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Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate

Report to the
California Environmental
Policy Council
in Response to
Executive Order
D-5-99

STATE WATER RESOURCES CONTROL BOARD

AIR RESOURCES BOARD

Office of Environmental Health Hazard Assessment

December 1999

Work performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate

Contents for Volumes 1–4

Volume 1: *Executive Summary*

Volume 2: *Background Information on the Use of Ethanol as a Fuel Oxygenate*

David W. Rice

Volume 3: *Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline*

Bart E. Croes, P.E.; Paul Allen, P.E.; Richard Bradley, P.E.;
Dongmin Luo, Ph.D.; Richard Vincent, P.E.; and Luis Woodhouse, Ph.D.

Volume 4: *Potential Ground and Surface Water Impacts*

Chapter 1: *Potential Scenarios for Ethanol-containing Gasoline Released into Surface and Subsurface Waters*

David W. Rice; Susan Powers, Ph.D.; and Pedro J.J. Alvarez, Ph.D.

Chapter 2: *A Critical Review: The Effect of Ethanol in Gasoline on the Fate and Transport of BTEX in the Subsurface*

Susan E. Powers, Ph.D.; and Stephen E. Heermann, Ph.D.

Chapter 3: *The Effect of Ethanol on BTEX Biodegradation and Natural Attenuation*

Pedro J.J. Alvarez, Ph.D., and Craig S. Hunt, Ph.D.

Chapter 4: *Screening Model Evaluation of the Effects of Ethanol on Benzene Plume Lengths*

Walt McNab, Ph.D.; Stephen E. Heermann, Ph.D.; and
Brendan P. Dooher, Ph.D.

Chapter 5: *Potential Impact of Ethanol-containing Gasoline on Surface Water Resources*

David W. Layton, Ph.D., and Jeffrey I. Daniels, Ph.D.

Chapter 6: *Environmental Transport and Fate of Fuel Hydrocarbon Alkylates*

Alfredo A. Marchetti, Ph.D.; Jeffrey I. Daniels, Ph.D.; and David W. Layton, Ph.D.

Chapter 7: *Evaluation of Analytical Methods for the Detection of Ethanol in Ground and Surface Waters*

Carolyn Koester, Ph.D.

Chapter 8: *Screening Analysis of Potential Groundwater Resource Impacts from Gasoline Containing Ethanol or MTBE Using an Empirically based, Probabilistic Screening Model*

Brendan P. Dooher, Ph.D.

Chapter 9: *Knowledge Gaps Regarding the Ground and Surface Water and Impacts of Ethanol-containing Gasoline and Recommendations for Future Research*

David W. Rice; Pedro J.J. Alvarez, Ph.D.; Susan E. Powers, Ph.D.; Harry R. Beller, Ph.D.; Staci R. Kane, Ph.D.; Jeffrey I. Daniels, Ph.D.; David W. Layton, Ph.D.; and Brendan P. Dooher, Ph.D.

Chapter 10: *Response to Comments*

David W. Rice

Volume 5: *Potential Health Risks of Ethanol in Gasoline*

Staff Report, Office of Environmental Health Hazard Assessment

UCRL-AR-135949 Vol. 1

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VOLUME 1

Executive Summary

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Front Cover Back

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UCRL-AR-135949 Vol. 1

Volume 1: Executive Summary

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December 1999

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AIR RESOURCES BOARD

Office of Environmental Health Hazard Assessment

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Volume 1: Executive Summary

This is the Executive Summary of the report entitled *Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate* for the California Environmental Policy Council. This report has been prepared by the California Air Resources Board, the State Water Resources Control Board (SWRCB), and the California Environmental Protection Agency's Office of Environmental Health Hazard Assessment (CalEPA/OEHHA). The report is divided into five volumes:

Volume 1: Executive Summary.

Volume 2: Background Information on the Use of Ethanol as a Fuel Oxygenate.

Volume 3: Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline.

Volume 4: Potential Ground and Surface Water Impacts.

Volume 5: Potential Health Risks of Ethanol in Gasoline.

Each volume is summarized below.

Volume 2: Background Information on the Use of Ethanol as a Fuel Oxygenate

2.1 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 no 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."

Recent legislation (Stats. 1999 Ch. 813; SB 529, Bowen) enacted Health and Safety Code Sec. 43840.8, which imposes new requirements regarding multimedia environmental assessments of proposed amendments to ARB's motor vehicle fuels specifications. There is a streamlined environmental review mechanism for amendments proposed prior to January 1, 2000 and adopted prior to July 1, 2000.

California Senate Bill 989 incorporates into state statutes most of the provisions of the Governor's MTBE Executive Order. Additionally, this bill prohibits the ARB from adopting new fuel specifications until a "multimedia" evaluation has been performed and submitted to the California Environmental Policy Council for final review and approval.

2.2 A systems-based approach is needed to evaluate risk management trade-offs and to assess health and environmental consequences of the use of ethanol as a fuel oxygenate.

A thorough systems-based approach would include:

1. Identification of the key attributes of gasohol[1] production, distribution, and use, including a fuel-cycle characterization.
2. Screening-level analysis and models to predict the likely environmental fate(s) of ethanol, gasohol, and alkylated-fuel components released into reference landscapes and consideration of potential exposure pathways. This assessment would contain:
   - A review of the existing state of knowledge,
   - The identification of physiochemical properties of the compounds of concern, and
   - Environmental-fate simulations for airborne emissions and subsurface releases.
3. Exposure assessments, including toxicity evaluations of ethanol, gasohol, and alkylated-fuel components that may be released.
4. Identification of key data and knowledge gaps and the specification of the kinds of studies needed to obtain the necessary data and to address any methodological issues related to assessing the use of ethanol, gasohol, and alkylated fuel.
5. Performance of selected experiments to address the identified data gaps.
6. Refinement of conceptual models and integration of new data into critical analyses of environmental transport and fate and multipathway exposures.

2.3 Ethanol is used in oxygenated[2] and reformulated[3] gasoline (8% in federal oxyfuel or 6% in federal reformulated gasoline [RFG], by volume) because it is a renewable, biomass-based source of fuel that benefits from tax incentives, and because it is perceived that its environmental impacts are less than those associated with the use of MTBE.

The ethanol used for fuel is made primarily from grains or other renewable agricultural and forestry feedstocks. Any feedstock that contains sugar, starch, or cellulose can be fermented and distilled into ethanol. To promote markets for ethanol, the United States Congress has approved a 5.4-cents/gallon federal subsidy for its use in gasoline.

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[1] Gasohol in this report refers to gasoline containing 10% ethanol.

[2] Oxygenated gasoline must contain at least 2.7% oxygen by weight unless a state obtains a waiver from the United States Environmental Protection Agency (US EPA). Such oxygenated gasoline is used in federally designated carbon monoxide nonattainment zones.

[3] Reformulated gasoline (RFG) contains a minimum average of 2% oxygen (by weight), no more than 1% benzene (by weight), and no heavy metals. RFG is used in locations that exceed the ozone standard. Currently, about 70% of gasoline used statewide is RFG.

Ethanol is a small chain molecule (C_2H_5OH) that contains 34.7% oxygen by weight and is infinitely soluble in water. In its pure (or neat) form, ethanol is a flammable, colorless liquid with a sweet alcohol odor. Ethanol is lighter than water; and if released rapidly in bulk onto water, ethanol will tend to remain on the surface of the water. When gasoline-containing ethanol is in contact with even small quantities of water, the ethanol will separate from the gasoline into the water. Pure ethanol and ethanol blends of gasoline are heavier than unblended gasoline.

Ethanol is very volatile and will evaporate into air approximately five times faster than MTBE. Like gasoline vapors, ethanol vapors are denser than air and tend to settle in low areas. In open-air areas, these vapors will tend to disperse rapidly.

When burned, ethanol releases less heat than gasoline. One and a half gallons of ethanol have approximately the same fuel combustion energy as one gallon of gasoline. Ethanol has a higher ignition temperature than gasoline (approximately 850°F versus approximately 495°F, respectively.). When pure ethanol is burned, the flame is less bright than a gasoline flame but is easily visible in daylight. Both ethanol and MTBE have similar octane ratings of about 110 and, when added to gasoline, increase the octane rating. (The long chain hydrocarbon known as octane[4] is used as a standard and is equal to 100).

Though pure ethanol is poisonous, it is less toxic than the benzene, toluene, ethyl benzene, and xylenes (BTEX) that are components of gasoline. Ethanol is present in pharmaceuticals, mouthwash products, alcoholic beverages, cleaning products, solvents, dyes, and explosives. Humans frequently ingest fermented beverages that contain about 12% ethanol by volume. Because ethanol is a metabolic byproduct, many organisms tolerate concentrations that may be encountered during accidental releases into the environment. A variety of indigenous microorganisms within the environment are capable of using ethanol as an energy source and will preferentially utilize ethanol over gasoline hydrocarbons, such as benzene.

Ethanol and ethanol blends of gasoline conduct electricity. (In contrast, unblended gasoline is an electrical insulator.) Because of its conductivity, pure ethanol is more corrosive than gasoline, and the compatibility of materials must be considered when designing large-volume, bulk ethanol storage tanks.

The California Energy Commission (CEC) anticipates that the use of alkylates[5] will be enhanced in non-oxygenated gasoline and some ethanol-containing gasolines in California to replace the octane normally provided by MTBE. For that reason, alkylates are also a focus of the analysis included in this report.

2.4 Additional amounts of alkylates, which are existing gasoline components, will likely be required to maintain octane levels in gasoline after the removal of the MTBE, a high-octane, anti-knock additive.

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[4] MTBE has a 110 octane rating, ethanol has 115 octane, alkylates provide 91 to 99 octane, and aromatics have 100 octane.

[5] Alkylates are gasoline blend stock produced by reacting isobutane with olefins. They consist of branched alkanes, have very low aromatic content, and contain no sulfur or olefins.

Alkylates consist of branched alkanes, mostly with 6 to 9 carbons, such as isooctane (2,2,4-trimethylpentane). Even though ethanol also has a high-octane level, its oxygen content is about twice that of MTBE; consequently, less ethanol is required to meet a specified oxygen content (for example, 2.5 wt% oxygen). The resulting octane deficit must be compensated for by adding high-octane blending components, such as alkylates.

Volume 3: Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline

To assist OEHHA in its health risk assessment, the ARB conducted an analysis to estimate the changes in outdoor air quality levels of potentially detrimental exhaust and evaporative components and subsequent reaction products that would result from substituting ethanol-blended gasoline for gasoline blended with MTBE. The ARB also included non-oxygenated gasoline in its analysis to provide a basis of comparison for the ethanol-containing gasolines. As stated previously, the CEC anticipates that the amount of alkylates will be increased in non-oxygenated gasoline and in some ethanol-containing gasolines to replace the octane normally provided by MTBE; consequently, these compounds were also a focus of the ARB analysis.

The ARB conducted four types of analyses:

1) A review of several recently published comprehensive assessments of the impact of oxygenated gasoline on the environment.
2) A literature review of studies that measure the direct impact of the use of ethanol in gasoline.
3) An evaluation of emission and air quality impacts from MTBE-free fuels in comparison to MTBE-containing fuel.
4) Closure of existing data gaps as part of this study and ongoing efforts that will not be completed until after the December 31, 1999, deadline in the Executive Order.

These analyses led to the following conclusions:

3.1 In comparison to the non-MTBE components of gasoline, the atmospheric formation of toxic compounds from ethanol and alkylates are relatively slow.

Because the maximum estimated outdoor air quality levels of ethanol and alkylates are at least a factor of 10 below any level of concern identified by OEHHA, the main issues are their products of incomplete combustion and atmospheric transformations. The major products of concern for ethanol are acetaldehyde (a toxic air contaminant) and peroxyacetyl nitrate (PAN, an eye irritant and cause of plant damage). These compounds are offset by reductions in formaldehyde (a toxic air contaminant) due to the elimination of MTBE. Alkylates eventually form acetaldehyde, formaldehyde, and PAN, as do many other existing components of gasoline. The greater the atmospheric lifetime of a compound, the more dilution and dispersion will reduce the impact of products of atmospheric transformations. The atmospheric lifetime for ethanol is similar to MTBE—about two to three days under polluted conditions and longer during periods of good air quality. Atmospheric lifetimes for alkylates range from one day to a week. Our findings from theoretical calculations using airshed models with state-of-the-science chemistry indicate that other components of gasoline, such as aromatic compounds and olefins, are primarily responsible for the formation of formaldehyde, acetaldehyde, and PAN due to both their greater abundance in gasoline and their shorter atmospheric lifetimes.

3.2 The inadvertent commingling of ethanol-containing and ethanol-free gasolines in vehicle fuel tanks results in a combined gasoline with a Reid vapor pressure (RVP) greater than the summertime California limit of 7.0 pounds per square inch (psi) and increased evaporative emissions of volatile organic compounds (VOCs). This effect will be mitigated by RVP reductions in the California Phase 3 Reformulated Gasoline (CaRFG3) regulations.

Even small amounts of ethanol cause an RVP increase of about 1 psi when it is added to an ethanol-free base gasoline. 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 with the potential for large-scale introduction. Thus, commingling would seldom happen in this large portion of California, representing 80% of the gasoline marketplace. California has requested the federal government for a waiver from the summertime oxygenate requirement to facilitate the phaseout of MTBE in these areas. If the waiver is granted, commingling will likely increase. Current estimates of the overall effect of commingling range from 0.1 to 0.4 psi, depending on assumptions for the market share of ethanol-containing gasolines, consumer's brand/grade loyalty, and the distribution of fuel tank levels before and after refueling events. The CaRFG3 regulations require a 0.1 psi RVP decrease to help mitigate the effect of commingling, and the ARB has committed to additional research to further quantify commingling impacts.

3.3 Ethanol-containing gasolines may lead to increases in evaporative emissions because rubber, plastics, and other materials are permeable to ethanol; moreover, ethanol may reduce the working capacity of the charcoal canisters used to control evaporative emissions on board motor vehicles. This issue has been addressed in the United States Environmental Protection Agency's (US EPA's) recently adopted Tier 2 emission standards. However, the current on-road motor vehicle fleet (other than flexible-fueled vehicles operated on alcohol blends) is not fully controlled from the perspective of evaporative ethanol emissions. Further research is needed to compare the effects of ethanol, MTBE (which also reduces the working capacity of charcoal canisters), and alkylates on evaporative emission from the existing California vehicle fleet.

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 evaporative emissions which occur during operation of the vehicle and stem from permeation through the fuel hoses and losses 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. “Diurnal” emissions are evaporative losses mainly from the charcoal canister and result from daily heating of the vehicle’s fuel tank and consequent saturation and overflow from the canister.

Because of the tendency of ethanol to evaporate more readily than other fuel components and because the smaller size of an ethanol molecule promotes permeation through hoses, hot-soak emissions tend to result in evaporative losses containing a proportionally greater amount of ethanol than was in the original fuel. Also, it is possible that ethanol’s propensity to be tightly held by activated carbon, in conjunction with its hygroscopic nature (that is, it attracts water), may decrease the working capacity of the charcoal canisters used to control evaporative emissions on board motor vehicles and result in increased diurnal emissions. However, data suggesting a reduced working capacity are somewhat conflicting in nature, but this may be partially due to the difficulty in sampling ethanol, and additional research is needed in this area.

Both early and late model–year vehicles (other than flexible-fueled vehicles operated on alcohol blends) are not fully controlled from the perspective of evaporative ethanol emissions. That is, the certification test procedures for evaporative emissions require the use of a fuel containing MTBE and, thus, do not completely take into account the use of commercially available ethanol-containing gasolines. Although more stringent evaporative emission standards were adopted in 1998 and are 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 US EPA recently adopted such changes under its Tier 2 regulations.

3.4 Because relatively little ethanol is produced in California, it will probably all be shipped by rail or truck. The estimated statewide impact on heavy-duty truck emissions is a 0.06% increase. Most likely , these impacts will be localized at the two central ethanol distribution locations and the 64 fuel storage terminals and will be addressed locally under the California Environmental Quality Act.

The bulk of the ethanol to be used in California will be transported by rail from the Midwest to two central distribution locations, trucked to 64 fuel storage terminals, and then splash-blended with gasoline. The increase in heavy-duty truck emissions would be about 0.06% of the statewide total, using estimates of truck travel for ethanol distribution made by the CEC. If increased local traffic and emissions from diesel trucks become local environmental concerns, they will be addressed locally in the context of use permits and permits to operate specific facilities under the California Environmental Quality Act.

3.5 So long as the CaRFG3 regulations address the potential for ethanol to increase evaporative emissions and cause more rail and truck traffic, the substitution of ethanol and alkylates for MTBE in California’s fuel supply will not have any significant air quality impacts. This finding is supported by theoretical calculations in the South Coast Air Basin using state-of-the-science tools, an analysis of the impact of uncertainties, air quality measurements in areas that have already introduced ethanol into their fuel supply, and an independent scientific peer review by the University of California.

We used the best available information on the emission characteristics of fuels that will be available in 2003, a comprehensive analysis of current (that is, 1997) air quality levels, and an airshed model for the South Coast Air Basin with state-of-the-science chemistry to estimate air quality in the future for the following four fuels:

- Current MTBE-based California Phase 2 Reformulated Gasoline (CaRFG2), assumed to be equivalent in both 1997 and 2003.
- Ethanol-based, fully complying CaRFG2 fuel with an oxygen content of 2.0 wt% (5.7% ethanol by volume) in 2003.
- Ethanol-based, fully complying CaRFG2 fuel with oxygen content of 3.5 wt% (10% ethanol by volume) in 2003.
- Non-oxygenated, fully complying CaRFG2 fuel in 2003.

Because the CaRFG3 regulations were not approved until December 9, 1999, we were unable to consider the new specifications in our emission and air quality predictions. However, because the regulations preserve the air quality benefits of CaRFG2 and apply equally to ethanol-blended and non-oxygenated gasolines, consideration of CaRFG3 will not affect our overall conclusions.

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. There are several differences between the 2003 MTBE baseline and the three 2003 MTBE-free fuel scenarios. Because fuel-related activities are the only inventoried source of MTBE, levels of MTBE decrease 100%. Ethanol levels for the ethanol-blended gasolines increase by 48% (2.0 wt% oxygen fuel) and 72% (3.5 wt% oxygen fuel), but acetaldehyde is predicted to increase (4%) for only the ethanol-blended gasoline at 3.5 wt% oxygen. PAN levels are not predicted to increase for either the ethanol-blended or non-oxygenated gasolines. Benzene levels 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 levels (2–4%) and essentially no change in ozone, nitrogen dioxide, nitric acid, and PPN (peroxypropionyl nitrate) levels. As expected, the non-oxygenated gasoline results in higher predicted eight-hour-average carbon monoxide levels (3%), and the 3.5 wt% oxygen ethanol-blend in lower carbon monoxide values (–9%). It should be noted that these are summertime levels—a time period when violations of the standard do not occur. Due to the wintertime oxygenate requirement for the South Coast Air Basin, carbon monoxide levels within the nonattainment area of Los Angeles County will not differ from the 2003 MTBE baseline.

Primarily due to the lack of ambient air quality measurements for many of the air contaminants of concern, we were unable to predict 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 levels, the conditions most conducive to formation of secondary air pollutants (for example, ozone, acetaldehyde, and PAN), the most emissions, and the highest number of gasoline-related emission sources in California.

Calculations that bracket the impact of motor vehicle emission inventory uncertainty and chlorine atom chemistry in coastal environments resulted in increases for all pollutants, but the only significant impact on relative differences among the 2003 fuels was a large increase in ethanol for the ethanol-blended gasolines. The use of the modeling tool in a relative sense bypasses concerns about other uncertainties.

Our review of studies of the impact of the use of ethanol-containing gasoline on air quality in Denver, Colorado; Albuquerque, New Mexico; Brazil; and other areas indicates that acetaldehyde levels are substantial only in Brazil, where the fuels contained either pure ethanol or 22% ethanol—much greater levels than the maximum of 10% ethanol allowed in California gasolines. Due to the lack of RVP requirements for gasolines in Brazil, the high acetaldehyde levels 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 levels, the observed levels of PAN are more than a factor of 10 below historical levels observed in southern California although the Brazilian measurements were not in the areas likely to have the highest PAN levels.

A draft version of this report was reviewed by four scientists approved by the University of California Office of the President under a process defined by Health and Safety Code section 57004. While the reviewers agreed with our basic findings on ethanol and alkylates, they noted the need for a number of corrections, clarifications, and caveats that we have incorporated into this final version of the report. Their comments and our responses are included in this report.

3.6 The results of this study do not necessarily extend to other states. California does not have an RVP exemption for ethanol-containing gasolines; and the CaRFG3 Predictive Model constrains emissions of cancer-potency-weighted toxic air contaminants, oxides of nitrogen (NO_X), and VOCs. States without these safeguards (that is, non-Federal Reformulated Gasoline areas) may have significant air quality impacts from replacement of MTBE with ethanol or aromatic compounds.

A previous ARB comparison of a 10% ethanol-gasoline blend with 8.0-psi RVP and a fully complying, MTBE-based gasoline meeting a 7.0-psi RVP limit concluded that while carbon monoxide emissions decreased by about 10% for the high-RVP fuel, emissions increased for NO_x (14%), combined exhaust and evaporative VOCs (32%), ozone-formation potential (17%), and cancer-potency-weighted toxic air contaminants (5%). The ozone formation potential calculations included the benefit of the carbon monoxide reduction. The results also show that there is a likelihood (between 92% and 100%) that emissions of NO_x, VOC, ozone formation potential, and cancer-potency-weighted toxics are greater with the high-RVP ethanol blend than with the fully complying gasoline. The high level of certainty associated with the results of the test program show that additional testing would not likely change the outcome of this evaluation and that additional tests on 1990 to 1995 model year vehicles and vehicles that employ control technologies similar to these are unnecessary. Thus, significant air quality impacts are likely in the parts of the United States (that is, non-Federal Reformulated Gasoline areas) where the US EPA allows a 1 psi RVP exemption for ethanol.

The CaRFG3 Predictive Model constrains exhaust emissions of NO_x, VOCs, and cancer-potency-weighted toxic air contaminants (that is, acetaldehyde, benzene, 1,3-butadiene, and formaldehyde), and evaporative emissions of VOCs and benzene. Thus, different fuel formulations (for example, ethanol-blended and non-oxygenated) will be manufactured to have similar emissions through the adjustment of various fuel properties, such as sulfur content, aromatic content, etc. As MTBE is removed from gasoline, the CaRFG3 Predictive Model will push California fuel suppliers toward an increased use of alkylates rather than aromatic compounds. Alkylates have no significant air quality impacts in comparison to the aromatic compounds that are powerful ozone and benzene precursors and likely to be used in other states if there is a corresponding ban on MTBE.

3.7 An air quality monitoring program is now in place to directly measure the impact of the phase-out of MTBE.

Our analysis of air quality impacts will be compared with field measurements that take place before and after the planned December 31, 2002, phaseout of MTBE. These types of studies were successfully conducted in California in 1996 during the implementation of CaRFG2. California's existing ambient air quality networks should be sufficient for all the criteria pollutants, MTBE, toxic air contaminants, and individual VOC compounds (that is, alkylates). Because PAN is not part of any routine air quality monitoring program, we began PAN measurements at two sites in the South Coast Air Basin last November. Because ethanol and acetaldehyde lead to PAN but not to PPN, and because their ratio may be a useful indicator of the impact of ethanol emissions on PAN air quality levels, the measurement program includes both PAN and PPN. We will investigate the possibility of adding ethanol measurements and expanding the monitoring program to other areas of the State.

Volume 4: Potential Ground and Surface Water Impacts

4.1 A comprehensive understanding of the effects of ethanol on the fate and transport of gasoline compounds is needed to determine if the economic and air quality benefits of adding such fuel alcohols to gasoline outweigh their potential detrimental effects on groundwater pollution and related health risks. Although California has implemented improved containment practices for underground storage tanks, releases of gasoline that may impact surface water and groundwater resources can still be expected.

An important consideration for the decision to use ethanol is the potential effect it may have on the fate and transport of toxic-gasoline components (in particular, BTEX). This fate-and-transport information is important for evaluating the impact that ethanol may have on the cleanup of gasoline releases and on California's water resources in general. The chapters in Volume 4 summarize the possible release scenarios associated with the use of ethanol as a fuel oxygenate (Chapter 1), the effect of ethanol on the fate and transport of BTEX compounds (Chapter 2), and on their natural attenuation and biodegradation (Chapter 3). We report the results of the predictive modeling performed to compare BTEX groundwater plumes in the presence of ethanol (Chapter 4). We consider the potential impacts of the use of ethanol-containing gasoline on surface-water resources (Chapter 5) and compare possible non-oxygenated fuel formulation to

MTBE- or ethanol-containing gasoline (Chapter 6). We evaluate the analytical methods available for the detection of ethanol in the environment (Chapter 7). We perform a comparative analysis of potential groundwater resource impacts for gasoline containing methyl tertiary butyl ether (MTBE) or ethanol (Chapter 8).

As a result of the research performed for this volume, we have identified important knowledge gaps regarding the anticipated environmental behavior of gasoline containing ethanol. Chapter 9 summarizes those knowledge gaps and provides recommendations for future research that would improve decision-making regarding the use of ethanol in oxygenated and reformulated gasolines in California.

4.2 During our evaluation of ground- and surface-water impacts, we began the development of a comprehensive life-cycle model.

This life-cycle model systematically addresses impacts from fugitive and accidental releases associated with the production, distribution, and use of ethanol-containing gasoline. Time constraints for producing this particular assessment limited its focus to only those scenarios of chronic or accidental releases of ethanol that are most likely to impact ground and surface waters. We were unable to consider fully other scenarios related to releases of substances as a consequence of the transportation and use of feedstocks required for ethanol production as well as from activities conducted at centralized blending centers. Also not considered were the additional implications of agricultural-related impacts from ethanol-fuel production. For example, increased corn-production for ethanol in California and elsewhere will require the application of additional herbicides/pesticides with subsequent releases to the environment. Including such scenarios will improve the breadth of understanding concerning the impacts of ethanol use in motor fuels and, for this reason, may warrant more complete evaluation in the future.

4.3 We examined the salient environmental properties of alkylates, which are non-oxygenated compounds likely to be used in greater amounts in gasoline after an MTBE phaseout.

However, the limited analyses we conducted were not completed within the context of an integrated life-cycle analysis concerning their production, storage, and use. Alkylates are complex solutions of isoalkanes; and some properties, such as biodegradability, may not be easily extrapolated to all alkylate components. In general, alkylate biodegradation rate is relatively slow compared to other organic compounds, and some components may not biodegrade in reasonable timeframes.

No toxicity data are available on the chronic effects of isooctane in humans. In addition, we did not address cancer risk and reproductive and developmental effects. Surface releases of alkylates, either on water or land, will probably result in the evaporation of most of the alkylate into the atmosphere. Overall, it appears that alkylates would not effect dramatic changes in the gasoline behaves in the environment and, thus, in the treatment of accidental releases.

4.4 Several abiotic processes or mechanisms that affect the fate of ethanol and ethanol-gasolines in the subsurface have been identified. These processes include infiltration, spreading at the capillary fringe, and leaching of chemicals into groundwater.

These abiotic processes can potentially impact the retention and distribution of gasohol or other petroleum products in the unsaturated zone, the size and the shape of a gasoline pool at the water table, and the flux of contaminants from the gasoline to the groundwater.

The extent of our knowledge about these processes ranges from sufficient to inadequate. We have very little information on the behavior of an ethanol gasoline as it infiltrates through the unsaturated zone. On the other hand, there is substantial knowledge about many of the mechanisms affecting saturated zone transport of gasoline containing ethanol. The net effect of ethanol on the length and longevity of a contaminant plume, however, requires an understanding of each of the steps that define the complete transport pathway. Rather than just deal with each of these steps individually, it is important to understand the complex interrelationships among the processes involved with the ultimate transport of gasoline components to a potential downgradient receptor.

4.5 The introduction of ethanol affects the migration and distribution of gasoline in the unsaturated zone in two primary ways:

- **Capillary forces are reduced, thereby changing the multiphase flow characteristics.**
- **Pore structure of some mineral types is altered by chemical interactions with ethanol.**

In the presence of ethanol, hydrocarbons can enter smaller pore spaces and drain more easily from unsaturated zone soils. This may impact the distributions of residual fuel hydrocarbons in the unsaturated zone and the periphery of free-product pools that may exist. Among the impacts may be the mobilization of existing unsaturated-zone contamination. As a result of the reduction in capillary forces, the height of the capillary fringe may also be reduced. The depth and the area of hydrocarbon pool on top of the water table may be altered (although 10% ethanol in gasoline is expected to have a very minor effect). Furthermore, the dehydration of clays and the formation of micro-fractures will increase permeability. The importance of these factors in multiphase flow has not been quantified.

Understanding this process is crucial because knowledge gaps about the early stages of the overall flow and transport preclude adequate prediction of the important impacts of ethanol on BTEX contamination resulting from subsequent processes. A high level of predictive uncertainty will remain until the relationship of each step to the overall process is understood sufficiently.

4.6 Ethanol in gasoline will affect the concentrations of BTEX that dissolve into groundwater and the residence time of fuel hydrocarbons in contact with the water table (saturated zone).

Although the dissolved equilibrium concentrations of gasoline components—benzene, toluene, ethylbenzene, and xylenes—increase in the presence of high concentrations of ethanol, the 10% ethanol expected to be added to gasoline in California should have only a minor effect on the dissolution of these gasoline components. Relatively hydrophobic compounds, such as xylenes, will be more affected than less hydrophobic compounds, such as benzene.

4.7 The presence of ethanol in groundwater may alter the processes of sorption and retardation and could contribute to increased benzene plume lengths.

The possible impact of these effects is dependent on the quantity of ethanol at the source. For gasoline containing 10% ethanol, these processes will likely be insignificant, whereas for neat ethanol spills, these processes may become important.

To better assess the overall impact of oxygenated gasolines on the length and the longevity of a BTEX groundwater plume, we need a better understanding of the significance of the size, the shape, and the composition of gasoline free product in contact with the water table. A thorough modeling effort to assess the sensitivity of the overall predictions to these unknown parameters would be an appropriate first step. If the predictions are sensitive to these parameters, then further experimental or modeling studies would be required to improve our ability to estimate them.

4.8 Biodegradation of fuel alcohols contributes to the depletion of electron-acceptor pools, and this depletion is likely to affect temporal and spatial transitions in electron-acceptor conditions during natural attenuation of petroleum-product releases.

Such geochemical transitions are important to study because they affect both BTEX degradation and migration rates. For example, both the changes in electron-acceptor availability and the presence of easily degradable ethanol could affect catabolic diversity and the relative abundance of specific BTEX-degrading bacteria.

4.9 Little is known about the effect of ethanol on microbial population shifts (that is, microbial ecology) and the resulting catabolic diversity.

Among the possible effects are enrichment of ethanol-degrading bacteria in relation to BTEX-degrading bacteria, fortuitous enrichment of bacteria that can degrade both ethanol and BTEX compounds, and decreases in populations of certain bacteria as a result of toxicity. Because the efficiency of bioremediation depends, in part, on the presence and expression of appropriate biodegradative capacities of the subsurface microbes, studying the microbial ecology of aquifers contaminated with gasoline-ethanol mixtures could be a fruitful avenue of research. Such studies should address response variability as a function of release scenario and site specificity to facilitate risk assessment and remedial action decisions.

To date, little research has been conducted on substrate interactions between BTEX and ethanol. Often, target pollutants are degraded by inducible enzymes whose expression can be repressed when easily degradable substrates (for example, ethanol) are present at high concentrations. Although biodegradation of contaminant mixtures is not very well understood at the biochemical level, preferential substrate degradation appears to be a concentration-dependent phenomenon related to repression of the enzymes needed to degrade the target compounds. Currently, little is known about the conditions leading to sequential or simultaneous degradation of BTEX in the presence of ethanol. This suggests the need to investigate the concentration-dependent effect that ethanol may have on the induction or repression of enzymes that catalyze BTEX degradation. However, considering that the co-occurrence of BTEX and ethanol may be a short-lived phenomenon relative to the overall duration of a gasoline plume, it is likely that the depletion of oxygen and other electron acceptors resulting from ethanol degradation will be a more important effect of ethanol than the substrate interactions between ethanol and BTEX.

Much of the relevant research to date reflects a reductionist approach to studying the effect of ethanol on natural attenuation. For example, to study the effect of ethanol on specific biodegradation activities, batch studies have often been used that eliminate confounding effects from other variables, such as BTEX and electron-acceptor concentration gradients, as well as mass-transport limitations. Similarly, pure cultures have been used to eliminate confounding effects of microbial population shifts. This work on individual processes generally facilitates hypothesis testing and yields results that are easier to interpret but may do so at the expense of oversimplifying the complex conditions encountered in the field. To determine how ethanol affects BTEX plume dimensions and treatment end points, future research should take on a more holistic approach that considers transport and degradation processes interactively.

4.10 Ethanol stimulates microbial processes that may affect aquifer porosity and hydraulic conductivity (for example, biofilm growth, mineral precipitation or dissolution, and nitrogen or methane gas generation).

It is important to study how the presence of ethanol influences the dynamics of anaerobic microbial communities and related processes that affect the hydraulic and chemical properties of the aquifer. Such research should delineate the conditions that lead to a significant accumulation of volatile fatty acids (VFA; potential degradation products of ethanol), and that could decrease the pH to levels that inhibit bioremediation. Emphasis should be placed on evaluating the potential for ethanol-induced methane production to restrict groundwater flow (thus, hindering the replenishment of nutrients and electron acceptors) and to pose an explosion hazard (which raises the possibility of requiring unique corrective-action measures).

4.11 The lack of BTEX and ethanol concentration data at gasohol leak sites is a major knowledge gap.

Although 10% gasohol is widely used in Iowa and Nebraska, the ethanol concentrations associated with gasohol releases are typically not measured because ethanol is not a regulated pollutant. There is a perception that no important differences exist between gasoline with and without 10% ethanol, but potential differences have not been evaluated.

Based on laboratory studies and theoretical considerations, we expect that ethanol may increase BTEX plume length by hindering BTEX biodegradation, enhancing light nonaqueous phase liquid (LNAPL) dissolution, and facilitating BTEX migration due to a decrease in sorption-related retardation during transport. Nevertheless, there is very little information about the subsurface characteristics of ethanol plumes or about the variability of their effect on BTEX fate and transport.

4.12 Several modeling efforts evaluating the behavior of benzene groundwater plumes in the presence of ethanol indicate that benzene plumes are likely to increase in length. The amount of this increase is not well known.

Because of the conservative assumptions used regarding unknown transport processes, the models used to forecast benzene plume lengths in the presence of ethanol systematically overestimate plume lengths. Each of these modeling efforts has taken a different approach and has used a different set of simplifying assumptions that may not reflect actual subsurface conditions. A key simplifying assumption among these studies is that the biodegradation rate of benzene is constant in space and in time and for all concentrations of benzene with in the plume. This assumption is very conservative; and if benzene biodegradation rates do actually increase downgradient from the ethanol degradation zone, then these modeling predictions significantly overestimate the extent of future benzene plumes. As information from laboratory, field, and historical-case studies becomes available, these simplifying assumptions can be refined; and more accurate and representative forecasts of gasoline-release plumes may be prepared. Improved modeling will aid in the identification of efficient and cost-effective cleanup approaches and resource management priorities.

4.13 During our analysis of potential groundwater impacts, we used a distance approach combined with known impact probabilities and estimated plume lengths to compare the probabilities of threat to public drinking water wells in California from MTBE or benzene releases (with or without ethanol) from leaking underground fuel tanks (LUFTs)..

This method provides an important advantage because it allows comparative estimates of potential future impacts between MTBE and benzene in the presence of ethanol. For comparative purposes only, this analysis develops a modeled estimated baseline for benzene impacts. This baseline estimate is then used to compare potential impacts from MTBE and benzene with ethanol present. The methodology described in Chapter 8 can act as a screening-level approach to identify vulnerable groundwater resource areas.

4.14 Based on the results of our analysis, an approximately 20% peak relative increase in public drinking water wells impacted by benzene was estimated if MTBE is replaced by ethanol.

The percent relative increase in impacts to public drinking-water wells is estimated to decline from this peak increase at about ten years after the initiation of the use of ethanol. However, the estimated, potential future increase in public wells impacted by MTBE is significantly higher if MTBE were to remain the primary fuel oxygenate. By the conclusion of the first ten-year period, estimated MTBE-well impacts increase by as much as 45% and continue to increase thereafter. This analysis is very conservative, especially with regard to MTBE. Known concentrations of MTBE at LUFT sites were not used in the analysis because only a limited number of LUST sites have a known concentration associated with them.

This approach may be subject to misinterpretations. Because we are examining an absolute probability, there is a concern that the results can be taken out of context. It is important that the relative probabilities be used, using the benzene-alone distributions as the baseline. These estimates are not intended to be used to predict or forecast actual impacts. The results of these estimates are to be used for relative comparison only.

4.15 Overall, the average yearly public drinking water source benzene detection rate is under 0.35%. Both toluene and total xylenes have a higher rate, 0.53% and 0.36% respectively. MTBE shows a 1.17% yearly detection rate, much higher than any of the BTEX constituents alone, although similar to the combined BTEX detection rate (1.15%).

The evaluation of known detection levels in public water sources is to provided some perspective to the magnitude of benzene or MTBE impacts in the past. Benzene shows a fairly constant detection rate over time, with a slight downward trend when yearly rates are compared. The use of ethanol as a fuel oxygenate would likely increase this detection rate which may stabilize at some higher level. MTBE shows definite upward detection trends; its continued use could, based on the trend results, result in more detections in water sources than benzene within the foreseeable future.

4.16 In assessing the probability that MTBE or benzene with or without the presence of ethanol may affect a drinking-water well or degrade a water supply, several unknowns must be estimated.

These include the concentration of benzene, MTBE, or ethanol at a gasoline-release site, the local hydrogeological regime, and the construction of nearby drinking-water wells and their radius of groundwater capture during use. The availability of this data is very limited, and existing data often have significant inaccuracies and errors.

Having accurate locations of public drinking-water wells is important to this effort, but database location information on these wells is often poor. Additionally, data on well construction and yield—necessary items to determine a well's intrinsic vulnerability—are not readily available, and collecting that data is costly although recent legislation has made it easier for groups that are performing environmental assessments to access this type of data.

4.17 The persistence of ethanol in surface water will be governed by its biodegradation rate, based on screening-level calculations.

Screening-level calculations for a scenario that simulates a discrete, seven-day period of watercraft discharges of fuel-borne ethanol to Donner Lake in northern California showed that the peak concentration of ethanol was only 2 μg/L, compared to about 8 μg/L for MTBE under the same release scenario. The difference in levels is due to the elevated biodegradation loss rate assumed to occur for ethanol—compared with the slower, volatilization-driven losses for MTBE. For accidental tank-car releases of ethanol to a river or stream, toxic levels of ethanol could occur in the immediate downstream area of a spill. The toxic levels of ethanol would be expected to occur at variable distances downstream from the hypothesized spill, with the extent of such toxic concentrations dependent on volumetric-discharge conditions. In addition, if only a portion of the tank-car inventory were released, the resulting concentrations would also be reduced proportionately.

Aside from the acute toxicity for aquatic species that might be affected by a spill and their associated recovery, it is unlikely that there would be any long-term toxic effects, because the ethanol will not persist in water due to its rapid degradation. The key uncertainty with regard to assessments of the impacts of ethanol releases to surface waters is the magnitude of the range of ethanol biodegradation rates.

4.18 Based on the health-protective concentrations for drinking water alone (which are summarized by the State of California Environmental Protection Agency, Office of Environmental Health Hazard Assessment in Volume 5 of this report), it is clear that any catastrophic or even major release of MTBE to surface water is far more likely to represent a potential public-health problem than a similar release of ethanol.

A quantitative risk assessment designed to compare the results of MTBE and ethanol releases to surface waters was not performed and was not the objective of this chapter. Instead, we performed a series of screening-level simulations of various releases to better understand the nature and magnitude of the impacts of ethanol and MTBE on surface waters, both temporally and spatially. However, based on the health-protective concentrations for drinking water alone (which are summarized by the State of California Environmental Protection Agency, Office of Environmental Health Hazard Assessment in Volume 5 of this report), it is clear that any catastrophic or even major release of MTBE to surface water is far more likely to represent a potential public-health problem than a similar release of ethanol. The draft health-protective concentration for oral exposures to drinking water for ethanol is 1,100,000 µg/L, whereas the public-health goal for drinking water for MTBE is only 13 µg/L—a difference of almost five orders of magnitude (that is, 10^5 or 100,000). The problem of MTBE release to surface water is further exacerbated because it appears to be recalcitrant to aerobic biodegradation.

4.19 Rainout of ethanol to surface waters is considered to be more than a factor of 40 greater than for MTBE (by mass per unit-volume), as a result of the large difference between the Henry's law constants for these two compounds.

The quantity of ethanol in rainout will only be about 10 µg/L for every part per billion by volume (ppb[v]) of ethanol in air compared to only 0.17 µg/L for MTBE. However, ethanol will biodegrade rapidly in surface water, but MTBE is recalcitrant to such removal. Nevertheless, for more accurate estimates of the levels of ethanol in rain, temperature-dependent values of the Henry's law constant need to be quantified in laboratory experiments. Compared to ethanol and MTBE, the concentration of isooctane (a representative alkylate) in rain is going to be negligible (estimated to be 0.000036 µg/L per 1 ppb[v] in air). Other isoalkanes are also likely to have very low concentrations in rainwater.

4.20 The literature reviewed indicates that the technology currently exists to enable researchers to detect ethanol at spill sites.

Sufficient methods also exist to determine ethanol at its taste threshold of 50 parts per million (ppm) in water. But no routine methods are currently able to detect ethanol below 50 parts per billion (ppb) in water. A novel method for ethanol analysis capable of 15-ppb detection limits has been reported. However, this solid-phase microextraction method requires validation before it can be applied routinely to the analysis of environmental samples. Thus, much time and effort must be invested to enable the detection of trace concentrations of ethanol. Until this is accomplished on a routine basis, it will be difficult to completely understand the fate and transport of ethanol in the environment.

4.21 The poor extraction efficiency of ethanol from water is the main contributor to its relatively high analytical detection limits.

Improved extraction methods will result in better detection limits. The literature reviewed for this study indicates that either direct injection of an aqueous solution or injection of the headspace above an aqueous liquid can be used to obtain detection limits of 10 ppm or less. Both of these techniques are easy and inexpensive to perform.

4.22 A number of recommendations have been made to address knowledge gaps in the potential ground- and surface-water impacts associated with using ethanol to replace MTBE. These recommendations include:

Expanded life-cycle analysis of the use of ethanol and non-oxygenated fuel compounds. A comprehensive life-cycle assessment of ethanol should include the evaluation of release scenarios associated with all stages of its manufacture, distribution, and utilization, including transportation and use of feedstocks and activities at blending centers. This complete analysis would account not only for the mass balance of ethanol in the environment but also for its direct and indirect impacts with respect to issues related to the environment, health, and safety. Accordingly, the objective of a complete life-cycle analysis is to provide a scientifically sound characterization of its input feedstocks and related byproducts as well as their potential impacts. A complete and comprehensive life-cycle analysis was not prepared for alkylates, but preparing one would also be beneficial in order to understand the nature and magnitude of environmental releases and their impacts.

Detailed field studies to refine conceptual models. Modeling based on detailed, site-specific information is needed. Data from a thoroughly studied field site would refine our conceptual models of critical processes controlling the net fate of gasohol in the subsurface. Because the results of these estimates are largely dependent on the input-parameter probability distributions, historical-case data that better constrain the uncertainty in these probability distributions will improve the predictive capability of any future modeling. The uncertainty inherent in using the complete distribution of benzene concentrations and velocities increases substantially the increase in expected probability for well impacts. Site-specific, maximum concentrations should be used, as opposed to a generic distribution that assumes no knowledge of the LUFT site.

A representative site where gasoline containing ethanol has been released should be evaluated in detail, including the collection and analysis of additional soil and groundwater samples needed to support microcosm and column studies. Additional sampling of field sites might be used to provide field verification of microcosm results and increase the number of sites upon which decision-making is based.

Groundwater capture zones should be included in the analysis. The approach we used to evaluate potential groundwater-resource impacts assumes that all plumes move towards a nearby well but without influence from the well itself. Further probabilistic modeling should be performed to ascertain the sensitivity of this approach to well-capture zones and known groundwater-flow directions.

Microcosm and aquifer column studies using field study materials. Microcosm and associated aquifer column studies are recommended to address knowledge gaps regarding the effect of ethanol on the biodegradation of BTEX compounds. The microcosm studies, which would involve aquifer solids and groundwater from several sites with different histories of fuel contamination, would address the following:

- Microbial ecology/catabolic diversity—assessment of changes in the relative abundance of BTEX-degrading bacteria resulting from exposure to gasoline with and without ethanol under various electron-accepting conditions (based on analysis of DNA that codes for specific aerobic and anaerobic BTEX-degrading enzymes).
- Degradation kinetics—generation of kinetic data (lag periods and degradation rates) for BTEX compounds and ethanol under various electron-accepting conditions in aquifer materials from areas with different histories of gasoline and oxygenate exposure.

The results from such studies will also show whether ethanol metabolism results in marked pH changes in naturally buffered systems as a result of VFA accumulation. The column studies will provide a means to examine whether the kinetic results for the microcosms (for one selected site) are generally consistent with the results in a more realistic, flow-through system. The column studies will also allow researchers to examine how the integrated effects of bacterial metabolism (for example, depletion of electron acceptors and variations in BTEX degradation rates under different electron-accepting conditions) and physical processes (for example, advection and dispersion) result in spatial heterogeneity in degradation processes. The kinetic BTEX and ethanol degradation data could be used in conjunction with existing laboratory data to derive input parameters for modeling.

Although the recommended studies will address some of the most critical knowledge gaps identified during the literature review, they cannot address all knowledge gaps because of time and cost constraints. As discussed earlier, a primary consequence of releases of ethanol-containing gasoline into the subsurface will be the rapid consumption of oxygen and the accelerated development of anaerobic conditions. Long lag times and relatively slow BTEX degradation rates characteristic of anaerobic conditions will constrain the scope of microbiological studies.

