identifying issues of concern, but all lacked a thorough review of ambient air studies in areas that had introduced ethanol as a gasoline oxygenate. Due to the

already broad scope of the prior assessments, they did not conduct a comprehensive modeling and data analysis to estimate future air quality concentrations for MTBE-free fuel scenarios, although several suggested that such studies should be undertaken. Both these needs are addressed in the following sections.

2.3. Ambient Air Quality Studies

We reviewed a total of sixteen journal articles and other documents that reported ambient air measurements in areas that used ethanol as a gasoline oxygenate. Studies conducted in Denver, Albuquerque, and Brazil provided the most useful insights to the future situation in California. The primary focus of these studies was on the change in ambient concentrations of acetaldehyde and PAN. Studies carried out in Alaska (Backer *et al.*, 1997) and Arizona (MathPro and EEA, 1998; Zielinska *et al.*, 1998) were not as useful because they did not include measurements before the introduction of ethanol or they did not include ambient air quality impacts. In Las Vegas and Chicago, ambient measurements of aldehydes and PAN were not conducted either before or after ethanol introduction.

2.3.1. Denver, Colorado

The Denver metropolitan area is the first region in the United States to implement the use of oxygenated gasoline in an effort to reduce ambient CO (Anderson *et al.*, 1994). The program has been mandated since the beginning of 1988 when the majority of the fuel sold contained 8% MTBE with the rest being a 10 vol% ethanol blend. Since then, the additive used has gradually shifted from largely MTBE to largely ethanol. Anderson *et al.* (1997) reported that the concentrations of formaldehyde and acetaldehyde during the winter of 1995/96, when nearly all of the gasoline was blended with ethanol, were not significantly different from those measured during the winter of 1988/89 when 95% of the gasoline was blended with MTBE. They concluded that photochemical production and destruction of these aldehydes suppress the effect of emissions changes.

2.3.2. Albuquerque, New Mexico

Albuquerque is one of the urban areas in the United States mandated to use oxygenated gasoline blends for improving air quality during the winter months. In the winter, over 99% of the gasoline contain 10 vol% ethanol. Gaffney *et al.* (1997; 1998) examined the air quality impacts of ethanol-blended gasoline by measuring the ambient concentrations of PAN and aldehydes in the summer of 1993 (prior to the introduction of ethanol-blended gasoline) and in the winters of 1994 and 1995 (after the introduction of ethanol-blended gasoline). Compared to the summertime data, they observed a 10% acetaldehyde increase during one winter, but a significant decrease (lower by a factor of five) in the other winter. The study observed an increase of PAN by a factor of two and four, respectively, in both winters that the authors attributed to the use of ethanol-containing gasoline. However, as pointed out by Whitten (1998), the study conducted by Gaffney *et al.* (1997; 1998) is not a convincing case for demonstrating the air quality impact of ethanol-containing gasoline. The major arguments are the lack of control conditions (i.e., no data for pre-ethanol wintertime conditions) and meteorological variation. For example, average concentrations of PAN varied by a factor of two between the two winters, largely due to meteorology.

2.3.3. Brazil

Brazil is the only country in the world where a national, large-scale ethanol fuel program has been implemented. The ethanol fuel was first introduced in 1979 and its use has increased steadily since then. In 1997, approximately nine million automobiles in Brazil ran on a gasohol fuel (gasoline blended with 22 vol% ethanol) and another four million ran on neat ethanol (Grosjean, 1997). Grosjean *et al.* (1990) measured ambient concentrations of aldehydes in three major urban cities of Brazil -- San Paulo, Rio de Janeiro, Salvador -- from 1986 to 1988 and reported that acetaldehyde was the most abundant carbonyl in terms of its maximum concentration (35 ppb), followed closely by formaldehyde (34 ppb). The results also showed that acetaldehyde concentrations in urban areas of Brazil were substantially higher than those measured elsewhere in the world, most likely caused by large-scale use of ethanol as a vehicle fuel. In contrast, the ambient concentrations of formaldehyde showed a small increase compared to those measured elsewhere. More recently, deAndrade *et al.* (1998) reported that the concentrations for formaldehyde and acetaldehyde measured in Salvador, Brazil ranged from 0.20 to 80 ppb and from 0.40 to 93 ppb, respectively. Tanner *et al.* (1988) observed up to 5 ppb of PAN, which they attributed to high ambient concentrations of acetaldehyde. These observations also agreed with model calculations of the photochemical processes. In addition, Grosjean and coworkers (1998a; 1998b; 1999a) measured ambient concentrations of ethanol and MTBE in Porto Alegre, Brazil from March 1996 to April 1997. Ambient concentrations of ethanol and MTBE ranged from 0.4 to 68.2 ppb and 0.2 to 17.1 ppb, respectively. Since there were no ambient data available prior to the use of ethanol-containing gasoline, these studies could not evaluate the direct impact on air quality before and after the introduction of ethanol into the fuel.

2.3.4. Conclusions of Review of Ambient Air Quality Studies

The studies of the impact of the use of ethanol-containing gasoline on air quality conducted in Denver, Albuquerque, and Brazil are not comprehensive but provide useful insight in how to design an ambient air monitoring program to directly measure the air quality impact of the MTBE phase-out (see Section 5.3). The impact on acetaldehyde concentrations is substantial only in Brazil, where the fuels contain either neat ethanol or 22 vol% ethanol. Due to the lack of RVP requirements for gasolines in Brazil, this acetaldehyde increase could be due to the addition of substantial evaporative emissions, rather than strictly the result of an ethanol-for-MTBE substitution. Even with increased acetaldehyde concentrations, the observed increase in PAN concentrations was modest and well below historical levels observed in southern California (Grosjean, 1999b).

3. Automotive Emission Issues

A number of issues related to emissions from vehicles operated on MTBE-free gasolines emerged from our review of prior assessments and comments from the public. Some of these issues were either not appropriate to the objectives of this ethanol fate and transport analysis or cannot be addressed by the automotive emission estimation procedures described in Section 4.1, and are discussed further below.

3.1. Proposed California Phase 3 Reformulated Gasoline Regulations

Executive Order D-5-99 directs the ARB to adopt Phase 3 Reformulated Gasoline (CaRFG3) regulations by December 1999. The regulations are to provide additional flexibility in lowering or removing oxygen, to maintain current emission and air quality benefits from the CaRFG2 regulations, and to allow compliance with the State Implementation Plan for achieving ambient air quality standards. The proposed amendments include a prohibition on the use of MTBE in gasoline, revised specifications for Phase 3 gasoline, and an improved and expanded Predictive Model (ARB, 1999a). Table 3.1 summarizes the proposed amendments to the flat, averaging, and cap limits of various fuel properties compared to the existing CaRFG2 limits. Since these regulations were not proposed until the majority of our analysis was complete, and because they are still subject to change, we did not consider them in our emission and air quality predictions. However, because the regulations apply equally to ethanol-blended and non-oxygenated gasolines, we do not anticipate that consideration of CaRFG3 will affect our overall conclusions.

Table 3.1. Proposed Amendments to the CaRFG2 Property Limits

Property	Flat Limits		Averaging Limits		Cap Limits	
	Original	Proposed	Original	Proposed	Original	Proposed
RVP, psi, max	7.0	7.0 ⁽¹⁾	Na ⁽²⁾	no change	7.0	6.4-7.2
Benzene, vol%, max	1.00	0.80	0.80	0.70	1.20	1.10
Sulfur, ppmw, max	40	20	30	15	80	60/30 ⁽³⁾
Aromatics, vol%, max	25	no change	22	no change	30	35
Olefins, vol%, max	6.0	no change	4.0	no change	10	no change
Oxygen, wt%	1.8 to 2.2	no change	na ⁽²⁾	no change	0-3.5	0-3.7 ⁽⁴⁾
T50 ^o F, max	210	211	200	201	220	225
T90 ^o F, max	300	305	290	295	330	335
Driveability Index ⁽⁵⁾	none	1225	na ⁽²⁾	na ⁽²⁾	None	none

(1) Equal to 6.9 psi if using the evaporative element of the Predictive Model.