Historical-case studies to develop statistical analyses. Additional data should be collected from sites where ethanol-containing gasoline has been released. These data should be used to develop population statistics for supporting the predictive modeling efforts and to interpret how the release scenario affects ethanol-plume characteristics. Emphasis should be placed on statistically analyzing BTEX data to determine how ethanol affects the stability and the dimensions of individual BTEX plumes. Such a survey would provide an integrated picture of the overall effects of ethanol on groundwater pollution and natural attenuation. This information would also provide a stronger basis for the selection and operation of appropriate remedial systems.

A possible outcome of the historical-case analysis would be a statistical comparison of gasoline-release plume lengths at locations where ethanol is present or absent as a fuel component. A reasonable objective is to gather at least 25 cases where ethanol was released as a gasoline component. This population would then be compared to existing historical-case data available for gasoline releases without ethanol.

Laboratory studies to improve Henry's law constants. To improve the prediction of the concentrations of ethanol in rainfall and surface waters, we recommend that temperature-dependent values of the Henry's law constant be determined in laboratory studies. Additionally, we recommend that further studies be conducted to predict more accurately the half-lives of ethanol in different kinds of surface waters in California. This is particularly important because of the important role that rapid natural biodegradation can play for the removal ethanol of from surface waters.

Development of laboratory analytical methods. Analysis methods must be developed to meet the data quality objectives of future studies. The poor extraction efficiency of ethanol from water is the main contributor to relatively high analytical detection limits. Improved extraction methods will result in better detection limits.

In order to eliminate problems with potential interferences, we recommend that gas chromatographic (GC) separation be used in all future ethanol analyses. There are two practical strategies that can be used for the sensitive detection of ethanol in the presence of interfering compounds. The first is to use the best possible GC procedure to separate ethanol from any interferences and then to detect ethanol with a nonspecific detector, such as a flame ionization detector. The second strategy is to perform a less rigorous GC separation coupled with a detector that would respond specifically to ethanol but would not respond to potentially interfering compounds (for example, an atomic emission detector or a mass spectrometer). Both of these strategies merit further consideration.

Development of a central database. More knowledge is required concerning the subsurface environment in California. One of the major unknowns in any hydrogeological investigation is the lack of knowledge of subsurface geology. A great deal can be learned even from the moderate to poor quality of data available in well logs maintained by the California Department of Water Resources. This data should be transcribed into electronic format for use by researchers attempting to draw conclusions on the subsurface.

As part of ethanol studies, we should use GeoTracker and the Geographic Environmental Information Management System (GEIMS) database as a central repository of data. GeoTracker and GEIMS were developed by Lawrence Livermore National Laboratory for the SWRCB pursuant to a mandate by the California State Legislature (AB 592, SB 1189) to investigate the feasibility of establishing a statewide geographic information system for LUFTs. The SWRCB already intends to use this system to help regulators assess sites.

Other agencies should be encouraged to supply their data to the system so that interagency cooperation may be fostered. As Senate Bill 989[6] allows responsible parties to access well construction and other details when under order from a regulatory agency, the associated data for wells in the state of California (lithologic logs, well construction, location, and yield) should be placed in an electronic database to expedite site assessments and decrease costs. This information can also assist in the evaluation of vulnerable groundwater areas as stated elsewhere in the same bill.

Data already collected by various state organizations should be systematically organized for use in decision analysis. This would permit further comparative analysis of impacted public drinking-water wells to gasoline continuing ethanol or MTBE and well-impacted LUFT sites.

Volume 5: Potential Health Risk of Ethanol in Gasoline

The objective of this volume is to present an evaluation of the public-health impacts of ethanol as an oxygenate in gasoline, and of non-oxygenated fuels, in place of methyl tertiary butyl ether (MTBE). Table 1 summarizes cancer and noncancer risks from selected air pollutants.

5.1. Existing state or United States public-health standards were used where available.

To quantify potential health risks, health assessment values for the compounds of concern were selected from current California or United States regulatory programs where these were available. In the absence of suitable regulatory standards, draft numbers currently under development for California regulatory programs were used. In the absence of these, draft health protective concentrations were developed for this report using established methodology.

5.2. Exposure assessments were based on estimates provided by the ARB and the SWRCB.

Evaluations of likely population exposures to fuel components and transformation products were presented in previous chapters of this report. The scenarios considered compared the use of fuel containing ethanol or MTBE as oxygenates, or fuel without oxygenates but otherwise complying with ARB regulations. The exposure estimates derived were used by OEHHA in assessing the relative public-health impacts of the proposed fuel compositions.

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[6] *Section 13752 of the Water Code is amended to read:* Reports made in accordance with paragraph (1) of subdivision (b) of Section 13751 shall not be made available for inspection by the public, but shall be made available to governmental agencies for use in making studies, or to any person who obtains a written authorization from the owner of the well. However, a report associated with a well located within two miles of an area affected or potentially affected by a known unauthorized release of a contaminant shall be made available to any person performing an environmental cleanup study associated with the unauthorized release, if the study is conducted under the order of a regulatory agency. A report released to a person conducting an environmental cleanup study shall not be used for any purpose other than for the purpose of conducting the study.

5.3. Cancer and noncancer risks from air pollutants were assessed.

For assessing health impacts of fuel-related air pollutants, the health assessment values for compounds of concern were compared to the model predictions provided by the ARB, and risk characterizations presented (Table 1). Risk characterizations for impacts of individual carcinogens, and for the cumulative impacts of all carcinogens considered, are presented. Risk characterizations for the critical noncancer effects (eye and respiratory irritation) are also provided. Some other pollutants for which exposure estimates were available were found to be unlikely to have significant health impacts. The chemicals considered were:

- The oxygenates MTBE and ethanol.
- Combustion products 1,3-butadiene, formaldehyde, acetaldehyde, carbon monoxide, nitrogen dioxide and particulate matter (PM_{10}).
- Evaporative emittents benzene, hexane, and toluene.
- Atmospheric transformation products peroxyacetyl nitrate (PAN), and ozone.

5.4. Existing levels of some air pollutants are a cause for concern, but predictions do not differ substantially between the proposed fuel types.

Under these exposure scenarios, the concentrations of irritants (including both air toxics and criteria pollutants) may achieve levels at which the margins of safety for short-term and long-term exposures are reduced. Adverse health effects are not necessarily expected at these levels, but more sensitive individuals may be affected. There were no substantial differences between the different fuel types with regard to the resulting levels of irritant air pollutants.

The upper-bound estimate of the cumulative cancer risks from air pollutants in the South Coast region, for all fuel use scenarios, is in the range 1 to 3×10^{-4} (Table 1). This is well above the level (10^{-6}) usually regarded as a negligible effect. There were no substantial differences between the different fuel types with regard to the cumulative cancer risks from air pollutants. Principal contributors to this risk are the fuel-related pollutants, benzene and 1,3-butadiene. Other pollutants (including formaldehyde and acetaldehyde, which may be partly related to oxygenate use in fuels, and MTBE) make a smaller contribution. While we have more confidence in the relative risk estimates than the absolute values of concentrations and risk, the results point to the continuing need for regulatory action to reduce toxic air contaminants from automobiles.

5.5. Effects of water pollution were considered.

Quantitative estimates of possible drinking-water contamination associated with different fuel-use scenarios were not available. However, possible toxic effects of drinking-water pollution by ethanol, MTBE, and tertiary butyl alcohol were considered. Other effects, such as changes in the groundwater distribution of benzene and other hydrocarbons, may need to be considered when data or model predictions of these processes become available.

5.6. Substantial uncertainties and research needs remain.

There are several major uncertainties and data gaps, both in the exposure-assessment needs for health-risk assessment and the toxicological assessment of compounds of concern. Some of these areas (particularly the assessment of water contamination, accidental-release scenarios, and life-cycle analysis) are being addressed by work currently in progress for SWRCB. Similarly, the ARB is continuing to refine and extend its modeling and measurement of both air toxics and criteria air pollutants. Other interested parties and academic specialists are also active in addressing these problems. As new data become available, their implication for public-health impacts of fuel use will need to be assessed.

Volume 5 Conclusions: *It appears that there are no substantial differences in the public-health impacts of the different nonMTBE fuel formulations considered in the scenarios for 2003.*

Although replacement of MTBE by either ethanol or non-oxygenated fuel is expected to have some benefits in terms of water contamination, these cannot be quantified at present. From our analysis, these substitutions had no substantial effects on public-health impacts of air pollution.

Table

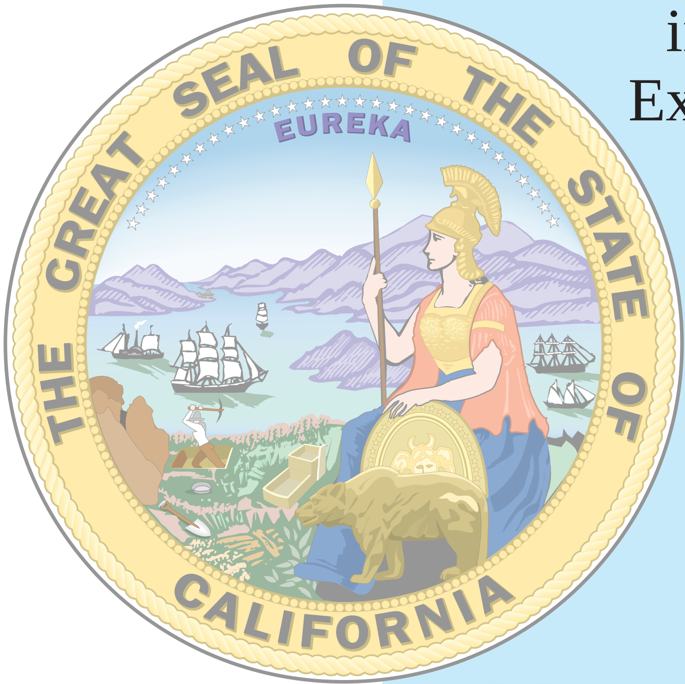
Table 1. **Cumulative cancer risks and noncancer hazard indexes from air pollutants in the South Coast region for all fuel scenarios.**

Risk description	Estimate range	1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 NonOxy
Cumulative lifetime cancer risk	Upper	2.9×10^{-4}	1.9×10^{-4}	1.8×10^{-4}	1.9×10^{-4}	1.8×10^{-4}
	Lower	2.7×10^{-4}	1.8×10^{-4}	1.7×10^{-4}	1.7×10^{-4}	1.7×10^{-4}
Cumulative Hazard Index (HI) for acute eye irritation	Upper	10.0	9.6	9.5	9.5	9.4
	Lower	6.9	6.7	6.6	6.6	6.5
Cumulative HI for acute respiratory irritation	Upper	4.0	3.8	3.8	3.7	3.8
	Lower	3.9	3.7	3.7	3.6	3.7
Cumulative HI for chronic respiratory irritation	Upper	5.5	5.1	5.1	5.2	5.0
	Lower	5.5	5.1	5.0	5.0	5.0

UCRL-AR-135949 Vol. 2

Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate

Report to the
California Environmental
Policy Council
in Response to
Executive Order
D-5-99



VOLUME 2

Background Information on the Use of Ethanol as a Fuel Oxygenate

STATE WATER RESOURCES CONTROL BOARD

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Office of Environmental Health Hazard Assessment

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Front Cover Back

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UCRL-AR-135949 Vol. 2

Volume 2: Background Information on the Use of Ethanol as a Fuel Oxygenate

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Table of Contents

Background Information on the Use of Ethanol as a Fuel Oxygenate

1.1. Scope of Report to the California Environmental Policy Council

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 no later than December 31, 2002 (State of California, 1999). Task 10 of the Executive Order states "the California Air Resources Board (CARB) 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."

This report has been prepared by the CARB and SWRCB in response to the Executive Order D-5-99 and is divided into five volumes:

- Volume 1: Executive Summary.
- Volume 2: Background Information on the Use of Ethanol as a Fuel Oxygenate.
- Volume 3: Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline.
- Volume 4: Potential Ground and Surface Water Impacts.
- Volume 5: Potential Health Risks of Ethanol in Gasoline.

This Volume 2 provides background information on the use of oxygenated fuels in general, the production of ethanol and its role as a fuel oxygenate, and the physical and chemical properties of ethanol as well as background information on key air and water issues associated with the multimedia evaluation of ethanol as a fuel oxygenate.

1.2. Clean Air Act and the Use of Oxygenated Fuels in California

Under the Clean Air Act (CAA) Amendments of 1990, areas of the country with poor air quality must add an oxygen-containing, organic compound to their gasoline to reduce air emissions. All gasoline sold in the specified, carbon monoxide nonattainment areas during winter months must contain at least 2.7% oxygen (by weight) unless a state obtains a waiver from the U.S. Environmental Protection Agency (US EPA) to implement a different oxygen standard in oxygenated fuel. California's oxygenated gasoline program limits oxygen content to a maximum of 2.2% to limit increases in nitrogen oxides (NOx) emissions that occur from adding oxygen to gasoline (Gomez *et al.,* 1998). Areas that exceed the ozone standard must meet federal requirements for the use of reformulated gasoline (RFG). The CAA requirements for RFG mandate that it must contain a minimum average of 2% oxygen (by weight), no more than 1% benzene (by weight), and no heavy metals. Throughout this report the use of the general term "gasohol" refers to either oxygenated fuel or RFG containing ethanol.

The 1977 CAA Amendments set requirements for "substantially similar gasoline" which mandate oxygenates be approved by the US EPA before they are allowed to be used in gasoline. Ethanol (EtOH), methanol (MeOH), MTBE, and ethyl tertiary butyl ether (ETBE) are currently added to gasoline to meet criteria for the CAA Amendments. Because 10% ethanol by volume blends did not meet the substantially similar definition, the US EPA has granted a waiver for blends of gasoline containing ethanol (Gomez *et al.*, 1998).

MTBE is the most commonly used fuel oxygenate (US EPA, 1999). It is added at 15% by volume to oxygenated fuel or at 11% to RFG and is currently used in over 85% of the nation's reformulated gasoline (US EPA, 1999). Concerns have been raised about the recently discovered widespread distribution of MTBE in ground and surface waters (Moran *et al.*, 1999; Zogorski *et al.*, 1997), consumer complaints of the pungent odor, and possible health effects. (Peaff, 1994; Bedard, 1995).

The state of California has also implemented its own RFG program—the California Cleaner Burning Gasoline (CBG) Program (Gomez, *et al*., 1998). Although MTBE has been the oxygenate used most frequently to meet the goals of this program, up to 10% ethanol (by volume) in gasoline would also be allowed. Currently, about 70% of the gasoline sold in California is RFG (California Energy Commission [CEC], 1999b).

1.3. Requirement for a Multimedia Assessment of New Fuel Components

1.3.1. Regulatory and Legislative Requirements

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). The findings of this assessment formed the basis for Executive Order D-5-99 issued by Governor Davis. That Executive Order precipitated this ethanol fate-and-transport analysis.

United States Environmental Protection Agency Administrator Carol Browner appointed a Blue Ribbon Panel (BRP) 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 (US EPA, 1999). Similar to the requirement in the Executive Order D-5-99, the BRP concluded that the US EPA should conduct a full, multimedia assessment (on air, soil, and water) of any major new additive to gasoline prior to its introduction. The BRP (1999) 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.

Recent legislation (Stats. 1999 Ch. 813; SB 529, Bowen) enacted Health and Safety Code Sec. 43840.8, which imposes new requirements regarding multimedia environmental assessments of proposed amendments to ARB's motor vehicle fuels specifications. There is a streamlined environmental review mechanism for amendments proposed prior to January 1, 2000 and adopted prior to July 1, 2000.

California Senate Bill 989 (California State Senate, 1999b) incorporates into state statues most of the provisions of the Governor’s MTBE Executive Order. Among the bill’s other provisions is the requirement that the SWRCB, on or before June 1, 2000, initiate a specified research program to quantify the probability and environmental significance of releases from petroleum underground storage tank (UST) systems that meet certain upgrade requirements and identify those areas of the state where groundwater is the most vulnerable to MTBE contamination, and to prioritize cleanups based on that identification. Additionally, after January 1, 2000, the bill prohibits the ARB from adopting new fuel specifications until a “multimedia” evaluation has been performed and submitted to the California Environmental Policy Council for final review and approval.

1.3.2. Systems-based Approach to Evaluating New Fuel Components

New fuels or potential additives must be evaluated against not only engine performance and emission requirements but also health and environmental criteria involving airborne toxics and associated health risks, ozone formation potential, and groundwater contamination resulting from production, distribution, and use. A systems-based approach is needed to evaluate risk management trade-offs and to assess health and environmental consequences of the use of ethanol as a fuel oxygenate. A thorough, systems-based approach would include:

1. Identification of the key attributes of gasohol production, distribution, and use, including a fuel-cycle characterization.
2. Screening-level analysis and models to predict the likely environmental fate(s) of ethanol, gasohol, and alkylated-fuel components released into reference landscapes and consideration of potential exposure pathways. This assessment would contain:
    - A review of the existing state of knowledge,
    - The identification of physiochemical properties of the compounds of concern, and
    - Environmental-fate simulations for airborne emissions and subsurface releases.
3. Exposure assessments, including toxicity evaluations of ethanol, gasohol, and alkylated-fuel components that may be released.
4. Identification of key data and knowledge gaps and the specification of the kinds of studies needed to obtain the necessary data and to address any methodological issues related to assessing the use of ethanol, gasohol, and alkylated fuel.
5. Performance of selected experiments to address the identified data gaps.
6. Refinement of conceptual models and integration of new data into critical analyses of environmental transport and fate and multipathway exposures.

1.4. Use of Ethanol as a Transportation Fuel Oxygenate

Ethanol is also widely used in oxygenated gasoline (8% in oxyfuel or 6% in RFG, by volume) because it is a renewable, biomass-based source of fuel and because it is perceived that its environmental impacts are less than those associated with the use of MTBE. To promote markets for ethanol, the United States Congress has approved a 5.4-cents/gal federal subsidy for its use in gasoline. Because of the subsidy, ethanol is sometimes used at 10% by volume in gasoline, even in areas that are not required to use RFG (RFA, 1999).

The use of fuel alcohols as gasoline additives is increasing worldwide, both as a substitute fuel for imported oil, and as oxygenates to minimize air pollution from combustion. In Brazil, for example, approximately one-half of all automobiles run on gasoline containing 22% ethanol with the remainder operating on hydrated ethanol (Petrobrás, 1995). In the United States, gasohol is already available in many states. A recent effort by some members of the House of Representatives to repeal the 5.4-cents/gallon tax subsidy for gasoline with ethanol earlier than its original (year 2000) end date was defeated. Instead, the tax subsidy was extended (*Chemical Market Reporter*, 1998). In addition, ongoing advances in biotechnology will continue to lower ethanol production costs (Lugar and Woolsey, 1999; Carver, 1996).

At the federal level, the BRP was convened in late 1998 to study the benefits and risks of the federal RFG program. In the final BRP report (US EPA, 1999), the Panel recommended that the use of MTBE in the nation’s gasoline be substantially reduced. Based on these recommendations, the United States Senate passed a resolution expressing support for a nationwide phase-out of MTBE and supported ethanol as its replacement.

In separate federal initiatives, the use of ethanol as a fuel source is being advocated as a means of promoting the use of renewable biomass fuels. President Clinton signed an Executive Order this year to accelerate the development and use of biomass fuels, products, and chemicals. Joined by the heads of the United States Departments of Agriculture and Energy, US EPA, and Senator Richard Lugar, Clinton announced the goal of tripling the use of bioenergy and bioproducts by 2010 (RFA, 1999).

Illinois Governor George Ryan recently dedicated the first fleet of urban transit buses in the country powered by E-15 Oxygenated Diesel, a blend of ethanol and diesel fuel that shows promise for cleaning up the environment while benefiting rural America. Known as E-15 OxyDiesel, the new fuel is a mixture of 15% ethanol, 80% diesel fuel, and 5% additives. The Illinois governor stated that the E-15 OxyDiesel promises a substantial reduction in black diesel exhaust and its effects, expanded opportunities in the ethanol industry, and new markets for Illinois corn (RFA, 1999). Prior to being tested in Chicago Transit Authority buses, E-15 OxyDiesel was tested in trucks operated by Archer Daniels Midland Corporation.

1.5. Production of Ethanol

The ethanol used for fuel is made primarily from grains or other renewable agricultural and forestry feedstocks (Canadian Renewable Fuels Association [CRFA], 1999). However, any feedstock that contains sugar, starch, or cellulose can be fermented and distilled into ethanol. The fact that ethanol can be made from liquid or solid waste (such as wood byproducts) or agricultural wastes (such as rice straw) is an advantage. In the United States, most ethanol is produced directly from corn (RFA, 1999).

There are basically seven steps in the whole-grain fermentation processes for producing ethanol (American Coalition for Ethanols [ACE], 1999):

1. The grain (such as corn) is milled into a fine powder called meal.
2. The meal is liquefied with the addition of water, enzymes, and heat (120º–150ºC).
3. During the process called saccharification, the liquefied starch is converted to fermentable sugars (dextrose).
4. Yeast is added to ferment the sugars to ethanol and carbon dioxide.
5. The alcohol is distilled to increase the ethanol content from 10% alcohol by volume to about 96%.
6. The alcohol is dehydrated to remove the remaining water. Most distillers use a molecular sieve for this step to produce anhydrous ethanol.
7. The ethanol is then denatured with 2–5% of some product that is added to make it unfit for human consumption. (California is specifying that unleaded gasoline be the denaturant used in fuel-grade ethanol.)

Although some smaller distillers produce ethanol as described above, most larger facilities separate the starch from the grain prior to fermentation (“wet-millers”) (ACE, 1999). The use of highly purified starch as the feedstock results in a much cleaner fuel product, whereas the ethanol fuel from whole-grain process contain a lot more impurities (Karaosmanoglu *et al.*, 1996) which do not need to be removed for ethanol to be suitable as a fuel additive.

1.6. Chemical and Physical Properties of Ethanol in Gasoline

Malcolm Pirnie, Inc. (1998) has published a good summary of the physical properties of ethanol compared to MTBE. Ethanol is a small chain molecule (C_2H_5OH) that contains 34.7% oxygen by weight and is infinitely soluble in water. In its pure form, ethanol is a flammable, colorless liquid with a sweet alcohol odor. Ethanol is lighter than water; and if released rapidly in bulk onto water, it will tend to remain on the surface of the water. When gasoline-containing ethanol is in contact with even small quantities of water, the ethanol will separate from the gasoline into the water. Pure ethanol and ethanol blends of gasoline are heavier than unblended gasoline.

Ethanol is very volatile and evaporates into air approximately five times faster than MTBE. Like gasoline vapors, ethanol vapors are denser than air and tend to settle near the ground in low areas. In open-air areas, these vapors disperse rapidly.

When burned, ethanol releases less heat than gasoline. One and a half gallons of ethanol have approximately the same fuel combustion energy as 1 gallon of gasoline. Ethanol has a higher ignition temperature than gasoline (approximately 850°F versus approximately 495°F). When pure ethanol is burned, the flame is less bright than a gasoline flame but is easily visible in daylight. Both ethanol and MTBE have similar octane ratings of about 110 and, when added to gasoline, increase the octane rating. (The long chain, branched hydrocarbon known as octane is used as a standard and is equal to a rating of 100 [Center for Transportation Research, no date]).

Though pure ethanol is poisonous, it is less acutely toxic than the benzene, toluene, ethyl benzene, and xylene (BTEX) components in gasoline. Ethanol is present in pharmaceuticals, mouthwash products, alcoholic beverages, cleaning products, solvents, dyes, and explosives (Verschueren, 1983). Humans frequently ingest fermented beverages that contain about 12% by volume ethanol. Because ethanol is a metabolic byproduct, many organisms tolerate concentrations that may be encountered during accidental releases into the environment (Dagley, 1984). A variety of indigenous microorganisms within the environment are capable of using ethanol as an energy source and will preferentially utilize ethanol over other gasoline hydrocarbons, such as benzene (Alvarez and Hunt, 1999).

Ethanol and ethanol blends of gasoline conduct electricity. In contrast, unblended gasoline is an electrical insulator. For this reason, pure ethanol is more corrosive than gasoline and materials-compatibility must be considered when designing large-volume, bulk-ethanol storage tanks. Aluminum, zinc, tin, lead-based solder, or brass fittings should not be used with pure ethanol or gasoline with high percentages of ethanol. When in contact with liquids that contain high percentages of ethanol, some nonmetallic materials also degrade, including natural rubber, polyurethane, cork-gasket materials, leather, polyester-bonded fiberglass laminate, polyvinyl chloride, polyamides, and methyl-methacrylate plastics (Center for Transportation Research, no date).

1.7. Increased Use of Alkylates as a Transportation Fuel Component

Because the California Energy Commission (CEC, 1999a) anticipates that alkylates[1] will be used in non-oxygenated gasoline and some ethanol-containing gasolines in California to replace the octane[2] normally provided by MTBE, these compounds are also a focus of the analysis included in this report.

Alkylates consist of branched alkanes and cycloalkanes, mostly with 6 to 9 carbons, such as iso-octane (2,2,4-trimethylpentane) and methylcyclopentane. Alkylates are already components in gasoline, but additional amounts will be required to maintain octane levels in gasoline after removal of MTBE, which is a high-octane, anti-knock additive. Even though ethanol also has a high-octane level, its oxygen content is about twice that of MTBE and, consequently, less is required to meet a specified oxygen content (for example, 2.5 wt% oxygen). The resulting octane deficit must be compensated for by adding high-octane blending components, such as alkylates.

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[1] Alkylates are a gasoline blendstock produced by reacting isobutane with light olefins in the presence of strong acid catalysts. They typically consist of branched alkanes, have very low aromatic content, and no sulfur or olefins (Northeast States for Coordinated Air Use Management [NESCAUM], 1999).

[2] MTBE has a 110 octane rating, ethanol has a 115 octane rating; alkylates provide 91 to 99 octane ratings, and aromatic compounds have a 100 octane rating (CEC, 1999a).

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Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate

Report to the
California Environmental
Policy Council
in Response to
Executive Order
D-5-99

VOLUME 3

AIR RESOURCES BOARD

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

December 1999

Front Cover Back

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California Environmental Protection Agency

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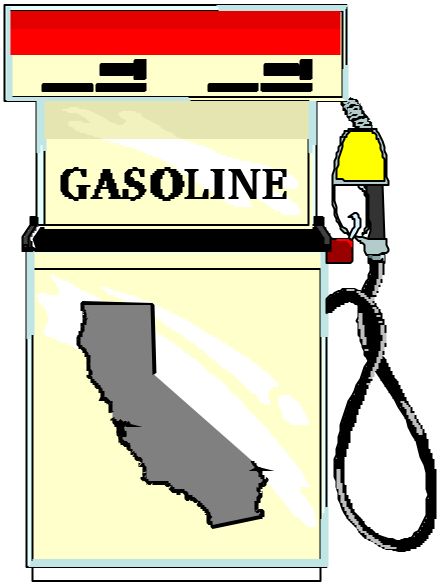
Environmental Policy Council



December 1999

Front Cover Back

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State of California
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Final Report to the California Environmental Policy Council

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This report has been reviewed by the staff of the Air Resources Board, peer reviewed by the University of California, and approved by the Air Resources Board on December 9, 1999 for submittal to the California Environmental Policy Council. Mention of trade names or commercial products does not constitute endorsement or recommendation for their use. To obtain this document in an alternative format, please contact the Air Resources Board ADA Coordinator at (916) 322-4505, TDD (916) 324-9531, or (800) 700-8326 for TDD calls from outside the Sacramento area. This report is available for viewing or downloading from the Air Resources Board Internet site, http://www.arb.ca.gov/cbg/ethanol/ethfate/ethfate.htm.

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Table of Contents

Appendices

List of Tables

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 outdoor air quality levels of potentially detrimental 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 the amount of alkylates will be increased in non-oxygenated gasoline and some ethanol-containing gasolines to replace the octane normally provided by MTBE; consequently these compounds were also a focus of our analysis.

We conducted four types of analyses: 1) a review of several recently published comprehensive assessments of the impact of oxygenated gasoline on the environment; 2) a literature review of studies that measure the direct impact of the use of ethanol in gasoline; 3) an evaluation of emission and air quality impacts from MTBE-free fuels in comparison to MTBE-containing fuel; and 4) closure of existing data gaps as part of this study and ongoing efforts that will not be complete until after the December 31, 1999 deadline in the Executive Order. These analyses led to the following conclusions.

1. **In comparison to the non-MTBE components of gasoline, the atmospheric formation of toxic compounds from ethanol and alkylates are relatively slow.**

Because the maximum estimated outdoor air quality levels of ethanol and alkylates are at least a factor of 10 below any level of concern identified by OEHHA, the main issues are their products of incomplete combustion and atmospheric transformations. The major products of concern for ethanol are acetaldehyde (a toxic air contaminant) and peroxyacetyl nitrate (PAN, an eye irritant and cause of plant damage). These compounds are offset by reductions in formaldehyde (a toxic air contaminant) due to the elimination of MTBE. Alkylates eventually form acetaldehyde, formaldehyde, and PAN, as do many other existing components of gasoline. The greater the atmospheric lifetime of a compound, the more dilution and dispersion will reduce the impact of products of atmospheric transformations. The atmospheric lifetime for ethanol is similar to MTBE, about two to three days under polluted conditions and longer during periods of good air quality. Atmospheric lifetimes for alkylates range from one day to a week. Our findings from theoretical calculations using airshed models with state-of-the-science chemistry indicate that other components of gasoline, such as aromatic compounds and olefins, are primarily responsible for the formation of formaldehyde, acetaldehyde, and PAN due to both their greater abundance in gasoline and their shorter atmospheric lifetimes.

2. **The inadvertent commingling of ethanol-containing and ethanol-free gasolines in vehicle fuel tanks results in a combined gasoline with a Reid vapor pressure (RVP) greater than the summertime California limit of 7.0 pounds per square inch (psi) and increased evaporative emissions of volatile organic compounds (VOCs). This effect will be mitigated by RVP reductions in the California Phase 3 Reformulated Gasoline (CaRFG3) regulations.**

Even small amounts of ethanol cause an RVP increase of about 1 psi when it is added to an ethanol-free base gasoline. 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 with the potential for large-scale introduction. Thus, commingling would seldom happen in this large portion of California, representing 80% of the gasoline marketplace. California has requested the federal government for a waiver from the summertime oxygenate requirement to facilitate the phase-out of MTBE in these areas. If the waiver is granted, commingling will likely increase. Current estimates of the overall effect of commingling range from 0.1 to 0.4 psi, depending on assumptions for the market share of ethanol-containing gasolines, consumer's brand/grade loyalty, and the distribution of fuel tank levels before and after refueling events. The CaRFG3 regulations require a 0.1 psi RVP decrease to help mitigate the effect of commingling, and the Air Resources Board has committed to additional research to further quantify commingling impacts.

3. **Ethanol-containing gasolines may lead to increases in evaporative emissions because rubber, plastics, and other materials are permeable to ethanol; moreover, ethanol may reduce the working capacity of the charcoal canisters used to control evaporative emissions on board motor vehicles. This issue has been addressed in the United States Environmental Protection Agency's (U.S. EPA's) recently adopted Tier 2 emission standards. However, the current on-road motor vehicle fleet (other than flexible-fueled vehicles operated on alcohol blends) is not fully controlled from the perspective of evaporative ethanol emissions. Further research is needed to compare the effects of ethanol, MTBE (which also reduces the working capacity of charcoal canisters), and alkylates on evaporative emission from the existing California vehicle fleet.**

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 evaporative emissions which occur during operation of the vehicle and stem from permeation through the fuel hoses and losses 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. “Diurnal” emissions are evaporative losses mainly from the charcoal canister and result from daily heating of the vehicle’s fuel tank and consequent saturation and overflow from the canister.

Because of the tendency of ethanol to evaporate more readily than other fuel components and because the smaller size of an ethanol molecule promotes permeation through hoses, hot soak emissions tend to result in evaporative losses containing a proportionally greater amount of ethanol than was in the original fuel. Also, it is possible that ethanol’s propensity to be tightly held by activated carbon, in conjunction with its hygroscopic nature (that is, it attracts water), may decrease the working capacity of the charcoal canisters used to control evaporative emissions on board motor vehicles and result in increased diurnal emissions. However, data suggesting a reduced working capacity are somewhat conflicting in nature, but this may be partially due to the difficulty in sampling ethanol, and additional research is needed in this area.

Both early and late model–year vehicles (other than flexible-fueled vehicles operated on alcohol blends) are not fully controlled from the perspective of evaporative ethanol emissions. That is, the certification test procedures for evaporative emissions require the use of a fuel containing MTBE and, thus, do not completely take into account the use of commercially available ethanol-containing gasolines. Although more stringent evaporative emission standards were adopted in 1998 and are 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 recently adopted such changes under its Tier 2 regulations.

4. **Because relatively little ethanol is produced in California, it will probably all be shipped by rail or truck. The estimated statewide impact on heavy-duty truck emissions is a 0.06% increase. Most likely, these impacts will be localized at the two central ethanol distribution locations and the 64 fuel storage terminals and will be addressed locally under the California Environmental Quality Act.**

The bulk of the ethanol used in California will be transported by rail from the Midwest to two central distribution locations, trucked to 64 fuel storage terminals, and then splash-blended with gasoline. The increase in heavy-duty truck emissions would be about 0.06% of the statewide total, using estimates of truck travel for ethanol distribution made by the California Energy Commission. If increased local traffic and emissions from diesel trucks become local environmental concerns, they will be addressed locally in the context of use permits and permits to operate specific facilities under the California Environmental Quality Act.

5. **So long as the CaRFG3 regulations address the potential for ethanol to increase evaporative emissions and cause more rail and truck traffic, the substitution of ethanol and alkylates for MTBE in California's fuel supply will not have any significant air quality impacts. This finding is supported by theoretical calculations in the South Coast Air Basin using state-of-the-science tools, an analysis of the impact of uncertainties, air quality measurements in areas that have already introduced ethanol into their fuel supply, and an independent scientific peer review by the University of California.**

We used the best available information on the emission characteristics of fuels that will be available in 2003, a comprehensive analysis of current (that is, 1997) air quality levels, and an airshed model for the South Coast Air Basin with state-of-the-science chemistry to estimate air quality in the future for the following four fuels:

- Current MTBE-based California Phase 2 Reformulated Gasoline (CaRFG2), assumed to be equivalent in both 1997 and 2003.
- Ethanol-based, fully complying CaRFG2 fuel with an oxygen content of 2.0 wt% (5.7% ethanol by volume) in 2003.
- Ethanol-based, fully complying CaRFG2 fuel with an oxygen content of 3.5 wt% (10% ethanol by volume) in 2003.

- Non-oxygenated, fully complying CaRFG2 fuel in 2003.

Because the CaRFG3 regulations were not approved until December 9, 1999, we were unable to consider the new specifications in our emission and air quality predictions. However, because the regulations preserve the air quality benefits of CaRFG2 and apply equally to ethanol-blended and non-oxygenated gasolines, consideration of CaRFG3 will not affect our overall conclusions.

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. There are several differences between the 2003 MTBE baseline and the three 2003 MTBE-free fuel scenarios. Because fuel-related activities are the only inventoried source of MTBE, levels of MTBE decrease 100%. Ethanol levels for the ethanol-blended gasolines increase by 48% (2.0 wt% oxygen fuel) and 72% (3.5 wt% oxygen fuel), but acetaldehyde is predicted to increase (4%) for only the ethanol-blended gasoline at 3.5 wt% oxygen. PAN levels are not predicted to increase for either the ethanol-blended or non-oxygenated gasolines. Benzene levels 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%) levels and essentially no change in ozone, nitrogen dioxide, nitric acid, and PPN (peroxypropionyl nitrate) levels. As expected, the non-oxygenated gasoline results in higher predicted eight-hour-average carbon monoxide levels (3%), and the 3.5 wt% oxygen ethanol-blend in lower carbon monoxide values (-9%). It should be noted that these are summertime levels-a time period when violations of the standard do not occur. Due to the wintertime oxygenate requirement for the South Coast Air Basin, carbon monoxide levels within the nonattainment area of Los Angeles County will not differ from the 2003 MTBE baseline.

Primarily due to the lack of ambient air quality measurements for many of the air contaminants of concern, we were unable to predict 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 levels, the conditions most conducive to formation of secondary air pollutants (for example, ozone, acetaldehyde, and PAN), the most emissions, and the highest number of gasoline-related emission sources in California.

Calculations that bracket the impact of motor vehicle emission inventory uncertainty and chlorine atom chemistry in coastal environments resulted in increases for all pollutants, but the only significant impact on relative differences among the 2003 fuels was a large increase in ethanol for the ethanol-blended gasolines. The use of the modeling tool in a relative sense bypasses concerns about other uncertainties.

Our review of studies of the impact of the use of ethanol-containing gasoline on air quality in Denver, Colorado; Albuquerque, New Mexico; Brazil; and other areas indicates that acetaldehyde levels are substantial only in Brazil, where the fuels contained either pure ethanol or 22% ethanol, much greater levels than the maximum of 10% ethanol allowed in California gasolines. Due to the lack of RVP requirements for gasolines in Brazil, the high acetaldehyde levels 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 levels, the observed levels of PAN are more than a factor of 10 below historical levels observed in southern California although the Brazilian measurements were not in the areas likely to have the highest PAN levels.

A draft version of this report was reviewed by four scientists approved by the University of California Office of the President under a process defined by Health and Safety Code section 57004. While the reviewers agreed with our basic findings on ethanol and alkylates, they noted the need for a number of corrections, clarifications, and caveats that we have incorporated into this final version of the report. Their comments and our responses are included in this report.

6. **The results of this study do not necessarily extend to other states. California does not have an RVP exemption for ethanol-containing gasolines; and the CaRFG3 Predictive Model constrains emissions of cancer-potency-weighted toxic air contaminants, oxides of nitrogen (NO_X), and VOCs. States without these safeguards (that is, non-Federal Reformulated Gasoline areas) may have significant air quality impacts from replacement of MTBE with ethanol or aromatic compounds.**

A previous ARB comparison of a 10% ethanol-gasoline blend with 8.0 psi RVP and a fully complying, MTBE-based gasoline meeting a 7.0 psi RVP limit concluded that while carbon monoxide emissions decreased by about 10% for the high-RVP fuel, emissions increased for NO_X (14%), combined exhaust and evaporative VOCs (32%), ozone formation potential (17%), and cancer-potency-weighted toxic air contaminants (5%). The ozone formation potential calculations included the benefit of the carbon monoxide reduction. The results also show that there is a likelihood (between 92% and 100%) that emissions of NO_X, VOC, ozone formation potential, and cancer-potency-weighted toxics are greater with the high-RVP ethanol blend than with the fully complying gasoline. The high level of certainty associated with the results of the test program show that additional testing would not likely change the outcome of this evaluation and that additional tests on 1990 to 1995 model year vehicles and vehicles that employ control technologies similar to these are unnecessary. Thus, significant air quality impacts are likely in the parts of the United States (that is, non-Federal Reformulated Gasoline areas) where the U.S. EPA allows a 1 psi RVP exemption for ethanol.

The CaRFG3 Predictive Model constrains exhaust emissions of NO_X, VOCs, and cancer-potency-weighted toxic air contaminants (that is, acetaldehyde, benzene, 1,3-butadiene, and formaldehyde), and evaporative emissions of VOCs and benzene. Thus, different fuel formulations (for example, ethanol-blended and non-oxygenated) will be manufactured to have similar emissions through the adjustment of various fuel properties such as sulfur content, aromatic content, etc. As MTBE is removed from gasoline, the CaRFG3 Predictive Model will push California fuel suppliers toward an increased use of alkylates rather than aromatic compounds. Alkylates have no significant air quality impacts in comparison to the aromatic compounds that are powerful ozone and benzene precursors and likely to be used in other states if there is a corresponding ban on MTBE.

7. **An air quality monitoring program is now in place to directly measure the impact of the phase-out of MTBE.**

Our analysis of air quality impacts will be compared with field measurements that take place before and after the planned December 31, 2002, phase-out of MTBE. These types of studies were successfully conducted in California in 1996 during the implementation of CaRFG2. California's existing ambient air quality networks should be sufficient for all the criteria pollutants, MTBE, toxic air contaminants, and individual VOC compounds (that is, alkylates). Because PAN is not part of any routine air quality monitoring program, we began PAN measurements at two sites in the South Coast Air Basin last November. Because ethanol and acetaldehyde lead to PAN but not to PPN, the measurement program includes both PAN and

PPN, [and because their ratio may be a useful indicator of the impact of ethanol emissions on PAN air quality levels]. We will investigate the possibility of adding ethanol measurements and expanding the monitoring program to other areas of the State.

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

The objective of this document is to meet the directives 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 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 alkylates[1] will be used in non-oxygenated gasoline and some ethanol-containing gasolines in California to replace the octane[2] normally provided by MTBE; consequently these compounds were also a focus of our analysis.

OEHHA requested information on the following air contaminants:

- Toxic air contaminants (acetaldehyde, benzene, 1,3-butadiene, and formaldehyde).
- Criteria air pollutants [carbon monoxide (CO), nitrogen dioxide (NO_2), ozone, and particulate matter (PM_{10}, $PM_{2.5}$)].
- Fuel oxygenates (ethanol and MTBE).
- Alkylates (C_6 to C_9 branched alkanes and cycloalkanes).
- Peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN).
- Nitric acid (HNO_3).

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[1] Alkylates are gasoline blendstock produced by reacting isobutane with olefins. They consist of branched alkanes, have very low aromatic content, and contain 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).

- Additional compounds of interest to OEHHA (*n*-heptane, *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. We did not consider global warming impacts, as this is being addressed under the California Phase 3 Reformulated Gasoline (CaRFG3) regulations (ARB, 1999a; 1999d) 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), assumed to be equivalent in both 1997 and 2003.
- Ethanol-based, fully complying CaRFG2 fuel with an oxygen content of 2.0 wt% (5.7% ethanol by volume)[3] in 2003.
- Ethanol-based, fully complying CaRFG2 fuel with an oxygen content of 3.5 wt% (10% ethanol by volume) in 2003.

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[3] The amount of an *oxygenate* such as ethanol or MTBE in gasoline is expressed as percent by volume. The amount of *oxygen* in gasoline is expressed as percent by weight (wt%). In this report, the amount of oxygenate in gasoline is referred to simply in terms of “%”, while the amount of oxygen in gasoline is referred to as “wt%”.

- Non-oxygenated, fully complying CaRFG2 fuel in 2003.

This analysis was conducted with the best available information on the emission characteristics of fuels that will be available in 2003, a comprehensive analysis of current air quality concentrations, and an airshed model with state-of-the-science photochemistry 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 Phase 3 regulations (ARB, 1999a; 1999d), a possible oxygenate waiver from the federal government, 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 ongoing 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 an independent scientific peer review by the University of California, comments on materials presented at public workshops on July 12, October 4, and November 10, 1999, and written and oral testimony at the public hearing of the Air Resources Board on December 9, 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 eight major assessments of the impact of oxygenated gasoline on the environment conducted prior to our analysis. Ethanol has been used 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

Atkinson (1994) has reviewed kinetic and mechanistic studies of the atmospheric chemistry of MTBE. The only significant atmospheric reaction for MTBE is with hydroxyl (OH) radicals. Two possible initial reactions are:

$$CH_3OC(CH_3)_3 + OH \rightarrow CH_2OC(CH_3)_3 + H_2O \quad (1)$$

$$\rightarrow CH_3OC(CH_3)_2CH_2 + H_2O \quad (2)$$

The rate constant for this reaction has been measured several times and the recommended value is $5.89\times10^{-13}(T/300)^2e^{483/T}$ cm^{3}molecule^{-1}s^{-1} over the temperature range 240-440 K, with a rate constant of 2.94×10^{-12} cm^{3}molecule^{-1}s^{-1} at 298 K. Based on several studies, the recommended reaction mechanism in the presence of NO has a product profile of *tertiary*-butyl formate (76%), formaldehyde (48%), methyl acetate (18%), and acetone (6%). *Tertiary*-butyl formate is less reactive in the atmosphere than is MTBE by about a factor of 4. Formation of *tertiary*-butyl nitrite was observed in one of the laboratory studies due to the $(CH_3)_3CO + NO \rightarrow (CH_3)_3CONO$ reaction competing with the $(CH_3)_3CO \rightarrow CH_3C(O)CH_3 + CH_3$ decomposition reaction; but under atmospheric conditions the decomposition reaction will totally dominate. The product profile is for NO being present and therefore applicable to urban areas, but possibly not to downwind areas with low NO_X concentrations. See Professor Atkinson's Comment #20 in Section D-1.1 in Appendix D for further details.

2.1.2. Ethanol

The most recent evaluations of the International Union of Pure and Applied Science (IUPAC, Atkinson *et al.*, 1997; 1999) and that of Atkinson (1994) recommend that the OH + ethanol reaction proceeds by:

$$OH + CH_3CH_2OH \rightarrow H_2O + CH_2CH_2OH \quad (3)$$

$$\rightarrow H_2O + CH_3CHOH \quad (4)$$

$$\rightarrow H_2O + CH_3CH_2O \quad (5)$$

with reactions (3) and (5) each accounting for 5^{+10}_{-5}% of the overall reaction at 298 K. The preferred IUPAC rate constant value for the reaction with the OH radical above is $5.56\times10^{-13}(T/300)^2e^{532/T}$ cm^{3}molecule^{-1}s^{-1} over the temperature range 270-340 K, with a rate constant of 3.2×10^{-12} cm^{3}molecule^{-1}s^{-1} at 298 K (Atkinson *et al.*, 1999). The relative importance of reaction (5) in the IUPAC evaluations and in Atkinson (1994) is based on the assumption that H-atom abstraction from the OH group in ethanol occurs with a rate constant equal to that for the corresponding reaction in methanol. The rate constant for reaction (3) is based on an estimation and on the elevated temperature data of Hess and Tully (see the above references). In the atmosphere, reaction (4) and reaction (5) give rise to the same products (acetaldehyde plus HO_2) and are hence indistinguishable.