(2) Not applicable.

(3) 60 ppmw will apply December 31, 2002; 30 ppmw will apply December 31, 2004.

(4) If the gasoline contains more than 3.5 weight percent but no more than 10 volume percent ethanol, the cap is 3.7 weight percent.

(5) Driveability Index=1.5*T10+3*T50+T90+20*(wt% oxygen).

3.2. Evaporative Emissions

3.2.1. Evaporative Processes

Motor vehicles are subject to evaporative fuel losses from many locations in the vehicle. These losses can be described by the following three processes -- running loss, hot soak, and diurnal emissions. "Running loss" emissions are those evaporative emissions which occur during operation of the vehicle and stem from permeation through the fuel hoses and loss from the carbon canister (a container filled with sorbent activated carbon used to store gasoline vapors). "Hot soak" emissions are vapor losses from a recently operated hot vehicle. Most of these losses are due to permeation through hoses. In older vehicles, the carburetor bowl is a prime source of hot soak emissions. "Diurnal" emissions are evaporative losses mainly from the carbon canister, and result from daily heating of the vehicle's fuel tank and consequent saturation and overflow from the canister.

3.2.2. Ethanol Evaporative Emissions

Direct evaporation of an ethanol-containing gasoline tends to result in emissions containing a greater proportion of ethanol than the original fuel. For example, a gasoline with an RVP of 8.0 psi and containing 10 wt% ethanol will evaporate over a period of 2 hours into a vapor containing approximately 13 wt% ethanol (Grisanti *et al.*, 1995). On the other hand, a determination of vapor

composition from an emitting vehicle is difficult since the evaporative source (whether a rubber hose or a canister) will affect vapor composition. All else being equal, one would expect that the tendency of ethanol to evaporate more readily than other fuel components should result in a greater proportion of ethanol in emissions measured by standard motor vehicle test procedures. Hot soak emissions from a test program conducted by ARB (1998b) using a blend of 10 vol% ethanol with an RVP of 7.8 psi confirmed that the proportion of ethanol in the vapor was higher than in the fuel. In this case, the proportion of ethanol in the vapor was on the order of 25 to 50 wt% (ARB, 1998b). Increases of similar magnitude were seen in earlier studies (Furey and King, 1980). These exceptionally high levels are likely due to the high permeability of rubber hoses with respect to ethanol (Furey and King, 1980). In summary, hot soak emissions tend to result in evaporative losses containing a proportionally greater amount of ethanol than was in the original fuel. The use of materials non-permeable to ethanol is an area requiring further research and development.

3.2.3. Impact of Ethanol-Containing Gasoline on Canister Function

The carbon canister is a primary component of the evaporative emission control system. Filled with sorbent activated carbon, it is designed to readily adsorb and release VOC vapors. During vapor generation (e.g., gasoline evaporation from a hot fuel tank), the canister receives and stores vapors. If saturated, the canister will vent excess vapors to the atmosphere. During vehicle operation, the canister is purged, with the vapor routed to the engine's intake manifold for combustion.

The amount of fuel vapor a canister can hold and subsequently release is designated the working capacity. Different chemical species are retained by the canister to different degrees. Oxygenates such as ethanol and MTBE bind more tightly to the activated carbon than hydrocarbons such as butane and isopentane (Furey and King, 1980). This may have the effect of reducing the canister's working capacity. Additionally, ethanol is hygroscopic (i.e., attracts water), and water is clearly known to reduce working capacity (Manos *et al.*, 1977). In summary, it is possible that ethanol's propensity to be tightly held by the activated carbon in conjunction with its hygroscopic nature may result in increased diurnal emissions. Data suggesting a reduced working capacity are somewhat conflicting in nature, which may be partially due to the difficulty in sampling ethanol (Grisanti *et al.*, 1995). Additional research is needed in the area.

3.2.4. Impact of Ethanol-Containing Gasoline on In-Use Emissions

The ethanol evaporative emissions associated with a particular vehicle will depend on that vehicle's technology and the stringency of its emission standards. Flexible-fueled vehicles (FFV) in California will be controlled for their evaporative emissions of ethanol since they must be certified on the appropriate test fuel. For example, a FFV certified to gasoline/ethanol will be certified to E10 (10 vol% ethanol), which is a worst-case blend from the standpoint of evaporative emissions. Both early and late model-year vehicles other than FFVs are not controlled from the perspective of evaporative ethanol emissions, i.e., the certification test procedures for evaporative emissions do not take into account the use of commercially available ethanol-containing gasolines. Although more stringent evaporative emission standards were adopted in 1998 and applicable to the 2004 to 2006 model years, the procedures were pertinent only to the fuels in use at the time of adoption, and thus did not include ethanol blends. Revised certification test procedures to include ethanol-containing gasolines will need to be developed in order to control any incremental evaporative emissions resulting from these fuel blends. The U.S. EPA is currently considering such changes under their proposed Tier 2 emissions program.

3.2.5. Impact of Commingling of Ethanol-Containing and Ethanol-Free Gasolines

Even small amounts of ethanol cause an RVP increase of about 1 psi when it is added to an ethanol-free base gasoline. To account for this unique property of ethanol, all ethanol containing CaRFG2 is blended with base gasoline that has an RVP of about 6.0 psi (by reducing high RVP components, such as pentanes and butanes) to produce a fuel that complies with the 7.0 psi limit. However, even if such a low RVP blendstock is used, the inadvertent commingling of ethanol-containing and ethanol-free gasolines in vehicle fuel tanks results in a combined gasoline with an RVP greater than 7.0 psi and increased evaporative VOC emissions. For example, in a 50-50 commingled blend where E10⁴ with an RVP of 7.0 psi is added to an equivalent volume of a ethanol-free gasoline with the same 7.0 psi RVP, the resulting RVP is about 7.5 psi and not the 7.0 psi as would be expected when two ethanol-free gasolines are commingled.⁵ NESCAUM (1999) reported that an unpublished study by Aulich and Richter (1999) confirmed that commingling does increase RVP and evaporative VOC emissions. The ethanol RVP increase was most pronounced in blends of 5 to 35 vol% E10 and less pronounced once the gasoline blends exceeded a 50 vol% E10 mixture. Gasoline with 2 vol% ethanol, or a mixture of 80 vol% gasoline with 20 vol% E10, showed RVP increases of 0.66 to 0.93 psi over the base fuel RVP. Aulich and Richter (1999) used gasolines with relatively high RVPs (9.85 and 9.9 psi) compared with the CaRFG2 limit of 7.0 psi, so clearly additional research is needed with CaRFG2-complying fuels.

As reported by the Blue Ribbon Panel (U.S. EPA, 1999), many factors are extremely important in determining the overall effect of commingling. These include the market share of ethanol-containing gasolines, station/brand loyalty, and the distribution of fuel tank levels before and after a refueling event. Caffrey and Machiele (1994) attempted to take these variables into account in modeling the effect of commingling in a mixed fuel marketplace. Their conclusions include the following:

- Brand loyalty and ethanol market share are much more important variables than the distribution of fuel tank levels before and after a refueling event.
- Depending on the combination of variables chosen, the overall effect of commingling in an MTBE-free market range from under 0.1 psi to over 0.4 psi.
- The effects of the increase in RVP commingling approaches a maximum when the market share for the ethanol-containing gasoline becomes 30 to 50%, and declines thereafter as ethanol takes a larger market share.

⁴ A gasoline containing 10 % ethanol by volume.

⁵ Commingling these two gasolines is equivalent to first combining the non-ethanol portion of both gasolines and then adding ethanol. The ethanol-free gasoline by definition has an RVP of 7.0 psi. The non-ethanol portion of the ethanol-containing gasoline had to have an RVP of 6.0 psi (since the subsequent addition of the ethanol produced a gasoline with an RVP of 7.0 psi). The non-ethanol components combine linearly producing a new fuel component having an RVP of about 6.5 psi (halfway between 6.0 and 7.0 psi). Then, adding in the ethanol component, which would now be about 5 vol% of the final blend, increases the RVP to about 8.5 psi. It is important to note that although the new 50-50 commingled blend would have an ethanol content of around 5 vol%, not 10 vol% as in the original ethanol-containing gasoline, the full 1.0 psi RVP increase would still occur (U.S. EPA, 1999).