Reaction (5) has not been shown experimentally to be negligible under atmospheric conditions, and the only experimental data concerning the importance of the three possible reaction channels are a branching ratio of $k_4/(k_3 + k_4 + k_5) = 0.75 \pm 0.15$ at room temperature (Meier *et al.*, 1985) and an acetaldehyde yield under atmospheric conditions of 80 ± 15% (Carter *et al.*, 1979). The formation of CH_3CHOH and CH_3CH_2O radicals from reactions (4) and (5) lead to the formation of acetaldehyde plus HO_2, independent of the presence or absence of NO, and hence the data of Carter *et al*. (1979) indicate that $(k_4 + k_5)/(k_3 + k_4 + k_5) = 0.80 \pm 0.15$. Formation of $HOCH_2CH_2$ radicals via reaction (3) leads to the formation of glycolaldehyde ($HOCH_2CHO$) (22%) and HCHO (78%) in the presence of NO (yields are for 298 K and atmospheric pressure of air), and to $HOCH_2CH_2OOH$, $HOCH_2CH_2OH$, $HOCH_2CHO$, and HCHO in the absence of NO. Atkinson (1997) has reviewed the atmospheric reactions of the

$HOCH_2CH_2$ radical. Formation of methyl nitrate is not expected to be of any significance; rather the formation of ethyl nitrate in very small overall yield (<0.1%) could occur from the reaction of the ethyl peroxy radical with NO.

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 via the following process:

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O \quad (6)$$

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$$CH_3CO + O_2 \rightarrow CH_3CO_3 \quad (7)$$

$$CH_3CO_3 + NO_2 \rightarrow CH_3C(O)OONO_2 \text{ (PAN)} \quad (8)$$

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 (Grosjean, 1997).

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 was most recently reviewed by Atkinson (1997). Under atmospheric conditions, the potential reaction pathways for alkylates include gas-phase reactions with OH and nitrate (NO_3) radicals. The gas-phase reactions of alkylates with ozone are of negligible importance.

Kinetic studies have been carried out for several alkylates and the rate constants with OH radicals obtained range from $(1 \text{ to } 10)\times10^{-12}$ $cm^3molecule^{-1}s^{-1}$ at 298 K (Atkinson, 1997). The measured rate constants of selected alkylates with NO_3 radicals range from $(0.5 \text{ to } 4.0)\times10^{-16}$ $cm^3molecule^{-1}s^{-1}$ at 298 K. The products observed and expected in the presence of NO include carbonyls, alkyl nitrates, hydroxycarbonyls, and hydroxynitrates. At low NO_X concentrations, the expected products include hydroperoxides, alcohols, hydroxycarbonyls, diols, and hydroxyhydroperoxides (Atkinson, 1997).

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 3.0×10^6 molecule/cm^3, representative of moderately polluted conditions in Los Angeles (George *et al.,* 1999). Maximum incremental reactivities (MIRs) -- measures of ozone formation potential -- of MTBE, ethanol, and alkylates were obtained from a recent reactivity assessment (Carter, 1999a). 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)
MTBE	**32**	**0.88**
Ethanol	**28**	**1.88**
Alkylates	**9-93**	**1.0-2.3**

[a] For a 12-hour daytime-average OH radical concentration of 3.0×10^6 molecule/cm^3.

[b] From Carter (1999a), using the techniques described in Carter (1994).

2.1.5. Chlorine Chemistry

There is an increasing recognition (e.g., De Haan *et al.*, 1999) that chlorine (Cl) atoms may play a role in the oxidation of organics in coastal areas. Several measurements of Cl_2 and photolyzable chlorine compounds in coastal areas in the eastern U.S. find nighttime concentrations of Cl_2 (and perhaps other species) of ~150 ppt (e.g., Spicer *et al.*, 1998). At dawn, photolysis generates highly reactive chlorine atoms at concentrations of up to ~10^5 molecule/cm^3. The Cl + MTBE rate constant is 1.66×10^{-10} cm^{3}molecule^{-1}s^{-1} (Wallington *et al.*, 1988) and the Cl + ethanol rate constant preferred by the IUPAC is 9.0×10^{-11} cm^{3}molecule^{-1}s^{-1} (Atkinson *et al.*, 1999), corresponding to lifetimes of 30 and 17 hours, respectively, at a Cl atom concentration of 10^5 molecule/cm^3. The rate constants for the reaction of selected alkylates with Cl atoms range from $(1.75 \text{ to } 3.9)\times10^{-10}$ cm^{3}molecule^{-1}s^{-1} (Atkinson, 1997), corresponding to lifetimes of 16 to 7 hours at a Cl atom concentration of 10^5 molecule/cm^3. Thus, Cl atom reactions will compete with OH radical-initiated reactions for these compounds in coastal areas during daylight hours. Product studies suggest that hydrogen abstraction in MTBE, ethanol, and alkylates is the major reaction pathway for Cl atoms as for OH radicals (Carter *et al.*, 1979)

2.1.6. Conclusions from 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 NO_3 radicals in the atmosphere are slow and of negligible importance. Reactions with Cl atoms in coastal areas may be important. Product studies showed that the major products in the presence of NO_X are *tertiary*-butyl formate, formaldehyde, and methyl acetate from MTBE, acetaldehyde and PAN from ethanol, and carbonyls, alkyl nitrates, hydroxycarbonyls, and hydroxynitrates from alkylates.

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

We reviewed eight 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

Governor Wilson signed Senate Bill S.B. 521 into law on October 8, 1997, enacting the MTBE Public Health and Environmental Protection Act of 1997. This legislation appropriated $500,000 to the University of California for 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). They concluded that 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% ethanol 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 are subject to the same Reid vapor pressure (RVP)[4] 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 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 implemented in Section 4.2.

2.2.2. Air Resources Board

As provided for in Health and Safety Code Section 43830(g), the ARB (1998b) investigated whether a 10% ethanol gasoline blend with 8.0 psi RVP would provide as good or better emission benefits as a fully complying, MTBE-based gasoline blended to be typical of the gasoline used during the summer and meeting a 7.0 psi RVP limit. An exhaust emission test program was conducted with 12 light-duty vehicles, and six of the vehicles were also tested for hot-soak and diurnal evaporative emissions. Running loss emissions were estimated with the assistance of General Motors using their vapor generation model, and with draft evaporative emissions models from the ARB and the USEPA.

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[4] 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.

A formal statistical analysis indicated that CO emissions decreased by about 10% for the high-RVP ethanol blend with increases in NO_X (14%), combined exhaust and evaporative NMOG (32%), ozone formation potential (17%), and potency-weighted toxic air contaminants (5%). The ozone formation potential calculations included the benefit of the CO reduction. The toxic compounds evaluated under this test program were benzene, 1,3-butadiene, formaldehyde, and acetaldehyde. The results also show that there is a likelihood between 92% and 100% that emissions of NO_X, NMOG, ozone formation potential, and potency-weighted toxics are greater with the high-RVP ethanol blend than with the fully complying gasoline. The data also show that the likelihood is almost 100% that CO emissions are higher with the fully complying gasoline than with the high-RVP ethanol blend. The high level of certainty associated with the results of the test program show that additional testing would not likely change the outcome of this evaluation and that additional tests on 1990 to 1995 model year vehicles and vehicles that employ control technologies similar to these are unnecessary. Based on these results, the ARB determined that an RVP exemption should not be granted to 10% ethanol blends.

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

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 the “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.*, 2000; Larsen, 2000), 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 3.4.5.

2.2.4. 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 issue will be discussed in Section 3.4.5.

2.2.5. 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 the 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.

2.2.6. 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% ethanol (E10) 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 CaRFG2.

2.2.7. 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.

2.2.8. 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.

2.2.9. Conclusions from 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 subsequent 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% 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 emission 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 contains 10% 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 drawbacks 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% ethanol) and another four million ran on neat (100%) 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 from 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 an 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% 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 PAN concentrations are modest and more than a factor of 10 below historical levels observed in southern California (Grosjean, 1999b) although the Brazilian measurements were not in the areas likely to have the highest PAN levels

3. 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. Various emissions associated with fuel additives and transportation of ethanol, and the possible increased evaporative emissions due to ethanol's high volatility, will need to be addressed with the Phase 3 Reformulated Gasoline specifications and other regulatory programs if they are found to be significant. This section does not include a full discussion of exhaust emissions, as we were able to determine the effect of MTBE-free fuels on exhaust using the automotive emission estimation procedures described in Section 4.1.

3.1. 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 directive specified that the CaRFG3 regulations should provide additional flexibility in lowering or removing oxygen, maintain current emission and air quality benefits from the CaRFG2 regulations, and allow compliance with the State Implementation Plan for achieving ambient air quality standards. On December 9, 1999, the Air Resources Board approved amendments to CaRFG2 in response to the Executive Order. The approved amendments include a prohibition on the use of MTBE in gasoline, revised specifications for Phase 3 reformulated gasoline, and an improved and expanded Predictive Model (ARB, 1999a; 1999d). Table 3.1 summarizes the approved amendments to the flat, averaging, and cap limits of various fuel properties compared with the existing CaRFG2 limits. Because the CaRFG3 regulations were not approved until December 9, 1999, we were unable to consider the new specifications in our emission and air quality predictions. However, because the regulations preserve the air quality benefits of CaRFG2 and apply equally to ethanol-blended and non-oxygenated gasolines, consideration of CaRFG3 will not affect our overall conclusions.

Table 3.1. Approved Amendments to the CaRFG2 Property Limits

Property	Flat Limits		Averaging Limits		Cap Limits	
	CaRFG2	CaRFG3	CaRFG2	CaRFG3	CaRFG2	CaRFG3
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 °F, max	210	213	200	203	220	220
T90 °F, max	300	305	290	295	330	330

(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 wt% but no more than 10% ethanol, the cap is 3.7 wt%.

3.2. Fuel Additives

3.2.1. 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.

3.2.2. 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% of the ethanol, and it could not contain pyroles, turpentines, 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.

3.3. Emissions Associated with Transportation of Ethanol

Since relatively little ethanol is produced in California, it will probably all be transported by rail from the Midwest to two central distribution locations, trucked to 64 fuel storage terminals, and then splash-blended with gasoline. The increase in heavy-duty truck emissions would be about 0.06% of the statewide total, using 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 addressed locally in the context of use permits and permits to operate specific facilities under the California Environmental Quality Act.

3.4. Automotive Evaporative Emissions

3.4.1. 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 evaporative emissions which occur during operation of the vehicle and stem from permeation through the fuel hoses and losses 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.

3.4.2. 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% 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). However, it is not clear if there is a problem with the hosing materials used in the existing vehicle fleet. 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.

3.4.3. 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, but this may be partially due to the difficulty in sampling ethanol (Grisanti *et al.*, 1995). Additional research is needed in the area.

3.4.4. Impact of Ethanol-Containing Gasoline on In-Use Evaporative 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% 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 recently adopted such changes under its Tier 2 regulations.

3.4.5. 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 E10[5] 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.[6] 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% E10 and less pronounced once the gasoline blends exceeded a 50% E10 mixture. Gasoline with 2% ethanol, or a mixture of 80% gasoline with 20% 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

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[5] A gasoline containing 10% ethanol by volume.

[6] 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% of the final blend, increases the RVP to about 7.5 psi. It is important to note that although the new 50-50 commingled blend would have an ethanol content of around 5%, not 10% as in the original ethanol-containing gasoline, the full 1.0 psi RVP increase would still occur (U.S. EPA, 1999).

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.

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 with the potential for large-scale introduction. Thus, commingling would seldom happen in this large portion of California, representing 80% of the gasoline marketplace. California has requested the federal government for a waiver from the summertime oxygenate requirement to facilitate the phase-out of MTBE in these areas. If the waiver is granted, commingling will likely increase. The CaRFG3 regulations require a 0.1 psi decrease in RVP to help mitigate the effect of commingling and the Air Resources Board has committed to additional research to further quantify commingling impacts.

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

The approved regulations for California Phase 3 reformulated gasoline (ARB, 1999a; 1999d) 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 approved 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 VOC emissions. Our review of the literature (see Appendix D) indicates the reactivity of CO is well established and regarded as having low uncertainty (Carter, 1999a). 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. Our conclusion is that an increase in the assigned reactivity of CO is not justified at this time.

3.5. Mileage Penalty for Gasolines With High Ethanol Content

Increasing the oxygen content of gasoline reduces fuel economy. Relative to typical current CaRFG2 made with MTBE, CaRFG2 containing 2 wt% oxygen as ethanol would only provide a slightly different fuel economy (change of 0.6% or less). CaRFG2 with 3.5 wt% oxygen as ethanol would likely provide less fuel economy (by ~2%) than current gasoline, while non-oxygenated CARFG2 would improve fuel economy by ~2%. However, mass emission rates should not change in proportion to the change in fuel economy. The Predictive Model tends to force emissions to meet constant standards regardless of the oxygen content. The model is built from data on emissions versus oxygen content of gasoline with emissions measured in mass per mile, not in mass per volume of fuel.

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 photochemical model with state-of-the-science chemistry 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, 1999a; 1999b) to establish the liquid gasoline profiles. In general the MathPro (1999a; 1999b) 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 Appendix 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 2003 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. Previous ARB modeling analyses found that CO emissions have a small impact (about 10 ppb) on concentrations of ozone. We used the same motor vehicle CO inventory for the MTBE and ethanol fuel scenarios with 2.0 wt% oxygen content, and decreased the CO emissions by 7.5% for the ethanol with 3.5 wt% oxygen scenario and increased the 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.

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 applied 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, NO_2, ozone, acetaldehyde, benzene, 1,3-butadiene, ethanol, formaldehyde, HNO_3, 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*-heptane, *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, PM_{10} and $PM_{2.5}$ concentrations are not expected to change due to the removal of MTBE from gasoline, as discussed in Section 4.2.3.2.

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 in 1997 and 2003 to vary from measured 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.

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

Year / Scenario	CO	NO_X	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	NO_X	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	NO_X	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%

4.2.2. Photochemical Model Results

We conducted two sets of model simulations. The original set of five scenarios uses our best estimates of emissions and atmospheric chemistry. An additional set of five scenarios brackets the effects of emission uncertainty and chlorine atom chemistry, uses updated MTBE and ethanol rate constants, and corrects boundary conditions for several species.

4.2.2.1. Original Model Simulations

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 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 population-weighted 24-hour-average 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. Because 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, NO_2, nitric acid, and 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.

4.2.2.2. Upper-Bound Model Simulations

Sensitivity analysis is an evaluation of the model response to variations in one or more of the model inputs. The sensitivity simulations performed in our study bracket the cumulative effect of 1) use of EMFAC2000 instead of EMFAC7G, 2) consideration of chlorine radical chemistry, 3) use of updated rate constants for the reactions of hydroxyl radical with ethanol and MTBE, and 4) revised boundary conditions.

The on-road motor vehicle emissions were increased to evaluate the potential impact of using EMFAC2000 (ARB, 1999) instead of EMFAC7G. EMFAC2000 was not available at the time of this study, but emissions from motor vehicles increase substantially with EMFAC2000. A large increase in hydrocarbon emissions will change the NO_X-to-hydrocarbon ratio and potentially impact the radical flux. This may increase the photochemical oxidation of ethanol and lead to an increase in acetaldehyde and PAN impacts. VOC emissions were multiplied by a factor of three to place an upper-limit to the impact of using EMFAC2000, which at one time proposed multiplication factors of 2.34 and 1.84 for the 2000 on-road motor vehicle emission inventory in the South Coast Air Basin for VOCs and NO_X, respectively. The factor of three is also consistent with an independent fuel-based inventory for the South Coast Air Basin in 1997 which proposes a multiplication factor of 3.5±0.6 for on-road motor vehicle hydrocarbon emissions of stabilized exhaust (Singer and Harley, 2000). The Singer and Harley (2000) fuel-based inventory is for stabilized exhaust emissions and does not include cold start or evaporative emissions, so it is not necessarily inconsistent with draft versions of EMFAC2000. We also have some concerns with Singer and Harley's methodology (primarily lack of freeway measurements where gm/gallon emission rates are likely to be lower) and view it as an upper-bound estimate. The motor vehicle CO emissions were also increased by a factor of three to represent the impact of using EMFAC2000, which proposes a significant (a factor of about three) increase of motor vehicle CO emissions.

In response to peer review comments provided by Professor Barbara Finlayson-Pitts (see Section D-1.2 in Appendix D), the chemical mechanism was modified to include chlorine (Cl) radical chemistry as described in Section 2.1.5. A proper representation would include reactions of Cl radical with all VOCs, including methane, 1,3-butadiene, isoprene, MTBE, ethanol, benzene, and their reaction products (for example, see Fantechi *et al.*, 1998), and reactions with other inorganic species. Hence, the addition of Cl radical reactions require a revision of the atmospheric chemical mechanism, which is outside the scope of this study. In addition, there are significant uncertainties in the reliability of Cl chemistry mechanisms because of limited smog chamber data for model testing (Carter, 1999b). A method to bracket the potential impact of adding Cl radical reactions is to focus on its effect on ethanol. We added a Cl radical reaction with ethanol, assuming the same lumped products as with the OH reaction with ethanol in the SAPRC97 chemical mechanism and using a reaction rate constant of 9.4×10^{11} $cm^3 molecule^{-1} s^{-1}$. Two additional assumptions were made to place an upper-limit on the potential effect of including the Cl radical reaction with ethanol. First, the reaction was assumed to occur throughout the entire day and, second, we assumed a constant Cl radical concentration of 10^4 atom cm^{-3} (Fantechi *et al.*, 1998) throughout the modeling domain. These Cl radical concentrations bracket the actual levels, which presumably occur only during the day and near coastal areas. Thus, the overall impact will be to greatly increase the oxidation of ethanol to acetaldehyde and PAN. The maximum impact will be for the 2003 Et3.5% scenario because of the higher ethanol emission rates in the inventory relative to the other scenarios.

In response to additional peer review comments (see Section D.1 of Appendix D), we increased the OH + ethanol rate constant by 0.03% and the OH + MTBE rate constant by 3.8%. The use of the revised kinetic rate constants will slightly increase the photochemical oxidation of ethanol and MTBE. We also revised the HONO, N_2O_5, and NO_3 boundary and region top concentrations in response to peer review comments.

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

Compound	Parameter	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
Acetaldehyde (Total)	1hr	-5%	-4%	-3%	-4%
Acetaldehyde (Total)	Daily	0%	0%	0%	0%
Acetaldehyde (Total)	PW	-13%	-13%	-10%	-14%
Acetaldehyde (Primary)	PW	-25%	-23%	4%	-26%
Acetaldehyde (Secondary)	PW	-12%	-12%	-11%	-13%
Benzene	1hr*	-36%	-36%	-36%	-36%
Benzene	Daily*	-29%	-32%	-29%	-33%
Benzene	PW	-33%	-34%	-32%	-36%
1,3-Butadiene	1hr	-50%	-50%	-50%	-50%
1,3-Butadiene	Daily	-60%	-60%	-60%	-60%
1,3-Butadiene	PW	-43%	-45%	-44%	-45%
CO	1hr*	-14%	-14%	-20%	-13%
CO	8hr*	-18%	-18%	-23%	-16%
CO	PW	-18%	-18%	-24%	-16%
Ethanol	1hr*	-6%	34%	53%	-6%
Ethanol	Daily*	-5%	39%	59%	-5%
Ethanol	PW	-5%	40%	63%	-5%
Formaldehyde (Total)	1hr	1%	0%	1%	0%
Formaldehyde (Total)	Daily	-13%	-16%	-14%	-16%
Formaldehyde (Total)	PW	-13%	-16%	-14%	-17%
Formaldehyde (Primary)	PW	-25%	-27%	-27%	-27%
Formaldehyde (Secondary)	PW	-11%	-14%	-12%	-15%
MTBE	1hr*	-31%	-100%	-100%	-100%
MTBE	Daily*	-31%	-100%	-100%	-100%
MTBE	PW	-34%	-100%	-100%	-100%
Nitric Acid	Daily	-12%	-12%	-12%	-12%
Nitric Acid	PW	-11%	-11%	-11%	-11%
NO	PW	-46%	-45%	-46%	-45%
NO_2	1hr	-8%	-8%	-8%	-8%
NO_2	Daily	-17%	-17%	-17%	-17%
NO_2	PW	-28%	-28%	-28%	-28%
Ozone	1hr	-6%	-7%	-7%	-7%
Ozone	8hr	-5%	-5%	-5%	-5%
PAN	1hr	-5%	-7%	-5%	-9%
PAN	Daily	-4%	-5%	-3%	-6%
PAN	PW	-4%	-4%	-3%	-6%
PPN	1hr	0%	0%	0%	0%
PPN	Daily	-1%	1%	-1%	4%
PPN	PW	-2%	-1%	-2%	-1%

1hr, 8hr, Daily, and PW are gridded region maximum 1hr, 8hr, daily hour averages, and population weighted summer daily average, respectively.

*=Data represent changes for grid cell containing Lynwood (location of highest estimated 1997 concentration).

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

Compound	Parameter	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
Acetaldehyde (Total)	1hr	1%	2%	1%
Acetaldehyde (Total)	Daily	0%	0%	0%
Acetaldehyde (Total)	PW	0%	4%	-1%
Acetaldehyde (Primary)	PW	4%	39%	-1%
Acetaldehyde (Secondary)	PW	0%	2%	-1%
Benzene	1hr*	0%	0%	0%
Benzene	Daily*	-4%	0%	-6%
Benzene	PW	-3%	1%	-5%
1,3-Butadiene	1hr*	0%	0%	0%
1,3-Butadiene	Daily*	0%	0%	0%
1,3-Butadiene	PW	-2%	-2%	-2%
CO	1hr*	0%	-7%	2%
CO	8hr*	0%	-7%	2%
CO	PW	0%	-7%	2%
Ethanol	1hr*	43%	63%	0%
Ethanol	Daily*	46%	67%	0%
Ethanol	PW	48%	72%	0%
Formaldehyde (Total)	1hr	-1%	0%	-1%
Formaldehyde (Total)	Daily	-3%	-1%	-4%
Formaldehyde (Total)	PW	-4%	-2%	-4%
Formaldehyde (Primary)	PW	-3%	-3%	-4%
Formaldehyde (Secondary)	PW	-4%	-1%	-4%
MTBE	1hr*	-100%	-100%	-100%
MTBE	Daily*	-100%	-100%	-100%
MTBE	PW	-100%	-100%	-100%
Nitric Acid	Daily	0%	-1%	0%
Nitric Acid	PW	0%	0%	0%
NO	PW	1%	0%	1%
NO_2	1hr	0%	0%	0%
NO_2	Daily	0%	0%	0%
NO_2	PW	0%	0%	0%
Ozone	1hr	-1%	-1%	-1%
Ozone	8hr	0%	0%	0%
PAN	1hr	-2%	0%	-5%
PAN	Daily	-1%	1%	-2%
PAN	PW	0%	1%	-1%
PPN	1Hr	0%	0%	0%
PPN	Daily	2%	-1%	4%
PPN	PW	0%	-1%	1%

1hr, 8hr, Daily, and PW are gridded region maximum 1hr, 8hr, daily hour averages, and population weighted summer daily average, respectively.

*=Data represent changes for grid cell containing Lynwood (location of highest estimated 1997 concentration).

Table 4.6. Changes in Gridded Region Model Results from 1997 MTBE Baseline for Upper-Bound Simulations

Compound	Parameter	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
Acetaldehyde (Total)	1hr	-30%	-28%	-23%	-30%
Acetaldehyde (Total)	Daily	-28%	-26%	-22%	-27%
Acetaldehyde (Total)	PW	-24%	-24%	-18%	-25%
Acetaldehyde (Primary)	PW	-32%	-24%	1%	-32%
Acetaldehyde (Secondary)	PW	-23%	-24%	-20%	-25%
Benzene	1hr*	-42%	-42%	-42%	-46%
Benzene	Daily*	-41%	-41%	-40%	-45%
Benzene	PW	-43%	-44%	-42%	-47%
1,3-Butadiene	1hr	-40%	-40%	-40%	-40%
1,3-Butadiene	Daily	-47%	-47%	-47%	-47%
1,3-Butadiene	PW	-44%	-46%	-46%	-46%
CO	1hr*	-29%	-29%	-32%	-26%
CO	8hr*	-28%	-28%	-31%	-25%
CO	PW	-27%	-27%	-31%	-25%
Ethanol	1hr*	-6%	97%	148%	-6%
Ethanol	Daily*	-5%	93%	145%	-6%
Ethanol	PW	-5%	102%	162%	-6%
Formaldehyde (Total)	1hr	-30%	-34%	-32%	-34%
Formaldehyde (Total)	Daily	-30%	-34%	-32%	-35%
Formaldehyde (Total)	PW	-25%	-30%	-27%	-31%
Formaldehyde (Primary)	PW	-33%	-35%	-36%	-36%
Formaldehyde (Secondary)	PW	-23%	-29%	-25%	-30%
MTBE	1hr*	-38%	-100%	-100%	-100%
MTBE	Daily*	-39%	-100%	-100%	-100%
MTBE	PW	-39%	-100%	-100%	-100%
Nitric Acid	Daily	-18%	-18%	-18%	-18%
Nitric Acid	PW	-15%	-14%	-15%	-14%
NO	PW	-41%	-40%	-40%	-39%
NO_2	1hr	-19%	-19%	-19%	-19%
NO_2	Daily	-19%	-19%	-19%	-19%
NO_2	PW	-26%	-26%	-26%	-26%
Ozone	1hr	-22%	-25%	-24%	-25%
Ozone	8hr	-20%	-23%	-21%	-23%
PAN	1hr	-37%	-40%	-35%	-43%
PAN	Daily	-33%	-36%	-33%	-37%
PAN	PW	-29%	-31%	-27%	-32%
PPN	1hr	-35%	-35%	-37%	-33%
PPN	Daily	-33%	-34%	-35%	-34%
PPN	PW	-27%	-28%	-29%	-27%

1hr, 8hr, Daily, and PW are gridded region maximum 1hr, 8hr, daily hour averages, and population weighted summer daily average, respectively.

*=Data represent changes for grid cell containing Lynwood (location of highest estimated 1997 concentration).

Table 4.7. Changes in Gridded Region Model Results from 2003 MTBE Baseline for Upper-Bound Simulations

Compound	Parameter	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
Acetaldehyde (Total)	1hr	2%	10%	-1%
Acetaldehyde (Total)	Daily	2%	7%	0%
Acetaldehyde (Total)	PW	0%	7%	-2%
Acetaldehyde (Primary)	PW	11%	49%	-1%
Acetaldehyde (Secondary)	PW	-1%	4%	-2%
Benzene	1hr*	0%	0%	-7%
Benzene	Daily*	-1%	1%	-7%
Benzene	PW	-1%	1%	-7%
1,3-Butadiene	1hr*	0%	0%	0%
1,3-Butadiene	Daily*	0%	0%	0%
1,3-Butadiene	PW	-3%	-3%	-3%
CO	1hr*	0%	-5%	4%
CO	8hr*	0%	-5%	3%
CO	PW	0%	-5%	3%
Ethanol	1hr*	110%	166%	0%
Ethanol	Daily*	104%	159%	-1%
Ethanol	PW	113%	177%	-1%
Formaldehyde (Total)	1hr	-5%	-2%	-6%
Formaldehyde (Total)	Daily	-6%	-2%	-7%
Formaldehyde (Total)	PW	-6%	-3%	-8%
Formaldehyde (Primary)	PW	-3%	-4%	-5%
Formaldehyde (Secondary)	PW	-7%	-2%	-8%
MTBE	1hr*	-100%	-100%	-100%
MTBE	Daily*	-100%	-100%	-100%
MTBE	PW	-100%	-100%	-100%
Nitric Acid	Daily	-1%	-1%	-1%
Nitric Acid	PW	1%	0%	1%
NO	PW	2%	1%	3%
NO_2	1hr	0%	0%	0%
NO_2	Daily	-1%	0%	-1%
NO_2	PW	0%	0%	0%
Ozone	1hr	-4%	-2%	-4%
Ozone	8hr	-3%	-2%	-3%
PAN	1hr	-4%	3%	-9%
PAN	Daily	-4%	1%	-6%
PAN	PW	-3%	1%	-5%
PPN	1Hr	0%	-3%	3%
PPN	Daily	-2%	-3%	-1%
PPN	PW	-2%	-2%	0%

1hr, 8hr, Daily, and PW are gridded region maximum 1hr, 8hr, daily hour averages, and population weighted summer daily average, respectively.

*=Data represent changes for grid cell containing Lynwood (location of highest estimated 1997 concentration).

Table 4.6 compares the changes in pollutant concentrations between the 1997 CaRFG2 base gasoline and the four 2003 fuel scenarios, while Table 4.7 compares the three 2003 MTBE-free fuel scenarios with the 2003 MTBE. The predicted domain maximum one-hour-average concentrations (see Table 5.3 in Appendix B) increase significantly for many species when the motor vehicle VOC emissions were increased by a factor of three. The major finding is that the predicted maximum one-hour-average concentrations for acetaldehyde and PAN from the ethanol-containing gasoline (Et3.5%) are now 1.4 ppb and 1.3 ppb, respectively, greater than the maximum predicted for the non-oxygenated gasoline (NonOxy). These acetaldehyde and PAN impacts from the ethanol-containing gasoline represent an upper limit because the factor of three increase in all on-road hydrocarbon emissions is larger than expected from EMFAC2000 when it becomes final, the assumed Cl radical concentrations are likely very high for inland areas, and the ozone episode modeled here is an extreme ozone event.

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 described in Appendix B, the box model simulations are consistent with the results from the three-dimensional airshed model that other VOCs, (that is, aromatic compounds, olefins) not ethanol, are primarily responsible for PAN formation.

4.2.3. Current and Future Air Quality

In order to perform a health-risk analysis, OEHHA requested maximum 1997 and 2003 population-weighted annual-average, maximum 24-hour-average, and maximum one-hour-average concentrations for the toxic air contaminants and fuel oxygenates, and concentrations for the appropriate averaging times for the criteria air pollutants (including PAN and PPN). 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 VOCs 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 (SCOS97-NARSTO) and Multiple Air Toxics Exposure Study (MATES) 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 also 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 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 used the region-wide population-weighted average of the daily-average model results. Results for the original and upper-bound modeling simulations are given in Table 4.8 and Table 4.9, respectively. The “upper baseline” and “lower baseline” in the tables reflect different assumptions of 1997 air quality due to incomplete measurements. For pollutants with more complete data (e.g., carbon monoxide, ozone), only a “best baseline” is given.

4.2.3.1. 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 4.8.

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 NO_2) 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 then applied model results to extrapolate each component separately. The separate components were then added to obtain total acetaldehyde and total formaldehyde. Table 4.8 reports the range of estimates developed using all except the correlation method.

Table 4.8. Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin Using Original Model Simulations

		Year / Scenario				
		1997	2003	2003	2003	2003
Pollutant / Avg. Type	**Estimate Type**	**MTBE**	**MTBE**	**Et2.0%**	**Et3.5%**	**NonOxy**
Benzene, ppb						
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
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
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
1,3-Butadiene, ppb						
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
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
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
Acetaldehyde, ppb						
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
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
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

Table 4.8. Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin Using Original Model Simulations-continued

		Year / Scenario				
		1997	2003	2003	2003	2003
Pollutant / Avg. Type	**Estimate Type**	**MTBE**	**MTBE**	**Et2.0%**	**Et3.5%**	**NonOxy**
Formaldehyde, ppb						
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**
Maximum Daily Average						
	Best Baseline	**14.0**	**12.2**	**11.8**	**12.1**	**11.7**
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**
Carbon Monoxide, ppm						
Maximum 1-Hour Average						
	Best Baseline	**22.5**	**19.2**	**19.2**	**18.0**	**19.7**[a]
Maximum 8-Hour Average						
	Best Baseline	**17.5**	**14.3**	**14.3**	**13.4**	**14.7**[a]
Nitrogen Dioxide, ppm						
Maximum 1-Hour Average						
	Best Baseline	**0.255**	**0.235**	**0.235**	**0.235**	**0.235**
Maximum Daily Average						
	Best Baseline	**0.117**	**0.098**	**0.097**	**0.097**	**0.097**
Maximum Annual Average						
	Best Baseline	**0.043**	**No significant difference expected among 2003 scenarios**			
Ozone, ppm						
Maximum 1-Hour Average						
	Best Baseline	**0.244**	**0.230**	**0.228**	**0.228**	**0.228**
Maximum 8-Hour Average						
	Best Baseline	**0.206**	**0.196**	**0.196**	**0.196**	**0.196**

[a] **This apparent increase is a function of the emission assumptions. Due to the wintertime oxygenate requirement for the South Coast Air Basin, carbon monoxide concentrations within the nonattainment area of Los Angeles County will not differ from the 2003 MTBE baseline.**

Table 4.8. Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin Using Original Model Simulations-continued

		Year / Scenario				
		1997	2003	2003	2003	2003
Pollutant / Avg. Type	**Estimate Type**	**MTBE**	**MTBE**	**Et2.0%**	**Et3.5%**	**NonOxy**
Particulate Matter (10 μm or less), μg/m^3						
Maximum Daily Average						
	Best Baseline	227	No difference expected among 2003 scenarios			
Maximum Annual Geometric Mean						
	Best Baseline	56	No difference expected among 2003 scenarios			
Particulate Matter (2.5 μm or less), μg/m^3						
Maximum Daily Average						
	Best Baseline	81	No difference expected among 2003 scenarios			
Maximum Annual Average						
	Best Baseline	25.9	No difference expected among 2003 scenarios			
Ethanol, ppb (Estimated from Summer Measurements)						
Maximum 1-Hour Average						
	Upper Baseline	108	101	145	165	101
	Lower Baseline	78	74	114	140	74
Maximum Daily Average						
	Upper Baseline	51	49	71	81	49
	Lower Baseline	47	45	64	75	45
Population-Weighted Annual Exposure						
	Upper Baseline	5.4	5.1	7.6	8.8	5.1
MTBE, ppb						
Maximum 1-Hour Average						
	Upper Baseline	67	46	0	0	0
	Lower Baseline	19	13	0	0	0
Maximum Daily Average						
	Upper Baseline	29	20	0	0	0
	Lower Baseline	13	9	0	0	0
Population-Weighted Annual Exposure						
	Upper Baseline	3.9	2.6	0	0	0
	Lower Baseline	3.6	2.4	0	0	0

Table 4.8. Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin Using Original Model Simulations-continued

		Year / Scenario				
		1997	2003	2003	2003	2003
Pollutant / Avg. Type	Estimate Type	MTBE	MTBE	Et2.0%	Et3.5%	NonOxy
PAN, ppb						
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
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
PPN[a], ppb						
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
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
Nitric Acid, ppb (Model Output Only)						
Maximum Daily Average						
	Model	36.7	32.4	32.3	32.2	32.3
Population-Weighted Summer Daily Exposure						
	Model	12.4	11.0	11.0	11.0	11.0

[a] PPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates.

4.2.3.2. CO, NO_2, Ozone, PM_{10}, and $PM_{2.5}$

For CO, NO_2, ozone, PM_{10}, 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 4.8. 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 Angles 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 emissions of these compounds 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.

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 for 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. 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. Range in estimates for ethanol and MTBE are given in Table 4.8.

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

Table 4.9. Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin Using Upper-Bound Model Simulations

		Year / Scenario				
		1997	2003	2003	2003	2003
Pollutant / Avg. Type	Estimate Type	MTBE	MTBE	Et2.0%	Et3.5%	NonOxy
Benzene, ppb						
Maximum 1-Hour Average						
	Upper Baseline	22.4	13.1	13.1	13.1	12.1
	Lower Baseline	11.6	6.8	6.8	6.8	6.3
Maximum Daily Average						
	Upper Baseline	9.5	5.6	5.6	5.7	5.2
	Lower Baseline	7.4	4.4	4.3	4.4	4.1
Population-Weighted Annual Exposure						
	Upper Baseline	1.19	0.68	0.67	0.69	0.63
	Lower Baseline	1.07	0.61	0.60	0.62	0.57
1,3-Butadiene, ppb						
Maximum 1-Hour Average						
	Upper Baseline	6.7	4.0	4.0	4.0	4.0
	Lower Baseline	3.1	1.9	1.9	1.9	1.9
Maximum Daily Average						
	Upper Baseline	2.9	1.5	1.5	1.5	1.5
	Lower Baseline	2.0	1.1	1.1	1.1	1.1
Population-Weighted Annual Exposure						
	Upper Baseline	0.36	0.20	0.19	0.20	0.20
	Lower Baseline	0.34	0.19	0.18	0.19	0.18
Acetaldehyde, ppb						
Maximum 1-Hour Average						
	Upper Baseline	17.7	12.4	12.7	13.6	12.3
	Lower Baseline	13.8	9.7	9.9	10.6	9.6
Maximum Daily Average						
	Upper Baseline	11.0	7.9	8.1	8.5	8.0
	Lower Baseline	5.1	3.7	3.8	4.0	3.7
Population-Weighted Annual Exposure						
	Upper	1.8	1.5	1.5	1.8	1.5
	Lower	1.8	1.4	1.5	1.7	1.4

Table 4.9. Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin Using Upper-Bound Model Simulations-continued

		Year / Scenario				
		1997	2003	2003	2003	2003
Pollutant / Avg. Type	**Estimate Type**	**MTBE**	**MTBE**	**Et2.0%**	**Et3.5%**	**NonOxy**
Formaldehyde, ppb						
Maximum 1-Hour Average						
	Upper Baseline	37.8	26.5	25.1	25.9	24.9
	Lower Baseline	20.3	14.2	13.5	13.9	13.4
Maximum Daily Average						
	Best Baseline	14.0	9.8	9.2	9.6	9.1
Population-Weighted Annual Exposure						
	Upper	4.7	3.7	3.4	3.5	3.4
	Lower	4.7	3.6	3.4	3.5	3.4
Carbon Monoxide, ppm						
Maximum 1-Hour Average						
	Best Baseline	22.5	16.1	16.1	15.3	16.6
Maximum 8-Hour Average						
	Best Baseline	17.5	12.7	12.7	12.1	13.1
Nitrogen Dioxide, ppm						
Maximum 1-Hour Average						
	Best Baseline	0.255	0.207	0.207	0.207	0.207
Maximum Daily Average						
	Best Baseline	0.117	0.095	0.095	0.095	0.095
Maximum Annual Average						
	Best Baseline	0.043	No difference expected among 2003 scenarios			
Ozone, ppm						
Maximum 1-Hour Average						
	Best Baseline	0.244	0.190	0.182	0.186	0.182
Maximum 8-Hour Average						
	Best Baseline	0.206	0.165	0.159	0.162	0.159

[a] **This apparent increase is a function of the emission assumptions. Due to the wintertime oxygenate requirement for the South Coast Air Basin, carbon monoxide concentrations within the nonattainment area of Los Angeles County will not differ from the 2003 MTBE baseline.**

Table 4.9. Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin Using Upper-Bound Model Simulations-continued

		Year / Scenario				
		1997	2003	2003	2003	2003
Pollutant / Avg. Type	Estimate Type	MTBE	MTBE	Et2.0%	Et3.5%	NonOxy
Particulate Matter (10 μm or less), μg/m^3						
Maximum Daily Average						
	Best Baseline	227	No difference expected among 2003 scenarios			
Maximum Annual Geometric Mean						
	Best Baseline	56	No difference expected among 2003 scenarios			
Particulate Matter (2.5 μm or less), μg/m^3						
Maximum Daily Average						
	Best Baseline	81	No difference expected among 2003 scenarios			
Maximum Annual Average						
	Best Baseline	25.9	No difference expected among 2003 scenarios			
Ethanol, ppb (Estimated from Summer Measurements)						
Maximum 1-Hour Average						
	Upper Baseline	108	101	213	268	101
	Lower Baseline	78	74	191	267	74
Maximum Daily Average						
	Upper Baseline	51	48	98	125	48
	Lower Baseline	47	45	93	121	44
Population-Weighted Annual Exposure						
	Upper Baseline	5.4	5.1	10.9	14.2	5.1
MTBE, ppb						
Maximum 1-Hour Average						
	Upper Baseline	67	41	0	0	0
	Lower Baseline	19	12	0	0	0
Maximum Daily Average						
	Upper Baseline	29	18	0	0	0
	Lower Baseline	13	8	0	0	0
Population-Weighted Annual Exposure						
	Upper Baseline	3.9	2.4	0	0	0
	Lower Baseline	3.6	2.2	0	0	0

Table 4.9. Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin Using Upper-Bound Model Simulations -continued

		Year / Scenario				
		1997	2003	2003	2003	2003
Pollutant / Avg. Type	Estimate Type	MTBE	MTBE	Et2.0%	Et3.5%	NonOxy
PAN, ppb						
Maximum 1-Hour Average						
	Upper Baseline	10.0	6.3	6.0	6.5	5.7
	Lower Baseline	5.0	3.1	3.0	3.2	2.9
Maximum Daily Average						
	Upper Baseline	5.0	3.3	3.2	3.4	3.1
	Lower Baseline	2.5	1.7	1.6	1.7	1.6
PPN[a], ppb						
Maximum 1-Hour Average						
	Upper Baseline	3.0	1.9	1.9	1.9	2.0
	Lower Baseline	1.5	1.0	1.0	0.9	1.0
Maximum Daily Average						
	Upper Baseline	2.0	1.3	1.3	1.3	1.3
	Lower Baseline	1.0	0.7	0.7	0.7	0.7
Nitric Acid, ppb (Model Output Only)						
Maximum Daily Average						
	Model	39.9	32.8	32.6	32.6	32.7
Population-Weighted Summer Daily Exposure						
	Model	12.4	10.6	10.6	10.6	10.6

[a] **PPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates.**

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 4.8.

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 4.8.

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

OEHHA requested information on maximum annual-average and maximum one-hour-average concentrations for alkylates, *n*-heptane, *n*-hexane, isobutene, toluene, and xylene isomers. We provided estimates in Table 4.10 by developing ratios between these compounds and CO using the techniques described in Section 4.2.3.1. 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 the alkylates, primarily due to lack of data. The maximum concentrations for *n*-heptane, *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 4.10. Estimated 1997 Maximum Toxic Concentrations

Compound	One-Hour Average (ppb)	Annual Average (ppb)
Total Alkylates	**146-216**	**15.6-23.0**
***n*-Heptane**	**2-7**	**0.2-0.7**
***n*-Hexane**	**11-22**	**1.2-2.4**
Isobutene	**20-36**	**2.2-3.8**
Toluene	**52-103**	**6-11**
***m*&*p*-Xylene**	**25-43**	**2.6-4.6**
***o*-Xylene**	**9-40**	**1.0-4.3**

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 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 4.11 and Table 4.12). This is especially true for the comparison to the 2003 MTBE baseline (Table 4.12). 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 for these pollutants in other air basins will be even smaller.

Table 4.11. Comparison of Emission and Modeled Air Quality Changes from 1997 MTBE Baseline

Scenario / Type of Change	CO	NO_X (NO_2)	NO_X (HNO_3)	Benzene	Butadiene	Acetaldehyde (Primary)	Formaldehyde (Primary)	Ethanol	MTBE
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%

[a] Air quality changes are based on changes in population-weighted daily-average model results for gridded region.

Table 4.12. Comparison of Emission and Modeled Air Quality Changes from 2003 MTBE Baseline

Scenario / Type of Change	CO	NO_X (NO_2)	NO_X (HNO_3)	Benzene	Butadiene	Acetaldehyde (Primary)	Formaldehyde (Primary)	Ethanol	MTBE
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%

[a] Air 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 Phase 3 regulations (ARB, 1999a; 1999d), a possible waiver from the oxygenate requirement of federal RFG 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 continue on-going efforts that will not be completed until after the December 31, 1999 deadline specified 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 the 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 neither 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**
Ethanol	**5.88**	**0.00**	**0.42**	**28.0**	**6.88**	**203.8**	**316.4**	**1.22**	**0.21**
NonOxy	**0.00**	**0.00**	**0.16**	**25.0**	**6.71**	**202.1**	**303.2**	**29.20**	**3.43**

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 approved CaRFG3 flat limit for sulfur of 20 ppm (ARB, 1999a; 1999d). Also, the RVP and olefin content of the ethanol-blended gasoline were lower than is expected for future ethanol-blended CaRFGs (under the approved variable-RVP provision). Gasolines with more reasonable values of sulfur, olefins, and RVP could have substantially different compositions than 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.*, 2000; Larsen, 2000). 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, NO_2, 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 might be recovered from gas chromatograms if a gas chromatography-flame ionization detector (GC-FID) with a DB column is used to measure ambient VOCs.

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California Environmental Protection Agency

Air Resources Board

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

Appendix A

Emissions

December 1999

Table of Contents

List of Tables

List of Figures

Attachments

Attachment A1	Peer Review of Organic Gas Emission Profiles
Attachment A2	Tables of Organic Gas Emission Profiles
Attachment A3	Tables of Organic Gas Profiles From Emission Testing

A-1. Introduction

The photochemical modeling described in Appendix B requires emission inventories as input. We evaluated emission impacts for four fuel scenarios for calendar year 2003. The scenarios are:

- 2003 MTBE-based California Phase 2 Reformulated Gasoline (CaRFG).
- 2003 Ethanol-based fully complying fuel (with oxygen content of 2.0 wt%).
- 2003 Ethanol-based fully complying fuel (with oxygen content of 3.5 wt%).
- 2003 Non-oxygenated fully complying fuel.

In addition, we include emission data for 1997 MTBE-based CaRFG to serve as a link to observed air quality in the South Coast Air Basin (SoCAB).

We focused our analysis on emissions of the following air contaminants:

- Criteria pollutant precursors [carbon monoxide (CO), oxides of nitrogen (NO_X), and reactive organic gases (ROG)].
- Toxic air contaminants (acetaldehyde, benzene, 1,3-butadiene, and formaldehyde).
- Fuel oxygenates (ethanol and MTBE).
- Alkylates (C_6 to C_9 branched alkanes and cycloalkanes).
- Additional compounds of interest to OEHHA (*n*-hexane, isobutene, toluene, and xylene isomers).