Current federal law requires all gasoline sold in southern California, Sacramento, and ,shortly, the San Joaquin Valley, to contain an oxygenate. Under an MTBE ban, ethanol would be the only possible oxygenate. Thus, commingling would seldom happen in this large portion of California, representing 80% of the gasoline marketplace.

3.2.6. Use of Reactivity in CO-for-Evaporative Emission Trade-Offs

The proposed regulations for California Phase 3 reformulated gasoline (ARB, 1999a) allow increased evaporative VOC emissions as the oxygen content of the fuel increases above 2 wt%, reducing CO emissions. This adjustment compensates for the ozone formation potential of CO. The proposed regulations use the MIR scale to make the adjustment. A recent modeling analysis (Whitten, 1999) suggests the reactivity of CO should be raised by 65%, allowing a greater increase in evaporative CO emissions.

Our review of the literature (see Appendix D) indicates the reactivity of CO is well established and regarded as having low uncertainty (Carter, 1999). Additionally, changes to the MIR scale on which California's reactivity regulations are based should only be undertaken after careful analysis and only when the scientific evidence and the advice of the ARB Reactivity Scientific Advisory Committee warrant such a change. We believe the Whitten (1999) analysis of the reactivity of CO focuses on an inappropriate metric for the comparison of three-dimensional photochemical models with MIR values. In addition, the approach by Whitten (1999) to eliminate CO chemistry creates a bias in the modeling analysis as CO produced by reactions of VOCs will also artificially contribute to a perceived decrease in the reactivity of CO. Our conclusion is that an increase in the reactivity of CO is not justified.

3.3. Fuel Additives

3.3.1. Denaturants

Denaturants comprise from 0.2 to 0.5 wt% of ethanol. Generally, they are gasoline or gasoline-blending materials. Therefore, they should not add any chemical species that are not already present in gasoline. There would be a small potential for denaturant at 0.5 wt% in ethanol to cause the final blended gasoline to violate the CaRFG2 regulatory limits and thereby cause slight increases in emissions. However, the potential for non-complying product always exists. That potential is limited by the ARB field inspection of gasoline, whatever may be the cause of non-compliance.

3.3.2. Co-Solvents

Co-solvents refer to a bulk additive to ethanol other than the denaturant. To our knowledge, no such additives are used. If one were added, it would be constrained by ASTM D 4806-98 "Denatured Fuel Ethanol for Blending with Gasoline" to comprise less than 7.4 vol% of the ethanol, and it could not contain pyroles, turpentine, ketones, or tars. Also, ASTM D 4806-98 excludes the addition of any aliphatic alcohol or ether to ethanol unless that species has been shown to cause no harm to fuel systems.

3.4. Emissions Associated with Transportation and Storage of Ethanol

Since ethanol is transported by rail from the Midwest, kept at fuel storage terminals refineries, and then splash-blended with gasoline, increased railway and truck traffic is expected. The increase in

diesel PM would be less than 0.06% of the statewide inventory of PM emissions, according to estimates of truck travel for ethanol distribution made by the California Energy Commission (ARB, 1999a). If increased local traffic and emissions from diesel trucks become local environmental concerns, they will be considered locally in the context of use permits and permits to operate specific facilities under the California Environmental Quality Act.

4. Estimates of the Impact of MTBE-Free Gasolines on Future Emissions and Air Quality

One of the major recommendations of the University of California assessment of MTBE (Keller et al., 1998) was to conduct modeling studies to predict the air quality concentration increases of acetaldehyde and PAN that would be expected to result from the large-scale substitution of ethanol for MTBE in the future. In order to fulfill this recommendation, we evaluated emission and air quality impacts in 2003 for the current MTBE-based CaRFG2, gasoline blended with 2.0 wt% oxygen as ethanol, gasoline blended with 3.5 wt% oxygen as ethanol, and gasoline without any oxygen. This analysis was conducted with the best available information on the emission characteristics of gasolines that will be available in 2003, and uses a comprehensive analysis of current air quality concentrations and a state-of-the-science photochemical model to estimate air quality in the future.

4.1. Predicted Emissions for the South Coast Air Basin

The photochemical modeling analysis requires estimates of organic gas emission profiles and mass emissions of VOC, NO_x, and CO for the four 2003 fuel scenarios. Estimates are also needed for 1997 MTBE-based CaRFG2 to provide a link with baseline air quality measured during 1997. Only a summary of the derivation of emissions for evaporative and exhaust emissions is presented here. Full details are available in Appendix A.

4.1.1. Organic Gas Emission Profile Assumptions

In order to develop the emission estimates for 1997 and 2003, we developed organic gas emission profiles for each fuel and applied the profiles to all gasoline-related emission inventory categories. The emission processes for which we developed profiles include:

- Liquid gasoline.
- Hot soak and running loss evaporative.
- Diurnal and resting loss evaporative.
- Start exhaust -- catalyst and non-catalyst.
- Stabilized exhaust -- catalyst and non-catalyst.

For 1997 MTBE-based CaRFG2, we used organic gas emission profiles developed from ARB surveillance data and presented at a public workshop in September 1998 (ARB, 1998a). We used the results of a linear-programming refinery model study sponsored by the California Energy Commission (MathPro, 1999ab) to establish the liquid gasoline profiles. In general the MathPro (1999ab) study

predicted significant removal of pentanes and an increased use of alkylates when MTBE is banned as a fuel oxygenate.

The liquid gasoline profiles were also applied to hot soak evaporative emissions for all the 2003 fuels as recommended from a peer review conducted by Professor Harley of the University of California at Berkeley (see Attachment A1). Running loss evaporative emissions were also speciated using the liquid gasoline profiles. Professor Harley calculated headspace vapors for all the 2003 fuels from the liquid gasoline composition (see Attachment A1) and we applied these to diurnal and resting loss evaporative emissions for the MTBE-free scenarios.

The emission profiles for the exhaust categories were established by adjusting the profiles for the MTBE-based CaRFG2 adopted in September 1998 (ARB, 1998a). The exhaust adjustments maintain consistency with the fuel composition. The adjustments for isobutene, identified as a major byproduct of MTBE combustion in the University of California MTBE report (Koshland *et al.*, 1998), were based on analysis of results from the Auto/Oil Program (1991; 1995), the ATL (1995) study, and an ARB (1998b) study contrasting MTBE-based CaRFG2 with a non-complying ethanol-containing gasoline. In addition, we input the fuel properties into the ARB Predictive Model for exhaust emissions of benzene and 1,3-butadiene (ARB, 1995), and into newly created models for evaporative benzene emissions and exhaust emissions of acetaldehyde and formaldehyde that distinguish between MTBE and ethanol as the oxygenate (ARB, 1999b). These profiles went through several iterations and were peer reviewed by Professor Harley in June 1999 (see Attachment A1 and Attachment D), and presented at public workshops on July 12 and October 4. What is presented in Appendix A is substantially different from what was presented earlier, having been extensively revised after errors were found by the peer review of Professor Harley and during the public comment period.

4.1.2. Mass Emissions

We estimated total mass emissions of VOC, NO_x, and CO for CaRFG2 using the current mobile source emissions model, MVEI7G. Stationary source emissions were assumed to be the same for all scenarios. For the three fully complying non-MTBE gasolines, the ARB Predictive Model (ARB, 1995) constrains the total mass emissions of VOC and NO_x, so emissions of these pollutants were held constant for all the 2003 scenarios.

Based on several vehicle emission test programs (NSTC, 1997) and ambient air studies (Dolislager, 1997), CO emissions decrease with increasing fuel oxygen content. Our previous modeling analyses show that the CO emission inventory has a small impact on concentrations of ozone and other secondary pollutants. We used the same motor vehicle CO inventory for the MTBE and ethanol fuel scenarios with 2.0 wt% oxygen content, and decreased CO emissions by 7.5% for the ethanol with 3.5 wt% oxygen scenario and increased CO emissions by 5% for the non-oxygenated scenario. Our nonlinear treatment of CO when the oxygenate is removed appears inconsistent with the findings of the NSTC (1997) that use of a 2.0 wt% oxygen wintertime gasoline results in a decrease of 10% in CO emissions. However, a substantial portion of the CO reductions that can be attributed to summertime CaRFG2 comes from properties of the fuel other than the oxygen content. This means that addition or removal of oxygen in CaRFG2 is likely to have less impact on CO emissions than from non-CaRFG2 wintertime gasolines.