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 (e.g., passenger cars, heavy-duty vehicles, fuel spillage, off-road mobile sources, etc.). 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 CaRFG, 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, 1998ab) to establish the liquid gasoline profiles. In general the MathPro (1998ab) 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 CaRFG 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 CaRFG 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 presented at public workshops on July 12 and October 4**.** What is presented here 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.

In order to determine if the organic gas emission profiles are reasonable, we conducted a limited emission testing program at the ARB laboratory in El Monte. 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.

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. In addition, most of the vehicles were aged, and several had unstable emission rates. 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.

This appendix describes the organic gas emission profiles, the emission estimates, and the fuel and vehicle testing results.

A-2. Development of Organic Gas Emission Profiles

This section documents the organic gas speciation profiles used as inputs the photchemical modeling. We estimated profiles for gasoline blended with 2.0 wt% oxygen as ethanol, gasoline blended with 3.5 wt% oxygen as ethanol, and gasoline without any oxygen. There are profiles for compositions of the liquid fuels, evaporative emissions, and exhaust emissions.

A-2.1. MTBE-Based CaRFG Profiles

A series of motor vehicle related profiles were presented at a public workshop on September 10, 1998 (ARB, 1998a). The speciation profiles were all based on MTBE-based CaRFG, and included:

- Liquid gasoline.

- Headspace vapors.
- Start exhaust -- catalyst and non-catalyst.
- Stabilized exhaust -- catalyst and non-catalyst.

The liquid gasoline speciation is based on tests of MTBE-based CaRFG conducted by the ARB in 1996 and 1997 (ARB, 1998b). The headspace vapor speciation for the MTBE-based CARFG was the mathematically derived speciation using an equilibrium model (Kirchstetter and Harley, 1997). The exhaust speciation is based on 1996 surveillance vehicle tests (ARB, 1998b) using the methodology discussed by Allen (1997). Vehicles were randomly selected in the Southern California region for the surveillance tests, and were tested "as received".

A-2.2. Non-MTBE-Based CaRFG Profiles

A-2.2.1. Overview of Profile Development

For gasoline compositions, we created organic gas speciation profiles by adjusting the ARB composition profile for CaRFG blended with 11 vol% MTBE. The adjustments are based on comparisons of gasoline compositions among the model fuels predicted in a linear programming refinery modeling study conducted by MathPro (1998ab). However, the benzene content of the compositions has been held constant at the value in the ARB profile for MTBE-blended CaRFG.

For diurnal and resting loss evaporative emissions, the profiles for the ethanol-blended and non-oxygenated CaRFGs are the headspace vapor compositions predicted by Professor Harley for the corresponding gasoline compositions (see Attachement A3). For hot soak and running loss evaporative emissions, the profiles have been set equal to the corresponding gasoline compositions.

For exhaust emissions, we have created profiles by making certain adjustments to the corresponding ARB profiles for CaRFG blended with 11 vol% MTBE. Some of the adjustments to create profiles for ethanol-blended CaRFGs are based on comparisons between the emission compositions measured by ARB in its recent testing of an MTBE-blended CaRFG and a gasoline with 10 vol% ethanol (ARB, 1998b). Likewise, some of the adjustments to create exhaust profiles for the non-oxygenated gasoline are based on comparisons of emission compositions by the Auto/Oil Program (1991, 1995). Also, in part, the adjustments of all the exhaust profiles are based on comparisons among the model fuels predicted by MathPro.

The contents of the four toxic species in exhaust (acetaldehyde, benzene, 1,3-butadiene, and formaldehyde) for the ethanol-blended and non-oxygenated CaRFGs have been determined by adjustments to the corresponding profiles for MTBE-blended CaRFG. The adjustments are based on applying the ARB Predictive Model (including a draft new element that distinguishes between MTBE and ethanol in predicting aldehyde emissions) to the fuels predicted by MathPro.

It must be noted that, in the absence of extensive emission data taken with representative commercial fuels, the emission profiles for MTBE-free CaRFGs are uncertain. Therefore, differences in outputs from the photochemical model must be interpreted with caution. Small differences could easily be due to the uncertainties in the inputs.

The immediately following sections describe the derivations in more detail. Section A-2.2.6 gives explicit directions for adjusting the profiles for MTBE-blended CaRFG to produce the profiles for the other fuels.

A-2.2.2. Limited Utility of Empirical Data

The data from ARB (1998b) and the Auto/Oil Program (1991; 1995) studies were adequate only for determining the amount of isobutene to remove from the MTBE-based exhaust and for determining the amounts of ethanol that should be added to the exhaust emissions. Neither study was useful for dealing with other species that are important to reactivity. The non-MTBE test fuels in both studies were matched in chemical composition to the MTBE test fuels. Such matching is not realistic; if applied to current typical MTBE-blended CaRFG, it would create ethanol-blended gasolines that would violate the ARB Reid Vapor Pressure (RVP) limit and non-oxygenated gasolines that would be deficient in octane.

To maintain an adequate octane number in non-oxygenated gasolines, refiners will typically use much higher contents of alkylates than in today’s MTBE-blended gasolines. According to the linear-programming results by MathPro (1998ab), branched alkanes will be more common in ethanol-blended CaRFGs, also. Adding ethanol at 3.5 wt% oxygen would essentially replace the octane. However, ethanol at 2.0 wt% oxygen would not provide sufficient octane, so additional octane-raising steps would be needed. These extra contents in the gasolines should be reflected in the emission streams.

Some exhaust and headspace data comparing commercially available CaRFGs have been taken recently in the ARB labs (see Section A-5). However, the seven vehicles used to test the fuels were generally not representative of the on-road fleet, and several showed large variability in NMOG emissions from test to test. Furthermore, the composition and RVP of the ethanol-blended CaRFG that was tested do not resemble the expected typical properties of ethanol-blended gasolines that will be in commercial production in 2003. Therefore, the recent empirical data have not been used in creating the profiles, but rather to provide a reality check on the relative increases and decreases in broad categories of compounds (see Section A-6).

A-2.2.3. Development of Gasoline Composition Profiles

Ethanol-Blended CaRFGs. Table 2.1 shows the available detail on the composition of the MTBE-blended and ethanol-blended CaRFGs predicted by MathPro (1998ab) for 2002. There are data for the entire fuels and for each fuel on the oxygenate-free basis. Note that MathPro modeled a single ethanol-blended gasoline with oxygen at 2.7 wt%.

Table 2.1. Compositions of CaRFGs Modeled by MathPro (vol%)

	MTBE-Blended[a]		EtOH-Blended[b]		
	actual	w/o MTBE	actual	w/o EtOH	No Oxygen[c]
n-Butane	0.6	0.65	0.5	0.54	0.1
C_5 and C_6 alkanes	6.1	6.9	4.3	4.6	11.3
C_7 to C_9 branched alkanes	14.4	16.3	28.4	30.1	32.5
Benzene	0.67	0.76	0.80	0.87	0.80
Total aromatics	24.0	27.1	20.0	21.7	20
Total olefins	4.3	4.9	2.9	3.1	5.0
Oxygenate	11.4	0.0	7.8	0.0	0
Other	39	43	35	38	30
Total	100.47	99.61	99.7	98.91	100
Oxgyen (wt%)	2.1	--	2.7	--	--

[a] "Ref. 2002, 1, CARB" on page 3 of Exhibit 8, Refinery Modeling Task 3, PB300-98-013I.

[b] "BAS U, Alk-100, 1, CARB" on page 3 of Exhibit 8, Refinery Modeling Task 3, PB300-98-013I.

[c] "HRG30, 1, CARB" on page 3 of Exhibit 8, Refinery Modeling Task 3, PB300-98-013I.

Note the contrasts between the MTBE- and ethanol-blended CaRFGs on the oxygenate-free basis. These changes include a significant removal of pentanes and an increased use of C_7 to C_9 branched alkanes. The reduction of pentanes is expected for ethanol-blended CaRFG, regardless of the ethanol content, to meet the limit on RVP. The near doubling in the content of C_7 to C_9 branched alkanes is reasonable for ethanol at 2.0 wt% oxygen because that amount of ethanol does not replace the octane provided by MTBE at 11 vol%. For ethanol at 3.5 wt% oxygen, the need for added C_7 to C_9 branched alkanes is not clear. However, we have applied the above ratios to the 3.5 wt% oxygen gasoline, too. This may lead to an overestimation of the content of C_7 to C_9 branched alkanes (and an under-estimation of the average ozone-forming potential) of that fuel because the cost of C_7 to C_9 branched alkanes will discourage refiners from using more than they need.

The MathPro (1998ab) predictions include greater benzene content in the ethanol-blended CaRFG than in the MTBE-blended CaRFG. The benzene content of the fuel is an important parameter because benzene emissions are influential in the computation of overall toxic emissions and because the estimated evaporative benzene emissions are proportional to the benzene content of the fuel. However, this prediction for a single gasoline constituent is less certain than the predictions for entire classes of compounds. Also, adopted "Phase 3 CaRFG" regulatory changes (ARB, 1999a) would discourage such an increase in benzene. Therefore, we believe that it would not be appropriate to change the benzene content of the CaRFG according to the type or lack of oxygenate.

Accordingly, to create the composition profiles for both of the ethanol-blended CaRFGs, the ARB profile for MTBE-blended CaRFG has been adjusted by multiplying certain contents on the oxygenate-free basis as follows:

- C_4 alkanes by 0.54/0.65=0.83
- C_5 and C_6 alkanes by 4.6/6.9=0.67
- C_7-C_9 branched alkanes by 30.1/16.3=1.85
- Aromatic species (except benzene) by 21.7/27.1=0.80
- Olefinic species by 3.1/4.9=0.63

Ethanol has then been inserted into the profiles at 5.75 wt% (2.0 wt% oxygen) and at 10.1 wt% (3.5 wt% oxygen). In re-normalizing to sum to 100%, steps have been taken to preserve these ethanol contents and to preserve the benzene content at its value in the profile for MTBE-blended CaRFG.

Non-oxygenated CaRFG. Table 2.1 shows the available detail on the composition of the MTBE-blended and non-oxygenated CaRFGs predicted by MathPro (1998ab) for 2002. As with the ethanol blended gasoline, we see a near doubling of the alkylate content.

In conformity with the derivation just presented for the ethanol-blended CaRFGs, we have adjusted the ARB profile for MTBE-blended CaRFG by multiplying certain contents on the oxygenate-free basis as follows:

- C_5 and C_6 alkanes by 11.3/6.9=1.64
- C_7-C_9 branched alkanes by 32.5/16.3=1.99
- Aromatic species (except benzene) by 20.0/27.1=0.74

The MathPro (1998ab) analysis indicates that the butanes in the MTBE-blended gasoline would be replaced by butenes in the non-oxygenated gasoline. We doubt that this is realistic. Lacking reliable information on the butane content of non-oxygenated CaRFG, we have made no adjustment of butanes in the MTBE-blended gasoline compositions in creating the non-oxygenated gasoline composition.

The olefinic content was not adjusted. At re-normalization to sum to 100%, the benzene content was kept at its value in the MTBE-blended gasoline profile.

A-2.2.4. Development of Evaporative Emission Profiles

For diurnal and resting loss evaporative emissions, all the liquid gasoline profiles (MTBE-blended, both ethanol-blended, and non-oxygenated CaRFGs) were input to a headspace prediction model developed by Professor Harley (see Attachment A3). For hot soak and running loss evaporative emissions, the liquid gasoline profiles were used directly. Since the benzene contents of all the fuels have been maintained equal, the benzene contents of the hot soak and running loss emission profiles are identical, and the benzene contents of the diurnal and resting emission profiles are nearly constant.

A-2.2.5. Development of Exhaust Emission Profiles

For both the ethanol-blended and non-oxygenated CaRFGs, three separate sets of adjustments have been made to the exhaust profiles for MTBE-blended CaRFG: (1) reduction of MTBE and isobutene; (2) adjustment of the four toxic species (acetaldehyde, benzene, 1,3-butadiene, and formaldehyde); and (3) adjustments to reflect the differences among fuels that result from the derivations in Section A-2.2.3. Ethanol was added to the ethanol-blended

CaRFG. Re-normalization to sum to 100% was carried out with preservation of the ethanol, toxic, and alkylate contents at the values determined by the adjustment procedures.

MTBE and Isobutene. Table 2.2 summarizes empirical data on the ratio of isobutene (a decomposition product of MTBE) in exhaust streams from MTBE-blended and MTBE-free gasolines. These numbers are fairly stable across studies, fuel type, and emission mode (starts versus stabilized exhaust). Therefore, we have used their mean, 0.53, to adjust the isobutene content in the ARB profiles for MTBE-blended CaRFG to yield the isobutene content in each exhaust profile for each non-MTBE CaRFG.

Table 2.2. Isobutene Ratios, Non-MTBE Gasoline to MTBE Gasoline

	ARB (1998b)	ATL (1995)	Auto/Oil	Auto/Oil
Starts (Bag 1 – Bag 2)				
EtOH-blended	**0.47**	**0.56**	**0.59**	
Non-oxygenated				**0.57**
Stabilized (Bag 2)				
EtOH-blended	**0.40**	**0.46**	**no data**	
Non-oxygenated				**0.68**

Toxic Emissions in Exhaust. The appropriate profile adjustments for benzene and 1,3-butadiene can be estimated with the ARB Predictive Model using as inputs the properties of the CaRFGs predicted by MathPro (1998ab) with benzene held constant. Using the MathPro (1998ab) MTBE-blended CaRFG as the baseline, one can predict the changes in the benzene/THC and 1,3-butadiene/THC ratios for ethanol-blended CaRFGs and non-oxygenated CaRFG. For the ethanol-blended gasoline, the 2.7 wt% oxygen in the predicted fuel has been replaced with 2.0 wt% and 3.5 wt% oxygen.

Since the ARB Predictive Model was developed mostly with data from MTBE-blended and non-oxygenated gasolines, it should not be used to predict aldehyde emissions for gasolines with ethanol. Therefore, we have re-regressed the Predictive Model database to construct new models for acetaldehyde and formaldehyde that distinguish between ethanol and MTBE as the source of oxygen. Applied to the MathPro fuels, these new models predict changes in acetaldehyde and formaldehyde for the ethanol-blended and non-oxygenated CaRFGs relative to the MTBE-blended CaRFG.

Table 2.3 and Table 2.4 show the results of these methods. [The columns headed by "Δ(xx/HC)" are the relative (%) changes of the profile contents for species xx.]

Table 2.3. Modeled Changes in Exhaust Benzene and 1,3-Butadiene Fractions

(from ARB Predictive Model; FTP-composite predictions for Tech 4)

CaRFG[a]	**ΔHC** (%)	**ΔBenz** (%)	**Δ(Benz/HC)** (%)[b]	**Δ1,3BD** (%)	**Δ(BD/HC)** (%)[b]
EtOH, 2.0 wt% O_2	**+0.9**	**-3.3**	***-4***	**-2.3**	***-2***
EtOH, 3.5 wt% O_2	**-1.1**	**-0.8**	***0***	**-2.3**	***-1***
Non-oxygenate	**+1.2**	**-11**	***-12***	**-0.8**	***-2***

[a] Fuel predicted by MathPro (1998ab); contrasted with MathPro's MTBE-blended CaRFG.

[b] Approximation: $\Delta(A/B)/(A/B) = \Delta A/A - \Delta B/B$.

Table 2.4. Modeled Changes in Aldehydes

(per oxygenate-specific models)

CaRFG[a]	**ΔHC**[b] **(%)**	**ΔForm**[c] (%)	**Δ(Form/HC)** (%)	**ΔAcet**[c] (%)	**Δ(Acet/HC)** (%)
EtOH, 2.0 wt% O_2	**+0.9**	**-5**	***-6***	**+28**	***+27***
EtOH, 3.5 wt% O_2	**-1.1**	**-9**	***-8***	**+133**	***+132***
Non-oxygenate	**+1.2**	**-10**	***-11***	**-4**	***-5***

[a] Fuel predicted by MathPro (1998ab); contrasted with MathPro's MTBE-blended CaRFG.

[b] From the current Predictive Model.

[c] From draft oxygenate-specific models applied to the oxygen contents.

The adjustments applied to both the ARB start and stabilized exhaust profiles for MTBE-blended CaRFG are shown in Table 2.5.

Table 2.5. Adjustments to TAC Fractions in Start and Stabilized Exhaust Profiles

CaRFG	**Acetaldehyde**	**Benzene**	**1,3-Butadiene**	**Formaldehyde**
EtOH, 2.0 wt% O_2	**1.27**	**0.96**	**0.98**	**0.94**
EtOH, 3.5 wt% O_2	**2.32**	**1.0**	**0.99**	**0.92**
Non-oxygenate	**0.95**	**0.88**	**0.98**	**0.89**

Branched Alkanes and Other Species. MathPro (1998ab) predicted a near doubling of the alkylate content in non-oxygenated CaRFG relative to MTBE-blended CaRFG. This information does not provide guidance on how much the amounts of alkylate species would increase in the exhaust streams, nor does it identify the specific species involved. However, a doubling of the C_7 to C_9 branched alkane contents should provide an upper bound on the effect in the exhaust.

Accordingly, each C_7 to C_9 branched alkane in the exhaust profiles for the MTBE-blended CaRFG has been doubled to represent exhaust for non-oxygenated CaRFG. (Recent testing by ARB of commercial fuels corroborates that exhaust contents of branched alkanes are proportional to the fuel contents as discussed in Section A-6).

Another issue is identifying the elements of the profiles that are to be displaced by the extra C_7 to C_9 branched alkanes. The adjustments just described for toxic species should not be allowed to be perturbed by additions to the alkanes. Also, since MathPro (1998ab) predicted higher C_5 and C_6 alkanes in the non-oxygenated CaRFG than in the MTBE-blended CaRFG, the added branched alkanes should not allowed to "dilute" them. Therefore, in adjusting the ARB exhaust profiles for MTBE-blended CaRFG, the added C_7 to C_9 branched alkanes have been allowed to displace olefinic contents (except 1,3-butadiene), aromatic contents (except benzene), alkanes other than C_5 and C_6, and aldehydes (except formaldehyde and acetaldehyde).

The above considerations apply also to the exhaust profiles for ethanol-blended CaRFG at 2.0 wt% oxygen. The ethanol-blended CaRFG modeled by MathPro (1998ab) has 1.85 times the alkylate content of the modeled MTBE-blended CaRFG. This factor has been applied to the C_7 to C_9 branched alkanes in the exhaust profiles for MTBE-blended CaRFG. However, the procedure for creating exhaust profiles for ethanol at 2.0 wt% oxygen differs somewhat from that for the non-oxygenated CaRFG, for two reasons:

- The C_5 and C_6 alkanes in MathPro's ethanol-blended gasoline are less than in the MTBE-blended gasoline.
- The presence of ethanol in a profile (versus no oxygenate content) will cause re-normalization to alter all contents differently than in the non-oxygenated case, except as specifically prevented for particular species.

Therefore, in the exhaust profiles for ethanol at 2.0 wt% oxygen, the added C_7 to C_9 branched alkanes have displaced olefinic contents (except 1,3-butadiene), aromatic contents (except benzene), all other alkanes, and aldehydes (except formaldehyde and acetaldehyde). Each C_7 to C_9 branched alkane has been fixed at 1.85 times its final value in the corresponding exhaust profile for MTBE-blended CaRFG.

No analogous changes have been made for the exhaust profiles for ethanol-blended CaRFG with 3.5 wt% oxygen. Recall that in creating the gasoline composition profile for the 3.5 wt% oxygen gasoline, extra branched alkanes have been added in the same amounts as added to the composition of the ethanol-blended CaRFG with 2.0 wt% oxygen. Since that step tends to cause an underestimation of the ozone-forming potential of the 3.5 wt% oxygen gasoline composition (see Section A-3), we think it would be inappropriate to further bias the modeling input set for the 3.5 wt% oxygen gasoline by adding low reactivity species to its exhaust profiles. While some such additions (or other changes) might occur for actual ethanol-blended CaRFGs with 3.5 wt% oxygen, there are no data to permit a quantification.

Ethanol. For the ethanol-blended CaRFGs, we estimated the appropriate amount of ethanol for the exhaust profiles from the ethanol contents measured in the ARB (1998b) emission comparison between MTBE-blended CaRFG and a splash-blended ethanol gasoline with 3.9 wt% oxygen. Figures 2.1 and 2.2 show emission profiles from that work. In Figure 2.1, the ethanol content of start exhaust is 6%. Under the assumption that the exhaust content is proportional to the fuel content, the estimated ethanol contents for CaRFGs with 2.0 wt% and 3.5 wt% oxygen are 3.0% and 5.3%, respectively. These values have been inserted into the start exhaust profiles. Figure 2.2 shows analogous data for stabilized exhaust measurements. In this case, we have not directly used the measured ethanol content (0.5%) because both it and the MTBE content of the exhaust from the MTBE-blended gasoline (0.26%) appear unreasonably low compared to other data. Therefore, we have taken their ratio, 1.96, as the basis for adjustment factors to the ARB stabilized exhaust profile for MTBE-blended CaRFG. Under the assumption of linearity with oxygen content, the adjustment factors for CaRFGs with 2.0 wt% and 3.5 wt% oxygen are 1.00 and 1.75, respectively.

A-2.2.6. Specifications for Creating Profiles

There is a different set of profiles for catalyst and non-catalyst exhaust emission. The following procedures for exhaust speciation apply to both categories.

A-2.2.6.1. Ethanol-Blended CaRFGs

A-2.2.6.1.1. Gasoline Composition

Remove MTBE from the ARB profile for MTBE-blended CaRFG. Multiply the following species by the indicated factors:

- *n*-butane -- 0.83
- Olefinic species -- 0.63
- C_7-C_9 branched alkanes -- 1.85
- C_5 and C_6 alkanes -- 0.67
- Aromatic species (except benzene) -- 0.80

For ethanol-blended CaRFG with 2.0 wt% oxygen, adjust all species in proportion so that their sum is [94.25% - benzene content] and insert 5.75 wt% ethanol plus the final benzene content. For ethanol-blended CaRFG with 3.5 wt% oxygen, adjust all species in proportion so that their sum is [89.1% - benzene content] and insert 10.1 wt% ethanol plus the final benzene content. In both cases, “final benzene content” is the fraction of benzene in the ARB profile for MTBE-blended CaRFG.

A-2.2.6.1.2. Hot Soak and Running Loss Evaporative Emissions

Use the gasoline compositions in Section A-2.2.6.1.1.

A-2.2.6.1.3. Diurnal and Resting Loss Evaporative Emissions

Use the headspace compositions for the two gasoline compositions in Section A-2.2.6.1.1 calculated by Professor Harley.

A-2.2.6.1.4. Starting Exhaust Emissions

For oxygen at 2.0 wt%, remove MTBE, methanol, and ethanol from the starting exhaust profile for MTBE-blended CaRFG. Multiply isobutene by 0.53. Adjust all species in proportion to sum to [100% minus the sum of final toxic species contents minus the total final C_7- C_9 branched alkane content and minus 3.0% ethanol]. The final toxic species contents are the contents in the starting exhaust profile for MTBE-blended CaRFG times the following factors:

- Acetaldehyde -- 1.27

- Benzene -- 0.96
- 1,3-Butadiene -- 0.98
- Formaldehyde -- 0.94

For each C_7 to C_9 branched alkane, the final content is the value in the starting exhaust profile for MTBE-blended CaRFG times 1.85. Insert the final toxic species contents, the final branched alkane contents, and 3.0% ethanol.

For oxygen at 3.5 wt%, remove MTBE and methanol from the starting exhaust profile for MTBE-blended CaRFG . Multiply isobutene by 0.53. Adjust all species in proportion to sum to [100% minus the sum of final toxic species contents and minus 5.3% ethanol]. The final toxic species contents are the contents in the starting exhaust profile for MTBE-blended CaRFG times the following factors:

- Acetaldehyde -- 2.32
- Benzene -- 1.00
- 1,3-Butadiene -- 0.99
- Formaldehyde -- 0.92

Insert the final toxic species contents and 5.3 wt% ethanol.

A-2.2.6.1.5. Stabilized Exhaust Emissions

For oxygen at 2.0 wt%, remove MTBE and methanol from the stabilized exhaust profile for MTBE-blended CaRFG . Multiply isobutene by 0.53. Adjust all species in proportion to sum to [100% minus the sum of final toxic species contents minus the total final C_7 to C_9 branched alkane content and minus the final ethanol content]. The final toxic species contents are the contents in the starting exhaust profile for MTBE-blended CaRFG times the following factors:

- Acetaldehyde -- 1.27
- Benzene -- 0.96
- 1,3-Butadiene -- 0.98
- Formaldehyde -- 0.94

For each C_7 to C_9 branched alkane, the final content is the value in the stabilized exhaust profile for MTBE-blended CaRFG times 1.85. The final ethanol content is 1.00 times the MTBE content of the stabilized exhaust profile for MTBE-blended CaRFG.

Insert the final toxic species contents, the final branched alkane contents, and the final ethanol content.

For oxygen at 3.5 wt%, remove MTBE and methanol from the stabilized exhaust profile for MTBE-blended CaRFG . Multiply isobutene by 0.53. Adjust all species in proportion to sum to [100% minus the sum of final toxic species contents and minus the final ethanol content]. The final toxic species contents are the contents in the stabilized exhaust profile for MTBE-blended CaRFG times the following factors:

- Acetaldehyde -- 2.32
- Benzene -- 1.00

- 1,3-Butadiene -- 0.99
- Formaldehyde -- 0.92

The final ethanol content is 1.75 times the MTBE content of the stabilized exhaust profile for MTBE-blended CaRFG.

Insert the final toxic species contents and the final ethanol content.

A-2.2.6.2. Non-Oxygenated CaRFG

A-2.2.6.2.1. Gasoline Composition

Remove MTBE from the ARB profile for MTBE-blended CaRFG. Multiply the following species by the indicated factors:

- C_5 and C_6 alkanes -- 1.64
- C_7-C_9 branched alkanes -- 1.99
- Aromatic species (except benzene) -- 0.74

Adjust all species in proportion so that their sum is [100% - benzene content]. Insert the benzene content equal to the benzene fraction of the MTBE-blended CaRFG

A-2.2.6.2.2. Extended Diurnal and Resting Loss Evaporative Emissions

Use the headspace compositions for the gasoline composition in Section A-2.2.6.2.1 calculated by Professor Harley.

A-2.2.6.2.3. Hot Soak and Running Loss Evaporative Emissions

Use the gasoline compositions in Section A-2.2.6.2.1.

A-2.2.6.2.4. Starting Exhaust and Stabilized Exhaust Emissions

Remove MTBE, methanol, and C_5 and C_6 alkanes from the starting exhaust or stabilized exhaust profile for MTBE-blended CaRFG. Multiply isobutene by 0.53. Adjust all species in proportion to sum to [100% minus the extracted C_5 and C_6 alkanes minus the sum of final toxic species contents minus the total C_7 - C_9 branched alkane content]. The final toxic species contents are the contents in the starting exhaust profile for MTBE-blended CaRFG times the following factors:

- Acetaldehyde -- 0.95
- Benzene -- 0.88
- 1,3-Butadiene -- 0.98
- Formaldehyde -- 0.89

For each C_7 - C_9 branched alkane, the final content is the value in the stabilized exhaust profile for MTBE-blended CaRFG times 2.0.

Insert the extracted C_5 and C_6 alkane contents, the final toxic species contents, and the final branched alkane contents.

A-2.3. CO Emissions

CO emissions are modeled as decreasing by 7.5% when oxygen is raised from 2.0 wt% (in the MTBE-blended CaRFG) to 3.5 wt% and as increasing by 5% when the oxygen is eliminated. It was left unchanged for ethanol-blended CaRFG with 2.0% oxygen.

The 7.5% increase for the higher oxygen content has been derived from data taken by ARB under the REPO5 test cycle (ARB, 1998b). According to FTP testing, the decrease in the CO inventory would be about 2.5% if oxygen were increased from 2.0 to 3.5 wt% of gasoline. However, the REPO5 data indicate that under "off-cycle" (non-FTP) operation, CO emissions are reduced much more. The staff has estimated the actual CO inventory reduction as 2.8 times the value calculated from FTP data. In contrast, available data do not show a difference between FTP and off-cycle testing in the effect of eliminating oxygen from gasoline. Therefore, the increase in the CO inventory estimated from FTP data, 5%, has been applied for the oxygen-free fuel.

Figure 2.1. “Starts” Comparison-ARB “MTBE-EtOH” Data

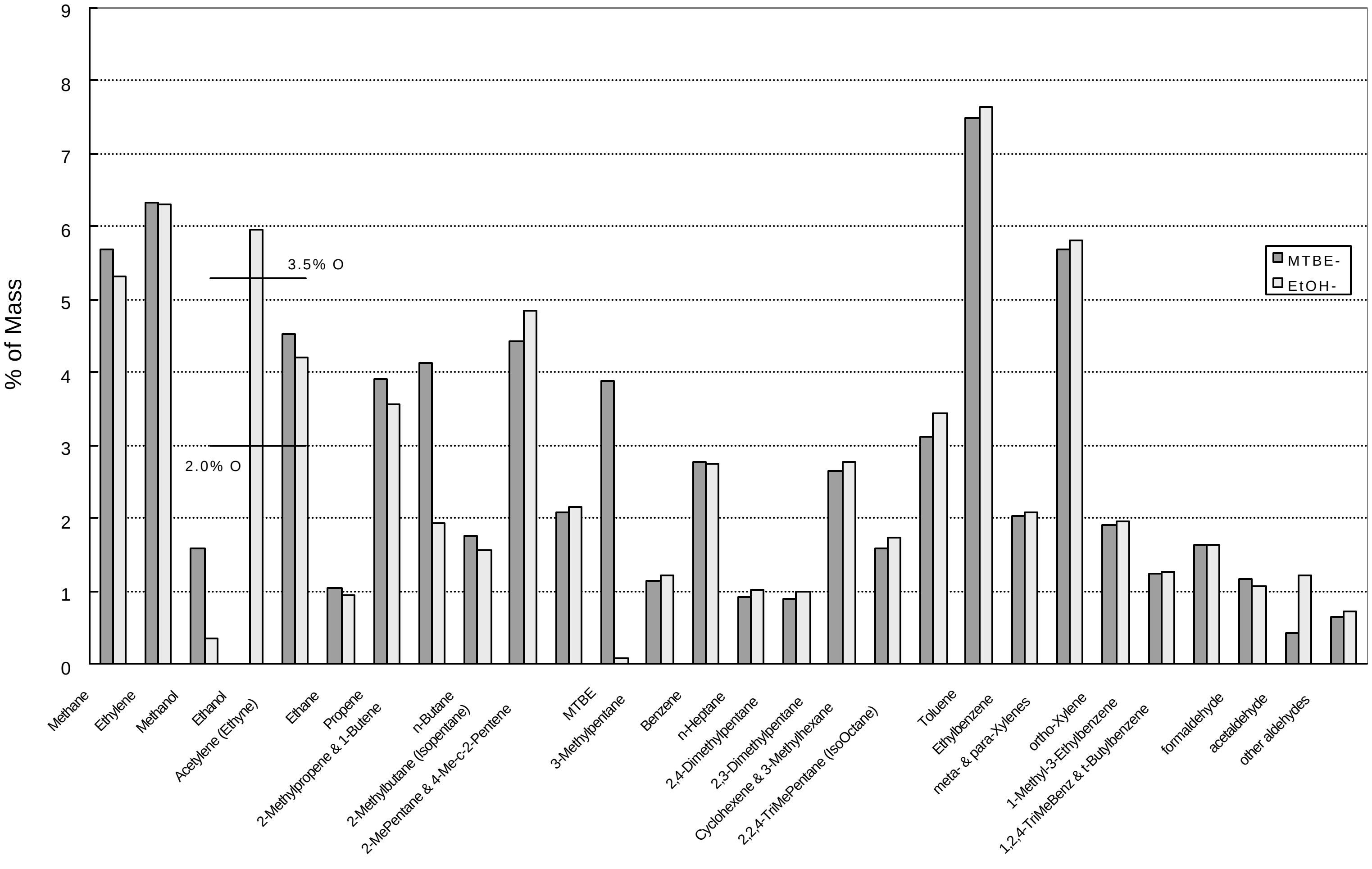
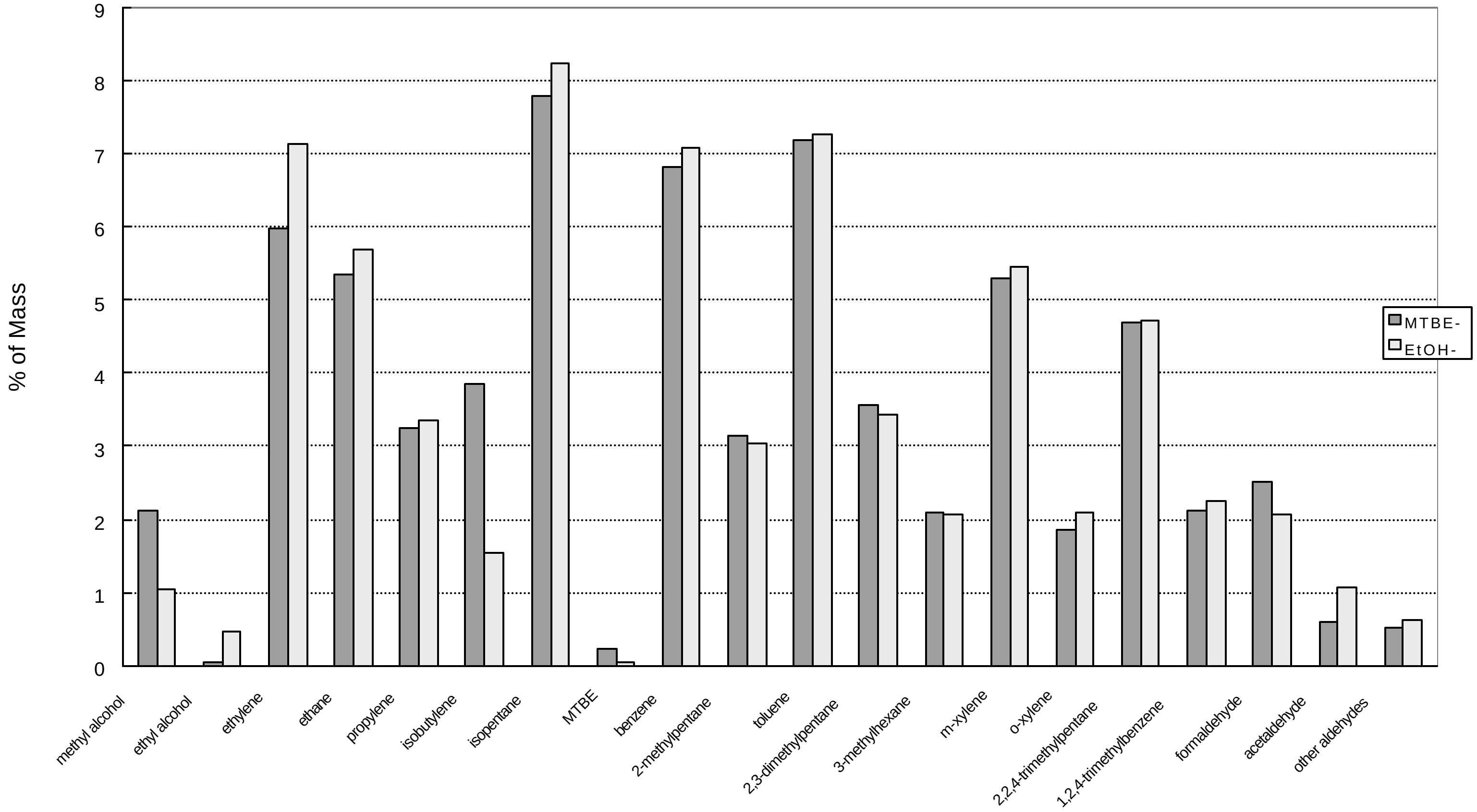


Figure 2.2. Bag 2 Comparison-ARB "MTBE-EtOH" Data (no methane)



A-3. Organic Gas Emission Profiles

Summaries of several important characteristics of the organic gas emission profiles derived in the preceding section are shown in Table 3.1 throughTable 3.7. Table 3.1 through Table 3.6 compare the weight percent of six selected organic gas species (ethanol, benzene, formaldehyde, acetaldehyde, 1,3-butadiene, and methane) for all categories and gasolines used in the photochemical modeling.

Table 3.1 shows the weight percent of ethanol in the motor vehicle emission categories. Ethanol is not present in any of the non-oxygenated gasoline emission categories. A very small amount of ethanol is in the MTBE gasoline exhaust emissions as measured in ARB surveillance testing. Table 3.2 shows the estimated benzene weight percent for the emission categories. Since there is no difference expected in the benzene content in any of the gasolines, there is not much difference in the expected benzene in any of the MTBE-free categories.

Table 3.3 through Table 3.6 show acetaldehyde, formaldehyde, 1,3-butadiene, and methane. These compounds are not found in the gasoline nor in the evaporative emissions, so only the exhaust comparisons are shown. Since acetaldehyde is a product of ethanol combustion, it is expected to be higher as the ethanol content of gasoline increases. As seen in Table 3.3, acetaldehyde emissions are expected to be highest for the ethanol blends. Formaldehyde emissions are highest for the MTBE-blended gasoline as shown in Table 3.4. In Table 3.5, exhaust emissions of 1,3-butadiene are similar for all four gasolines.

Organic gas emission inventories include methane, which has a very low reactivity. Therefore, the methane fraction is very important in determining overall reactivity of the TOG emissions. Methane fractions are expected to decrease for the catalyst stabilized emission category as the vehicle fleet becomes cleaner over time. ARB studies have estimated that the average fleet methane fraction for 2003 will be approximately 18.7%. Photochemical simulations for 2003 were based on this methane estimate for catalyst stabilized exhaust. All other compounds were adjusted slightly by an equal percentage to yield a species profile totaling to 100%. All comparisons of profiles in this document are based on 1996 emission profiles (Allen, 1997). These profiles are the best organic gas speciation profiles to represent fleet emissions, since the 1996 surveillance data is used as the basis of the exhaust TOG emission speciation.

Table 3.7 shows the specific reactivity for all emission categories. The maximum incremental reactivity (Carter, 1994) values used to calculate the specific reactivity for each category are the same as those adopted for use in the ARB Low-Emission Vehicles program and developed using the SAPRC90 chemical mechanism. We have also calculated the specific reactivity for MIR values based on the SAPRC97 mechanism used in the airshed modeling described in Appendix B. These are shown in Figure 3.7 after the parentheses. The SAPRC97 specific reactivities are higher for exhaust and headspace organic gas mixtures and about the same as SAPRC90 for the liquid fuel. The relative differences in specific reactivity between gasolines are about the same for all categories for both SAPRC90 and SAPRC97.

Table 3.8 shows the ARB organic gas profile assignments for each emission category. The methane fraction in catalyst stabilized exhaust increases from 1997 to 2003. The profiles in parentheses denote the 2003 profile for each fuel. The methane fractions for non-MTBE gasolines were increased by the same percentage as we expect will occur for the MTBE gasoline

Figure 3.1 through 3.6 show a more complete comparison of the species profiles for each emission category. There are about 180 organic species identified in motor vehicle emissions. These figures contain seven categories of "lumped" species (butanes, pentanes, C_6+ alkanes, etc.) and eleven explicit species. Figure 3.1 and Figure 3.2 show the profiles for the liquid gasoline and headspace vapors. The non-oxygenated gasoline has the highest alkane and lowest aromatic content. The remaining figures are for catalyst and non-catalyst vehicle exhaust emissions. The largest difference in exhaust gas composition is due to the increased alkanes in the ethanol-blended gasoline with 2.0 wt% oxygen and the non-oxygenated gasolines. The replacement of MTBE with ethanol leads to higher ethanol and acetaldehyde emissions.

Attachment A1 displays the complete speciation profiles for all categories of gasoline organic gas emissions used in the photochemical modeling.