We calculated emissions of benzene, 1,3-butadiene, acetaldehyde, formaldehyde, ethanol, and MTBE by applying the organic gas emission profiles to VOC mass emission estimates for gasoline-related categories (e.g., passenger cars, heavy-duty vehicles, fuel spillage, off-road mobile

sources, etc.). The resulting emission inventories for the South Coast Air Basin (SoCAB) are shown in Table 4.1 to Table 4.3 for CO, NO_x, reactive organic gases (ROG), benzene, 1,3-butadiene, acetaldehyde, formaldehyde, ethanol, and MTBE. Table 4.1 summarizes the total emissions (mobile, area, stationary, and natural sources) for an average ozone episode day for the five fuel scenarios. Table 4.2 and Table 4.3 present emission changes relative to the 1997 and 2003 MTBE baselines, respectively. In comparison to the 1997 MTBE baseline inventory, emissions of all compounds (except acetaldehyde and ethanol for the ethanol-blended gasolines) are substantially reduced. Among the four 2003 scenarios, there are differences for all compounds but NO_x and ROG.

Table 4.1. South Coast Air Basin Emissions (tons/day)

Year / Scenario	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
1997 Baseline (MTBE-based CaRFG2)	5440	1083	1037	17.83	3.46	6.78	21.71	33.55	31.15
2003 Baseline (MTBE-based CaRFG2)	4295	851	895	11.82	2.59	6.00	18.89	32.10	21.09
2003 Ethanol at 2.0 wt% Oxygen	4295	851	893	11.67	2.53	6.37	18.52	46.00	0.01
2003 Ethanol at 3.5 wt% Oxygen	4052	851	894	11.98	2.55	7.78	18.41	53.46	0.01
2003 Non-Oxygenate	4457	851	893	10.97	2.53	5.93	18.22	31.96	0.01

Table 4.2. Emission Changes from 1997 MTBE Baseline

Scenario	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
2003 Baseline (MTBE-based CaRFG2)	-21%	-21%	-14%	-34%	-25%	-12%	-13%	-4%	-32%
2003 Ethanol at 2.0 wt% Oxygen	-21%	-21%	-14%	-35%	-27%	-6%	-15%	37%	-100%
2003 Ethanol at 3.5 wt% Oxygen	-26%	-21%	-14%	-33%	-26%	15%	-15%	59%	-100%
2003 Non-Oxygenate	-18%	-21%	-14%	-38%	-27%	-13%	-16%	-5%	-100%

Table 4.3. Emission Changes from 2003 MTBE Baseline

Scenario	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
2003 Ethanol Blend at 2.0 wt% Oxygen	0%	0%	0%	-1%	-2%	6%	-2%	43%	-100%
2003 Ethanol Blend at 3.5 wt% Oxygen	-6%	0%	0%	1%	-1%	30%	-3%	67%	-100%
2003 Non-Oxygenate	4%	0%	0%	-7%	-2%	-1%	-4%	0%	-100%

4.2. Predicted Air Quality for the South Coast Air Basin

We used photochemical modeling to predict air quality concentrations for episodic ozone conditions in 1997 and 2003, and apply these results to measured 1997 air quality during the entire year to estimate pollutant concentrations in 2003. Full details for the photochemical modeling are given in Appendix B, and Appendix C describes the air quality observed in 1997 and predicted for 2003.

4.2.1. Photochemical Model Description

We applied the Urban Airshed Model with the Flexible Chemical Mechanism interface (UAM-FCM) for the August 26 to 28, 1987 ozone episode in the SoCAB. Input files for winds, temperature, and diffusion break were developed using special air quality and meteorological data collected during the 1987 Southern California Air Quality Study (Lawson 1990; Lawson *et al.*, 1995). We simulated initial and boundary conditions, together with emission inventories for calendar years 1997 and 2003, using the meteorology from the 1987 episode. Fixing the meteorological conditions in this way allows the effects of fuel changes to be directly calculated. We used an extended version of the SAPRC-97 photochemical mechanism (Carter *et al.*, 1997) to simulate atmospheric chemical transformations. The mechanism includes explicit chemical reactions for CO, NO₂, ozone, acetaldehyde, benzene, 1,3-butadiene, ethanol, formaldehyde, HNO₃, MTBE, PAN, and PPN. The mechanism tracks secondary formation of acetaldehyde and formaldehyde separately from the contribution of direct emissions. The SAPRC-97 mechanism lumps alkylates, *n*-hexane, isobutene, toluene, and xylene isomers with similarly reacting compounds, but we did extend the mechanism to include explicit treatments of these compounds. OEHHA determined that the maximum 1997 concentrations we provided were at least an order of magnitude below any level of concern (see Section 4.2.3.5). The UAM-FCM does not include representations of the chemical and physical processes that form particulate matter. However, PM₁₀ and PM_{2.5} concentrations are not expected to change due to the removal of MTBE from gasoline, as discussed in Section 4.2.3.1.

To establish baseline conditions, we simulated 1997 mass emissions with the organic gas emission profiles for CaRFG2. Calendar year 2003 was evaluated for CaRFG2 and the three fully complying non-MTBE gasolines. We assumed boundary conditions to vary from 1987 concentrations consistent with the emission inventory. However, initial concentrations are held constant. Model results for the first and second days of the simulation are greatly influenced by the initial conditions for ozone and its precursors. Therefore, only the results for the third day (i.e., August 28) of the simulations are reported.

4.2.2. Photochemical Model Results

For all five scenarios, we processed UAM-FCM results for the maximum one-hour-average, eight-hour-average (CO and ozone only), and 24-hour-average concentrations for all compounds of interest. Table 4.4 compares the changes in population-weighted 24-hour-average pollutant concentrations between the 1997 CaRFG2 base gasoline and the four 2003 fuel scenarios to give the reader a sense of temporally and spatially integrated patterns across the modeling domain. All pollutants but PPN show decreases from the 1997 baseline to the 2003 baseline ("2003 MTBE") due to reductions in overall emissions. The predicted decreases are especially pronounced for the toxic air contaminants, ranging from 13% for formaldehyde and acetaldehyde to 33% for benzene and 43% for 1,3-butadiene. The domain maximum one-hour-average ozone is predicted to decrease 6% between

1997 and 2003. The reductions from 1997 to 2003 for the three MTBE-free scenarios are similar to the 2003 MTBE baseline for all compounds but ethanol.

Table 4.5 compares the changes in concentration between the 2003 MTBE baseline and the three 2003 MTBE-free fuel scenarios. Since fuel-related activities are the only inventoried source of MTBE, concentrations decrease 100%. Ethanol concentrations for the ethanol-blended gasoline increase by 48% (2.0 wt% oxygen) and 72% (3.5 wt% oxygen), but changes in secondary acetaldehyde from this ethanol increase are modest (0 to 2%), and total acetaldehyde is predicted to increase (4%) for only the ethanol-blended gasoline at 3.5 wt% oxygen. PAN concentrations are not predicted to increase for either ethanol-blended gasoline. Benzene concentrations increase slightly (1%) for the ethanol-blended gasoline at 3.5 wt% oxygen, with decreases predicted for the other two gasolines. All three MTBE-free gasolines produce modest reductions in 1,3-butadiene (2%) and formaldehyde (2 to 4%) concentrations and essentially no change in ozone, NO₂, nitric acid, or PPN concentrations. As expected, the non-oxygenated gasoline results in higher predicted eight-hour-average CO concentrations (3%) and the 3.5 wt% oxygen ethanol-blend in lower CO values (-9%). It should be noted that these are summertime concentrations, a time period when violations of the standard do not occur. It is not clear if any of these impacts are statistically significant, due to uncertainties in the model inputs and the model itself as discussed in Section 5.

Sensitivity analysis is an evaluation of the model response to variations in one or more of the model inputs. Sensitivity simulations for a subset of the fuel scenarios were conducted to evaluate the potential impact of using EMFAC2000 (ARB, 1999c) instead of EMFAC7G. EMFAC2000 was not available at the time of this study, but emissions from motor vehicles, primarily VOCs, increase substantially with EMFAC2000. A large increase in VOC emissions will change the VOC to NO_x ratio and potentially impact the radical flux. This may increase the photochemical oxidation of ethanol and lead to increased acetaldehyde and PAN impacts. For this purpose, gasoline-related VOC emissions were multiplied by a factor of three to place an upper-limit to the impact of using EMFAC2000, which proposes multiplication factors of 2.34 and 1.84 for the 2000 on-road motor vehicle emission inventory in the SoCAB for VOCs and NO_x, respectively. The factor of three is also consistent with an independent fuel-based inventory for the SoCAB in 1997 which proposes a multiplication factor of 3.5±0.6 for on-road motor vehicle VOC emissions of stabilized exhaust (Singer and Harley, 1999).

The major finding of the sensitivity analysis is that the predicted maximum one-hour-average concentrations for acetaldehyde and PAN from the ethanol-blended at 3.5 wt% oxygen were 1.3 ppb greater than the maximum predicted for the non-oxygenated gasoline. These represent increases of 10% in acetaldehyde and 12% in PAN in comparison to the non-oxygenated gasoline. Population-weighted 24-hour-average acetaldehyde and PAN concentrations increase by 50% and 8%, respectively. These acetaldehyde and PAN impacts from the ethanol-containing gasoline represent an upper limit because the factor of three increase in all on-road VOC emissions is larger than expected from EMFAC2000 when it becomes final and the ozone episode modeled here is an high ozone event with high photochemical formation of acetaldehyde and PAN from ethanol. We plan to redo our analysis when EMFAC2000 becomes final.

Table 4.4. Changes in Gridded Region Model Results from 1997 MTBE Baseline

Compound	Parameter	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
Acetaldehyde (Primary)	PW	-25%	-23%	4%	-26%
Acetaldehyde (Secondary)	PW	-12%	-12%	-11%	-13%
Acetaldehyde (Total)	PW	-13%	-13%	-10%	-14%
Benzene	PW	-33%	-34%	-32%	-36%
1,3-Butadiene	PW	-43%	-45%	-44%	-45%
CO	8hr	-25%	-25%	-32%	-23%
Ethanol	PW	-5%	40%	63%	-5%
Formaldehyde (Primary)	PW	-25%	-27%	-27%	-27%
Formaldehyde (Secondary)	PW	-11%	-14%	-12%	-15%
Formaldehyde (Total)	PW	-13%	-16%	-14%	-17%
MTBE	PW	-34%	-100%	-100%	-100%
Nitric Acid	PW	-11%	-11%	-11%	-11%
NO	PW	-46%	-45%	-46%	-45%
NO ₂	1hr	-8%	-8%	-8%	-8%
Ozone	1hr	-6%	-7%	-7%	-7%
	8hr	-5%	-5%	-5%	-5%
PAN	1hr	-5%	-7%	-5%	-9%
	PW	-4%	-4%	-3%	-6%
PPN	1hr	0%	0%	0%	0%
	PW	-2%	-1%	-2%	-1%

1hr = Gridded Region Maximum 1-Hour Average

8hr = Gridded Region Maximum 8-Hour Average

PW = Gridded Region Population-Weighted Summer Daily Average

Table 4.5. Changes in Gridded Region Model Results from 2003 MTBE Baseline

Compound	Parameter	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
Acetaldehyde (Primary)	PW	4%	39%	-1%
Acetaldehyde (Secondary)	PW	0%	2%	-1%
Acetaldehyde (Total)	PW	0%	4%	-1%
Benzene	PW	-3%	1%	-5%
1,3-Butadiene	PW	-2%	-2%	-2%
CO	8hr	0%	-9%	3%
Ethanol	PW	48%	72%	0%
Formaldehyde (Primary)	PW	-3%	-3%	-4%
Formaldehyde (Secondary)	PW	-4%	-1%	-4%
Formaldehyde (Total)	PW	-4%	-2%	-4%
MTBE	PW	-100%	-100%	-100%
Nitric Acid	PW	0%	0%	0%
NO	PW	1%	0%	1%
NO ₂	1hr	0%	0%	0%
Ozone	1hr	-1%	-1%	-1%
	8hr	0%	0%	0%
PAN	1hr	-2%	0%	-5%
	PW	0%	1%	-1%
PPN	1Hr	0%	0%	0%
	PW	0%	-1%	1%

1hr = Gridded Region Maximum 1-Hour Average

8hr = Gridded Region Maximum 8-Hour Average

PW = Gridded Region Population-Weighted Summer Daily Average

In addition to the three-dimensional airshed model simulations, we also investigated the ozone, PAN, and PPN (which includes higher molecular weight acyl peroxy nitrates) formation potentials for each of the explicit VOCs and lumped species in the SAPRC-97 chemical mechanism. This was used primarily to explain the lack of sensitivity of PAN formation to the ethanol content of the gasoline. We implemented the SAPRC-97 chemical mechanism in a box model with observed air quality for ten scenarios spanning the past three decades in southern California, and two cases in Brazil with widespread use of ethanol. As fully described in Appendix B, the box model simulations are consistent with the results from the three-dimensional airshed model that ethanol substitution scenarios will not necessarily lead to a substantial increase in PAN concentrations.

4.2.3. Current and Future Air Quality

In order to perform a health-risk analysis, OEHHA requested maximum 1997 and 2003 concentrations for the appropriate averaging times for the criteria air pollutants (including PAN and PPN), and population-weighted annual-average, maximum 24-hour-average, and maximum one-hour-average concentrations for the toxic air contaminants and fuel oxygenates. Analyses were only done for the SoCAB, the most populated and most polluted air basin in California. This is also the area in California (and perhaps the world) with the most air quality data, speciated VOC and toxic air contaminants in particular. Ambient air quality data for criteria pollutants in 1996-1998 were used to represent the 1997 baseline to account for natural year-to-year meteorological fluctuations. Only 1996-1997 toxics data were used to represent the 1997 baseline since 1998 data were not readily available at the time of the analysis. Data from before 1996 were not used because fuels used then did not satisfy the CaRFG2 requirements. We used data from the following sources:

- 1996-1998 Criteria Pollutant Monitoring Network in the SoCAB.
- 1996-1997 ARB Toxic Air Contaminant Network in the SoCAB (“TAC data”).
- 1996 SoCAB VOC Monitoring Study by Desert Research Institute (“DRI data”).
- 1996 Desert Research Institute Sepulveda Tunnel Study.
- 1996 and 1997 UC Berkeley Caldecott Tunnel Studies.
- 1997 ARB Emission Inventory for the SoCAB.

Data from the 1997 Southern California Ozone Study and Multiple Air Toxics Exposure Study II data were not readily available at the time of our analysis. Although we originally proposed to include data from a 1999 UC Berkeley Tunnel Study conducted in July, these data were not available at the time of our analysis.

The photochemical modeling results were used to establish future air quality concentrations. For estimating future maximum one-hour-average and 24-hour-average concentrations, we normally used the maximum concentrations in the gridded modeling region for the third day of the model simulation. For the population-weighted annual-average exposure estimates, we normally used the region-wide population-weighted average of the daily-average model results.

4.2.3.1. CO, NO₂, Ozone, PM₁₀, and PM_{2.5}

We used maximum concentrations observed in 1996-1998 to represent the 1997 baseline and scaled them to 2003 with the photochemical modeling results. The predicted concentrations for the 1997 MTBE baseline, the 2003 MTBE baseline, the 2.0 wt% oxygen content ethanol-blended gasoline

("Et2.0%"), the 3.5 wt% oxygen content ethanol-blended gasoline ("Et3.5%"), and the non-oxygenated gasoline ("NonOxy") are reported in Table 4.6. The apparent CO increase is a function of the emission assumptions for summertime conditions applied to the winter, when CO concentrations exceed the state and national ambient air quality standards. Due to the wintertime oxygenate requirement for the SoCAB, CO concentrations within the nonattainment area of Los Angeles County will not differ from the 2003 MTBE baseline.