Table 3.1. Ethanol Emissions (wt%)

Ethanol	Liquid	Hot Soak	Headspace	Catalyst Start Exhaust	Catalyst Hot Exhaust	Non-cat Start Exhaust	Non-cat Hot Exhaust
MTBE	**0.00**	**0.00**	**0.00**	**0.09**	**0.07**	**0.06**	**0.01**
Non-Oxygenate	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
EtOH 2.0%	**5.75**	**5.75**	**9.35**	**3.00**	**2.01**	**3.00**	**1.86**
EtOH 3.5%	**10.10**	**10.10**	**9.56**	**5.28**	**3.58**	**5.28**	**3.24**

Table 3.2. Benzene Emissions (wt%)

Benzene	Liquid	Hot Soak	Headspace	Catalyst Start Exhaust	Catalyst Hot Exhaust	Non-cat Start Exhaust	Non-cat Hot Exhaust
MTBE	**1.00**	**1.00**	**0.36**	**2.47**	**2.73**	**2.75**	**3.44**
Non-oxygenate	**1.00**	**1.00**	**0.69**	**2.17**	**2.40**	**2.42**	**3.03**
EtOH 2.0%	**1.00**	**1.00**	**0.80**	**2.37**	**2.62**	**2.64**	**3.30**
EtOH 3.5%	**1.00**	**1.00**	**0.80**	**2.43**	**2.73**	**2.74**	**3.45**

Table 3.3. Acetaldehyde Emissions (wt%)

Acetaldehyde	Catalyst Start Exhaust	Catalyst Hot Exhaust	Non-cat Start Exhaust	Non-cat Hot Exhaust
MTBE	**0.40**	**0.25**	**0.35**	**0.75**
Non-oxygenate	**0.38**	**0.24**	**0.33**	**0.71**
EtOH 2.0%	**0.51**	**0.32**	**0.44**	**0.95**
EtOH 3.5%	**0.91**	**0.58**	**0.81**	**1.74**

Table 3.4. Formaldehyde Emissions (wt%)

Formaldehyde	Catalyst Start Exhaust	Catalyst Hot Exhaust	Non-cat Start Exhaust	Non-cat Hot Exhaust
MTBE	1.31	1.76	1.46	3.12
Non-oxygenate	1.17	1.57	1.30	2.78
EtOH 2.0%	1.23	1.65	1.37	2.93
EtOH 3.5%	1.19	1.62	1.34	2.88

Table 3.5. 1,3-Butadiene Emissions (wt%)

1,3-Butadiene	Catalyst Start Exhaust	Catalyst Hot Exhaust	Non-cat Start Exhaust	Non-cat Hot Exhaust
MTBE	0.70	0.57	0.78	0.83
Non-oxygenate	0.69	0.56	0.76	0.81
EtOH 2.0%	0.69	0.56	0.76	0.81
EtOH 3.5%	0.68	0.56	0.77	0.82

Table 3.6. Methane Emissions (wt%)

Methane	Catalyst Start Exhaust	Catalyst Hot Exhaust	Non-cat Start Exhaust	Non-cat Hot Exhaust
MTBE	5.28	15.82	6.53	5.58
Non-oxygenate	4.79	14.57	5.95	5.16
EtOH 2.0%	4.82	14.75	5.96	5.19
EtOH 3.5%	5.20	15.85	6.52	5.59

Table 3.7. Specific Reactivity (SAPRC90/SAPRC97)

(grams ozone/gram NMOG)

Specific Reactivity	Liquid	Hot Soak	Headspace	Catalyst Start Exhaust	Catalyst Hot Exhaust	Non-cat Start Exhaust	Non-cat Hot Exhaust
MTBE	2.54/2.52	2.54/2.52	1.58/1.85	3.61/3.99	3.53/4.01	3.50/3.97	3.97/4.38
Non-oxygenate	2.16/2.13	2.16/2.13	1.66/1.83	3.39/3.72	3.30/3.71	3.32/3.71	3.72/4.08
EtOH 2%	2.30/2.25	2.30/2.25	1.66/1.79	3.41/3.74	3.33/3.75	3.33/3.73	3.75/4.12
EtOH 3.5%	2.25/2.22	2.25/2.22	1.64/1.78	3.60/4.00	3.48/3.97	3.50/3.99	3.94/4.37

Table 3.8. Organic Gas Profile Assignment

ARB Profile Number	Liquid	Hot Soak	Headspace	Catalyst Start Exhaust	Catalyst Hot Exhaust	Non-cat Start Exhaust	Non-cat Hot Exhaust
MTBE	**419**	**419**	**906**	**877**	**876(441)**	**402**	**401**
Non-oxygenate	**650**	**650**	**449**	**643**	**642(636)**	**641**	**640**
EtOH 2%	**660**	**660**	**450**	**649**	**648(637)**	**647**	**646**
EtOH 3.5%	**670**	**670**	**451**	**674**	**673(677)**	**676**	**675**

Figure 3.1. Liquid Gasoline

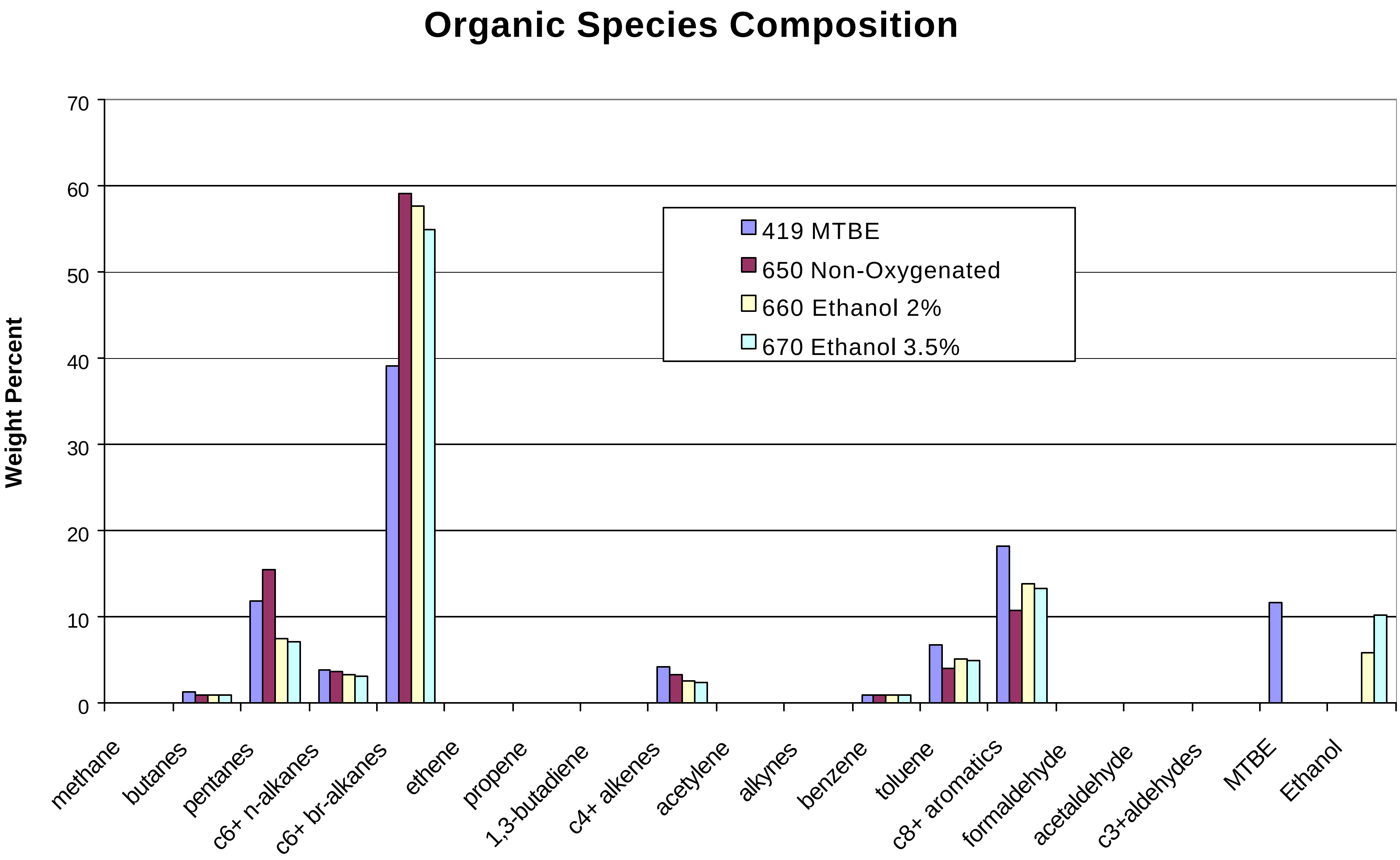


Figure 3.2. Headspace Vapors

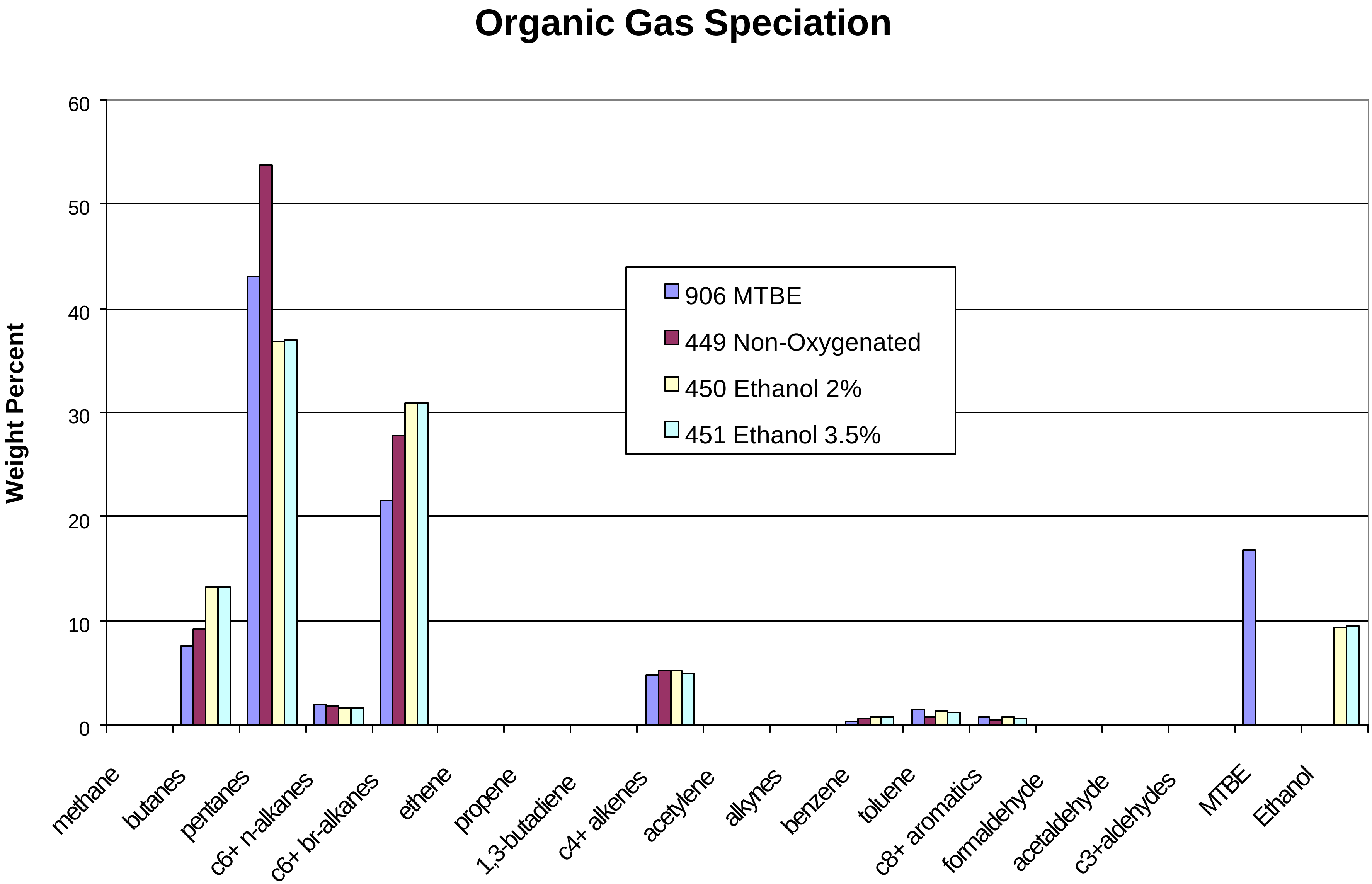


Figure 3.3. Catalyst Stabilized Exhaust

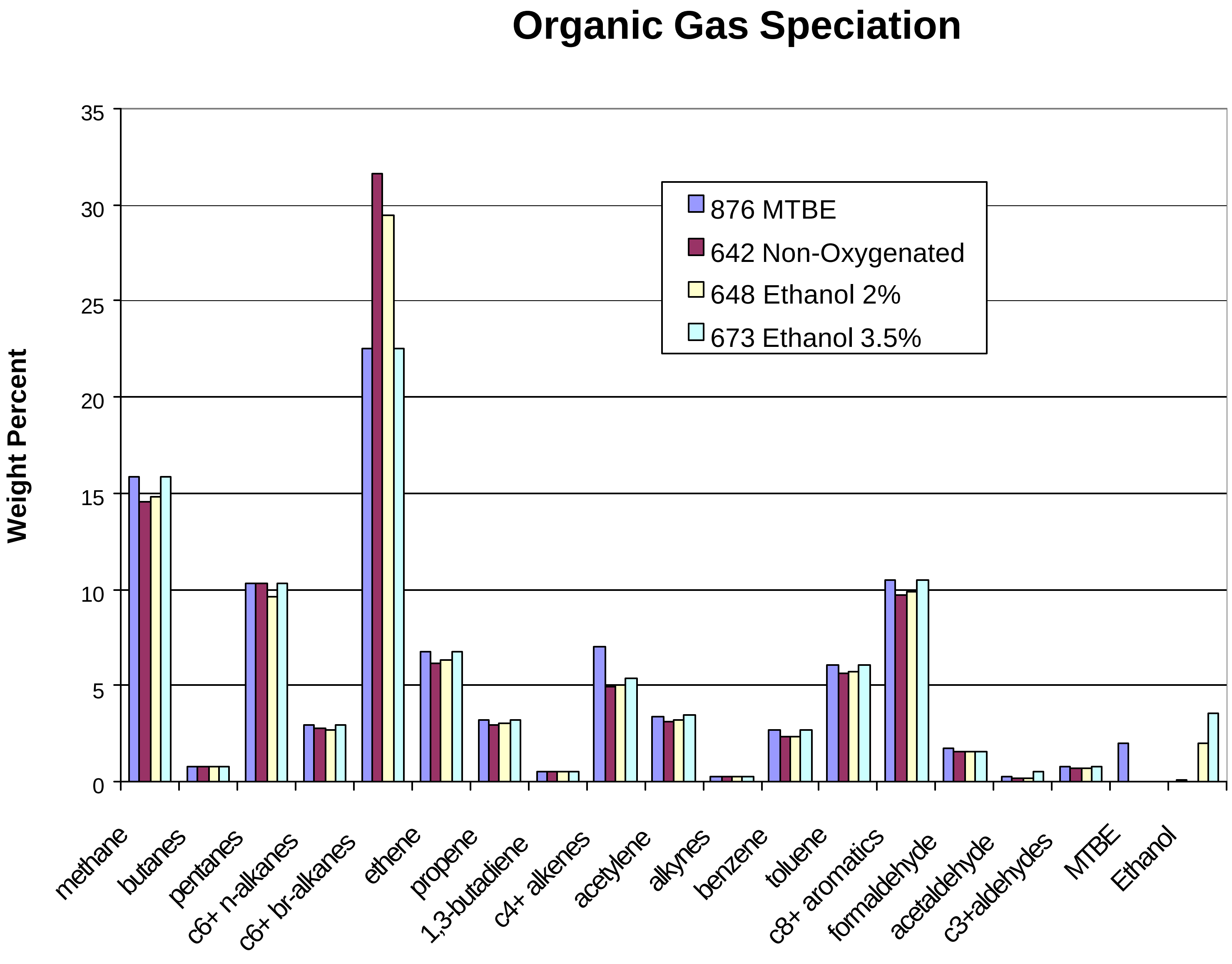


Figure 3.4. Catalyst Start Exhaust

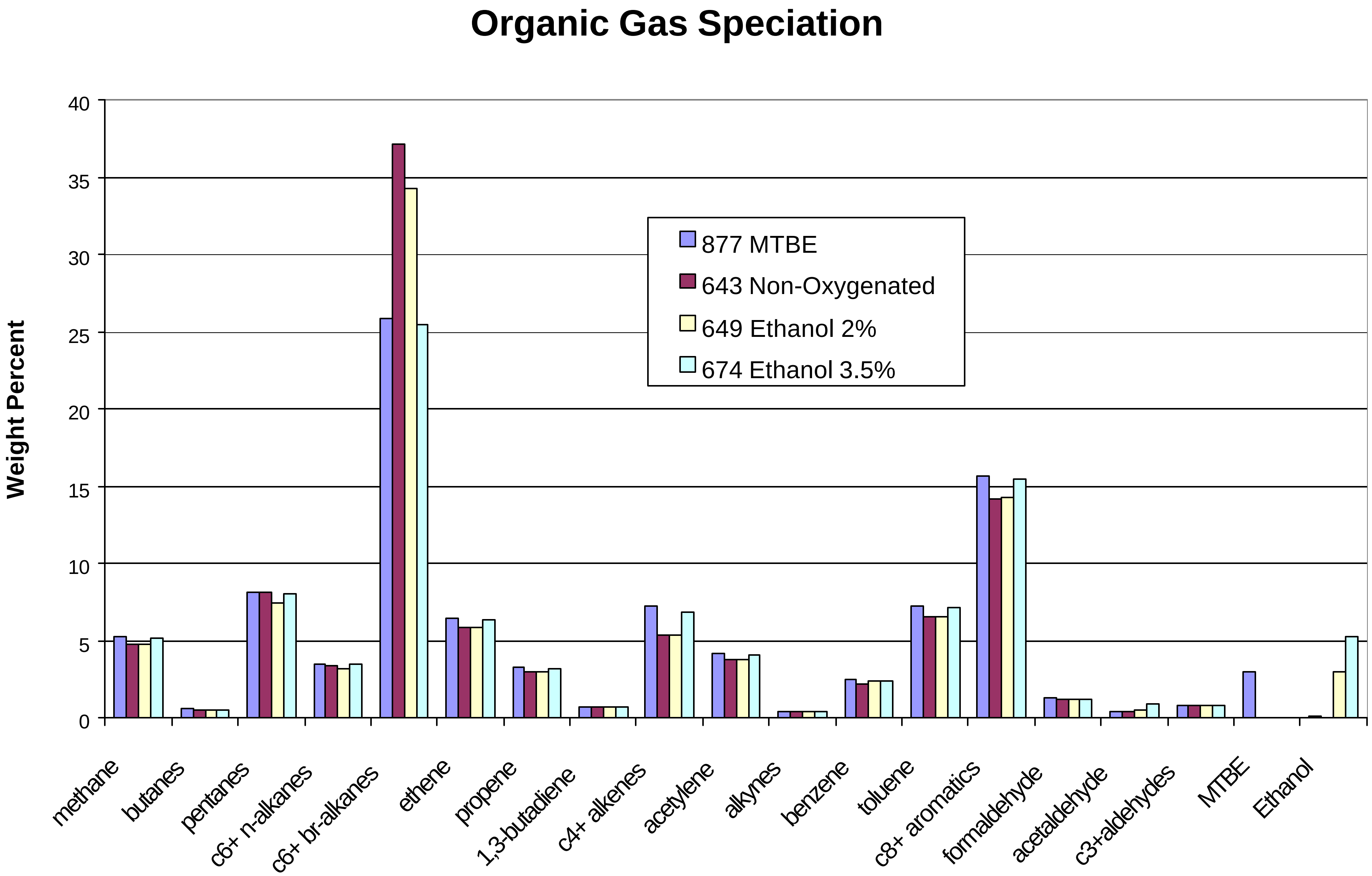


Figure 3.5. Non-Catalyst Stabilized Exhaust

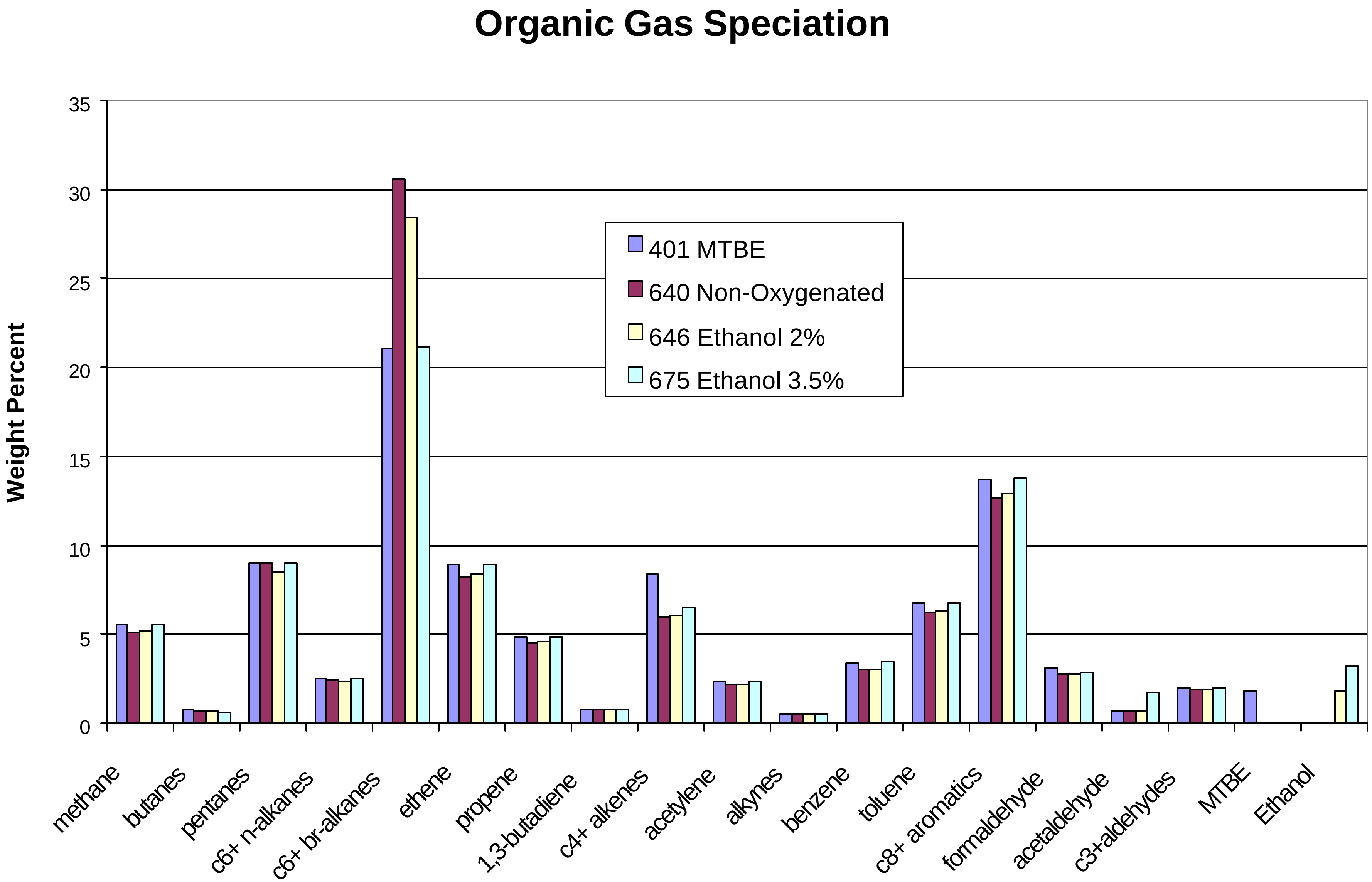
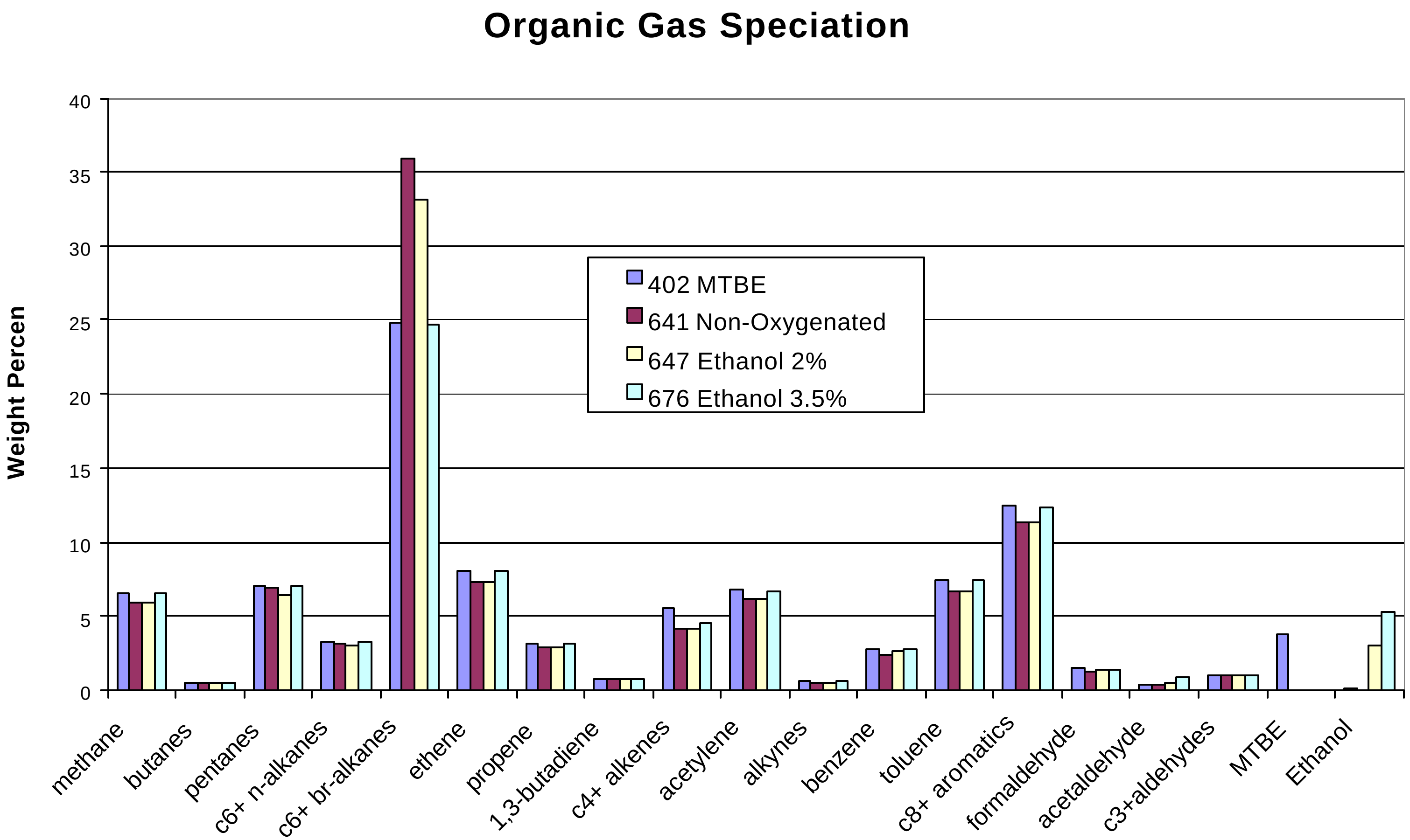


Figure 3.6. Non-Catalyst Start Exhaust



A-4. Emission Inventories

The development of emission estimates for each of the fuel scenarios involved a number of steps. This section briefly outlines the procedures used and presents detailed emission inventories for all the scenarios.

A-4.1. County-Level Emission Inventories

The inventories for the 1997 and 2003 baseline fuels (MTBE blends) were obtained from the ARB emission inventory database -- California Emissions Forecasting System (CEFS). These inventories are available at the county level. The inventories are the ozone planning inventories which reflect emissions on a summer day with high ozone. Since the official ARB inventory is updated regularly as better information becomes available, it is important to document the date of data retrieval. Area sources, including on-road and other mobile sources, were produced on May 26, 1999. Point sources were produced on June 10, 1999.

The on-road motor vehicle portion of the inventory was based on the Motor Vehicle Emission Inventory model MVEI7G (version 1.0c) because EMFAC2000 (ARB, 1999c) was not available. The off-road mobile source emissions were prepared with methodologies used previous to the development of the new ARB off-road emissions model.

These inventories represent mass emissions of principal criteria pollutants in units of tons per day. The pollutants include total organic gases, oxides of nitrogen, oxides of sulfur, carbon monoxide, and particulate matter. Estimates of emissions of individual organic gas constituents such as benzene were developed by combining the organic gas mass emissions from the inventory with the speciation profiles described earlier.

Table 4.1 through Table 4.5 present the summer ozone planning inventories for the South Coast Air Basin for each of the fuel scenarios. The pollutants of major interest include carbon monoxide (CO), nitrogen oxides (NO_X), reactive organic gases (ROG), benzene, 1,3-butadiene, acetaldehyde, formaldehyde, ethanol, and methyl *tertiary*-butyl ether (MTBE). In addition, emission inventory data for total alkylates and six additional VOCs (toluene, *m&p*-xylene, *o*-xylene, *n*-hexane, *n*-heptane, and isobutene) are presented in Table 4.6. The compounds in Table 4.6 were judged to be of minimal concern as discussed in Appendix C and were not modeled separately.

Table 4.1. 1997 MTBE-Based California Phase 2 Reformulated Gasoline (CaRFG)

	South Coast Air Basin Emissions					Tons/Day			27-Oct-99
Scenario: MTBE Summer 1997	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
STATIONARY SOURCES									
FUEL COMBUSTION									
ELECTRIC UTILITIES	3.87	16.58	.88	.061	.	.011	.146	.	
COGENERATION	2.79	6.89	.61	.007	.	.002	.053	.	
OIL AND GAS PRODUCTION (COMBUSTION)	1.57	10.66	.81	.031	.	.002	.095	.	
PETROLEUM REFINING (COMBUSTION)	8.56	17.72	1.4	.02	.002	.002	.139	.	.004
MANUFACTURING AND INDUSTRIAL	16.78	43.99	4.94	.211	.004	.071	.625	.	.002
FOOD AND AGRICULTURAL PROCESSING	.46	1.21	.2	.016	.	.	.033	.	.
SERVICE AND COMMERCIAL	12.78	26.27	3.48	.103	.002	.044	.394	.	.002
OTHER (FUEL COMBUSTION)	4.14	2.89	.6	.016	.004	.003	.032	.	.007
FUEL COMBUSTION - Subtotal	50.95	126.21	12.92	.466	.011	.136	1.518	.	.014
WASTE DISPOSAL									
SEWAGE TREATMENT	.03	.	.09				.014		
LANDFILLS	.55	.54	1.32				.044		
INCINERATORS	.12	.34	.01	.006			.		
OTHER (WASTE DISPOSAL)	.	.01	.79	.					
WASTE DISPOSAL - Subtotal	.7	.89	2.21	.006			.058		
CLEANING AND SURFACE COATINGS									
LAUNDERING	.	.	.64						
DEGREASING	.	.	85.53						
COATINGS AND RELATED PROCESS SOLVENTS	.22	.36	92.98	.069				1.965	.001
PRINTING	.02	.07	5.05					.53	
OTHER (CLEANING AND SURFACE COATINGS)	.	.	13.38	.003			.	.003	
CLEANING AND SURFACE COATINGS - Subtotal	.24	.43	197.56	.071			.	2.498	.001
PETROLEUM PRODUCTION AND MARKETING									
OIL AND GAS PRODUCTION	.02	.06	12.4	.187			.		.001
PETROLEUM REFINING	6.28	10.93	8.99	.13			.014		.134
PETROLEUM MARKETING	.08	.	23.57	.145					3.197
OTHER (PETROLEUM PRODUCTION AND MARKETING)	.05	.01	.2	.004					.001
PETROLEUM PRODUCTION AND MARKETING - Subtotal	6.43	11.01	45.16	.466			.014		3.334
INDUSTRIAL PROCESSES									
CHEMICAL	.04	.57	13.75	.001			.	.001	
FOOD AND AGRICULTURE	.21	.12	3.19					1.04	
MINERAL PROCESSES	2.67	9.93	.58						
METAL PROCESSES	1.74	.69	.65						
WOOD AND PAPER	.	.	.04						
GLASS AND RELATED PRODUCTS	.	1.48	.03						
OTHER (INDUSTRIAL PROCESSES)	1.4	1.15	2.61	.			.335		.
INDUSTRIAL PROCESSES - Subtotal	6.06	13.94	20.84	.001			.336	1.041	.

Table 4.1. 1997 MTBE-Based California Phase 2 Reformulated Gasoline (CaRFG) (continued)

South Coast Air Basin Emissions Tons/Day 27-Oct-99

Scenario: MTBE Summer 1997	CO	NO_X	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
STATIONARY SOURCES - Subtotal	64.38	152.49	278.71	1.011	.011	.136	1.926	3.539	3.349
AREA-WIDE SOURCES									
SOLVENT EVAPORATION									
CONSUMER PRODUCTS	.	.	87.13				.029	25.241	
ARCHITECTURAL COATINGS AND RELATED PROCESS SOLVENTS	.	.	68.02	.067				.252	
PESTICIDES/FERTILIZERS	.	.	13.81	.596			.002	1.557	
ASPHALT PAVING	.	.	.48						
OTHER (SOLVENT EVAPORATION)	.	.	.17	.002					
SOLVENT EVAPORATION - Subtotal	.	.	169.61	.665			.031	27.05	
MISCELLANEOUS PROCESSES									
RESIDENTIAL FUEL COMBUSTION	40.78	22.65	2.75	.068		.173	.322		
FARMING OPERATIONS	.	.	10.92					2.731	
FIRES	7.54	.18	.53						
WASTE BURNING AND DISPOSAL	17.7	.74	1.39		.021				
UTILITY EQUIPMENT	229.58	.3	14.74	.55	.133	.12	.499	.002	.297
OTHER (MISCELLANEOUS PROCESSES)	.04	.24	1.7						
MISCELLANEOUS PROCESSES - Subtotal	295.65	24.11	32.03	.618	.153	.293	.821	2.732	.297
AREA-WIDE SOURCES - Subtotal	295.65	24.11	201.64	1.283	.153	.293	.852	29.782	.297
MOBILE SOURCES									
ON-ROAD MOTOR VEHICLES									
CATALYST COLD EXHAUST	1150.4	90.72	117.17	3.091	.876	.501	1.639	.113	3.779
CATALYST HOT EXHAUST	1832.7	327.43	107.86	3.55	.742	.326	2.289	.092	2.615
NON-CATALYST COLD EXHAUST	90.02	1.96	15.49	.461	.131	.059	.245	.01	.637
NON-CATALYST HOT EXHAUST	402.33	37.09	46.22	1.725	.416	.376	1.564	.005	.933
HOT SOAK EVAPORATIVES	.	.	34.59	1.188					4.489
DIURNAL EVAPORATIVES	.	.	29.48	.106					4.962
RUNNING EVAPORATIVES	.	.	42.51	1.46					5.517
RESTING EVAPORATIVES	.	.	19.4	.07					3.265
DIESEL EXHAUST	128.07	201.46	20.98	.478	.045	1.756	3.514	.002	
ON-ROAD MOTOR VEHICLES - Subtotal	3603.59	658.65	433.7	12.128	2.21	3.017	9.251	.221	26.195

Table 4.1. 1997 MTBE-Based California Phase 2 Reformulated Gasoline (CaRFG) (continued)

South Coast Air Basin Emissions Tons/Day 27-Oct-99

Scenario: MTBE Summer 1997	CO	NO_X	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
OTHER MOBILE SOURCES									
AIRCRAFT	87.08	15.13	15.56	.438	.312	.776	2.482		.008
TRAINS	5.02	31.38	2.08	.047	.004	.174	.348	.	
SHIPS AND COMMERCIAL BOATS	4.49	40.81	5.17	.12	.012	.417	.836	.001	.002
RECREATIONAL BOATS	246.18	2.15	41.74	1.554	.374	.359	1.446	.005	.837
OFF-ROAD RECREATIONAL VEHICLES	70.65	.41	9.4	.351	.085	.076	.318	.001	.19
COMMERCIAL/INDUSTRIAL MOBILE EQUIPMENT	885.	152.65	38.92	.88	.157	1.506	4.187	.003	.27
FARM EQUIPMENT	7.15	2.7	.51	.014	.002	.029	.061	.	.004
OTHER MOBILE SOURCES - Subtotal	1305.57	245.23	113.37	3.404	.946	3.337	9.679	.009	1.311
MOBILE SOURCES - Subtotal	4909.16	903.89	547.08	15.532	3.156	6.354	18.93	.231	27.507
NATURAL (NON-ANTHROPOGENIC) SOURCES									
NATURAL SOURCES									
WILDFIRES	170.39	2.6	9.41		.14				
NATURAL SOURCES - Subtotal	170.39	2.6	9.41		.14				
NATURAL (NON-ANTHROPOGENIC) SOURCES - Subtotal	170.39	2.6	9.41		.14				
ALL SOURCES - Total	5439.59	1083.09	1036.83	17.826	3.46	6.783	21.709	33.552	31.154

Table 4.2. 2003 MTBE-Based CaRFG

	South Coast Air Basin Emissions				Tons/Day				27-Oct-99
Scenario: MTBE Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
STATIONARY SOURCES									
FUEL COMBUSTION									
ELECTRIC UTILITIES	1.71	6.51	.39	.027	.	.005	.064	.	.
COGENERATION	2.81	5.71	.61	.007	.	.002	.053	.	.
OIL AND GAS PRODUCTION (COMBUSTION)	1.57	7.9	.81	.031	.	.002	.095	.	.
PETROLEUM REFINING (COMBUSTION)	8.56	7.73	1.4	.02	.002	.002	.139	.	.004
MANUFACTURING AND INDUSTRIAL	17.39	38.74	5.43	.244	.004	.072	.701	.	.003
FOOD AND AGRICULTURAL PROCESSING	.48	.9	.21	.017	.	.	.035	.	.
SERVICE AND COMMERCIAL	14.06	21.83	3.72	.117	.002	.048	.427	.	.002
OTHER (FUEL COMBUSTION)	4.41	1.85	.64	.018	.004	.004	.033	.	.008
FUEL COMBUSTION - Subtotal	51.	91.17	13.21	.481	.012	.136	1.547	.	.016
WASTE DISPOSAL									
SEWAGE TREATMENT	.03	.	.07	.	.	.	.006	.	.
LANDFILLS	.6	.59	1.35	.	.	.	.048	.	.
INCINERATORS	.13	.34	.02	.007	.	.	.	.	.
OTHER (WASTE DISPOSAL)	.	.01	.8	.	.	.	.	.	.
WASTE DISPOSAL - Subtotal	.77	.95	2.24	.007	.	.	.055	.	.
CLEANING AND SURFACE COATINGS									
LAUNDERING	.	.01	.71	.	.	.	.	.	.
DEGREASING	.	.	99.98	.	.	.	.	.	.
COATINGS AND RELATED PROCESS SOLVENTS	.26	.42	96.4	.071	.	.	.	1.771	.001
PRINTING	.02	.08	5.08	.	.	.	.	.643	.
OTHER (CLEANING AND SURFACE COATINGS)	.	.	12.08	.002	.	.	.	.003	.
CLEANING AND SURFACE COATINGS - Subtotal	.29	.51	214.26	.074	.	.	.	2.417	.001
PETROLEUM PRODUCTION AND MARKETING									
OIL AND GAS PRODUCTION	.02	.06	10.76	.165	.	.	.	.	.001
PETROLEUM REFINING	6.33	5.32	8.03	.112	.	.	.014	.	.136
PETROLEUM MARKETING	.09	.	24.1	.154	.	.	.	.	3.245
OTHER (PETROLEUM PRODUCTION AND MARKETING)	.05	.01	.2	.005	.	.	.	.	.001
PETROLEUM PRODUCTION AND MARKETING - Subtotal	6.5	5.39	43.09	.436	.	.	.014	.	3.384
INDUSTRIAL PROCESSES									
CHEMICAL	.04	.54	17.19	.001	.	.	.	.001	.
FOOD AND AGRICULTURE	.22	.11	3.28	.	.	.	.	1.091	.
MINERAL PROCESSES	2.84	6.49	.65	.	.	.	.	.	.
METAL PROCESSES	1.96	.75	.75	.	.	.	.	.	.
WOOD AND PAPER	.	.	.04	.	.	.	.	.	.
GLASS AND RELATED PRODUCTS	.	.26	.03	.	.	.	.	.	.
OTHER (INDUSTRIAL PROCESSES)	1.67	.94	2.94	.	.	.	.357	.	.
INDUSTRIAL PROCESSES - Subtotal	6.74	9.09	24.89	.001	.	.	.358	1.091	.
STATIONARY SOURCES - Subtotal	65.29	107.12	297.69	1.	.012	.136	1.974	3.508	3.401

Table 4.2. 2003 MTBE-Based CaRFG (continued)

South Coast Air Basin Emissions Tons/Day 27-Oct-99

Scenario: MTBE Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
AREA-WIDE SOURCES									
SOLVENT EVAPORATION									
CONSUMER PRODUCTS	.	.	83.19	.	.	.	.028	24.1	.
ARCHITECTURAL COATINGS AND RELATED PROCESS SOLVENTS	.	.	72.77	.072	.	.	.	.27	.
PESTICIDES/FERTILIZERS	.	.	13.42	.595	.	.	.002	1.464	.
ASPHALT PAVING	.	.	.55	.	.	.	.	.	.
OTHER (SOLVENT EVAPORATION)	.	.	.19	.002	.	.	.	.	.
SOLVENT EVAPORATION - Subtotal	.	.	170.12	.67	.	.	.029	25.834	.
MISCELLANEOUS PROCESSES									
RESIDENTIAL FUEL COMBUSTION	43.99	23.68	2.95	.071	.	.187	.344	.	.
FARMING OPERATIONS	.	.	10.38	.	.	.	.	2.612	.
FIRES	8.06	.19	.56	.	.	.	.	.	.
WASTE BURNING AND DISPOSAL	30.89	1.44	2.34	.	.035	.	.	.	.
UTILITY EQUIPMENT	204.59	.41	11.91	.444	.107	.097	.403	.001	.24
OTHER (MISCELLANEOUS PROCESSES)	.05	.28	1.81	.	.	.	.	.	.
MISCELLANEOUS PROCESSES - Subtotal	287.57	26.	29.96	.515	.142	.284	.747	2.613	.24
AREA-WIDE SOURCES - Subtotal	287.57	26.	200.08	1.185	.142	.284	.776	28.448	.24
MOBILE SOURCES									
ON-ROAD MOTOR VEHICLES									
CATALYST COLD EXHAUST	757.45	71.4	82.09	2.164	.62	.349	1.152	.079	2.653
CATALYST HOT EXHAUST	1290.2	223.04	62.26	2.05	.428	.187	1.321	.053	1.509
NON-CATALYST COLD EXHAUST	27.12	.59	4.78	.142	.04	.018	.075	.003	.196
NON-CATALYST HOT EXHAUST	143.27	12.97	16.84	.628	.152	.137	.57	.002	.34
HOT SOAK EVAPORATIVES	.	.	19.83	.198	.	.	.	.	2.292
DIURNAL EVAPORATIVES	.	.	18.85	.068	.	.	.	.	3.173
RUNNING EVAPORATIVES	.	.	35.02	.35	.	.	.	.	4.048
RESTING EVAPORATIVES	.	.	10.93	.039	.	.	.	.	1.84
DIESEL EXHAUST	141.72	177.19	15.82	.36	.034	1.324	2.649	.002	.
ON-ROAD MOTOR VEHICLES - Subtotal	2359.79	485.2	266.42	6.001	1.273	2.015	5.768	.138	16.052

Table 4.2. 2003 MTBE-Based CaRFG (continued)

South Coast Air Basin Emissions Tons/Day 27-Oct-99

Scenario: MTBE Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
OTHER MOBILE SOURCES									
AIRCRAFT	92.63	17.24	16.92	.472	.343	.858	2.745	.	.008
TRAINS	4.79	30.01	1.99	.045	.004	.166	.333	.	.
SHIPS AND COMMERCIAL BOATS	4.85	44.48	5.59	.129	.013	.451	.904	.001	.002
RECREATIONAL BOATS	297.9	2.6	50.51	1.88	.453	.434	1.75	.005	1.013
OFF-ROAD RECREATIONAL VEHICLES	62.44	.46	3.84	.143	.035	.031	.13	.	.078
COMMERCIAL/INDUSTRIAL MOBILE EQUIPMENT	941.55	132.63	41.63	.947	.17	1.595	4.446	.003	.295
FARM EQUIPMENT	7.73	2.78	.56	.016	.003	.032	.068	.	.004
OTHER MOBILE SOURCES - Subtotal	1411.89	230.2	121.05	3.633	1.02	3.568	10.377	.01	1.4
MOBILE SOURCES - Subtotal	3771.68	715.39	387.47	9.634	2.293	5.583	16.144	.148	17.452
NATURAL (NON-ANTHROPOGENIC) SOURCES									
NATURAL SOURCES									
WILDFIRES	170.39	2.6	9.41	.	.14	.	.	.	.
NATURAL SOURCES - Subtotal	170.39	2.6	9.41	.	.14	.	.	.	.
NATURAL (NON-ANTHROPOGENIC) SOURCES - Subtotal	170.39	2.6	9.41	.	.14	.	.	.	.
ALL SOURCES - Total	4294.94	851.11	894.65	11.819	2.587	6.003	18.895	32.104	21.093

Table 4.3. 2003 Ethanol-Based Fully Complying Fuel (with Oxygen Content of 2.0 wt%)

	South Coast Air Basin Emissions				Tons/Day				27-Oct-99
Scenario: ET20 Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
STATIONARY SOURCES									
FUEL COMBUSTION									
ELECTRIC UTILITIES	1.71	6.51	.39	.027	.	.005	.064	.	
COGENERATION	2.81	5.71	.61	.007	.	.002	.053	.	
OIL AND GAS PRODUCTION (COMBUSTION)	1.57	7.9	.81	.031	.	.002	.095	.	.
PETROLEUM REFINING (COMBUSTION)	8.56	7.73	1.4	.02	.002	.003	.138	.004	
MANUFACTURING AND INDUSTRIAL	17.39	38.74	5.43	.244	.004	.072	.7	.003	.
FOOD AND AGRICULTURAL PROCESSING	.48	.9	.21	.017	.	.	.035	.	
SERVICE AND COMMERCIAL	14.06	21.83	3.72	.116	.002	.048	.427	.002	.
OTHER (FUEL COMBUSTION)	4.41	1.85	.64	.017	.004	.005	.032	.008	
FUEL COMBUSTION - Subtotal	51.	91.17	13.21	.48	.012	.137	1.545	.016	.
WASTE DISPOSAL									
SEWAGE TREATMENT	.03	.	.07	.	.	.	.006	.	
LANDFILLS	.6	.59	1.35	.	.	.	.048	.	
INCINERATORS	.13	.34	.02	.007	.	.	.	.	
OTHER (WASTE DISPOSAL)	.	.01	.8	.	.	.	.	.	
WASTE DISPOSAL - Subtotal	.77	.95	2.24	.007	.	.	.055	.	
CLEANING AND SURFACE COATINGS									
LAUNDERING	.	.01	.71						
DEGREASING	.	.	99.98						
COATINGS AND RELATED PROCESS SOLVENTS	.26	.42	96.4	.071	.	.	.	1.772	.
PRINTING	.02	.08	5.08	.	.	.	.	.643	
OTHER (CLEANING AND SURFACE COATINGS)	.	.	12.08	.002	.	.	.	.003	.
CLEANING AND SURFACE COATINGS - Subtotal	.29	.51	214.26	.074	.	.	.	2.417	.
PETROLEUM PRODUCTION AND MARKETING									
OIL AND GAS PRODUCTION	.02	.06	10.76	.165	.	.	.	.	.
PETROLEUM REFINING	6.33	5.32	8.03	.116	.	.	.014	.076	
PETROLEUM MARKETING	.09	.	24.1	.224	.	.	.	1.771	.
OTHER (PETROLEUM PRODUCTION AND MARKETING)	.05	.01	.2	.005	.	.	.	.001	
PETROLEUM PRODUCTION AND MARKETING - Subtotal	6.5	5.39	43.09	.51	.	.	.014	1.847	.
INDUSTRIAL PROCESSES									
CHEMICAL	.04	.54	17.19	.001	.	.	.	.001	
FOOD AND AGRICULTURE	.22	.11	3.28	.	.	.	.	1.091	.
MINERAL PROCESSES	2.84	6.49	.65						
METAL PROCESSES	1.96	.75	.75						
WOOD AND PAPER	.	.	.04						
GLASS AND RELATED PRODUCTS	.	.26	.03						
OTHER (INDUSTRIAL PROCESSES)	1.67	.94	2.94	.	.	.	.357	.	
INDUSTRIAL PROCESSES - Subtotal	6.74	9.09	24.89	.001	.	.	.358	1.092	.
STATIONARY SOURCES - Subtotal	65.29	107.12	297.69	1.072	.012	.137	1.972	5.373	.

Table 4.3. 2003 Ethanol-Based Fully Complying Fuel (with Oxygen Content of 2.0 wt%) (continued)

South Coast Air Basin Emissions Tons/Day 27-Oct-99

Scenario: ET20 Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
AREA-WIDE SOURCES									
SOLVENT EVAPORATION									
CONSUMER PRODUCTS	.	.	83.19	.	.	.	.028	24.1	.
ARCHITECTURAL COATINGS AND RELATED PROCESS SOLVENTS	.	.	72.77	.072	.	.	.	.27	.
PESTICIDES/FERTILIZERS	.	.	13.42	.595	.	.	.002	1.464	.
ASPHALT PAVING	.	.	.55						
OTHER (SOLVENT EVAPORATION)	.	.	.19	.002	.	.	.	.	.
SOLVENT EVAPORATION - Subtotal	.	.	170.12	.67	.	.	.029	25.834	.
MISCELLANEOUS PROCESSES									
RESIDENTIAL FUEL COMBUSTION	43.99	23.68	2.95	.071	.	.187	.344	.	.
FARMING OPERATIONS	.	.	10.38	.	.	.	.	2.612	.
FIRES	8.06	.19	.56						
WASTE BURNING AND DISPOSAL	30.89	1.44	2.34	.	.035	.	.	.	.
UTILITY EQUIPMENT	204.59	.41	11.88	.427	.105	.123	.379	.24	.
OTHER (MISCELLANEOUS PROCESSES)	.05	.28	1.81						
MISCELLANEOUS PROCESSES - Subtotal	287.57	26.	29.93	.497	.14	.31	.723	2.853	.
AREA-WIDE SOURCES - Subtotal	287.57	26.	200.05	1.167	.14	.31	.752	28.687	.
MOBILE SOURCES									
ON-ROAD MOTOR VEHICLES									
CATALYST COLD EXHAUST	757.45	71.4	81.36	2.069	.599	.443	1.074	2.618	.
CATALYST HOT EXHAUST	1290.2	223.04	61.93	1.943	.414	.236	1.226	1.49	.
NON-CATALYST COLD EXHAUST	27.12	.59	4.77	.136	.039	.023	.071	.155	.
NON-CATALYST HOT EXHAUST	143.27	12.97	16.8	.603	.149	.174	.536	.34	.
HOT SOAK EVAPORATIVES	.	.	19.85	.198	.	.	.	1.141	.
DIURNAL EVAPORATIVES	.	.	18.86	.151	.	.	.	1.763	.
RUNNING EVAPORATIVES	.	.	35.05	.35	.	.	.	2.015	.
RESTING EVAPORATIVES	.	.	10.93	.087	.	.	.	1.022	.
DIESEL EXHAUST	141.72	177.19	15.82	.36	.034	1.324	2.649	.002	.
ON-ROAD MOTOR VEHICLES - Subtotal	2359.79	485.2	265.36	5.9	1.235	2.2	5.556	10.546	.