We conducted a qualitative analysis for particulate matter. $PM_{2.5}$ can be approximated as the sum of nitrates, sulfates, organic carbon, elemental carbon, and secondary organic carbon. PM_{10} is roughly the sum of $PM_{2.5}$ and coarse dust. Gasoline-fueled motor vehicles are a relatively small contributor to sulfates and elemental carbon in the SoCAB and they are not expected to be a function of the fuel oxygenate. Nitrates and organic carbon are not expected to change because NO_x and VOC emissions are fixed. The maximum 24-hour-average concentration for HNO_3 , the main nitrate precursor, decreases by 11% from 1997 to 2003, and does not change among the 2003 fuel scenarios. Odum *et al.* (1997) concluded that the aromatic content of fuels is primarily responsible for forming secondary organic aerosols. Since there was very little variation in aromatic content among the fuels, PM_{10} and $PM_{2.5}$ concentrations are not expected to change appreciably as a result of the introduction of MTBE-free gasolines. Vehicle activity is not likely to vary with the fuel, so coarse dust can be assumed to be constant as well. Therefore, the removal of MTBE is not expected to have an impact on PM_{10} and $PM_{2.5}$ concentrations.

Table 4.6. Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin

Pollutant / Avg. Type	Estimate Type	Year / Scenario				
		1997 MTBE	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
Benzene, ppb						
Population-Weighted Annual Exposure						
	Upper Baseline	1.19	0.80	0.78	0.81	0.76
	Lower Baseline	1.07	0.72	0.70	0.73	0.69
Maximum Daily Average						
	Upper Baseline	9.5	6.8	6.5	6.8	6.4
	Lower Baseline	7.4	5.3	5.1	5.3	4.9
Maximum 1-Hour Average						
	Upper Baseline	22.4	14.3	14.3	14.3	14.3
	Lower Baseline	11.6	7.4	7.4	7.4	7.4
1,3-Butadiene, ppb						
Population-Weighted Annual Exposure						
	Upper Baseline	0.36	0.20	0.20	0.20	0.20
	Lower Baseline	0.34	0.19	0.19	0.19	0.19
Maximum Daily Average						
	Upper Baseline	2.9	1.2	1.2	1.2	1.2
	Lower Baseline	2.0	0.8	0.8	0.8	0.8
Maximum 1-Hour Average						
	Upper Baseline	6.7	3.4	3.4	3.4	3.4
	Lower Baseline	3.1	1.6	1.6	1.6	1.6
Acetaldehyde, ppb						
Population-Weighted Annual Exposure						
	Upper	1.8	1.6	1.6	1.8	1.6
	Lower	1.8	1.5	1.6	1.7	1.5
Maximum Daily Average						
	Upper Baseline	6.2	6.2	6.2	6.2	6.2
	Lower Baseline	5.1	5.1	5.1	5.1	5.1
Maximum 1-Hour Average						
	Upper Baseline	17.7	16.7	16.9	17.1	16.9
	Lower Baseline	13.8	13.1	13.2	13.4	13.2

Pollutant / Avg. Type	Estimate Type	Year / Scenario				
		1997 MTBE	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
Formaldehyde, ppb						
Population-Weighted Annual Exposure						
	Upper	4.7	4.2	4.1	4.1	4.0
	Lower	4.7	4.1	4.0	4.0	4.0
Maximum Daily Average						
	Best Baseline	14.0	12.2	11.8	12.1	11.7
Maximum 1-Hour Average						
	Upper Baseline	37.8	38.3	37.8	38.1	37.8
	Lower Baseline	20.3	20.6	20.3	20.5	20.3
Carbon Monoxide, ppm						
Maximum 8-Hour Average						
	Best Baseline	17.5	14.3	14.3	13.4	14.7 ^a
Maximum 1-Hour Average						
	Best Baseline	22.5	19.2	19.2	18.0	19.7 ^a
Nitrogen Dioxide, ppm						
Maximum Annual-Average Exposure						
	Best Baseline	0.043	No difference expected among 2003 scenarios			
Maximum Daily Average						
	Best Baseline	0.117	0.098	0.097	0.097	0.097
Maximum 1-Hour Average						
	Best Baseline	0.255	0.235	0.235	0.235	0.235
Ozone, ppm						
Maximum 8-Hur Average						
	Best Baseline	0.206	0.196	0.196	0.196	0.196
Maximum 1-Hour Average						
	Best Baseline	0.244	0.230	0.228	0.228	0.228

^aThis apparent increase is a function of the emission assumptions. Due to the wintertime oxygenate requirement for the SoCAB, CO concentrations within the nonattainment area of Los Angeles County will not differ from the 2003 MTBE baseline.

Pollutant / Avg. Type	Estimate Type	Year / Scenario				
		1997 MTBE	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
Particulate Matter (10 μm or less), mg/m^3						
Maximum Annual Geometric Mean						
	Best Baseline	56	No difference expected among 2003 scenarios			
Maximum Daily Average						
	Best Baseline	227	No difference expected among 2003 scenarios			
Particulate Matter (2.5 μm or less), mg/m^3						
Maximum Annual Geometric Mean						
		na ^a	No difference expected among 2003 scenarios			
Maximum Daily Average						
		na ^a	No difference expected among 2003 scenarios			
Ethanol, ppb (Estimated from Summer Measurements)						
Population-Weighted Annual Exposure						
	Best Baseline	5.4	5.1	7.6	8.8	5.1
Maximum Daily Average						
	Upper Baseline	51	49	71	81	49
	Lower Baseline	47	45	64	75	45
Maximum 1-Hour Average						
	Upper Baseline	108	101	145	165	101
	Lower Baseline	78	74	114	140	74
MTBE, ppb						
Population-Weighted Annual Exposure						
	Upper Baseline	3.9	2.6	0.0	0.0	0.0
	Lower Baseline	3.6	2.4	0.0	0.0	0.0
Maximum Daily Average						
	Upper Baseline	29	20	0	0	0
	Lower Baseline	13	9	0	0	0
Maximum 1-Hour Average						
	Upper Baseline	67	46	0	0	0
	Lower Baseline	19	13	0	0	0

^aCalifornia's PM_{2.5} monitoring network has been deployed for less than a year and insufficient measurements are available to establish baseline air quality concentrations.

Pollutant / Avg. Type	Estimate Type	Year / Scenario				
		1997 MTBE	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
PAN, ppb						
	Maximum Daily Average					
	Upper Baseline	5.0	4.8	4.8	4.9	4.7
	Lower Baseline	2.5	2.4	2.4	2.4	2.4
	Maximum 1-Hour Average					
	Upper Baseline	10.0	9.5	9.3	9.5	9.1
	Lower Baseline	5.0	4.8	4.7	4.8	4.5
PPN^a, ppb						
	Maximum Daily Average					
	Upper Baseline	2.0	2.0	2.0	2.0	2.1
	Lower Baseline	1.0	1.0	1.0	1.0	1.0
	Maximum 1-Hour Average					
	Upper Baseline	3.0	3.0	3.0	3.0	3.0
	Lower Baseline	1.5	1.5	1.5	1.5	1.5
Nitric Acid, ppb (Model Output Only)						
	Population-Weighted Summer Daily Exposure					
	Model	12.4	11.0	11.0	11.0	11.0
	Maximum Daily Average					
	Model	36.7	32.4	32.3	32.2	32.3

^aPPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates.

4.2.3.2. Acetaldehyde, Benzene, 1,3-Butadiene, and Formaldehyde

We used two different approaches to estimate 1997 benzene and 1,3-butadiene concentrations. First, we used measured concentrations directly from the TAC sampling network. In addition, we used least-squares linear regression (forced through the origin after accounting for background concentration) to develop ratios between these toxic air contaminants and CO. We found good correlations with CO for benzene and 1,3-butadiene. We used the regression results to estimate concentrations at locations where there are no direct TAC measurements, but there are CO measurements. The latter approach allowed us to estimate pollutant concentrations at nineteen locations, rather than the five locations for which toxics sampling data are available. Model results for benzene and 1,3-butadiene were used to extrapolate from the 1997 base year to the various 2003 scenarios. The range of estimates developed using the different approaches is given in Table 4.6.