Table 4.3. 2003 Ethanol-Based Fully Complying Fuel (with Oxygen Content of 2.0 wt%) (continued)

South Coast Air Basin Emissions Tons/Day 27-Oct-99

Scenario: ET20 Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
OTHER MOBILE SOURCES									
AIRCRAFT	92.63	17.24	16.92	.472	.343	.858	2.745	.	.008
TRAINS	4.79	30.01	1.99	.045	.004	.166	.333	.	.
SHIPS AND COMMERCIAL BOATS	4.85	44.48	5.59	.129	.013	.451	.904	.003	.
RECREATIONAL BOATS	297.9	2.6	50.4	1.805	.443	.544	1.648	1.013	.
OFF-ROAD RECREATIONAL VEHICLES	62.44	.46	3.84	.138	.034	.04	.122	.078	.
COMMERCIAL/INDUSTRIAL MOBILE EQUIPMENT	941.55	132.63	41.6	.925	.167	1.627	4.417	.297	.
FARM EQUIPMENT	7.73	2.78	.56	.015	.003	.033	.068	.004	.
OTHER MOBILE SOURCES - Subtotal	1411.89	230.2	120.89	3.53	1.007	3.719	10.237	1.394	.008
MOBILE SOURCES - Subtotal	3771.68	715.39	386.26	9.429	2.242	5.919	15.793	11.94	.008
NATURAL (NON-ANTHROPOGENIC) SOURCES									
NATURAL SOURCES									
WILDFIRES	170.39	2.6	9.41	.	.14	.	.	.	.
NATURAL SOURCES - Subtotal	170.39	2.6	9.41	.	.14	.	.	.	.
NATURAL (NON-ANTHROPOGENIC) SOURCES - Subtotal	170.39	2.6	9.41	.	.14	.	.	.	.
ALL SOURCES - Total	4294.94	851.11	893.41	11.669	2.533	6.367	18.518	45.999	.008

Table 4.4. 2003 Ethanol-Based Fully Complying Fuel (with Oxygen Content of 3.5 wt%)

		South Coast Air Basin Emissions			Tons/Day				27-Oct-99
Scenario: ET35 Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
STATIONARY SOURCES									
FUEL COMBUSTION									
ELECTRIC UTILITIES	1.71	6.51	.39	.027	.	.005	.064	.	.
COGENERATION	2.81	5.71	.61	.007	.	.002	.053	.	.
OIL AND GAS PRODUCTION (COMBUSTION)	1.57	7.9	.81	.031	.	.002	.095	.	.
PETROLEUM REFINING (COMBUSTION)	8.56	7.73	1.4	.02	.002	.003	.138	.006	.
MANUFACTURING AND INDUSTRIAL	17.39	38.74	5.43	.244	.004	.072	.7	.005	.
FOOD AND AGRICULTURAL PROCESSING	.48	.9	.21	.017	.	.	.035	.	.
SERVICE AND COMMERCIAL	14.06	21.83	3.72	.117	.002	.048	.427	.004	.
OTHER (FUEL COMBUSTION)	4.41	1.85	.64	.018	.004	.005	.032	.013	.
FUEL COMBUSTION - Subtotal	51.	91.17	13.21	.482	.012	.138	1.546	.028	.
WASTE DISPOSAL									
SEWAGE TREATMENT	.03	.	.07	.	.	.	.006	.	.
LANDFILLS	.6	.59	1.35	.	.	.	.048	.	.
INCINERATORS	.13	.34	.02	.007	.	.	.	.	.
OTHER (WASTE DISPOSAL)	.	.01	.8	.	.	.	.	.	.
WASTE DISPOSAL - Subtotal	.77	.95	2.24	.007	.	.	.055	.	.
CLEANING AND SURFACE COATING0S									
LAUNDERING	.	.01	.71	.	.	.	.	.	.
DEGREASING	.	.	99.98	.	.	.	.	.	.
COATINGS AND RELATED PROCESS SOLVENTS	.26	.42	96.4	.071	.	.	.	1.772	.
PRINTING	.02	.08	5.08	.	.	.	.	.643	.
OTHER (CLEANING AND SURFACE COATINGS)	.	.	12.08	.002	.	.	.	.003	.
CLEANING AND SURFACE COATINGS - Subtotal	.29	.51	214.26	.074	.	.	.	2.417	.
PETROLEUM PRODUCTION AND MARKETING									
OIL AND GAS PRODUCTION	.02	.06	10.76	.164	.	.	.	.	.
PETROLEUM REFINING	6.33	5.32	8.03	.108	.	.	.014	.077	.
PETROLEUM MARKETING	.09	.	24.1	.221	.	.	.	2.016	.
OTHER (PETROLEUM PRODUCTION AND MARKETING)	.05	.01	.2	.004	.	.	.	.001	.
PETROLEUM PRODUCTION AND MARKETING - Subtotal	6.5	5.39	43.09	.496	.	.	.014	2.095	.
INDUSTRIAL PROCESSES									
CHEMICAL	.04	.54	17.19	.001	.	.	.	.001	.
FOOD AND AGRICULTURE	.22	.11	3.28	.	.	.	.	1.091	.
MINERAL PROCESSES	2.84	6.49	.65	.	.	.	.	.	.
METAL PROCESSES	1.96	.75	.75	.	.	.	.	.	.
WOOD AND PAPER	.	.	.04	.	.	.	.	.	.
GLASS AND RELATED PRODUCTS	.	.26	.03	.	.	.	.	.	.
OTHER (INDUSTRIAL PROCESSES)	1.67	.94	2.94	.	.	.	.357	.	.
INDUSTRIAL PROCESSES - Subtotal	6.74	9.09	24.89	.001	.	.	.357	1.092	.
STATIONARY SOURCES - Subtotal	65.29	107.12	297.69	1.06	.012	.138	1.973	5.632	.

Table 4.4. 2003 Ethanol-Based Fully Complying Fuel (with Oxygen Content of 3.5 wt%) (continued)

South Coast Air Basin Emissions Tons/Day 27-Oct-99

Scenario: ET35 Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
AREA-WIDE SOURCES									
SOLVENT EVAPORATION									
CONSUMER PRODUCTS	.	.	83.19	.	.	.	.028	24.1	.
ARCHITECTURAL COATINGS AND RELATED PROCESS SOLVENTS	.	.	72.77	.072	.	.	.	.27	.
PESTICIDES/FERTILIZERS	.	.	13.42	.595	.	.	.002	1.464	.
ASPHALT PAVING	.	.	.55	.	.	.	.	.	.
OTHER (SOLVENT EVAPORATION)	.	.	.19	.002	.	.	.	.	.
SOLVENT EVAPORATION - Subtotal	.	.	170.12	.669	.	.	.029	25.834	.
MISCELLANEOUS PROCESSES									
RESIDENTIAL FUEL COMBUSTION	43.99	23.68	2.95	.071	.	.187	.344	.	.
FARMING OPERATIONS	.	.	10.38	.	.	.	.	2.596	.
FIRES	8.06	.19	.56	.	.	.	.	.	.
WASTE BURNING AND DISPOSAL	30.89	1.44	2.34	.	.035	.	.	.	.
UTILITY EQUIPMENT	193.67	.41	11.91	.446	.106	.225	.372	.418	.
OTHER (MISCELLANEOUS PROCESSES)	.05	.28	1.81	.	.	.	.	.	.
MISCELLANEOUS PROCESSES - Subtotal	276.65	26.	29.95	.516	.141	.413	.716	3.014	.
AREA-WIDE SOURCES - Subtotal	276.65	26.	200.08	1.186	.141	.413	.745	28.848	.
MOBILE SOURCES									
ON-ROAD MOTOR VEHICLES									
CATALYST COLD EXHAUST	700.64	71.4	81.81	2.124	.596	.799	1.037	4.606	.
CATALYST HOT EXHAUST	1193.4	223.04	62.23	2.053	.425	.436	1.218	2.689	.
NON-CATALYST COLD EXHAUST	25.08	.59	4.78	.142	.04	.042	.069	.273	.
NON-CATALYST HOT EXHAUST	132.52	12.97	16.83	.63	.151	.319	.526	.591	.
HOT SOAK EVAPORATIVES	.	.	19.85	.198	.	.	.	2.004	.
DIURNAL EVAPORATIVES	.	.	18.86	.151	.	.	.	1.803	.
RUNNING EVAPORATIVES	.	.	35.05	.35	.	.	.	3.54	.
RESTING EVAPORATIVES	.	.	10.93	.087	.	.	.	1.045	.
DIESEL EXHAUST	141.72	177.19	15.82	.36	.034	1.324	2.649	.002	.
ON-ROAD MOTOR VEHICLES - Subtotal	2193.44	485.2	266.15	6.096	1.245	2.919	5.499	16.553	.

Table 4.4. 2003 Ethanol-Based Fully Complying Fuel (with Oxygen Content of 3.5 wt%) (continued)

	South Coast Air Basin Emissions				Tons/Day				27-Oct-99
Scenario: ET35 Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
OTHER MOBILE SOURCES									
AIRCRAFT	92.63	17.24	16.92	.472	.343	.858	2.745	.	.008
TRAINS	4.79	30.01	1.99	.045	.004	.166	.333	.	.
SHIPS AND COMMERCIAL BOATS	4.79	44.48	5.59	.129	.013	.452	.904	.005	.
RECREATIONAL BOATS	275.59	2.6	50.49	1.885	.449	.976	1.618	1.762	.
OFF-ROAD RECREATIONAL VEHICLES	57.76	.46	3.84	.144	.034	.073	.12	.135	.
COMMERCIAL/INDUSTRIAL MOBILE EQUIPMENT	903.73	132.63	41.62	.948	.169	1.753	4.408	.515	.
FARM EQUIPMENT	7.23	2.78	.56	.016	.003	.035	.068	.007	.
OTHER MOBILE SOURCES - Subtotal	1346.52	230.2	121.02	3.64	1.015	4.312	10.196	2.424	.008
MOBILE SOURCES - Subtotal	3539.96	715.39	387.17	9.736	2.26	7.231	15.694	18.976	.008
NATURAL (NON-ANTHROPOGENIC) SOURCES									
NATURAL SOURCES									
WILDFIRES	170.39	2.6	9.41	.	.14	.	.	.	.
NATURAL SOURCES - Subtotal	170.39	2.6	9.41	.	.14	.	.	.	.
NATURAL (NON-ANTHROPOGENIC) SOURCES - Subtotal	170.39	2.6	9.41	.	.14	.	.	.	.
ALL SOURCES - Total	4052.3	851.11	894.35	11.982	2.553	7.781	18.412	53.456	.008

Table 4.5. 2003 Non-Oxygenated Fully Complying Fuel

	South Coast Air Basin Emissions				Tons/Day				27-Oct-99
Scenario: UNOX Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
STATIONARY SOURCES									
FUEL COMBUSTION									
ELECTRIC UTILITIES	1.71	6.51	.39	.027	.	.005	.064	.	
COGENERATION	2.81	5.71	.61	.007	.	.002	.053	.	
OIL AND GAS PRODUCTION (COMBUSTION)	1.57	7.9	.81	.031	.	.002	.095	.	.
PETROLEUM REFINING (COMBUSTION)	8.56	7.73	1.39	.02	.002	.002	.138	.	
MANUFACTURING AND INDUSTRIAL	17.39	38.74	5.43	.244	.004	.072	.7	.	.
FOOD AND AGRICULTURAL PROCESSING	.48	.9	.21	.017	.	.	.035	.	
SERVICE AND COMMERCIAL	14.06	21.83	3.72	.116	.002	.048	.426	.	.
OTHER (FUEL COMBUSTION)	4.41	1.85	.64	.016	.004	.004	.031	.	
FUEL COMBUSTION - Subtotal	51.	91.17	13.21	.478	.012	.135	1.544	.	.
WASTE DISPOSAL									
SEWAGE TREATMENT	.03	.	.07	.	.	.	.006	.	
LANDFILLS	.6	.59	1.35	.	.	.	.048	.	
INCINERATORS	.13	.34	.02	.007	.	.	.	.	
OTHER (WASTE DISPOSAL)	.	.01	.8	.	.	.	.	.	
WASTE DISPOSAL - Subtotal	.77	.95	2.24	.007	.	.	.055	.	
CLEANING AND SURFACE COATINGS									
LAUNDERING	.	.01	.71						
DEGREASING	.	.	99.98						
COATINGS AND RELATED PROCESS SOLVENTS	.26	.42	96.4	.071	.	.	.	1.771	.
PRINTING	.02	.08	5.08	.	.	.	.	.643	
OTHER (CLEANING AND SURFACE COATINGS)	.	.	12.08	.002	.	.	.	.003	.
CLEANING AND SURFACE COATINGS - Subtotal	.29	.51	214.26	.074	.	.	.	2.417	.
PETROLEUM PRODUCTION AND MARKETING									
OIL AND GAS PRODUCTION	.02	.06	10.76	.165	.	.	.	.	.
PETROLEUM REFINING	6.33	5.32	8.03	.115	.	.	.014	.	
PETROLEUM MARKETING	.09	.	24.1	.207	.	.	.	.	.
OTHER (PETROLEUM PRODUCTION AND MARKETING)	.05	.01	.2	.005	.	.	.	.	
PETROLEUM PRODUCTION AND MARKETING - Subtotal	6.5	5.39	43.09	.491	.	.	.014	.	.
INDUSTRIAL PROCESSES									
CHEMICAL	.04	.54	17.19	.001	.	.	.	.001	
FOOD AND AGRICULTURE	.22	.11	3.28	.	.	.	.	1.091	.
MINERAL PROCESSES	2.84	6.49	.65						
METAL PROCESSES	1.96	.75	.75						
WOOD AND PAPER	.	.	.04						
GLASS AND RELATED PRODUCTS	.	.26	.03						
OTHER (INDUSTRIAL PROCESSES)	1.67	.94	2.94	.	.	.	.357	.	
INDUSTRIAL PROCESSES - Subtotal	6.74	9.09	24.89	.001	.	.	.358	1.091	.
STATIONARY SOURCES - Subtotal	65.29	107.12	297.68	1.052	.012	.135	1.971	3.508	.

Table 4.5. 2003 Non-Oxygenated Fully Complying Fuel (continued)

South Coast Air Basin Emissions Tons/Day 27-Oct-99

Scenario: UNOX Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
AREA-WIDE SOURCES									
SOLVENT EVAPORATION									
CONSUMER PRODUCTS	.	.	83.19	.	.	.	.028	24.1	.
ARCHITECTURAL COATINGS AND RELATED PROCESS SOLVENTS	.	.	72.77	.072	.	.	.	.27	.
PESTICIDES/FERTILIZERS	.	.	13.42	.595	.	.	.002	1.464	.
ASPHALT PAVING	.	.	.55						
OTHER (SOLVENT EVAPORATION)	.	.	.19	.002	.	.	.	.	.
SOLVENT EVAPORATION - Subtotal	.	.	170.12	.67	.	.	.029	25.834	.
MISCELLANEOUS PROCESSES									
RESIDENTIAL FUEL COMBUSTION	43.99	23.68	2.95	.071	.	.187	.344	.	.
FARMING OPERATIONS	.	.	10.38	.	.	.	.	2.612	.
FIRES	8.06	.19	.56						
WASTE BURNING AND DISPOSAL	30.89	1.44	2.34	.	.035	.	.	.	.
UTILITY EQUIPMENT	211.87	.41	11.86	.391	.105	.092	.359	.	.
OTHER (MISCELLANEOUS PROCESSES)	.05	.28	1.81						
MISCELLANEOUS PROCESSES - Subtotal	294.85	26.	29.9	.462	.14	.279	.703	2.612	.
AREA-WIDE SOURCES - Subtotal	294.85	26.	200.03	1.131	.14	.279	.732	28.446	.
MOBILE SOURCES									
ON-ROAD MOTOR VEHICLES									
CATALYST COLD EXHAUST	795.32	71.4	81.36	1.897	.599	.332	1.018	.	.
CATALYST HOT EXHAUST	1354.7	223.04	61.5	1.777	.414	.176	1.159	.	.
NON-CATALYST COLD EXHAUST	28.47	.59	4.75	.125	.039	.017	.067	.	.
NON-CATALYST HOT EXHAUST	150.43	12.97	16.76	.553	.149	.13	.507	.	.
HOT SOAK EVAPORATIVES	.	.	19.83	.198	.	.	.	.	.
DIURNAL EVAPORATIVES	.	.	18.85	.13	.	.	.	.	.
RUNNING EVAPORATIVES	.	.	35.02	.35	.	.	.	.	.
RESTING EVAPORATIVES	.	.	10.93	.075	.	.	.	.	.
DIESEL EXHAUST	141.72	177.19	15.82	.36	.034	1.324	2.649	.002	.
ON-ROAD MOTOR VEHICLES - Subtotal	2470.7	485.2	264.82	5.467	1.235	1.979	5.4	.002	.

Table 4.5. 2003 Non-Oxygenated Fully Complying Fuel (continued)

		South Coast Air Basin Emissions				Tons/Day			27-Oct-99
Scenario: UNOX Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
OTHER MOBILE SOURCES									
AIRCRAFT	92.63	17.24	16.92	.472	.343	.858	2.745	.	.008
TRAINS	4.79	30.01	1.99	.045	.004	.166	.333	.	.
SHIPS AND COMMERCIAL BOATS	4.89	44.48	5.59	.129	.013	.451	.904	.001	.
RECREATIONAL BOATS	312.78	2.6	50.28	1.655	.443	.414	1.563	.	.
OFF-ROAD RECREATIONAL VEHICLES	65.56	.46	3.83	.126	.034	.03	.116	.	.
COMMERCIAL/INDUSTRIAL MOBILE EQUIPMENT	966.76	132.63	41.56	.881	.167	1.589	4.392	.002	.
FARM EQUIPMENT	8.06	2.78	.56	.015	.003	.032	.068	.	.
OTHER MOBILE SOURCES - Subtotal	1455.47	230.2	120.73	3.324	1.007	3.54	10.12	.003	.008
MOBILE SOURCES - Subtotal	3926.16	715.39	385.55	8.791	2.242	5.519	15.52	.004	.008
NATURAL (NON-ANTHROPOGENIC) SOURCES									
NATURAL SOURCES									
WILDFIRES	170.39	2.6	9.41	.	.14	.	.	.	.
NATURAL SOURCES - Subtotal	170.39	2.6	9.41	.	.14	.	.	.	.
NATURAL (NON-ANTHROPOGENIC) SOURCES - Subtotal	170.39	2.6	9.41	.	.14	.	.	.	.
ALL SOURCES - Total	4456.7	851.11	892.67	10.974	2.533	5.933	18.223	31.959	.008

Table 4.6. Emission Inventory Data of Selected Compounds in 1997 Baseline and 2003 Scenarios for the SoCAB (tons/day)

Compounds	1997 MTBE	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
Toluene	77.54	61.93	59.35	60.56	58.31
***m*&*p*-Xylene**	28.90	18.72	16.92	17.72	16.22
***o*-Xylene**	12.33	9.30	8.66	8.93	8.39
***n*-Hexane**	22.82	19.94	19.11	19.42	20.11
***n*-Heptane**	7.71	6.71	6.94	7.11	6.99
Isobutene	14.66	10.01	5.12	6.65	5.08
Total Alkylates[a]	277.00	260.91	296.65	274.36	302.68

[a] C_6+ branched alkanes and cycloalkanes.

A-4.2. Gridded Emission Inventories

The photochemical modeling was performed for the Southern California Air Quality Study (SCAQS) grid region which is the inner grid shown in Figure 4.1. This region is somewhat larger than the South Coast Air Basin. As a result, there are about 10 to 40% more emissions in the modeling region than the Air Basin depending on the year and pollutant.

The 1997 and 2003 baseline MTBE gridded inventories were developed using ARB countywide inventory estimates for ozone precursors (CO, NO_X, and TOG). All countywide area source emissions were gridded using the same area source surrogates used to grid the 1997 Southern California Ozone Study (SCOS97-NARSTO) gridded inventory (SAI, 1997). Both the spatial and temporal distributions for 1997 and 2003 for each area source category are the same for each county as in the SCOS97-NARSTO gridded inventory.

Vegetative emissions used in the 1997 SCAQMD SIP update modeling were incorporated into the ARB area source emissions to complete the area source inventory and were assumed constant for all 1997 and 2003 simulations. The total vegetative emissions from the SCAQS August episode are 103.5, 128.8, and 139.8 tons/day for August 26, 27, and 28, respectively. All the area source emissions are modeled as surface sources.

All other emissions sources are contained in the ARB point source emission inventory and have associated UTM coordinates. Emissions for these sources are allocated to the proper grid cells and are also modeled as surface sources unless there are associated stack records, in which case the point source is modeled as an elevated source with calculated plume rise.

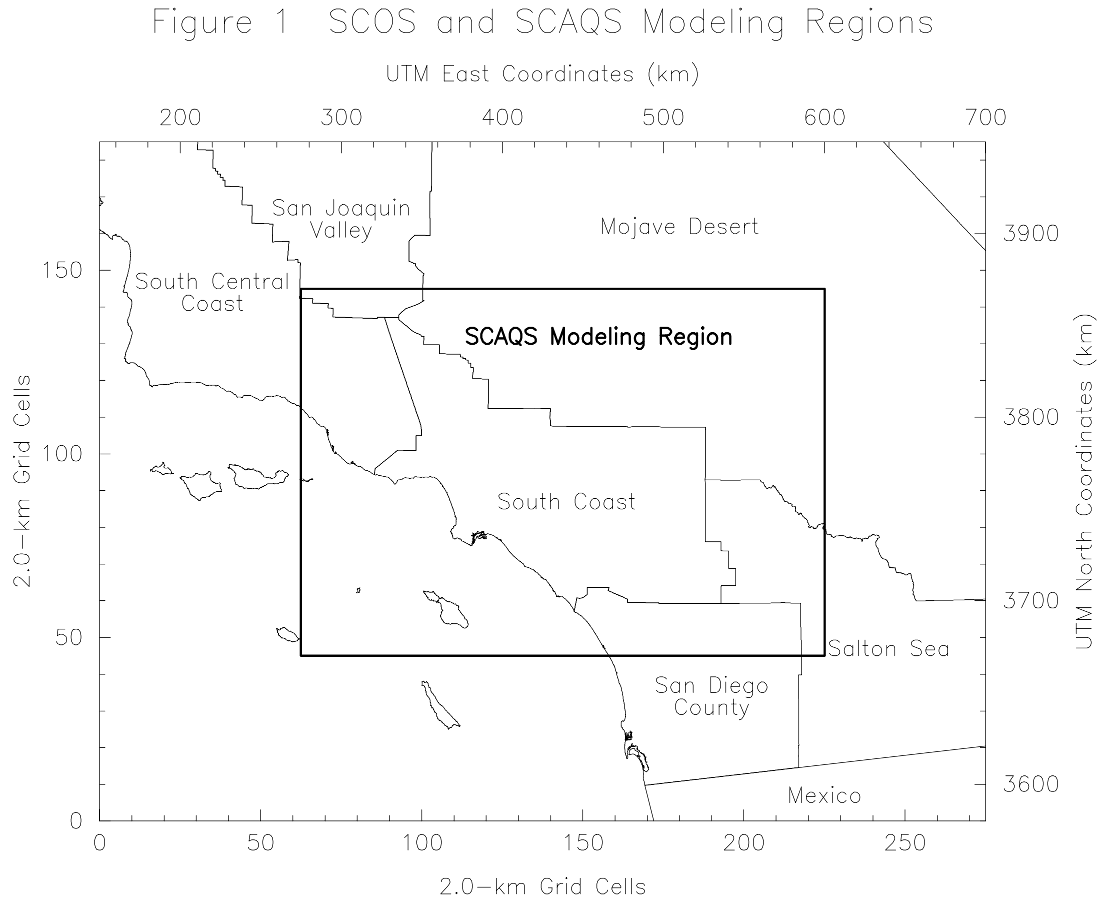


Figure 4.1. SCOS97-NARSTO and SCAQS Modeling Regions

The ozone precursor inventory contains estimates of CO, NO_X (as NO_2), and TOG. Both NO_X and TOG emissions must be resolved to individual chemical species before processing further to SAPRC97 model species. NO_X emissions are assumed to be 88% NO, 10% NO_2 , and 2% HONO. TOG is resolved to chemical species through the use of organic gas species profiles. Species profiles for all gasoline-related sources have been discussed in Section A-3 and vary with each alternate gasoline. Species profiles for all other organic gas emission sources are constant for all simulations.

Emission totals within the modeling region for ozone precursors are shown in Table 4.7, for the MTBE gasoline scenarios for 1997 and 2003. NO_X and TOG emissions are constant for all 2003 scenarios. ROG emissions vary only slightly between the 2003 scenarios due to minor variations in methane emissions estimated to occur in vehicle exhaust. Motor vehicle CO emissions are the same for the MTBE and ethanol 2 wt% oxygen scenarios. Motor vehicle CO emissions are increased by 5% for the non-oxgenated gasoline scenario and reduced by 7.5% for the ethanol 3.5 wt% oxygen scenario (relative to the MTBE fleet emissions).

Table 4.7. CO, NO_X, and ROG Emissions for the SCAQS Modeling Region

(CO is for MTBE Scenarios)

YEAR	CO (tons/day)	NO_X (tons/day)	ROG (tons/day)
1997	6,400	1,300	2,100
2003	5,000	1,050	1,900

The change in total emissions for a given pollutant from 1997 to 2003 may be different for the South Coast Air Basin than the modeling region. Both growth rates and emission controls are different inside and outside the Air Basin. For all scenarios, the same organic gas speciation profiles were used consistently throughout the modeling region.

All organic gas emission categories associated with gasoline combustion or evaporation are speciated with the gasoline specific profiles discussed in Section A-2. Emission sources that were speciated with gasoline specific profiles include gasoline marketing, distribution, storage, on and off-road mobile sources, and utility equipment. Besides the change in CO emissions discussed above, the only significant change between 2003 simulations is from the changing gasoline composition.

The organic gas speciation process results in emission estimates for over 450 separate compounds. The modeling is done with a more consolidated set of compounds. While this detailed inventory is available, it is easier to understand in terms of the SAPRC97 model species. The mechanism used in this study, which we refer to as the SAPRC97 toxics mechanism, includes several compounds not modeled explicitly in the base SAPRC97 mechanism. Organic gas emissions are partitioned into nine important lumped organic gas model species and seventeen explicit compounds as shown in Table 4.8.

The photochemical model requires a surface-level emission file and an elevated emission file. The surface emission file contains all the organic gas emissions from gasoline related sources. The majority of elevated sources are NO_X emissions from large boilers. The SCAQS region surface emission totals for each of the above model species are shown in Table 4.9.

Table 4.8. SAPRC97 Toxic Mechanism Model Species

Explicit Species	Lumped species
ACET – acetone	**ALK1 – lower alkanes**
MEK – methyl ethyl ketone	**ALK2 – higher alkanes**
BALD – benzaldehyde	**ARO1 – lower aromatics**
GLY – glyoxal	**ARO2 – higher aromatics**
MGLYOX – methylglyoxal	**OLE1 – external alkenes**
CH4 – methane	**OLE2 – internal alkenes**
ETHE – ethene	**OLE3 – biogenic alkenes**
ISOP – isoprene	**RCHO – higher aldehydes**
BUTD – 1,3-butadiene	**CRES – cresols**
C6H6 – benzene	
PDCB – *p*-dichlorobenzene	
DICM – dichloromethane	
PERC – perchloroethylene	
FORM – formaldehyde	
ALD – acetaldehyde	
ETOH – ethanol	
MTBE –methyl *tertiary*-butyl ether	

Table 4.9. SCAQS Region Surface Emissions (kilomoles/day)

Species	1997 MTBE	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
CO	205,065.4	160,157.0	160,157.0	140,408.4	166,739.9
NO	21,704.8	17,445.8	17,350.9	17,350.9	17,350.9
NO2	2,466.3	1,982.4	1,971.6	1,971.6	1,971.6
HONO	480.2	386.0	383.9	383.9	383.9
RCHO	94.1	81.0	79.6	80.8	79.4
BALD	17.7	13.4	12.7	13.4	12.6
ACET	320.9	305.2	303.9	304.6	303.9
MEK	169.1	167.9	167.7	167.9	167.6
CRES	0.4	0.4	0.4	0.4	0.4
GLY	1.0	1.2	1.2	1.2	1.2
MGLY	0.7	0.8	0.8	0.8	0.8
CH4	30,105.7	29,804.7	29,777.3	29,857.4	29,769.8
ETHE	1,947.2	1,548.0	1,489.7	1,544.6	1,479.8
ISOP	1,118.2	1,114.5	1,114.4	1,114.7	1,114.1
BUTD	88.7	70.3	69.2	69.6	69.2
C6H6	253.5	170.2	161.7	172.2	158.3
PDCB	13.1	12.6	12.6	12.6	12.6
DICM	33.5	37.3	37.3	37.3	37.3
PERC	109.7	128.9	128.9	128.9	128.9
FORM	663.6	556.7	535.0	539.7	533.0
ALD	139.6	119.2	120.5	162.6	117.6
ETOH	778.4	757.6	1,080.0	1,256.6	754.2
MTBE	375.3	255.5	0.0	0.0	0.0
ALK1	4,679.7	3,993.8	3,875.7	3,881.5	4,176.8
ALK2	2,134.2	2,066.1	2,327.6	2,165.7	2,329.8
ARO1	1,009.5	788.4	750.7	766.9	733.1
ARO2	790.0	597.3	554.8	571.4	536.1
OLE1	1,030.0	779.2	661.6	708.7	657.2
OLE2	254.1	181.6	164.4	169.3	168.8
OLE3	561.2	561.0	561.0	561.0	561.0

A-5. Emission Testing

The availability of both ethanol-blended and non-oxygenated commercial CaRFG gasolines presented the opportunity to provide a reality check on the organic gas emission profiles developed in Section A-2. Because of the limited time available to conduct the ethanol fate and transport analysis, we were not able to test a fully representative number of vehicle not conduct tests of diurnal or running loss evaporative emissions.

A-5.1. Emission Testing Protocol

This section describes the protocol for the test program.

A-5.1.1. Fuels

One fuel will be a regular, unleaded, non-oxygenated gasoline. The second will be a regular gasoline blended with about 2 wt% oxygen (from ethanol). The MTBE content in this fuel should be below 1% by weight. The third gasoline will be a California commercial Phase 2 summer grade fuel with about 2 wt% oxygen (from MTBE). Complete speciation analyses for hydrocarbons, carbonyls, and alcohols will be required for all emission test samples in this program.

We obtained commercially available compliant non-MTBE gasolines in drums from fuel distributors (Chevron and Tosco in the San Francisco Bay Area). The gasolines must meet CaRFG specifications except for oxygen content. The ARB underground tank CaRFG summer grade gasoline with MTBE will be used as the third fuel. A fuel sample was obtained from each drum delivered and analyzed (complete organic gas speciation and all specifications for CaRFG). The test sequence for the two non-MTBE gasolines will be based on Table 5.1 to avoid potential biases.

A-5.1.2. Test Vehicles

One or two vehicles were selected per week from July 19 through September 15 (7 vehicles total). The desired source of vehicles is the Vehicle Surveillance Program. State vehicles with E-plates may be selected for this project when surveillance vehicles are not available. Vehicles will be selected based on the baseline FTP emission levels for hot running Bag 2 total hydrocarbon (THC). At least half of the vehicles in this project must have Bag 2 THC emissions in the range of 0.5 to 4 grams/mile. Other than this emission criterion, vehicles were randomly selected from the Surveillance Program.

Table 5.1. Fuel Test Sequence for Project 2R9905

Vehicle Number	UC Test #1	UC Test #2	UC Test #3
1	50	51	52
2	50	52	51
3	50	51	52
4	50	52	51
5	50	51	52
6	50	52	51
7	50	51	52

Fuel Code 50: California Phase 2 commercial summer grade gasoline with MTBE

Fuel Code 51: Phase 2 Chevron Non-Oxygenated gasoline

Fuel Code 52: Phase 2 Tosco 2% oxygenated gasoline with ethanol

A-5.1.3. Test Cyles

Each vehicle will undergo one cold start Unified Cycle (UC) for each fuel. Regular bag samples will be collected and analyzed at the end of the test. An extra bag will be sampled at the end of the first 100 seconds of the cold start UC test Bag 1. A modified aldehyde sample cart will be used to collect the first 100 seconds bag. Second-by-second modal data, bag results, and speciated HC bag analyses are required for all sample bags including the first 100 seconds bag. One composite background bag is acceptable for the regular 3 bag speciation analyses and the first 100 seconds sample analyses. The first 100 second sample will be labeled and reported as sample #4. Modal analyses from the dyno only provide the HC readings for the first 100 seconds; the methane readings for the first 100 seconds sample can only be based on the Pre-concentrated Direct Flame Ionization Detector (PDFID) instrument readings. The non-methane hydrocarbon (NMHC) readings for the first 100 second sample and the dilution ratio will be calculated daily by the on-site project engineer.

A-5.1.4. Vehicle Preconditioning

Test vehicles will be first classified into two groups, one group with adaptive learning and another group without adaptive learning capability. Adaptive learning is defined as vehicles with closed-loop fuel control. Cars equipped with oxygen sensors in the early 80's were the first group of vehicles with adaptive learning.

Each acceptable test vehicle with adaptive learning shall be subjected to the following preconditioning schedule:

- Drain the tank fuel
- Add 5 gallons of the correct test fuel

- Run the vehicle on the road for 50 miles (include key on/key off)
- Drain the tank fuel
- Add 3 gallons test fuel
- Start engine - one min. idle
- Drain fuel tank
- Add enough fuel to fill the tank to 40%
- Run one dummy CVS-72
- Engine off - five min. soak.
- Start engine - one min. idle
- Engine off - five min. soak
- Start engine - one min. idle
- Engine off - five min. soak
- Run one dummy CVS-72
- Cold soak the vehicle at least 12 hours, but not more than 36 hours prior to a UC or truncated UC

Each acceptable test vehicle without adaptive learning shall be subjected to the following preconditioning schedule:

- Drain the tank fuel
- Add 5 gallons of the correct test fuel
- Run the vehicle on the road for 25 miles
- Drain the tank fuel
- Add enough fuel to fill the tank 40%
- Run one dummy CVS-72
- Cold soak the vehicle at least 12 hours, but not more than 36 hours prior to a UC or truncated UC

A-5.1.5. Data Reporting and Quality Control

The test engineer will verify the test results including modal data right after each UC test. Driving violations are acceptable in this test program unless there are too many stalls (>3) that will obviously impact the results. The on-site project engineer will coordinate with MLD to obtain the preliminary GC/DYNO QC results within 2 days. Since a discrepancy exists between the modal data and composite data, the current MLD GC/DYNO QC criteria (based on composite data) may have to be adjusted to account for the difference between the modal and composite data. If the test vehicle successfully completes all three UC tests and passes the MLD QC, the test engineer will release this vehicle back to the Surveillance program.

A-5.2. Gasoline Headspace Analysis

We developed a method to sample and analyze gasoline headspace samples. The following is a brief description of the method.

- Gasoline samples are received in 1-liter metal containers and are stored in a refrigerator at approximately 0°C. One 60-ml portion of each gasoline is transferred to a 60-ml amber glass bottle and the bottles are refrigerated. Using pipettes, 10-ml of each gasoline sample is transferred from its 60-ml bottle to a 40-ml glass vial. The glass vials have plastic screw caps fitted with a Teflon lined septum. The bottles are capped immediately after introduction of the samples.
- The Mobile Source Operations Division, according to their standard procedure, makes sample bags (6-liter capacity) with Tedlar material. The bags are fitted with a QuickConnect connector and a port with a Teflon lined septum. The bags are filled with zero nitrogen to their full capacity and evacuated. This process is repeated once. Each bag is then filled with one liter of zero nitrogen.
- All sample vials and sample bags are placed inside a variable volume SHED (sealed housing for evaporative determination) maintained at 100°F for two hours. At the end of the two hours, using a gas-tight syringe, 0.3 ml of the headspace vapor is extracted from the vial and injected into the sample bag through the septum port. The bag is filled with 50-ml zero nitrogen through this port and another four liters of zero nitrogen through the QuickConnect. The bags are kept at room temperature for two hours before gas chromatography analysis.
- A gas chromatograph equipped with a flame ionization detector using standard operating procedures MLD 102 for the light-end hydrocarbons and MLD 103 for the mid-range hydrocarbons is used to analyze the samples. Both these methods are currently available on the ARB web site (http://www.arb.ca.gov/testmeth/testmeth.htm) under the mobile source programs, Low Emission Vehicle II, non-methane organic gas test procedures, attachment M to the recent regulatory action as procedures 1002 and 1003.
- The above procedures are also used to analyze motor vehicle exhaust and evaporative emissions along with the alcohol and carbonyl test methods, numbers 1001 and 1004 respectively.

A-5.3. Vehicle and Fuel Selection Processes

A-5.3.1. Vehicle Selection Process

This test program was targeted for testing at least five vehicles within two months. In order to obtain a representative fleet from a small number of vehicles, this program focused on vehicles with significant impacts on the mass emissions. The 1996-97 emission inventory data showed that 30% of the entire fleet was responsible for 80% of the total hydrocarbon (THC) emissions. These mid-range emission vehicles were selected based on the following criteria: Any vehicles with the FTP Bag 2 THC emissions in the range of 0.5 to 4 grams/mile. At least 50% of the test vehicles in this program are required to meet the criterion.

Seven vehicles were completed in this test program at the end of September. Five vehicles were randomly selected from the Vehicle Surveillance program. The two other vehicles were selected from the State vehicles with E plates. The average odometer reading for the seven vehicles is about 101,000 miles. The average model year for the seven vehicles is 81. Four of the seven test vehicles meet the emission criteria set for this program. The average FTP Bag 2 THC emissions is 1.07 gm/mile. A description of each vehicle is presented in Table 5.3.

A-5.3.2. Fuel Selection Process

The original test plan only requested two fuels to be tested in each vehicle, one is the Chevron non-oxygenated gasoline and the other is the Tosco 2%-oxygenated gasoline with ethanol. Ten barrels of each fuel were obtained from refineries located in northern California. ARB proposed to include the commercial Phase 2 gasoline with MTBE in the program. Therefore, all seven vehicles in this test program were tested with three different fuels by a random order within each vehicle. In summary, the three fuels are as follows:

- Chevron Non-Oxygenated Gasoline
- Tosco 2% Oxygenated Gasoline with Ethanol
- ARB Commercial Phase 2 gasoline with MTBE.

At least two fuel samples were taken from each barrel when it is opened. All fuel samples were analyzed in the ARB fuel analysis laboratory. ARB chemists check fuel parameters in compliance with Phase 2 gasoline specifications as well as detailed hydrocarbon analysis (speciation) for each fuel sample. The fuel analysis data are summarized in the following table.

Table 5.2. Summary of Fuel Properties

Sample I.D.	EtOH (wt%)	MTBE (wt%)	Benzene (vol%)	Total Aromatics (vol%)	RVP psi	T50 (deg F)	T90 (deg F)	Sulfur (ppm)	Olefins (vol%)
Fuel 50	**0.00**	**10.67**	**0.57**	**23.9**	**6.79**	**201.0**	**311.0**	**14.00**	**3.60**
Fuel 51	**0.00**	**0.00**	**0.16**	**25.0**	**6.71**	**202.1**	**303.2**	**29.20**	**3.43**
Fuel 52	**5.88**	**0.00**	**0.42**	**28.0**	**6.88**	**203.8**	**316.4**	**1.22**	**0.21**

Fuel 50	**Commercial Phase 2 gasoline with MTBE**
Fuel 51	**Chevron Phase 2 non-oxygenated gasoline**
Fuel 52	**Tosco Phase 2 oxygenated gasoline with ethanol**

.

Table 5.3. Description of Vehicles

Project	**2R9905**	**2R9905**	**2R9905**	**2R9905**	**2R9905**	**2R9905**	**2R9905**
Vehicle Number	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Model Year	76	75	92	79	80	90	76
Manufacturer	General Motor	Mercedes	Ford	General Motor	Honda	General Motor	Ford
Division	Oldsmobile	Mercedes	Ford	Chevolet	Honda	Buick	Ford
Model Year	Delta88 Royale	450 SEL	Tempo GS	Malibu	Accord LX	Lesabre	Granada
Bag 2 FTP HC (g/mile)	1.535	1.708	0.015	0.204	0.509	0.016	3.942
Odometer (mile)	136660	150623	30151	153643	76095	57870	101020
Cylinder	8	8	4	6	4	6	8
Displacement (liter)	5.736	4.523	2.294	3.785	1.753	3.786	4.949
Drive	2R	2R	2F	2R	2F	2F	2R
Vehicle Class	Passenger Car	Passenger Car	Passenger Car	Passenger Car	Passenger Car	Passenger Car	Passenger Car
Transmission	Automatic 3 speed	Automatic 3 speed	Automatic 3 speed	Automatic 3 speed	Automatic 3 speed	Automatic 4 speed	Automatic 3 speed
Exhaust Gas Recirculation	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Oxygen Sensor	No	No	Yes	No	No	Yes	No
Fuel Injection	Carburetor	Electronic Multipoint	Electronic Multipoint	Carburetor	Carburetor	Electronic Multipoint	Carburetor
Reactor	Oxidizing Catalyst	Oxidizing Catalyst	Three-Way Catalyst Double Bed Closed Loop	Oxidizing Catalyst	Oxidizing Catalyst	Three-Way Catalyst Single Bed Closed Loop	Oxidizing Catalyst

A-5.4. Mass Emission Test Results

Table 5.4 summarizes the test results for the seven vehicles for carbon monoxide, oxides of nitrogen and non-methane hydrocarbons.

Table 5.4. Exhaust Emission Test Results (g/mi)

Vehicle	No. of	Test	Test	CO		NOx		NMHC	
Number	Tests	Type	Fuel	Bag2	Bag1-Bag3	Bag2	Bag1-Bag3[a]	Bag2	Bag1-Bag3
1	1	FTP	MTBE	36.566	28.324	0.964	0.000	1.367	1.391
2	1	FTP	MTBE	5.848	27.157	1.778	0.000	1.615	0.640
3	1	FTP	MTBE	0.635	3.647	0.105	0.367	0.004	0.423
4	1	FTP	MTBE	0.476	10.706	0.535	0.000	0.082	1.349
5	1	FTP	MTBE	7.745	5.396	2.059	0.028	0.445	0.829
1	1	UC	MTBE	33.870	21.371	2.012	0.618	0.900	3.879
1	1	UC	NonOxy	46.804	119.311	1.954	0.186	1.250	6.105
1	1	UC	Etoh	21.163	87.399	2.175	0.000	0.783	3.886
2	1	UC	MTBE	2.366	88.620	2.646	0.054	0.359	1.692
2	1	UC	NonOxy	4.784	98.584	2.985	0.000	1.840	3.038
3	1	UC	MTBE	3.542	14.679	0.342	0.796	0.013	1.552
3	2	UC	NonOxy	4.419	17.324	0.289	1.112	0.019	1.453
3	1	UC	Etoh	4.419	17.696	0.225	1.115	0.016	1.692
4	1	UC	MTBE	9.613	36.799	1.560	0.191	0.307	3.740
4	2	UC	NonOxy	42.774	57.301	0.246	0.401	1.064	6.705
4	1	UC	Etoh	15.524	43.944	0.454	0.368	0.471	4.243
5	1	UC	MTBE	32.635	19.897	2.239	0.796	1.291	5.833
5	2	UC	NonOxy	32.104	38.950	2.304	1.057	1.103	5.860
5	1	UC	Etoh	10.537	26.390	2.098	1.169	0.505	3.714
6	1	UC	NonOxy	2.202	9.451	0.143	0.518	0.014	1.570
6	1	UC	Etoh	4.156	39.009	0.128	0.519	0.018	2.038
7	1	UC	NonOxy	40.861	61.622	1.878	3.142	1.367	6.326
7	1	UC	Etoh	38.393	47.693	2.216	0.000	1.367	6.878

a: Negative values of bag1-bag3 set to zero.

Bag2 represents hot stablized emissions.

Bag1 minus Bag3 represents start emissions.

FTP: Federal Test Procedure.

UC: Unified Cycle.

Ethanol and MTBE fuels are 2.0 wt% oxygen; NonOxy fuel is non-oxygenated fuel (0 wt% oxygen) .

A-5.5. Organic Species Test Results

Full speciation was conducted on the liquid gasoline, headspace, and exhaust emissions. Summarized results are presented in Figure 5.1 through Figure 5.4 and Table 5.5 through Table 5.8. Complete speciation details for all species for each barrel of gasoline and each vehicle is included in Attachment A2.

Figure 5.1. Liquid Gasoline Organic Gas Species Test Results

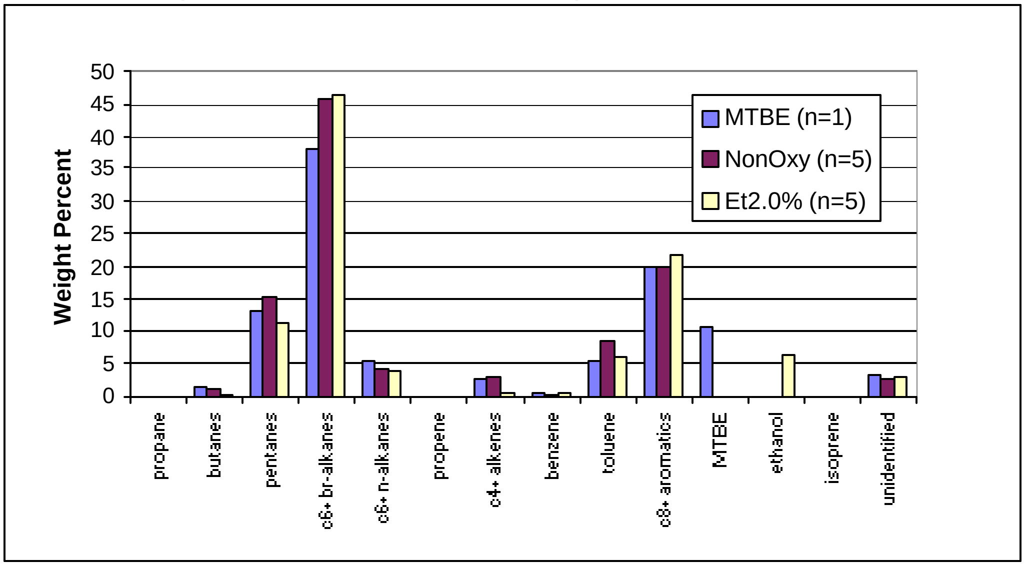


Table 5.5. Liquid Gasoline Organic Gas Species Test Results (wt%)

Group	MTBE (n=1)	NonOxy (n=5)		Et2.0% (n=5)	
Name	**Mean**	**Mean**	**COV**	**Mean**	**COV**
Propane	0.01	0.00	n/a	0.00	7%
Butanes	1.14	0.94	6%	0.41	2%
Pentanes	12.82	15.29	3%	11.26	2%
C6+ br-alkanes	37.83	45.50	2%	46.27	2%
C6+ n-alkanes	5.26	4.23	1%	3.78	0%
Propene	0.00	0.00	20%	0.00	0%
C4+ alkenes	2.69	2.75	2%	0.52	10%
Benzene	0.78	0.26	2%	0.57	1%
Toluene	5.41	8.56	1%	6.17	1%
C8+ aromatics	19.88	19.94	6%	21.88	3%
MTBE	10.90	0.06	11%	0.10	1%
Ethanol	0.00			6.34	5%
Isoprene	0.01	0.00	8%	0.00	0%
Unidentified	3.29	2.49	7%	2.75	37%
TOTAL	100.00	100.03		100.05	
MIR	2.42	2.55	3%	2.51	3%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).