We considered three different approaches to estimate 1997 acetaldehyde and formaldehyde concentrations. First, we used measured concentrations directly from the toxics sampling network. Second, to derive maximum one-hour-average concentrations from 24-hour-average measurements, we used the corresponding ratio for ozone. Third, we attempted to develop relationships between aldehydes and both CO and total oxidant (sum of ozone and NO₂) so aldehyde values could be estimated at many more locations than are sampled with the TAC monitoring network. Our attempt to correlate aldehydes with CO and oxidant was not considered sufficiently reliable and was abandoned.

Future year maximum one-hour and daily acetaldehyde and formaldehyde estimates were extrapolated from 1997 using modeled results for total acetaldehyde and total formaldehyde. To estimate future year population-weighted exposure, we first split 1997 estimates into primary and secondary components and applied model results to extrapolate each component separately. The separate components were then added to obtain total acetaldehyde and total formaldehyde. Table 4.6 reports the range of estimates developed using all except the correlation method.

4.2.3.3. Ethanol and MTBE

The only ethanol air quality data readily available were those collected by DRI in the summers of 1995 and 1996. We used the 1996 data as the basis for estimating representative concentrations for 1997. The highest ethanol concentrations are expected in winter. Given only summer data, it was challenging to estimate concentrations in a different season. We opted to use CO as an index of mixing and dispersion to extrapolate from measured maximum ethanol concentrations in the summer to a different season. The results are reported in . Similar to other pollutants, we attempted to correlate ethanol with CO, but results were poor. This was not surprising, given that on-road vehicles currently emit less than 1% of the estimated ethanol emissions in the SoCAB.

We used the two approaches described above for benzene and 1,3-butadiene to estimate MTBE concentrations. We found good correlations with CO for some data sets and not others. A range in estimates is given in Table 4.6.

4.2.3.4. PAN and PPN

Grosjean (1999b) analyzed prior measurement programs for PAN and PPN. They have no direct sources and form *in situ* in the atmosphere. PAN has been measured earlier and more frequently in the SoCAB than anywhere else in the world (about 25 studies that span some 35 years). The highest PAN concentrations were recorded during early studies (and often outside the summer ozone season), e.g., 60 to 65 ppb in the late 1960s. Many of the subsequent studies lasted only a few days, weeks, or months, thus providing us with no consistent basis to assess long-term trends. High concentrations of PAN (40 ppb or more) have been recorded until about 1980, and concentrations of PAN appear to have decreased substantially thereafter. No PAN concentration higher than 10 ppb has been reported since 1991. Consistent with the downward trend observed for maximum one-hour-average PAN concentrations, 24-hour-average PAN concentrations have declined from 15 to 20 ppb in the late 1960s and until 1980, to 5 to 12 ppb in the late 1980s, and 2 to 5 ppb in 1993. Seasonal variations of PAN are sparsely documented, especially so in the last decade (no data since 1987). Results from earlier studies indicate that high concentrations of PAN were often recorded outside of the traditional smog season, and that the coastal and central regions of the SoCAB may experience higher concentrations of PAN during the late fall than during the summer months. However, even though PAN has not been monitored routinely over a long period, many special studies demonstrate a downwind trend on average. Ozone data can be used to predict the time of maximum PAN but not to estimate

PAN concentrations and their diurnal, seasonal, and spatial variations. It appears that thermal decomposition of PAN may account for much of the differences between diurnal, spatial, and seasonal variations of ambient PAN and those of ambient ozone. A wide range of estimates for PAN concentrations is given in Table 4.6.

Even less information is available for PPN than for PAN. Ambient concentrations of PPN have been reported in only nine studies. The highest concentrations of PPN were up to 5 to 6 ppb in earlier studies and 1 ppb or less in recent years. Twenty-four-hour-average concentrations range from 0.1 to 1.8 ppb. There are no data on seasonal variations or annual averages. Diurnal variations of ambient PPN are closely related to those of PAN. The slopes of the linear regressions of ambient PPN versus ambient PAN at all locations studied in 1993 and 1997 range from 0.10 to 0.17 (average = 0.15). These values may serve as a baseline when using the PPN-to-PAN concentration ratio as an indicator of the possible impact of replacing MTBE by ethanol on future PAN air quality in the SoCAB. A wide range of estimates for PPN concentrations is given in Table 4.6.

4.2.3.5. Alkylates, *n*-Hexane, Isobutene, Toluene, and Xylene Isomers

OEHHA requested information on maximum annual-average and maximum one-hour-average concentrations for alkylates, *n*-hexane, isobutene, toluene, and xylene isomers. We provided estimates in Table 4.7 by developing ratios between these compounds and CO using the techniques described in Section 4.2.3.2. In general, we observed good correlation with CO for all compounds for all but a few datasets. OEHHA later concluded that there is no indication of a toxicological problem with any of alkylates, primarily due to lack of data. The maximum concentrations for *n*-hexane, isobutene, toluene, and xylene isomers are at least an order of magnitude below any level of concern, so there was no need to establish 2003 concentrations (which require photochemical modeling).

Table 4.7. Estimated 1997 Maximum Toxic Concentrations

Compound	Annual Average (ppb)	One-Hour Average (ppb)
Total Alkylates	15.6-23.0	146-216
Toluene	6-11	52-103
<i>m</i> & <i>p</i> -Xylene	2.6-4.6	25-43
<i>o</i> -Xylene	1.0-4.3	9-40
Isobutene	2.2-3.8	20-36
<i>n</i> -Hexane	1.2-2.4	11-22

4.3. Air Quality Impacts for Other Areas of California

Primarily due to the lack of ambient air quality measurements for many of the air contaminants of concern, we were unable to predict the future air quality for other areas of California. However, our analysis for the South Coast Air Basin can be considered the worst-case situation in comparison to other air basins. It has the highest baseline air quality concentrations, the conditions most conducive to formation of secondary air pollutants (e.g., ozone, acetaldehyde, PAN), the most emissions, and the highest number of gasoline-related emission sources in California. For most of the directly emitted air

pollutants, the predicted air quality impacts are roughly equal to the emission impacts (as shown in Table 4.8 and Table 4.9). This is especially true for the comparison to the 2003 MTBE baseline (Table 4.9). Once EMFAC2000 becomes available, it will be relatively straightforward to estimate the emission impacts of the MTBE-free fuels and we can safely infer that the air quality impacts will be similar. Since the air quality impacts for the secondary air pollutants were modest for the high photochemistry episode that was modeled, we can safely assume that impacts in other air basins for these pollutants will be even smaller.

Table 4.8. Comparison of Emission and Modeled Air Quality Changes from 1997 MTBE Baseline

Scenario / Type of Change	NO _x		NO _x			Acetaldehyde	Formaldehyde	Ethanol	MTBE
	CO	(NO ₂)	(HNO ₃)	Benzene	Butadiene	(Primary)	(Primary)		
2003 Baseline Inventory (MTBE-based CaRFG2)									
Emissions	-21%	-21%	-21%	-34%	-25%	-12%	-13%	-4%	-32%
Air Quality ^a	-18%	-28%	-11%	-33%	-43%	-25%	-25%	-5%	-34%
2003 Ethanol Blend at 2.0 wt% Oxygen									
Emissions	-21%	-21%	-21%	-35%	-27%	-6%	-15%	37%	-100%
Air Quality ^a	-18%	-28%	-11%	-34%	-45%	-23%	-27%	40%	-100%
2003 Ethanol Blend at 3.5 wt% Oxygen									
Emissions	-26%	-21%	-21%	-33%	-26%	15%	-15%	59%	-100%
Air Quality ^a	-24%	-28%	-11%	-32%	-44%	4%	-27%	63%	-100%
2003 Non-Oxygenate									
Emissions	-18%	-21%	-21%	-38%	-27%	-13%	-16%	-5%	-100%
Air Quality ^a	-16%	-28%	-11%	-36%	-45%	-26%	-27%	-5%	-100%

^aAir quality changes are based on changes in population-weighted daily-average model results for gridded region.