Figure 5.2. Gasoline Headspace Organic Gas Species Test Results

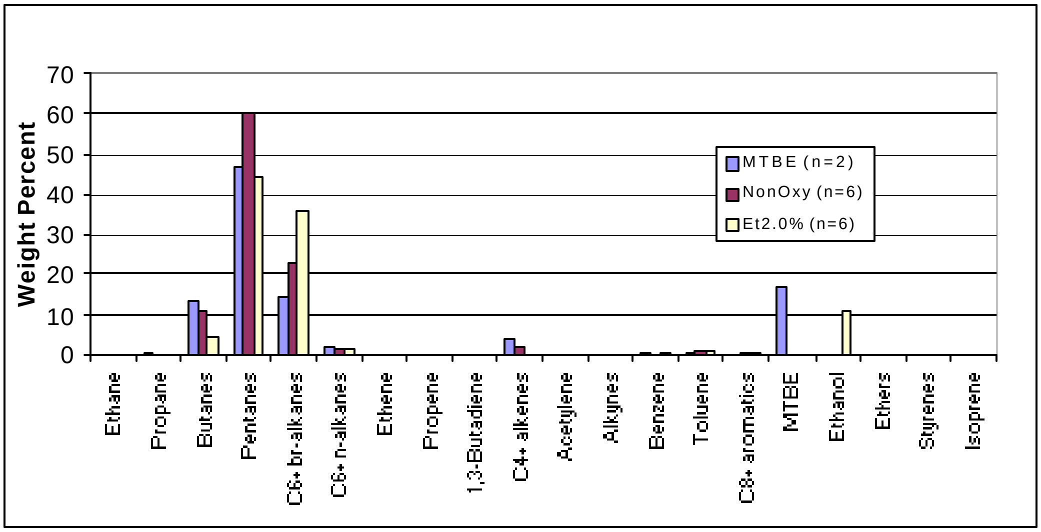


Table 5.6. Gasoline Headspace Organic Gas Species Test Results (wt%)

Group	MTBE (n=2)		NonOxy (n=6)		Et2.0% (n=6)	
Name	**Mean**	**COV**	**Mean**	**COV**	**Mean**	**COV**
Ethane	0.15	18%	0.00	n/a	0.00	n/a
Propane	0.30	28%	0.00	n/a	0.05	8%
Butanes	13.86	23%	11.01	11%	4.35	7%
Pentanes	46.93	6%	60.39	4%	44.48	5%
C6+ br-alkanes	14.21	32%	23.15	11%	35.92	2%
C6+ n-alkanes	2.07	32%	1.82	16%	1.59	6%
Ethene	0.04	17%	0.00	n/a	0.00	n/a
Propene	0.08	28%	0.00	n/a	0.00	n/a
1,3-Butadiene	0.02	141%	0.00	n/a	0.00	n/a
C4+ alkenes	4.00	2%	2.08	5%	0.26	8%
Acetylene	0.00	n/a	0.00	n/a	0.00	n/a
Alkynes	0.00	n/a	0.00	n/a	0.00	n/a
Benzene	0.45	0%	0.19	0%	0.39	0%
Toluene	0.60	62%	1.01	34%	1.18	17%
C8+ aromatics	0.22	46%	0.43	50%	0.67	37%
MTBE	17.08	3%	0.00	n/a	0.00	n/a
Ethanol	0.00	n/a	0.00	n/a	11.19	11%
Ethers	0.00	n/a	0.00	n/a	0.00	n/a
Styrenes	0.00	n/a	0.00	n/a	0.00	n/a
Isoprene	0.01	141%	0.00	n/a	0.00	n/a
TOTAL	100.01		100.08		100.06	
MIR	1.47	1%	1.45	3%	1.43	1%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).

The COVs were calculated before the mean and standard deviation were rounded.

MIR means Maximum Incremental Reactivity (g ozone/g NMOG).

Figure 5.3. Exhaust Gasoline Organic Gas Species Test Results (Hot Stabilized Emissions)

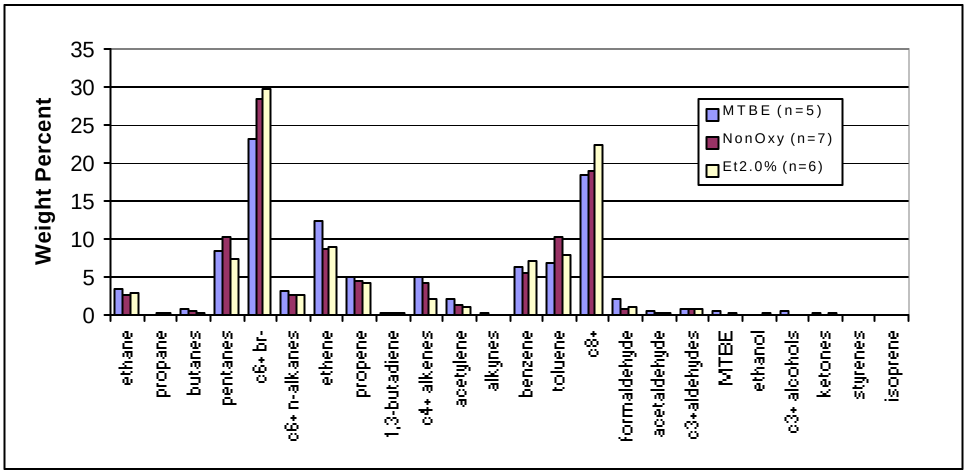


Table 5.7. Exhaust Gasoline Organic Gas Species Test Results (Hot Stabilized Emissions, wt%)

Group	MTBE (n=5)		NonOxy (n=7)		Et2.0% (n=6)	
Name	Mean	COV	Mean	COV	Mean	COV
Ethane	3.42	79%	2.56	68%	2.79	40%
Propane	0.08	76%	0.22	173%	0.35	131%
Butanes	0.66	60%	0.60	39%	0.39	31%
Pentanes	8.50	17%	10.24	19%	7.42	19%
C6+ br-alkanes	23.25	29%	28.30	17%	29.74	19%
C6+ n-alkanes	3.03	35%	2.54	20%	2.67	22%
Ethene	12.27	60%	8.63	49%	8.94	51%
Propene	4.95	51%	4.42	32%	4.10	39%
1,3-Butadiene	0.16	77%	0.23	134%	0.14	136%
C4+ alkenes	5.00	59%	4.21	47%	2.11	83%
Acetylene	2.01	77%	1.20	125%	1.05	94%
Alkynes	0.21	91%	0.07	85%	0.11	123%
Benzene	6.27	45%	5.55	46%	7.20	43%
Toluene	6.74	18%	10.37	10%	7.79	8%
C8+ aromatics	18.55	48%	18.82	31%	22.33	41%
Formaldehyde	2.19	176%	0.71	177%	0.98	137%
Acetaldehyde	0.62	167%	0.24	159%	0.38	166%
C3+aldehydes	0.74	160%	0.74	143%	0.77	138%
MTBE	0.41	32%	0.08	171%	0.24	137%
Ethanol					0.15	173%
C3+ alcohols	0.62	192%	0.06	265%	0.10	176%
Ketones	0.26	79%	0.10	101%	0.18	122%
Styrenes	0.06	62%	0.10	160%	0.07	157%
Isoprene	0.01	224%	0.02	145%		
TOTAL	100.00		100.00		100.00	
MIR	3.98	11%	3.63	9%	3.72	5%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).
Hot stabilized emissions are represented by Bag 2 of Unified Cycle.

Figure 5.4. Exhaust Gasoline Organic Gas Species Test Results (Start Emissions)

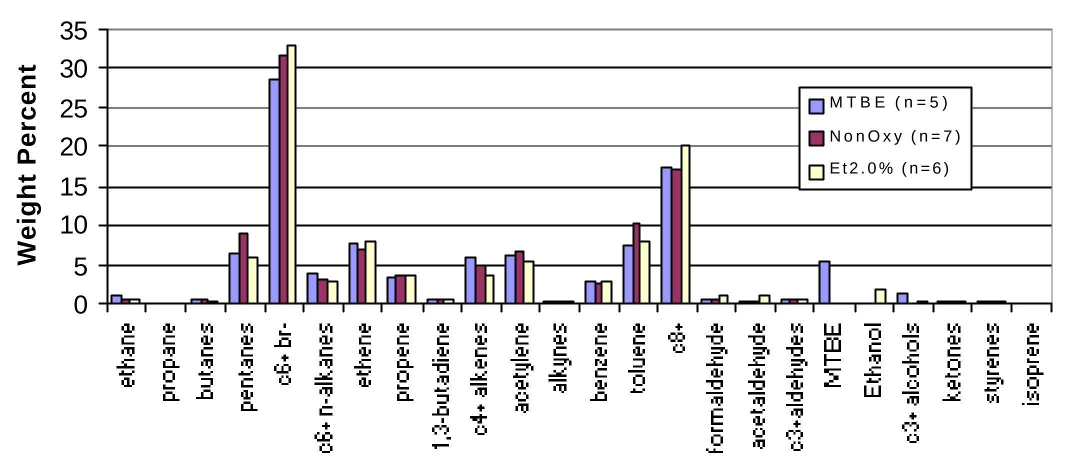


Table 5.8. Exhaust Gasoline Organic Gas Species Test Results (Start Emissions, wt%)

Group	MTBE (n=5)		NonOxy (n=7)		Et2.0% (n=6)	
Name	Mean	COV	Mean	COV	Mean	COV
Ethane	0.90	75%	0.72	49%	0.70	30%
Propane	0.07	92%	0.05	52%	0.06	52%
Butanes	0.49	54%	0.55	47%	0.32	38%
Pentanes	6.28	61%	8.96	20%	5.77	16%
C6+ br-alkanes	28.59	39%	31.69	22%	32.82	19%
C6+ n-alkanes	3.81	37%	2.98	22%	2.79	23%
Ethene	7.62	62%	7.05	34%	7.96	34%
Propene	3.43	58%	3.61	38%	3.74	32%
1,3-Butadiene	0.59	55%	0.49	47%	0.54	77%
C4+ alkenes	5.76	28%	4.89	30%	3.66	33%
Acetylene	6.05	86%	6.75	71%	5.53	58%
Alkynes	0.36	91%	0.30	82%	0.36	69%
Benzene	2.79	58%	2.32	40%	2.62	27%
Toluene	7.30	14%	10.36	7%	8.02	6%
C8+ aromatics	17.32	27%	17.01	19%	20.15	27%
Formaldehyde	0.65	78%	0.67	76%	0.84	35%
Acetaldehyde	0.28	71%	0.37	70%	0.79	33%
C3+aldehydes	0.47	55%	0.49	61%	0.56	45%
MTBE	5.49	64%	0.10	67%	0.10	61%
Ethanol			0.04	265%	1.89	66%
C3+ alcohols	1.33	42%	0.08	130%	0.22	85%
Ketones	0.24	65%	0.27	69%	0.26	37%
Styrenes	0.16	39%	0.19	36%	0.24	56%
Isoprene	0.04	118%	0.05	113%	0.07	125%
TOTAL	100.00		100.00		100.00	
MIR	3.47	19%	3.45	9%	3.72	5%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).
Start emissions are represented by Bag 1 minus Bag 3 of Unified Cycle.

A-6. Comparison of Emission Testing with Profiles

A-6.1. Limitations of Test Program

The data obtained from testing three commercially available CaRFGs have only limited utility for evaluating the liquid gasoline compositions, headspace compositions, and exhaust emission profiles developed according to the procedures of Section A-2. The specific reactivities (overall MIRs) calculated from the test data cannot be expected to equal the reactivities of typical future MTBE-free CaRFGs and their emissions. The uncertainty about the validity of the test results stems from several factors:

- The MTBE-free gasolines have some properties that are probably atypical of future ethanol-blended CaRFGs. Most important, 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 "Phase 3" flat limit for sulfur of 20 ppm (ARB, 1999a). Also, the RVP and olefinic 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.
- The test vehicles as a group are aged; the mean model year among the vehicles for which the exhaust was speciated is 1981. They do not represent well the emission-control technology that is on the road today, let alone the technology in 2003. Only two have 3-way catalysts, and only three are fuel-injected. Only one is a Japanese brand.
- Several of the vehicles apparently had unstable exhaust emission rates. Many of the differences between gasolines within the same vehicle (up to a factor of five) are too large to be attributed to fuel effects; so, temporal variability in emissions may be assumed. However, we cannot estimate that variability well and separate it from the true fuel effects because no observations on the MTBE-free gasoline were replicated.
- In only four vehicles were all three test gasolines tested. For some of the vehicles, exhaust aldehydes and isobutene were not reported for some gasolines.
- Only one MTBE-blended, one ethanol-blended, and one non-oxygenated gasoline were tested. Hence, there is no information on the variability of emission measurements within a class of gasoline.
- The test data for the MTBE-free gasolines are from the Unified Cycle, whereas the modeling profiles are based on FTP data.

The headspace measurements from the test gasolines are of interest to compare with the headspace compositions used to represent diurnal emissions in the ozone modeling. Table 6.1 shows ratios of some species and groups between the headspaces and their whole gasolines. Except for the olefins, the ratios are similar for the sampled gasolines and the profiles.

Table 6.1. Headspace to Liquid Gasoline Ratios for Organic Gases

	Test Data[a]		Profiles	
	Et2.0%	**NonOxy**	**Et2.0%**	**NonOxy**
Ethanol	1.76		1.63	
C4+ olefins	0.49	0.76	2.1	1.6
C8+ aromatic	0.031	0.022	0.051	0.044
Toluene	0.19	0.12	0.26	0.22
Benzene	0.75	0.74	0.80	0.69
C6+ br. alkanes	0.78	0.51	0.53	0.47
Butanes	10.6	11.6	13.8	10.5
Pentanes	3.9	3.9	4.9	3.5

[a] Ratios are of means across all vehicles. Number of vehicles varies by fuel. Means exclude zeros in the data.

For start exhaust emission, Table 6.2 shows the ratios of species between the ethanol-blended and MTBE-blended gasoline and between the non-oxygenated and MTBE-blended gasoline, for the test results and for the model profiles.

Table 6.2. Ratios of Organic Gases Between Gasolines for Starts Exhaustt

	Test Data[a]		Profiles[b]	
	EtOH/MTBE	**NonOxy/MTBE**	**EtOH/MTBE**	**NonOxy/MTBE**
Ethanol	1.9 wt%[c]	--	3.0 wt%[c]	--
C4+ olefins	0.64	0.85	0.76	0.76
C8+ aromatics	1.16	0.98	0.91	0.91
Toluene	1.10	1.42	0.91	0.91
Benzene	0.94	0.83	0.96	0.88
C6+ br. alkanes	1.15	1.11	1.34	1.45
Butanes	0.66	1.13	0.92	0.92
Pentanes	0.92	1.54	0.91	1.0
Isobutene	0.26	0.47	0.48	0.48
Formaldehyde	1.03	0.97	0.94	0.89
Acetaldehyde	2.31	1.26	1.26	0.94

[a] Ratios are of means across all vehicles. Number of vehicles varies by gasoline. Means exclude zeros in the data.

[b] Non-catalyst.

[c] For ethanol, the entry is the content of the test emissions or profile.

As mentioned above, the design of the experiment and the variability of results do not permit an attempt to corroborate the exhaust quantitatively. However, some qualitative observations about the table may be in order.

- As in the profiles, isobutene is less plentiful in the emissions from the MTBE-free test gasolines than from the MTBE-blended test gasoline. This is expected because isobutene is a product of combustion of MTBE.
- The C_6+ branched alkanes (which include branched alkanes and cycloalkanes) are more plentiful in the emissions from the MTBE-free test gasolines than from the MTBE-blended test gasoline. This is consistent with the assumption in the profile development that each C_7 to C_9 branched alkane (but not cycloalkane) in the MTBE exhaust profiles should be increased (by 1.85 for the ethanol-blended gasoline and by 2.0 for the non-oxygenated 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. The ratio for acetaldehyde from the ethanol-blended test gasoline (2.31) is much higher than in the profiles. It may be due to large vehicle-to-vehicle variations in the acetaldehyde exhaust fraction (as well as temporal instability within vehicles).
- 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.

A-7. References

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Attachment A1

Peer Review of Organic Gas Emission Profiles

UNIVERSITY OF CALIFORNIA, BERKELEY

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June 23, 1999

John DaMassa
Planning and Technical Support Division
California Air Resources Board
2020 L Street
Sacramento, CA 95814

Re: Review of Organic Gas Speciation Profiles of Exhaust and Evaporative Emissions from Alternate Gasoline Formulations

Dear John:

I have reviewed the speciation profiles that Paul Allen sent via E-mail on June 8, and am providing my comments and analysis of these profiles to you in this letter. Separate sets of speciation profiles were provided corresponding to 4 different gasoline formulations. Each of the profiles is identified by profile number; these profile numbers will be used in the comments that follow. Note that any changes to base profiles for RFG with 2% oxygen from MTBE will also affect the profiles for other fuels, since they were obtained by adjusting the base (MTBE) profiles.

	MTBE @ 2%	Ethanol @ 2%	Ethanol @ 3.5%	RFG without oxygenates
Liquid fuel	419	660	670	650
Diurnal evap.	906	661	671	651
Hot soak evap.	420	662	672	652
Catalyst exhaust stabilized	876	663	673	653
Catalyst exhaust starts	877	664	674	654
Non-cat exhaust stabilized	401	665	675	655
Non-cat exhaust starts	402	666	676	656

DISCLAIMER: Given the time available to complete my review, and the complexity of the information provided, it was not possible to review the values specified for all chemical species in each profile. I have emphasized in my review 16-20 of the most abundant species in unburned fuel and exhaust emissions, as well as formaldehyde, acetaldehyde, benzene, and 1,3-butadiene. My review identifies some areas where further consideration of the profiles by ARB staff is recommended; I leave it to ARB staff to decide in the end whether the profiles are correct and appropriate for use in air quality modeling.

SUMMARY OF COMMENTS:

Here I identify the most important issues recommended for further consideration, ranked subjectively in terms of how revisions may affect the assessment of ozone formation and air toxic concentrations in subsequent air quality modeling.

- There are numerous problems with the hot soak profiles for all 4 fuels:
  - there appear to be duplicate entries for ethyltoluene isomers.
  - the benzene content varies much more widely in the hot soak profiles than it does in the fuels. Furthermore, variations in hot soak benzene content do not agree with benzene changes in liquid fuel composition.
  - the composition of hot soak emissions does not appear to be well-correlated to the liquid fuel composition for other species including toluene, m-xylene, and 2,2,4-trimethylpentane.

- The benzene content of diurnal emissions appears low given the assumed benzene levels in liquid gasoline; variations in benzene content in diurnal emissions across fuels are not consistent with changes in fuel composition.

- The oxygenate content in exhaust emissions profiles may be too low, especially for ethanol but also MTBE to a lesser degree.

- Acetaldehyde emissions are expected to increase when ethanol is added to gasoline. Further increases are expected when ethanol content is increased from 2 to 3.5% oxygen, yet all of the exhaust profiles are nearly identical in acetaldehyde content when ethanol increases from 2 to 3.5% oxygen in the fuel.

- The ethanol content in diurnal evaporative emissions (profiles 661 and 671) may not scale linearly with fuel ethanol content, due to non-ideal solution behavior.

- Isobutene content in exhaust profiles 653 and 655 looks high for gasoline without oxygenates.

- Butadiene emissions may increase in exhaust profiles 653-656 if the olefin content of the fuel increases.

- The methane content in catalyst-equipped stabilized engine exhaust in 1996 appears high compared to on-road data.

- Acetylene in non-catalyst stabilized exhaust profiles is too low.

More detailed comments, tables and figures, are attached. Please call me at (510) 643-9168 if you have any questions. I hope these comments are useful to you in your assessment of various alternate gasoline formulations.

Sincerely,

Rob Harley

Robert Harley
Associate Professor

DETAILED COMMENTS: Review of Organic Gas Speciation Profiles of Exhaust and Evaporative Emissions from Alternate Gasoline Formulations.

Comment 1: CAT STABILIZED EXHAUST PROFILE FOR RFG w/MTBE. The stabilized exhaust profile for catalyst-equipped engines (profile 876) is compared in the attached Figure 1 with the on-road running emissions profile measured in the Caldecott tunnel in summer 1996 for 20 individual species that together account for >70% of non-methane organic compound emissions in profile 876 and in the tunnel. The tunnel profile is similar to profile 876 for all species except MTBE, which accounted for 5.0% of tunnel VOC (5.5% of tunnel NMOC), whereas profile 876 includes only 2.0% by weight MTBE. Methane is not shown in Figure 1; it accounted for 15.8% of VOC in profile 876 versus 9.1% of VOC in the Caldecott tunnel. A 1996 emissions-weighted average of the profiles for cat and non-cat stabilized exhaust should give around 10% methane to agree with on-road data.

Comment 2: CAT STABILIZED EXHAUST PROFILES FOR ALL 4 FUELS. The stabilized exhaust profiles for all 4 fuels for catalyst-equipped engines (profiles 876, 663, 673, and 653) are compared for selected species in Figure 2. Abundances of species shown in Figure 2 are similar across all profiles, except for five species shown at the right: isobutene, formaldehyde (HCHO), acetaldehyde (CCHO), MTBE, and ethanol. Changes for these species are expected if changes are made in gasoline oxygenate content.

While addition of MTBE to gasoline is expected to lead to increased emissions of isobutene in vehicle exhaust (Hoekman, 1992; Kirchstetter et al., 1999), further consideration should be given as to whether isobutene would increase as much as shown in Figure 2 when switching from RFG containing ethanol to RFG without any oxygenate.

Given that ethanol accounts for 5.75 and 10.1% of gasoline mass (these values correspond to 2 and 3.5% by weight oxygen, respectively), it is surprising in profiles 663 and 673 that ethanol accounts for only 0.25 and 0.5% of exhaust VOC mass. I would predict that roughly half of the exhaust would be unburned fuel, and so would expect as much as an order of magnitude higher ethanol (3-5%) in exhaust emissions depending on fuel ethanol content. Further consideration of this issue is recommended.

Comment 3: EXHAUST PROFILES FOR RFG w/MTBE. For gasoline containing 2% oxygen as MTBE, a comparison of exhaust profiles for catalyst/non-catalyst engines and stabilized/start emissions is presented in Figure 3. Isopentane is higher in the stabilized profiles than in the start profiles. Aromatics (toluene, ethylbenzene, xylenes, and 1,2,4-trimethylbenzene) are less abundant in the catalyst stabilized exhaust profile (876) when compared to the other profiles shown in Figure 3. Acetylene in the non-catalyst stabilized exhaust profile (401) is the lowest of all profiles shown in Figure 3, which is unexpected because vehicles with catalytic converters are expected to have the lower acetylene levels. ARB staff should consider specifying a higher acetylene fraction in profile 401. I am concerned that using the highest-emitting vehicles from ARB in-use surveillance testing may not accurately represent non-catalyst engine emissions.

Comment 4: LIQUID FUEL. In Figures 4 and 5, liquid fuel composition in profile 419 is compared against measured fuel composition in the SF Bay Area from summer 1996 (Kirchstetter et al., 1999). The profiles are similiar in terms of distribution of species across organic compound categories (Figure 4) and for the top 16 identified species listed in profile 419 (Figure 5). These 16 species account for >60% of the mass in profile 419. Profile 419 seems reasonable in comparison to the liquid fuel data from the Bay Area, although differences exist in the specific isomers and types of alkanes present. Further comparisons of profile 419 against Los Angeles area gasoline composition measured during summer 1996 (Norbeck et al., 1998) could be helpful.

Comment 5: HOT SOAK. Duplicate entries exist in the hot soak emission profile (420) for all 3 isomers of ethyltoluene (also called methyl-ethyl-benzene). ARB staff should consider deleting the entries for SAROAD codes 45211, 45212, and 98164 in profile 420, which duplicate entries for SAROAD codes 99915, 99912, and 99914, respectively. If this change is made, the profile will need to be renormalized to sum to 100%, and the hot soak profiles for other fuels (numbers 652, 662, and 672) should be rederived based on the revised profile 420.

The benzene content in hot soak emissions varies widely across fuels, from a low of 3.3% to a high of 4.9% by weight. Given the modest changes specified in fuel benzene content, the changes appear too large, and furthermore the highest hot soak benzene content is specified for the liquid fuel having the lowest benzene (profile 652). A large decrease in hot soak benzene occurs between profiles 662 and 672, while fuel benzene hardly changes.

The composition of hot soak evaporative emissions may approach, in some cases, the composition of liquid gasoline, especially for older vehicles with carburetors. Large differences exist in the relative abundances of toluene (15.1% in profile 420 vs. 6.7% in liquid fuel), m-xylene (8.8% in profile 420 vs. 3.5% in liquid fuel), and 2,2,4-trimethylpentane (2.1% in profile 420 vs. 5.5% in liquid fuel).

Comment 6: DIURNAL. A gasoline headspace vapor profile (906) is used to represent the speciation of diurnal evaporative emissions. This profile was derived using vapor-liquid equilibrium theory and measured composition of liquid gasoline from the Bay Area in summer 1996 (see Kirchstetter et al., 1999). This profile is likely to describe the compostion of displaced gasoline vapor emissions that occur during refueling (Furey and Nagel, 1986). For diurnal emissions from vehicles equipped with correctly-functioning activated carbon canister control systems, other factors such as differing uptake rates of individual VOC, canister carryover effects, and permeation of VOC through fuel system elastomers, can affect VOC composition (Urbanic et al., 1989; Burns et al., 1992). Therefore, an equilibrium headspace vapor composition profile may not represent all diurnal evaporative emissions correctly. Also the benzene levels in profile 906 were calculated from Bay Area liquid gasoline composition which included 0.58% benzene, as opposed to 1.00 wt% benzene in profile 419 (unburned fuel profile, RFG w/MTBE). Therefore profile 906 is likely to understate the benzene content of diurnal evaporative emissions relative to what is specified in the liquid fuel in profile 419.

The level of benzene in diurnal profile 651 (0.52% for RFG w/o oxygenate) is not consistent with benzene content in the liquid fuel, which is the lowest of all 4 fuels, whereas the corresponding diurnal profile has the highest benzene value.

The presence of ethanol in headspace vapor/diurnal evaporative emissions may not scale linearly with ethanol content in fuel, because ethanol exhibits non-ideal behavior in solution with non-polar gasoline hydrocarbons (Bennett et al., 1993), and the activity coefficient increases as ethanol content decreases. Therefore, decreases in ethanol in the liquid may be offset in part by increases in its activity coefficient. Further analysis of profiles 661 and 671 is recommended.

ARB staff should move isomers of ethyltoluene listed in the diurnal evap profiles to list them under SAROAD codes 99915, 99912, and 99914, for consistent labeling of these species across all 7 profiles for each fuel.

Comment 7: BUTADIENE. 1,3-butadiene is present in exhaust emissions, but is not present in any of the evaporative emissions profiles supplied by ARB. This is appropriate. At present there are only minor differences in butadiene weight fractions across the different fuels. Increases in olefin content in unburned fuel may increase butadiene emissions in vehicle exhaust (e.g., Table 3 of Gorse et al., 1991). Therefore, ARB staff should consider whether converting 80% of butane content to butene to construct profile 650 would lead to increased butadiene in the exhaust profiles for gasoline without oxygenate.

Comment 8: ACETALDEHYDE. Profiles 673-676 correspond to exhaust emissions for gasoline with 3.5% oxygen as ethanol. Given the higher fuel ethanol levels, emissions of acetaldehyde should increase compared to profiles 663-666 where ethanol is present at only 2% oxygen, yet the profiles are virtually identical in terms of acetaldehyde content.

Comment 9: OTHER. There are errors in the molecular weights assigned to some of the chemical species in the speciation profiles that were sent to me. Recommended corrections are listed in the attached Table 1. Depending on the chemical mechanism and emission processing procedures used in air quality modeling, these errors in molecular weights could affect conversion of emission rates from mass to molar units. Also, in estimating headspace vapor composition from liquid fuel composition, accurate molecular weights are needed to convert between mass fractions and mol fractions. The most important change is likely methylcyclohexane (43261) where the molecular weight should be 98.2 rather than 85.2 g mol^{-1}.

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TABLE 1: Recommended Changes to Molecular Weights for Individual VOC

SAROAD:	Species Name:	Molecular Weight:
99912	m-ethyltoluene	120.19
99914	p-ethyltoluene	120.19
99915	o-ethyltoluene	120.19
98179	1-ethyl-2-n-propylbenzene	148.25
45250	isomer of dimethylethylbenzene	134.22
45251	"	"
45252	"	"
45254	"	"
45257	"	"
91099	"	"
45256	1-(1,1-dme)-3,5-dimethylbenzene	162.26
91115	t-1-butyl-3,5-dimethylbenzene	162.26
91117	1,3,5-triethylbenzene	162.26
91119	1,2,4-triethylbenzene	162.26
46751	dihydronaphthalene	130.19
91122	pentamethylbenzene	148.23
43261	methylcyclohexane	98.18
90116	propylcylopentane	112.21
91057	trimethylcyclohexane isomer	126.24
91061	"	"
91064	"	"
91066	"	"
91074	"	"
91077	butylcyclopentane	"
91085	"	"
91067	2-methyl-1-octene	126.24
91080	trans-3-nonene	126.24
91084	cis-3-nonene	126.24
43222	1,3-butadiyne	50.06
91097	ethylnonane	156.3

Figure 1: Comparison of Stabilized Exhaust Profile 876 with On-Road Emissions Profile (1996 Caldecott tunnel)

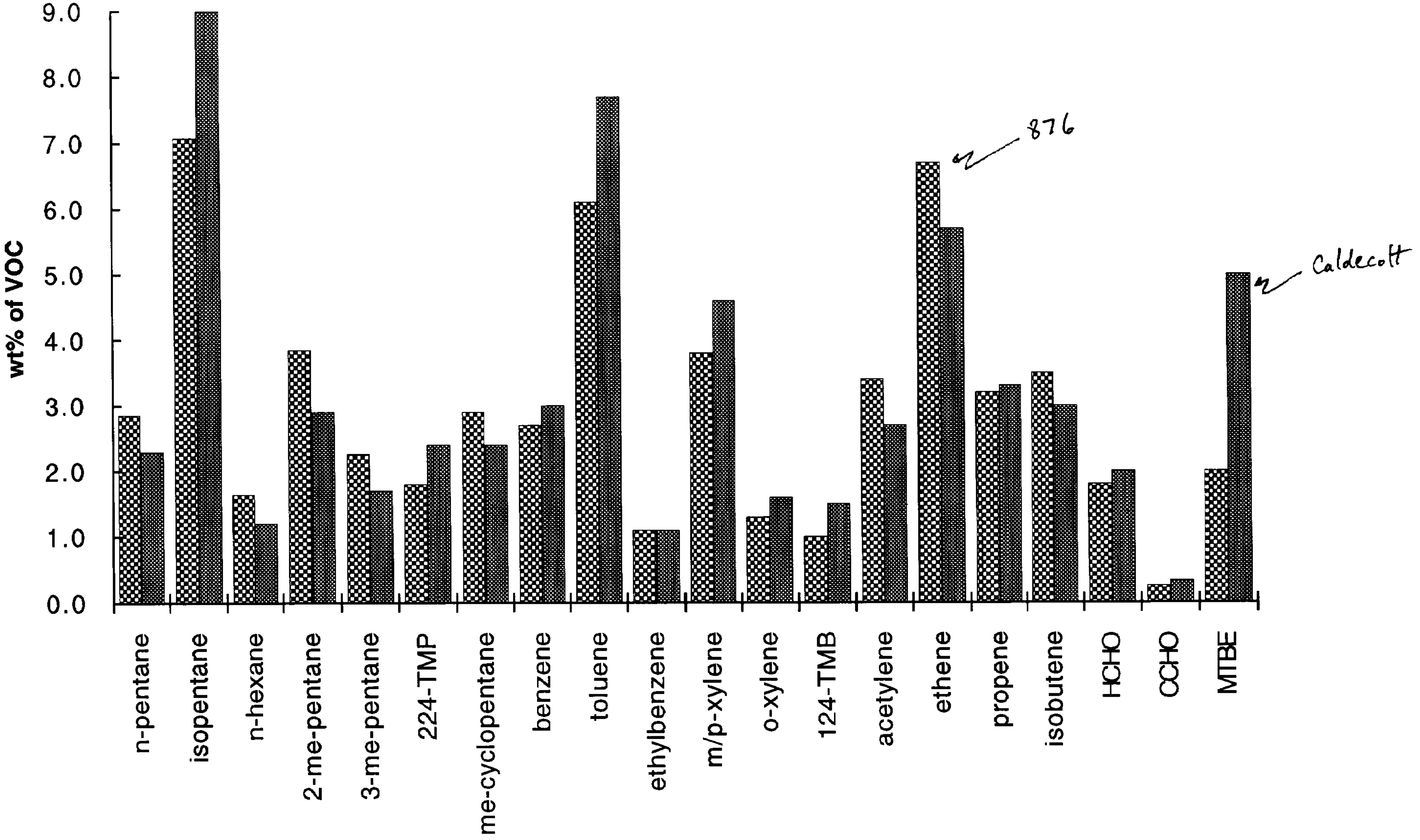


Figure 2: Comparison of Stabilized Exhaust Profiles for RFG with MTBE (876), 2% as ETOH (663), 3.5% as ETOH (673), and w/o oxy (653), in that order

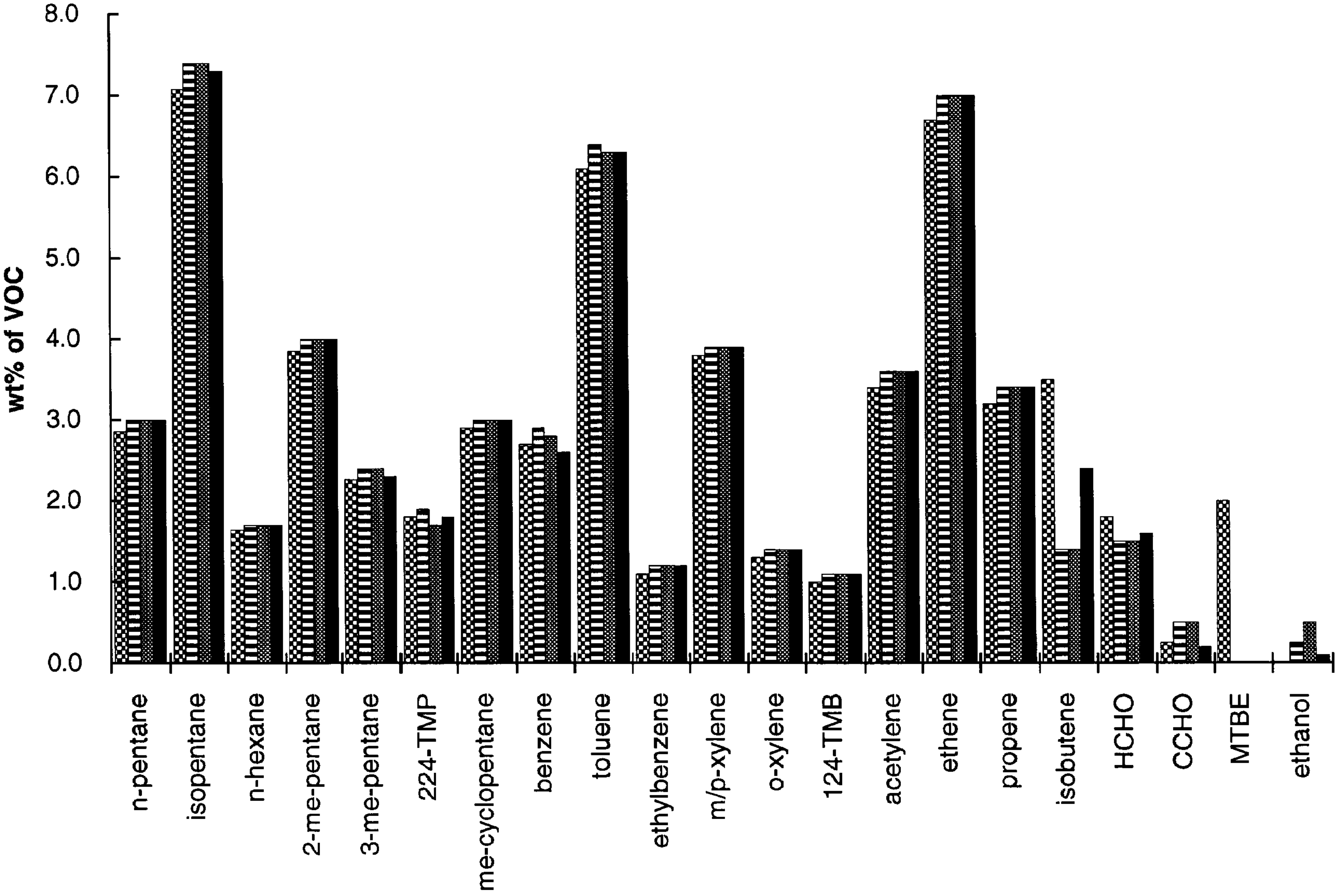


Figure 3: Comparison of Exhaust Speciation Profiles for RFG with MTBE (Profiles are CAT STAB, CAT STRT, NON-CAT STAB, and NON-CAT STRT in that order)

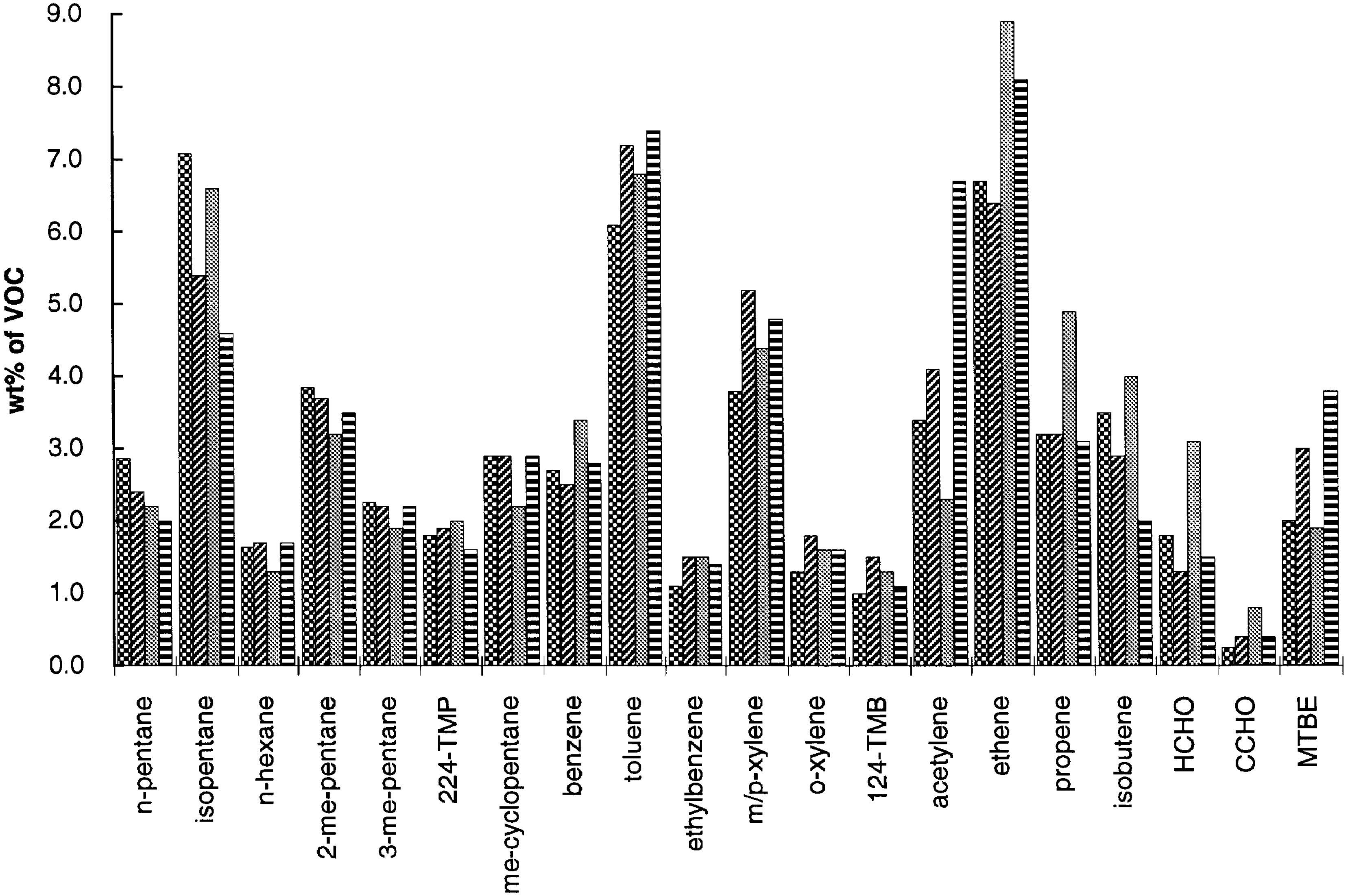


Figure 4: Comparison of Gasoline Composition, Profile 419 (left bars) vs. Bay Area Summer 1996 Composite (right bars)

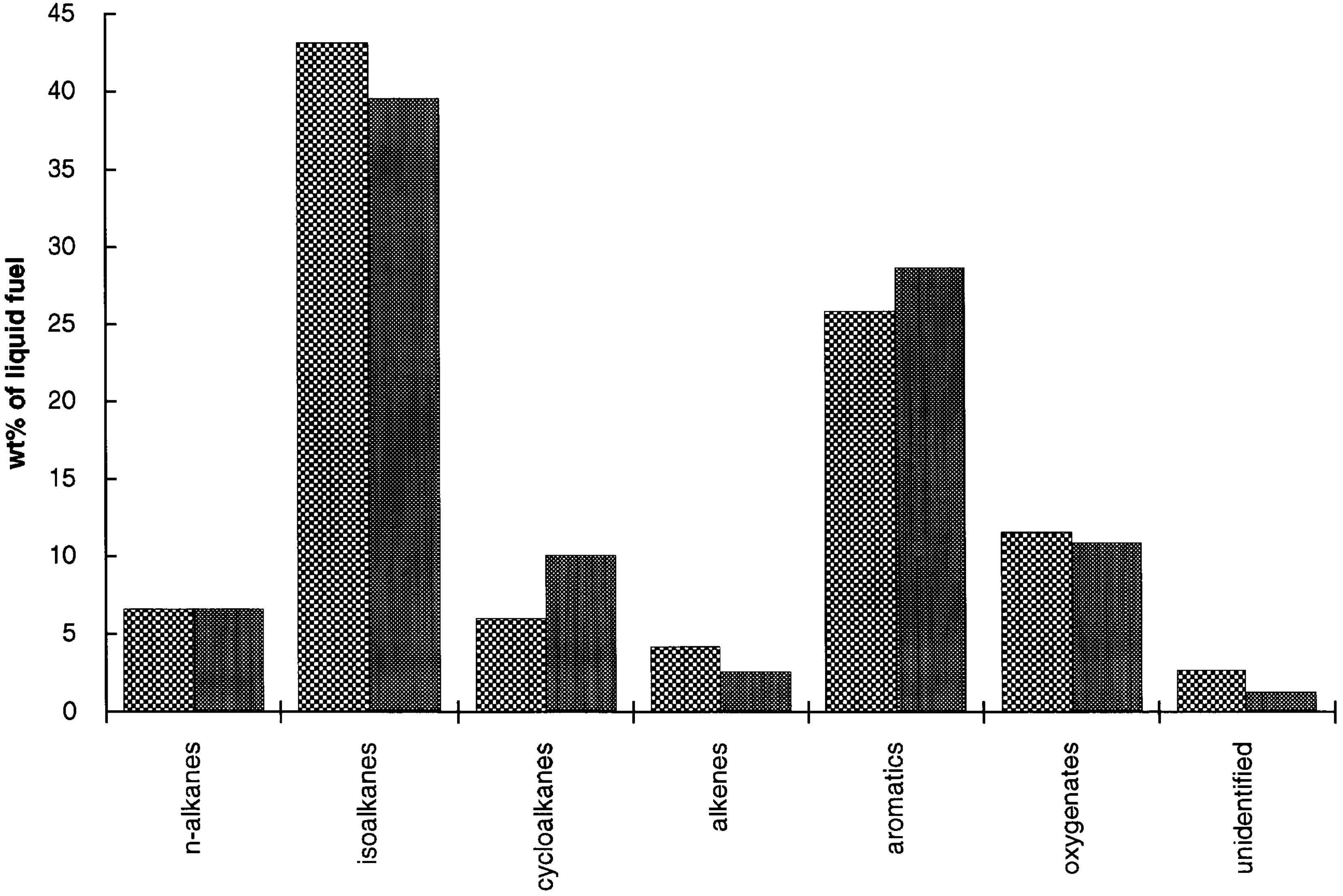
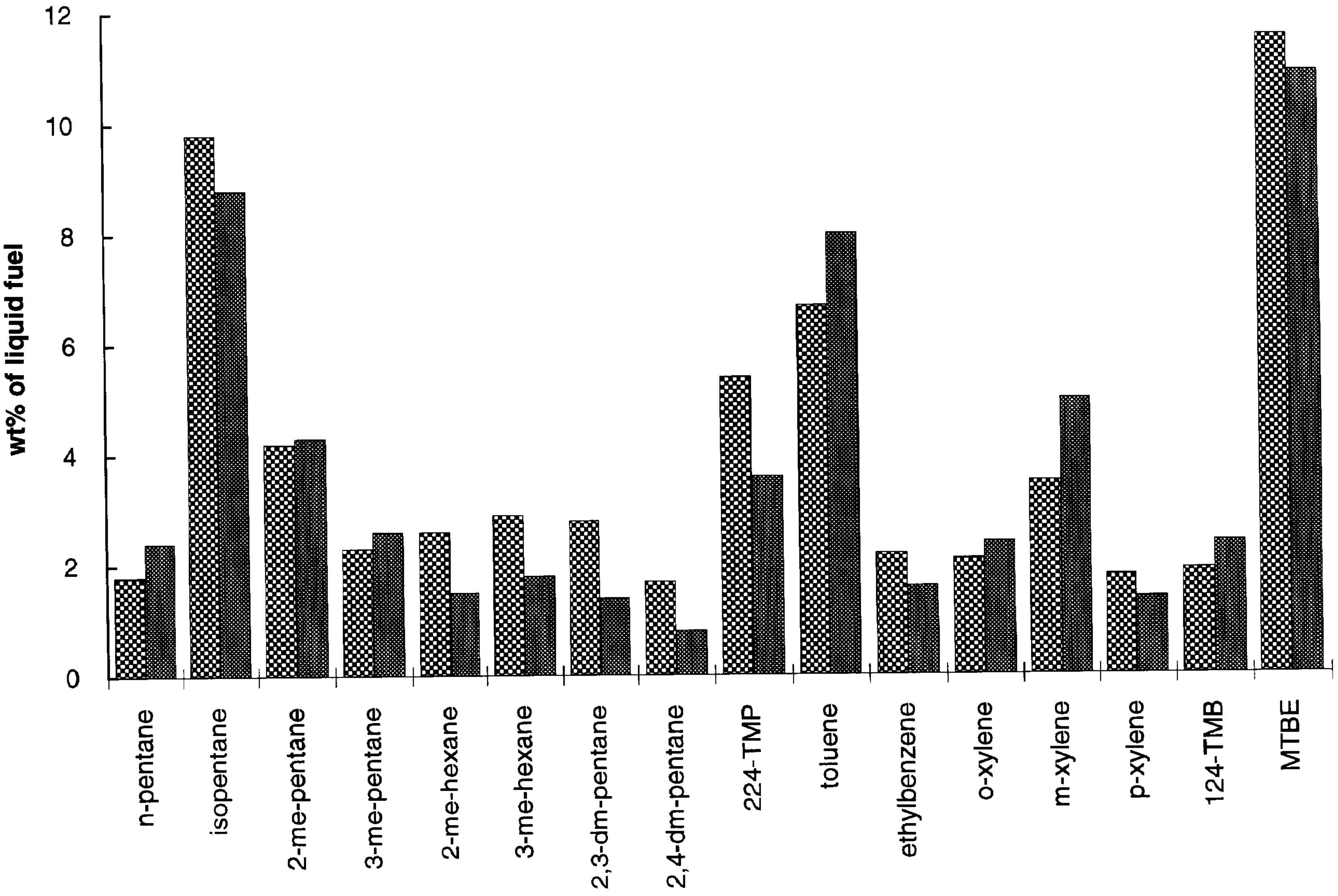


Figure 5: Comparison of Gasoline Composition, Profile 419 (left bars) vs. Bay Area Summer 1996 Composite (right bars)



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July 16, 1999

John DaMassa
Planning and Technical Support Division
California Air Resources Board
2020 L Street
Sacramento, CA 95814

Re: Review of Organic Gas Speciation Profiles of Exhaust and Evaporative Emissions from Alternate Gasoline Formulations

Dear John:

In the second phase of the speciation profile review, new headspace vapor profiles were developed using vapor-liquid equilibrium theory and liquid fuel composition profiles provided by ARB. Headspace vapor profiles were developed for 4 liquid fuels (gasoline with MTBE @ 2 wt% oxygen, gasoline with ethanol @ 2 wt% oxygen, gasoline with ethanol @ 3.5 wt% oxygen, and gasoline without oxygenates).