Table 4.9. Comparison of Emission and Modeled Air Quality Changes from 2003 MTBE Baseline

Scenario / Type of Change	NO _x		NO _x			Acetaldehyde	Formaldehyde	Ethanol	MTBE
	CO	(NO ₂)	(HNO ₃)	Benzene	Butadiene	(Primary)	(Primary)		
2003 Ethanol Blend at 2.0 wt% Oxygen									
Emissions	0%	0%	0%	-1%	-2%	6%	-2%	43%	-100%
Air Quality ^a	0%	0%	0%	-3%	-2%	4%	-3%	48%	-100%
2003 Ethanol Blend at 3.5 wt% Oxygen									
Emissions	-6%	0%	0%	1%	-1%	30%	-3%	67%	-100%
Air Quality ^a	-7%	0%	0%	1%	-2%	39%	-3%	72%	-100%
2003 Non-Oxygenate									
Emissions	4%	0%	0%	-7%	-2%	-1%	-4%	0%	-100%
Air Quality ^a	2%	0%	0%	-5%	-2%	-1%	-4%	0%	-100%

^aAir quality changes are based on changes in population-weighted daily-average model results for gridded region.

5. On-Going Efforts to Address Uncertainties

Our predictions of future emissions and air quality provide only an initial estimate because of significant data gaps: 1) several uncertainties in how oil refiners will reformulate gasoline in response to California's proposed Phase 3 regulations (ARB, 1999a), a possible summertime oxygenate waiver from the United States Congress, and market forces; 2) uncertainties in the inputs and mathematical formulation of the photochemical model; and 3) incomplete ambient measurements for some of the air contaminants. The fourth component of our analysis is to close these data gaps as part of this study and on-going efforts that will not be complete until after the December 31, 1999 deadline in the Executive Order. We report here the results of a limited emission testing program with two commercial MTBE-free CaRFG2 gasolines that provide a reality check on the emission estimates, and progress in our long-term efforts to improve the photochemical model and collect ambient air quality data.

5.1. Emission Testing

The availability of both ethanol-blended and non-oxygenated commercial CaRFG2 gasolines presented the opportunity to provide a reality check on the organic gas emission profiles developed in Section 4.1.1. Because of the limited time available to conduct our analysis, we were not able to test a fully representative number of vehicles nor conduct tests of diurnal or running loss evaporative emissions. We conducted emission testing at the ARB laboratory in El Monte. Full details are presented in Appendix A. We tested three fuels:

- ARB commercial MTBE-based Phase 2 regular-grade gasoline.
- Tosco ethanol-blended regular-grade gasoline (with oxygen content of 2.05 wt%).
- Chevron non-oxygenated regular-grade gasoline.

The measured fuel properties are summarized in Table 5.1.

Table 5.1. Properties for Three Commercial Fuels

Fuel	EtOH (wt%)	MTBE (wt%)	Benzene (vol%)	Aromatics (vol%)	RVP (psi)	T50 (deg F)	T90 (deg F)	Sulfur (ppm)	Olefins (vol%)
MTBE	0.00	10.67	0.57	23.9	6.79	201.0	311.0	14.00	3.60
NonOxy	0.00	0.00	0.16	25.0	6.71	202.1	303.2	29.20	3.43
Ethanol	5.88	0.00	0.42	28.0	6.88	203.8	316.4	1.22	0.21

We conducted full VOC speciation of the liquid gasoline, the headspace vapors, and exhaust tests of seven vehicles. The Tosco and Chevron gasolines are not representative of fuels expected to be sold in 2003, and we were not able to draw quantitative conclusions. Most importantly, the sulfur content is very low (~1 ppm) in the ethanol-blended gasoline; and in the non-oxygenated gasoline it is much higher (29 ppm) than the proposed CaRFG3 flat limit for sulfur of 20 ppm (ARB, 1999a). Also, the RVP and olefin content of the ethanol-blended gasoline were lower than is expected for future ethanol-blended

CaRFGs (under the proposed variable-RVP provision). Gasolines with more reasonable values of sulfur and olefins and RVP could have substantially different compositions that did the test gasolines. In addition, most of the vehicles were aged (mean model year was 1981), and several had unstable emission rates (up to a factor of five).

With these limitations in mind, the test results are consistent, for several broad categories of organic gases, with the emission profiles prepared by ARB and by Professor Harley using limited data. Except for the olefins, the headspace to liquid fuel ratios for species are similar for the commercial gasolines and the predicted profiles by Professor Harley. As in the profiles, isobutene is reduced and alkylates are increased in the emissions from the MTBE-free test gasolines than from the MTBE-blended test gasoline. As in the profiles, the formaldehyde is slightly greater from the ethanol-blended test gasoline than from the non-oxygenated test gasoline, and the acetaldehyde is substantially greater. However, the ratio for acetaldehyde from the ethanol-blended test gasoline is much higher than in the profiles. Unlike the profiles, the exhausts from the MTBE-free gasolines were higher in aromatics and olefins than was the exhaust from MTBE-blended test gasoline. With consideration of the problems in the test design and the data variability, the test results do not contradict the model profiles.

5.2. Improvements in Photochemical Models

Photochemical models have uncertainties in their mathematical formulation, representations of physical and chemical process (e.g., deposition, diffusion, photochemistry), and model inputs for emissions, meteorology, and air quality. We are currently funding research to quantify model uncertainty, and to improve the model's representations of horizontal diffusivity, mixing heights, and photolysis. We are currently processing the measurements collected during the 1997 Southern California Air Quality Study (SCOS97-NARSTO) to prepare model inputs. This effort will result in improved representations of meteorology and boundary conditions (especially above the surface) for more recent ozone episodes than the 1987 case. There is much more research in these areas being conducted nationally. As model improvements become available, particularly in the area of improved chemistry for ethanol and the alkylates, we will determine their impact on our conclusions.

5.3. Ambient Air Quality Measurement Program

Our analysis of air quality impacts should be confirmed with field measurements that take place before and after the planned December 31, 2002 phase-out of MTBE. These types of studies were already conducted in California during the implementation of CaRFG2 in 1996 (Kirchstetter and Harley, 1999ab; Gertler *et al.*, 1999; Larsen, 1999). California's existing ambient air quality networks should be sufficient for all the criteria pollutants, MTBE, toxic air contaminants, and individual VOC compounds (i.e., alkylates). However, ethanol and PAN are not part of any routine air monitoring program.

In November 1999, we started a PAN and PPN monitoring program at two sites in the SoCAB. Since ethanol and acetaldehyde lead to PAN but not to PPN, the PPN-to-PAN ratio may be a useful indicator of the impact of ethanol on PAN air quality. During 1987, high PAN concentrations were observed at coastal sites (up to 19 ppb) during the winter and at Claremont (up to 30 ppb) during the summer (Grosjean, 1999b). Therefore, we are conducting year-around measurements at a high precursor site (Burbank) and a high ozone site (Azusa). Both sites are part of the Photochemical Assessment Monitoring Stations (PAMS) program and have daily (eight 3-hour averages) speciated

hydrocarbon data for three months during the summer, and 24-hour averages on a one-day-in-six schedule year-around. Burbank is an existing toxic air contaminant (TAC) monitoring site and we moved the existing sampler at Fontana to Azusa so that we will have year-around 24-hour-average formaldehyde and acetaldehyde data on a one-day-in-twelve schedule. The existing hourly ozone, NO, NO₂, and temperature measurements at Azusa and Burbank, coupled with the speciated hydrocarbon and aldehyde measurements, will allow us to conduct a thorough analysis of the effects of precursors and thermal decomposition on PAN and PPN concentrations. We will investigate the possibility of adding ethanol measurements to the TAC program in the future. Fung (1999) has proposed that data on ambient ethanol can be recovered from gas chromatograms as the ethanol peak is recorded but never reported.

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