The theoretical calculations of headspace vapor composition presented here were made because ARB staff had concerns about the applicability and consistency of available vehicle test data used to characterize speciation of diurnal evaporative emissions, especially for ethanol-containing gasoline blends. However, it should be noted that while headspace vapor composition can be used to represent the speciation of some vapor displacement emissions that occur during vehicle refueling (Furey and Nagel, 1986), the presence of control equipment such as activated carbon canisters can affect the speciation of diurnal evaporative emissions (Urbanic et al., 1989). Therefore, calculated headspace vapor composition profiles developed here may not represent the composition of diurnal evaporative emissions. Furthermore, while the vapor-liquid equilibrium theory and methods used here have been verified for pure hydrocarbon and hydrocarbon-MTBE mixtures, measured headspace vapor composition profiles for ethanol-containing gasolines were not available from ARB at the time this report was prepared. Predicted headspace vapor composition profiles for the ethanol-containing gasolines should be evaluated using measured values before these profiles can be considered for use.

METHODS

Liquid fuel profiles were sent by Paul Allen via E-mail on June 8, together with profiles for other exhaust and evaporative emission categories. On July 8, I was advised of the following revisions to profile 650 (liquid fuel profile for gasoline without oxygenates): benzene, 0.799 wt%; 1-butene, 0.008 wt%; n-butane, 0.807 wt%; isobutane, 0.136 wt%. These resulted from a change in ARB's recipe for predicting the composition of gasoline without oxygenates: the recipe step of converting 80% of butanes to 1-butene was deleted. On July 15, I was advised that one further revision had been made to the fuel profiles: benzene had been set uniformly at 1.0 wt% in the liquid phase for all 4 fuels. I did not renormalize the liquid fuel profiles after these changes; the revised sum of species was within 100.0±0.1 wt% in all cases.

Starting from the composition specified for liquid fuel, vapor-liquid equilibrium theory was used to predict headspace vapor composition. This procedure has been described and verified by comparing predicted and measured headspace vapor profiles (Furey and Nagel, 1986; Kirchstetter et al., 1999). These studies both caution that assuming ideal solution behavior is not appropriate for gasoline containing ethanol.

For ideal solutions, the partial pressure (P_i) of a species in the headspace above the liquid is given by Raoult's law:

$$P_i = x_i P_{i,sat}$$

where x_i is the mole fraction of the species in the liquid phase, and $P_{i,sat}$ is the saturation vapor pressure of the pure liquid. To predict vapor pressures for non-ideal solutions, activity coefficients γ_i must be included:

$$P_i = \gamma_i x_i P_{i,sat}$$

Tables II and III of Bennett et al. (1993) present measured vapor and liquid-phase mole fractions for various equilibrium mixtures containing MTBE or ethanol plus a paraffin (2,2,4-trimethylpentane), an olefin (1-heptene), a naphthene (methylcyclohexane), and an aromatic (toluene). Activity coefficients were back-calculated from measured liquid (x_i) and vapor (y_i) mole fractions and measured vapor pressure (P_{tot}):

$$\gamma_i = \frac{y_i P_{tot}}{x_i P_{i,sat}}$$

Pure liquid vapor pressures ($P_{i,sat}$) were calculated for the conditions of each experiment for each species using the Wagner equation (see Appendix A).

Activity coefficients for MTBE and ethanol are presented in Figures 1 and 2 as a function of the mole fraction of oxygenate in the liquid phase. Figure 1 shows that MTBE's behavior in solution with a mixture of hydrocarbons is closely approximated by Raoult's law (i.e., $\gamma_{MTBE} = 1$), whereas the partial pressure of ethanol in the headspace exceeds the Raoult's law prediction by factors of 2-5 for ethanol mole fractions of 10-20% in the liquid (this range corresponds approximately to 5-10 vol% ethanol in fuel). Figures 1 and 2 also indicate that the effect of temperature on activity coefficients is small over the range from 25 to 60°C.

Activity coefficients listed in Table 1 were used to estimate headspace vapor composition for each of the 4 liquid fuel profiles provided by ARB. Separate activity coefficients were specified for each fuel; near-ideal solution behavior was expected for gasoline without oxygenates and gasoline with MTBE. A small increment in aromatics (γ=1.2) in headspace vapors for these two fuels was suggested by data of Bennett et al. (1993) for toluene. Larger departures from ideal solution behavior were specified for the gasoline-ethanol blends, as shown in Table 1.

Table 1: Activity Coefficients Used to Estimate Headspace Vapor Composition for Alternate Liquid Fuel Formulations

	Fuel 419	Fuel 650	Fuel 660	Fuel 670
Compound Class	MTBE @ 2%	No oxygenates	Ethanol @ 2%	Ethanol @ 3.5%
Paraffins	1.1	1.0	1.6	1.8
Naphthenes	1.1	1.0	1.6	1.7
Olefins	1.1	1.0	1.5	1.6
Aromatics	1.2	1.2	1.6	1.7
MTBE	1.0	N/A	N/A	N/A
Alcohols	10.[a]	10.[a]	4.5	2.8

[a] Highly non-ideal behavior is expected from Figure 2 for small amounts of alcohols that may be present in fuels that are nominally "without ethanol".

Figure 1: Activity Coefficient for MTBE vs. MTBE Content in Liquid Phase

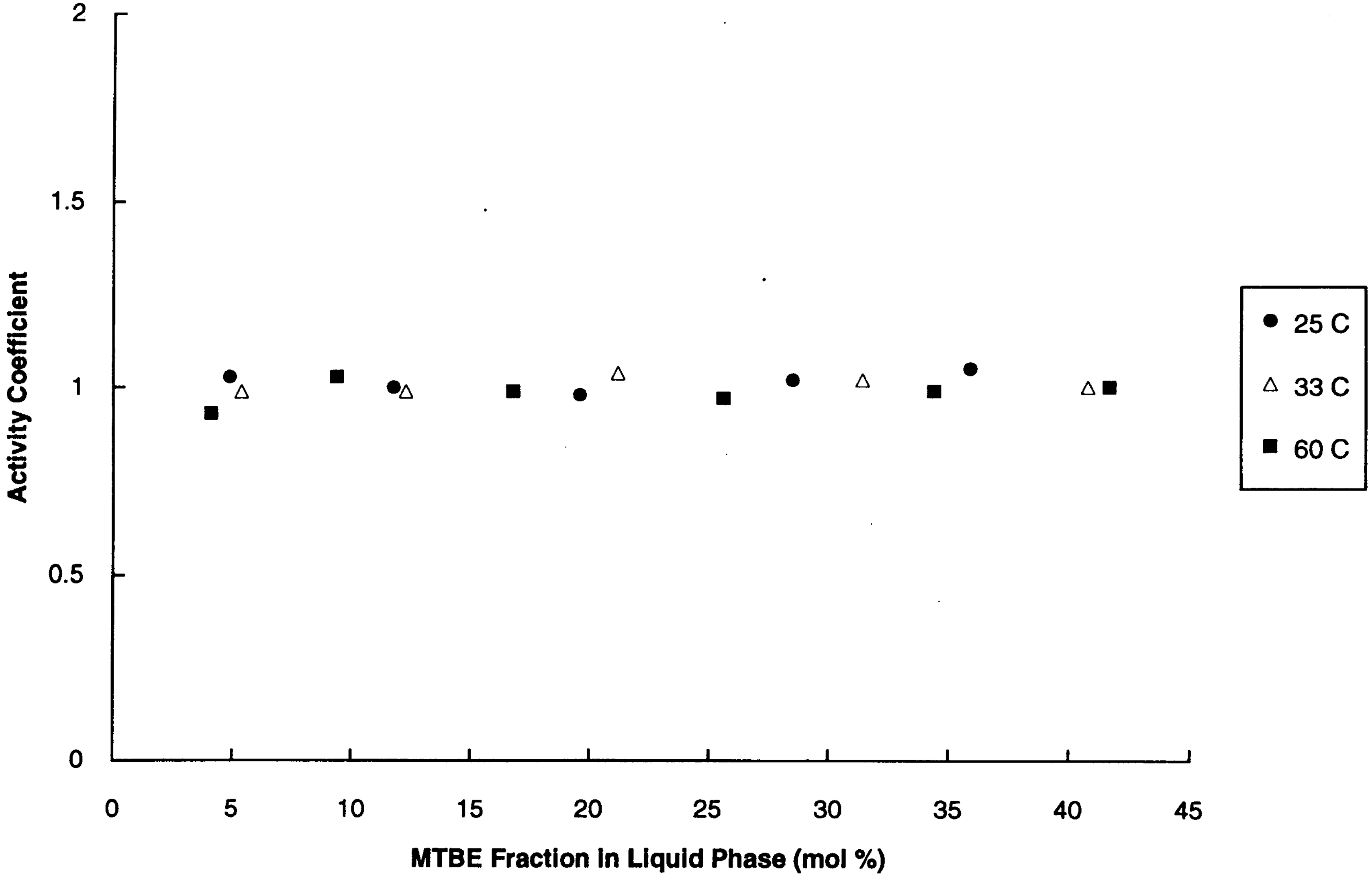
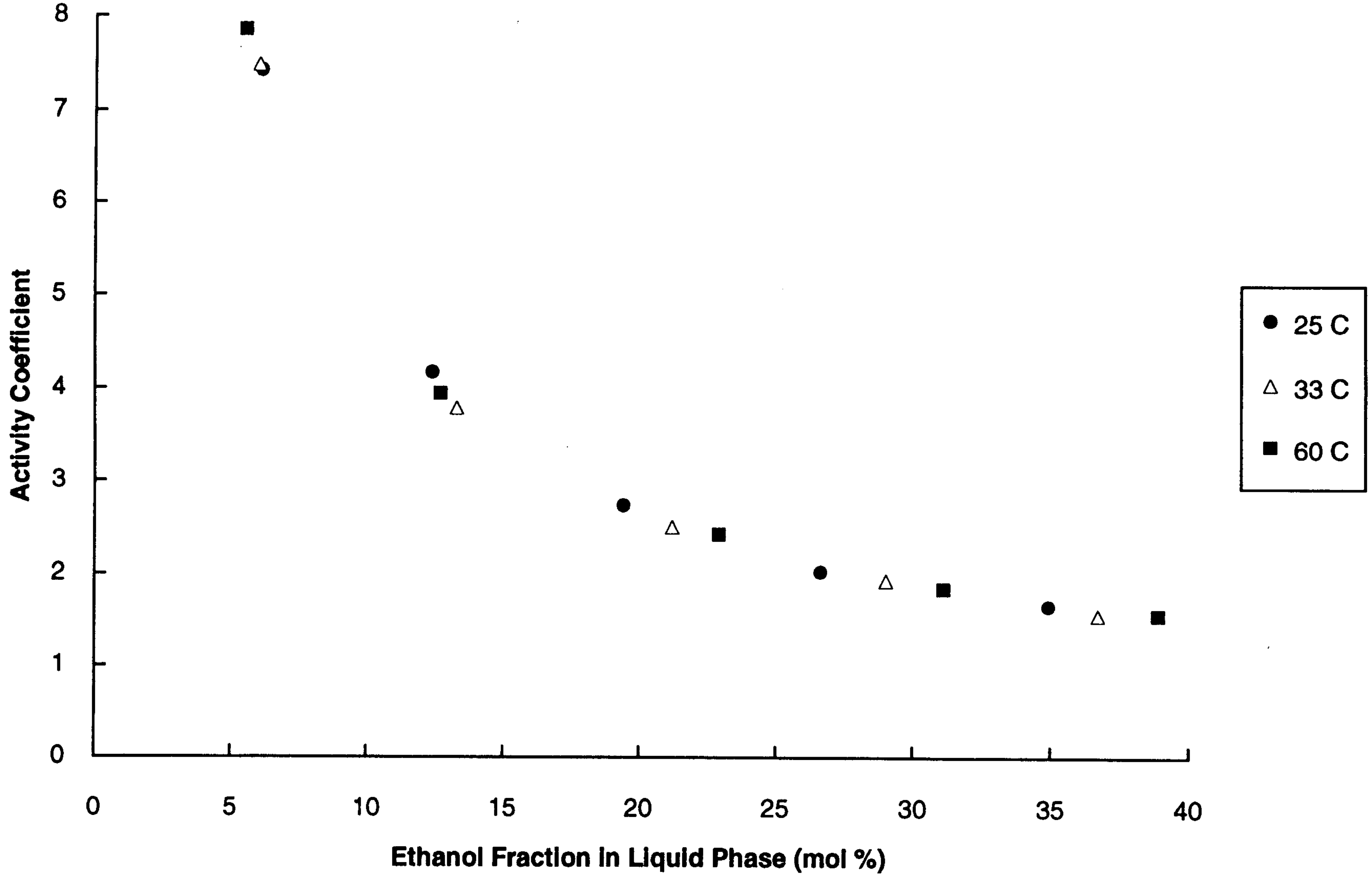


Figure 2: Activity Coefficient for Ethanol vs. Ethanol Content in Liquid Phase



RESULTS

A summary of the most abundant species in gasoline headspace vapors is presented in Table 2. Isopentane accounts for about a third of headspace vapor mass, except for gasoline without oxygenates where it is nearly half of the total. Ethanol or MTBE also are abundant in the headspace when present in the liquid fuels. The other most abundant species are alkanes with low molecular weights and high vapor pressures: n-butane, n-pentane, and 2-methylpentane. The 23 species listed in Table 2 together account for 90% or more of the total headspace vapors for each fuel. Full headspace vapor speciation profiles are provided in Appendix B.

DISCUSSION

In each of the oxygenated fuels, the oxygenate accounts for a significant fraction of headspace vapor mass. MTBE comprises ~15 wt% of headspace vapors when added at 2 wt% oxygen in liquid fuel, and ethanol is in the range 9-10 wt% of headspace vapors for both fuels containing ethanol. Ethanol in the liquid phase almost doubles from 5.75 to 10.1 wt% between the two fuels containing ethanol, but its fraction in the headspace hardly changes. This non-linear relationship between fuel and headspace vapor composition is due to the decrease in ethanol's activity coefficient as the ethanol increases in the liquid, as shown in Figure 2. The relationship between the weight fraction of ethanol in the liquid phase and in headspace vapors should be confirmed in the laboratory by measuring headspace vapor composition for real gasoline samples with different ethanol contents.

Olefins are an important part of the headspace vapor composition profiles because they are highly reactive in the atmosphere compared to other compounds such as alkanes, MTBE, and ethanol (Carter, 1994). The list of the most abundant species in headspace vapors (Table 2) includes four C_5 olefins: 2-methyl-2-butene, trans-2-pentene, 2-methyl-1-butene, and cis-2-pentene. Although none of these species are abundant in liquid fuels (all are <0.5% except for 2-methyl-2-butene in gasoline with MTBE), their high vapor pressures lead to increased amounts of these compounds in headspace vapors. Laboratory studies of fuel composition and evaporative emissions should pay special attention to identifying and quantifying olefins and diolefins in the C_4-C_6 range.

In addition to impacts on ozone, an important part of the air quality assessment for the alternate fuels will be consideration of air toxics including benzene. Table 2 indicates increased benzene levels in headspace vapors for the ethanol-containing fuels. The predictions of benzene in the headspace vapors of ethanol-containing gasoline blends should be verified against laboratory measurements of headspace vapor composition.

Table 2: Comparison of Most Abundant Species in Gasoline Headspace Vapors

	MTBE 2%		**ETOH 2%**		**ETOH 3.5%**		**NO OXY**	
Species Name	weight percent in head space	rank	weight percent in head space	rank	weight percent in head space	rank	weight percent in head space	rank
isopentane	36.5	1	32.0	1	32.2	1	46.8	1
ethyl alcohol	0.0	n/a	9.3	3	9.6	3	0.0	n/a
methyl t-butyl ether (MTBE)	15.2	2	0.0	n/a	0.0	n/a	0.0	n/a
n-butane	9.5	3	10.3	2	10.4	2	7.4	2
n-pentane	5.1	4	4.5	4	4.5	4	6.6	3
2-methylpentane	5.1	5	4.5	5	4.5	5	6.5	4
3-methylpentane	2.5	6	2.2	12	2.2	12	3.3	5
isobutane	2.2	7	2.9	7	2.9	7	1.7	9
2,3-dimethylbutane	1.8	8	1.5	13	1.6	13	2.3	7
2,2,4-trimethylpentane	1.7	9	4.1	6	4.1	6	2.6	6
2-methyl-2-butene	1.6	10	1.2	15	1.2	15	1.2	15
toluene	1.4	11	1.3	14	1.2	14	0.9	17
methylcyclopentane	1.3	12	1.1	16	1.0	16	1.6	12
2,3-dimethylpentane	1.2	13	2.9	8	2.9	8	1.9	8
trans-2-pentene	1.1	14	0.9	18	0.8	18	0.9	16
3-methylhexane	1.1	15	2.7	9	2.7	9	1.7	10
n-hexane	1.1	16	0.9	17	0.9	17	1.4	14
2-methylhexane	1.1	17	2.6	10	2.6	10	1.7	11
2,4-dimethylpentane	1.0	18	2.5	11	2.5	11	1.6	13
2-methyl-1-butene	0.77	19	0.59	22	0.57	22	0.60	19
benzene	0.64	20	0.80	19	0.80	19	0.69	18
cis-2-pentene	0.60	21	0.47	24	0.45	25	0.47	21
n-heptane	0.48	22	0.63	20	0.63	20	0.38	23
sum of above species	93		90		90		92	

In addition to calculating headspace vapor composition, the total vapor pressure P_{tot} for each gasoline at 100°F (38°C) was estimated as

$$P_{tot} = \sum_i P_i$$

where P_i is the partial pressure of species i in headspace vapors calculated as described above. Calculated vapor pressures for each fuel are 7.6 psi for gasoline with MTBE, 8.3 and 8.5 psi for gasoline with ethanol at 2 and 3.5 wt% oxygen, and 7.1 psi for gasoline without oxygenates. Note that predictions of absolute vapor pressure may be less accurate than predictions of the relative abundance of species in headspace vapors. Furthermore, these calculations do not reproduce exactly the conditions of the Reid Vapor Pressure test used to certify fuels. Nevertheless, the detailed liquid fuel formulations provided by ARB, especially those for gasolines with ethanol, may not be representative of fuels that comply with California's summertime RVP limits.

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ACKNOWLEDGMENTS

I am grateful to Shannon Coulter-Burke, a student at UC Berkeley, for assisting me with the calculation of headspace vapor composition profiles.

Sincerely,

Robert Harley

Robert Harley
Associate Professor

APPENDIX A: FURTHER DESCRIPTION OF METHODOLOGY USED TO PREDICT HEADSPACE VAPOR COMPOSITION

For each of the pure compounds present in gasoline, the saturation pressure at 100 F (T=311 K) was calculated using the Wagner equation:

$$\ln P_r = \frac{at + bt^{1.5} + ct^3 + dt^6}{1 - t}$$

where a, b, c, and d are constants specific to each species and τ=1- T_r. P_r and T_r are the reduced pressure and temperature: $P_r = P_{i,sat}/P_c$ and $T_r = T/T_c$ where $P_{i,sat}$ is the saturation vapor pressure (atm), T is the temperature (K), and P_c and T_c are the critical pressure and temperature of pure species i. Values of all parameters needed in the Wagner equation are tabulated in Appendix 1 of Reid et al. (1987). For some compounds, the vapor pressure was estimated using alternate equations such as Antoine or Frost-Kalkwarf-Thodos, again using data from Appendix 1 of Reid et al. (1987).

The liquid fuel profiles that were provided specify composition in terms of weight fractions (w_i) instead of mole fractions (x_i). The following formula was used to convert the liquid profiles from mass to molar basis, using the molecular weights M_i for each species:

$$x_i = \frac{w_i / M_i}{\sum_i w_i / M_i}$$

Likewise the final headspace vapor composition profiles were converted from mole fraction (y_i) to weight fraction (w_i) using the following formula:

$$w_i = \frac{y_i M_i}{\sum_i y_i M_i}.$$

SAROAD Number	**Species Name**	**MTBE 2% wt % headspace**	**ETOH 2% wt % headspace**	**ETOH 3.5% wt % headspace**	**NO OXY wt % headspace**
45201	benzene	0.64	0.80	0.80	0.69
45202	toluene	1.36	1.31	1.24	0.86
45203	ethylbenzene	0.16	0.15	0.14	0.10
45209	n-propylbenzene	0.01	0.01	0.01	0.01
98043	isopropylbenzene (cumene)	0.00	0.00	0.00	0.00
91098	n-butylbenzene	0.00	0.00	0.00	0.00
98047	isobutylbenzene	0.00	0.00	0.00	0.00
45216	sec-butylbenzene	0.00	0.00	0.00	0.00
91111	s-pentylbenzene	0.00	0.00	0.00	0.00
91121	n-hexylbenzene	0.00	0.00	0.00	0.00
45205	m-xylene	0.23	0.22	0.21	0.14
45204	o-xylene	0.11	0.11	0.10	0.07
45206	p-xylene	0.12	0.12	0.11	0.08
99912	1-methyl-3-ethylbenzene	0.04	0.03	0.03	0.02
99914	1-methyl-4-ethylbenzene	0.01	0.01	0.01	0.01
99915	1-methyl-2-ethylbenzene	0.01	0.01	0.01	0.01
98152	1-methyl-3n-propylbenzene	0.00	0.00	0.00	0.00
98182	1-methyl-4n-propylbenzene	0.00	0.00	0.00	0.00
45113	1,3-diethylbenzene (meta)	0.00	0.00	0.00	0.00
98153	1-methyl-3-isopropylbenzene	0.00	0.00	0.00	0.00
91096	1-methyl-2-isopropylbenzene	0.00	0.00	0.00	0.00
98154	1,2-diethylbenzene (ortho)	0.00	0.00	0.00	0.00
91094	1-methyl-4-isopropylbenzene	0.00	0.00	0.00	0.00
98179	1-ethyl-2n-propylbenzene	0.00	0.00	0.00	0.00
45245	c11 dialkyl benzenes	0.00	0.00	0.00	0.00
91100	1-methyl-4-t-butylbenzene	0.00	0.00	0.00	0.00
45237	1,3-dipropylbenzene	0.00	0.00	0.00	0.00
91113	1,2-isodipropylbenzene	0.00	0.00	0.00	0.00
91120	1-methyl-4-n-pentylbenzene	0.00	0.00	0.00	0.00
91116	1,3-n-dipropylbenzene	0.00	0.00	0.00	0.00
45247	c12 dialkyl benzenes	0.00	0.00	0.00	0.00
45208	1,2,4-trimethylbenzene	0.03	0.03	0.03	0.02
45207	1,3,5-trimethylbenzene	0.02	0.02	0.01	0.01
45225	1,2,3-trimethylbenzene	0.00	0.00	0.00	0.00
45252	1,2-dimethyl-4-ethylbenzene	0.00	0.00	0.00	0.00
45257	1,3-dimethyl-5-ethylbenzene	0.00	0.00	0.00	0.00
45250	1,4-dimethyl-2-ethylbenzene	0.00	0.00	0.00	0.00
45251	1,3-dimethyl-4-ethylbenzene	0.00	0.00	0.00	0.00
45254	1,2-dimethyl-3-ethylbenzene	0.00	0.00	0.00	0.00
45253	1,3-dimethyl-2-ethylbenzene	0.00	0.00	0.00	0.00
91117	1,3,5-triethylbenzene	0.00	0.00	0.00	0.00
91119	1,2,4-triethylbenzene	0.00	0.00	0.00	0.00
98044	indan	0.00	0.00	0.00	0.00
98046	naphthalene	0.00	0.00	0.00	0.00
91104	1,2,3,5-tetramethylbenzene	0.00	0.00	0.00	0.00
91108	2-methylindan	0.00	0.00	0.00	0.00
91106	5-methylindan	0.00	0.00	0.00	0.00
91103	1,2,4,5-tetramethylbenzene	0.00	0.00	0.00	0.00
91107	4-methylindan	0.00	0.00	0.00	0.00
46751	dihydronaphthalene	0.00	0.00	0.00	0.00
91123	2-methylnaphthalene	0.00	0.00	0.00	0.00
91124	1-methylnaphthalene	0.00	0.00	0.00	0.00
91122	pentamethylbenzene	0.00	0.00	0.00	0.00
43242	cyclopentane	0.25	0.22	0.21	0.32

43262	methylcyclopentane	1.26	1.10	1.05	1.61
43248	cyclohexane	0.13	0.11	0.11	0.17
43261	methylcyclohexane	0.22	0.53	0.50	0.34
91018	1-c-3-dimethylcyclopentane	0.19	0.46	0.43	0.29
91019	1-t-3-dimethylcyclopentane	0.17	0.42	0.40	0.27
91021	1-t-2-dimethylcyclopentane	0.14	0.35	0.33	0.22
98057	ethylcyclopentane	0.05	0.13	0.12	0.08
91029	1-c-2-dimethylcyclopentane	0.05	0.12	0.12	0.08
90064	dimethylcyclopentane	0.03	0.07	0.06	0.04
91038	1c,2t,3-trimethylcyclopentane	0.03	0.07	0.07	0.05
43116	c8 cycloparaffins	0.02	0.05	0.05	0.03
91031	1c,2t,4-trimethylcyclopentane	0.04	0.09	0.08	0.06
91032	1t,2c,3-trimethylcyclopentane	0.01	0.02	0.02	0.01
91047	t-1,2-dimethylcyclohexane	0.01	0.02	0.02	0.01
91050	1c,2c,3-trimethylcyclopentane	0.01	0.02	0.02	0.01
98180	cis-1,3-dimethylcyclohexane	0.01	0.02	0.02	0.02
98181	trans-1,4-dimethylcyclohexane	0.01	0.03	0.02	0.02
91045	t-2-ethylmethylcyclopentane	0.01	0.01	0.01	0.01
90116	propylcyclopentane	0.00	0.01	0.01	0.01
91055	c-1,2-dimethylcyclohexane	0.00	0.01	0.01	0.00
91033	1,1,2-trimethylcyclopentane	0.00	0.01	0.01	0.01
98059	trans-1,3-dimethylcyclohexane	0.00	0.01	0.01	0.00
91041	1,1-dimethylcyclohexane	0.00	0.00	0.00	0.00
91046	1,1-methylethylcyclopentane	0.00	0.00	0.00	0.00
91077	i-butylcyclopentane	0.00	0.01	0.01	0.01
91057	1,1,4-trimethylcyclohexane	0.00	0.01	0.01	0.00
91061	c-1,c-3,5-trimethylcyclohexane	0.00	0.00	0.00	0.00
91081	1,1-methylethylcyclohexane	0.00	0.00	0.00	0.00
91066	c1,t2,t4-trimethylcyclohexane	0.00	0.00	0.00	0.00
91085	n-butylcyclopentane	0.00	0.00	0.00	0.00
90120	propylcyclohexane	0.00	0.00	0.00	0.00
91064	1,1,3-trimethylcyclohexane	0.00	0.00	0.00	0.00
91074	1,1,2-trimethylcyclohexane	0.00	0.00	0.00	0.00
98060	trimethylcyclohexane	0.00	0.00	0.00	0.00
90101	butylcyclohexane	0.00	0.00	0.00	0.00
43213	1-butene	0.11	0.09	0.09	0.09
43225	2-methyl-1-butene	0.77	0.59	0.57	0.60
43224	1-pentene	0.42	0.32	0.31	0.33
43223	3-methyl-1-butene	0.10	0.07	0.07	0.07
98040	2-methyl-1-pentene	0.12	0.09	0.09	0.09
43245	1-hexene	0.07	0.05	0.05	0.05
98135	4-methyl-1-pentene	0.03	0.03	0.02	0.03
43211	3-methyl-1-pentene	0.02	0.02	0.02	0.02
43234	2,3-dimethyl-1-butene	0.01	0.01	0.01	0.01
91000	3,3-dimethyl-1-pentene	0.06	0.05	0.05	0.05
91008	4-methyl-1-hexene	0.01	0.01	0.01	0.01
90063	2,4-dimethyl-1-pentene	0.00	0.00	0.00	0.00
91005	5-methyl-1-hexene	0.00	0.00	0.00	0.00
43267	1-nonene	0.00	0.00	0.00	0.00
91067	2-methyl-1-octene	0.00	0.00	0.00	0.00
43216	trans-2-butene	0.09	0.07	0.07	0.07
43217	cis-2-butene	0.08	0.06	0.06	0.07
43228	2-methyl-2-butene	1.59	1.23	1.17	1.24
43226	trans-2-pentene	1.12	0.87	0.83	0.88
43227	cis-2-pentene	0.60	0.47	0.45	0.47
43292	cyclopentene	0.15	0.12	0.11	0.12
98004	2-methyl-2-pentene	0.18	0.14	0.13	0.14

92000	1-methylcyclopentene	0.16	0.12	0.12	0.12
98034	trans-2-hexene	0.16	0.12	0.12	0.12
43272	3-methylcyclopentene	0.10	0.08	0.08	0.08
98035	cis-2-hexene	0.08	0.06	0.06	0.06
98136	trans-3-hexene	0.08	0.06	0.06	0.07
43293	4-methyl-trans-2-pentene	0.10	0.08	0.07	0.08
98163	3-methyl-cis-2-pentene	0.04	0.03	0.03	0.03
43273	cyclohexene	0.03	0.02	0.02	0.02
98003	cis-3-hexene	0.03	0.02	0.02	0.02
90029	3-methyl-cis-2-hexene	0.06	0.04	0.04	0.04
91027	3-methyl-trans-2-hexene	0.05	0.04	0.04	0.04
98006	trans-3-heptene	0.05	0.04	0.03	0.04
91001	4,4-dimethyl-2-pentene	0.02	0.02	0.02	0.02
91026	trans-2-heptene	0.02	0.02	0.02	0.02
91028	cis-2-heptene	0.02	0.02	0.02	0.02
90031	4-methyl-trans-2-hexene	0.02	0.01	0.01	0.01
90032	3-methyl-trans-3-hexene	0.02	0.01	0.01	0.01
91024	3-methyl-cis-3-hexene	0.01	0.01	0.01	0.01
91006	2-methyl-trans-3-hexene	0.01	0.01	0.01	0.01
98007	3-ethyl-2-pentene	0.01	0.01	0.01	0.01
91011	3,4-dimethyl-2-pentene	0.01	0.01	0.01	0.01
91017	5-methyl-cis-2-hexene	0.00	0.00	0.00	0.00
43263	trans-2-octene	0.00	0.00	0.00	0.00
43250	trans-4-octene	0.00	0.00	0.00	0.00
43266	cis-2-octene	0.00	0.00	0.00	0.00
91084	cis-3-nonene	0.00	0.00	0.00	0.00
91080	trans-3-nonene	0.00	0.00	0.00	0.00
91092	2,3-dimethyl-2-octene	0.00	0.00	0.00	0.00
90100	trans-1,3-pentadiene	0.07	0.05	0.05	0.05
43243	isoprene	0.03	0.02	0.02	0.02
90026	1,3-cyclopentadiene	0.02	0.02	0.02	0.02
99999	unidentified	0.00	0.00	0.00	0.00
43301	methyl alcohol	0.09	0.04	0.02	0.08
43302	ethyl alcohol	0.00	9.35	9.56	0.00
43303	n-propyl alcohol	0.03	0.01	0.01	0.03
43378	methyl t-butyl ether (MTBE)	15.20	0.00	0.00	0.00
43212	n-butane	9.49	10.31	10.36	7.42
43220	n-pentane	5.11	4.48	4.50	6.54
43231	n-hexane	1.08	0.94	0.95	1.38
43232	n-heptane	0.48	0.63	0.63	0.38
43233	n-octane	0.06	0.08	0.08	0.05
43235	n-nonane	0.01	0.01	0.01	0.00
43238	n-decane	0.00	0.00	0.00	0.00
43241	n-undecane	0.00	0.00	0.00	0.00
43255	n-dodecane	0.00	0.00	0.00	0.00
43214	isobutane	2.23	2.92	2.92	1.74
98132	isopentane	36.51	32.03	32.17	46.78
43229	2-methylpentane	5.10	4.48	4.50	6.54
43230	3-methylpentane	2.54	2.23	2.24	3.26
43295	3-methylhexane	1.10	2.67	2.68	1.72
43275	2-methylhexane	1.08	2.61	2.62	1.67
43300	3-ethylpentane	0.10	0.25	0.25	0.16
43298	3-methylheptane	0.10	0.24	0.24	0.15
98140	2-methylheptane	0.10	0.23	0.23	0.15
43297	4-methylheptane	0.04	0.10	0.10	0.06
91039	3-ethylhexane	0.01	0.02	0.02	0.01
98172	3-methyloctane	0.01	0.03	0.03	0.02

98146	2-methyloctane	0.01	0.02	0.02	0.02
98173	4-methyloctane	0.01	0.02	0.02	0.01
91071	3-ethylheptane	0.00	0.01	0.01	0.00
90047	2-methylnonane	0.00	0.00	0.00	0.00
91090	3-methylnonane	0.00	0.00	0.00	0.00
91088	5-methylnonane	0.00	0.00	0.00	0.00
91089	3-ethyloctane	0.00	0.00	0.00	0.00
91097	3-ethylnonane	0.00	0.00	0.00	0.00
98130	2,2-dimethylpropane	0.07	0.06	0.06	0.09
98001	2,3-dimethylbutane	1.76	1.55	1.55	2.26
43291	2,2-dimethylbutane	0.43	0.38	0.38	0.55
43274	2,3-dimethylpentane	1.19	2.89	2.90	1.85
43271	2,4-dimethylpentane	1.03	2.49	2.51	1.60
90040	3,3-dimethylpentane	0.10	0.25	0.25	0.16
90042	2,2-dimethylpentane	0.01	0.01	0.01	0.01
43277	2,4-dimethylhexane	0.17	0.41	0.41	0.26
43278	2,5-dimethylhexane	0.12	0.30	0.30	0.19
98139	2,3-dimethylhexane	0.09	0.23	0.23	0.15
98138	2,2-dimethylhexane	0.03	0.08	0.08	0.05
91036	3-methyl-3-ethylpentane	0.01	0.04	0.04	0.02
98150	3,4-dimethylhexane	0.01	0.03	0.03	0.02
91034	2-methyl-3-ethylpentane	0.01	0.02	0.02	0.01
98171	3,3-dimethylhexane	0.01	0.02	0.02	0.01
98143	2,5-dimethylheptane	0.01	0.03	0.03	0.02
98145	2,3-dimethylheptane	0.01	0.01	0.01	0.01
91063	3,3-dimethylheptane	0.00	0.01	0.01	0.01
91069	3,4-dimethylheptane	0.00	0.01	0.01	0.01
91060	4,4-dimethylheptane	0.00	0.01	0.01	0.00
98144	3,5-dimethylheptane	0.00	0.00	0.00	0.00
98142	2,4-dimethylheptane	0.00	0.00	0.00	0.00
98176	2,5-dimethyloctane	0.00	0.00	0.00	0.00
98184	3,3-dimethyloctane	0.00	0.00	0.00	0.00
98149	2,4-dimethyloctane	0.00	0.00	0.00	0.00
98177	2,6-dimethyloctane	0.00	0.00	0.00	0.00
91086	3,6-dimethyloctane	0.00	0.00	0.00	0.00
98175	2,2-dimethyloctane	0.00	0.00	0.00	0.00
43160	2,2,3-trimethylbutane	0.02	0.06	0.06	0.04
43276	2,2,4-trimethylpentane	1.70	4.11	4.13	2.64
43279	2,3,4-trimethylpentane	0.25	0.61	0.62	0.39
43280	2,3,3-trimethylpentane	0.18	0.45	0.45	0.29
43296	2,2,3-trimethylpentane	0.03	0.07	0.07	0.04
98033	2,2,5-trimethylhexane	0.08	0.19	0.19	0.12
91053	2,3,4-trimethylhexane	0.01	0.02	0.02	0.02
98141	2,3,5-trimethylhexane	0.01	0.02	0.02	0.01
91059	2,2,3,trimethylhexane	0.01	0.01	0.01	0.01
45222	2,2,4-trimethylhexane	0.00	0.00	0.01	0.00
45223	2,4,4-trimethylhexane	0.00	0.00	0.00	0.00

Attachment A2

Tables of Organic Gas Emission Profiles

Organic Gas Speciation (Weight Percent)

		Liquid Gasoline			
CNUM	CHEMNAME	MTBE	Non-Oxy	EtOH 2%	EtOH3.5%
1	methyl alcohol	0.010	0.000	0.010	0.010
2	ethyl alcohol	0.000	0.000	5.750	10.100
3	n-propyl alcohol	0.020	0.000	0.020	0.020
4	cis-2-butene	0.010	0.010	0.010	0.010
	isobutane	0.170	0.140	0.160	0.150
	n-butane	1.010	0.810	0.800	0.760
	trans-2-butene	0.010	0.010	0.010	0.010
	1-butene	0.010	0.010	0.010	0.010
5	cis-2-pentene	0.220	0.170	0.130	0.130
	cyclopentane	0.140	0.180	0.090	0.080
	cyclopentene	0.070	0.060	0.040	0.040
	isopentane	9.800	12.820	6.260	5.970
	isoprene	0.010	0.010	0.010	0.010
	methyl t-butyl ether (MTBE)	11.550	0.000	0.000	0.000
	n-pentane	1.810	2.370	1.160	1.100
	trans-1,3-pentadiene	0.030	0.020	0.020	0.020
	trans-2-pentene	0.400	0.320	0.240	0.230
	1-pentene	0.120	0.100	0.070	0.070
	1,3-cyclopentadiene	0.010	0.010	0.010	0.010
	2-methyl-1-butene	0.230	0.180	0.140	0.130
	2-methyl-2-butene	0.610	0.490	0.370	0.350
	2,2-dimethylpropane	0.010	0.010	0.010	0.010
	3-methyl-1-butene	0.020	0.020	0.010	0.010
6	benzene	1.000	1.000	1.000	1.000
	cis-2-hexene	0.090	0.070	0.050	0.050
	cis-3-hexene	0.030	0.020	0.020	0.020
	cyclohexane	0.220	0.290	0.140	0.130
	cyclohexene	0.030	0.020	0.020	0.020
	methylcyclopentane	1.540	2.010	0.980	0.940
	n-hexane	1.190	1.560	0.760	0.720
	trans-2-hexene	0.170	0.140	0.100	0.100

CNUM	CHEMNAME	Liquid Gasoline			
		MTBE	Non-Oxy	EtOH 2%	EtOH3.5%
	trans-3-hexene	0.090	0.070	0.050	0.050
6	1-hexene	0.060	0.050	0.040	0.030
	1-methylcyclopentene	0.170	0.140	0.100	0.100
	2-methyl-1-pentene	0.110	0.090	0.070	0.060
	2-methyl-2-pentene	0.190	0.150	0.110	0.110
	2-methylpentane	4.170	5.450	2.660	2.540
	2,2-dimethylbutane	0.240	0.310	0.150	0.150
	2,3-dimethyl-1-butene	0.010	0.010	0.010	0.010
	2,3-dimethylbutane	1.310	1.710	0.840	0.800
	3-methyl-cis-2-pentene	0.040	0.030	0.020	0.020
	3-methyl-1-pentene	0.020	0.020	0.010	0.010
	3-methylcyclopentene	0.110	0.090	0.070	0.060
	3-methylpentane	2.330	3.050	1.490	1.420
	4-methyl-trans-2-pentene	0.070	0.060	0.040	0.040
	4-methyl-1-pentene	0.030	0.020	0.020	0.020
7	cis-2-heptene	0.060	0.050	0.040	0.030
	dimethylcyclopentane	0.060	0.090	0.110	0.100
	ethylcyclopentane	0.210	0.330	0.370	0.350
	methylcyclohexane	0.750	1.190	1.320	1.260
	n-heptane	1.640	1.310	1.560	1.490
	toluene	6.690	3.950	5.100	4.870
	trans-2-heptene	0.060	0.050	0.040	0.030
	trans-3-heptene	0.130	0.100	0.080	0.070
	1-c-2-dimethylcyclopentane	0.170	0.270	0.300	0.290
	1-c-3-dimethylcyclopentane	0.490	0.780	0.860	0.820
	1-t-2-dimethylcyclopentane	0.360	0.570	0.630	0.600
	1-t-3-dimethylcyclopentane	0.450	0.710	0.790	0.760
	2-methyl-trans-3-hexene	0.030	0.020	0.020	0.020
	2-methylhexane	2.610	4.140	4.600	4.390
	2,2-dimethylpentane	0.010	0.020	0.020	0.020
	2,2,3-trimethylbutane	0.040	0.060	0.070	0.040
	2,3-dimethylpentane	2.780	4.410	4.900	4.680
	2,4-dimethyl-1-pentene	0.010	0.010	0.010	0.010
7	2,4-dimethylpentane	1.720	2.730	3.030	2.890

CNUM	CHEMNAME	Liquid Gasoline			
		MTBE	Non-Oxy	EtOH 2%	EtOH3.5%
	3-ethyl-2-pentene	0.030	0.020	0.020	0.020
	3-ethylpentane	0.280	0.440	0.490	0.470
	3-methyl-cis-2-hexene	0.160	0.130	0.100	0.090
	3-methyl-cis-3-hexene	0.040	0.030	0.020	0.020
	3-methyl-trans-2-hexene	0.140	0.110	0.080	0.080
	3-methyl-trans-3-hexene	0.050	0.040	0.030	0.030
	3-methylhexane	2.860	4.540	5.040	4.810
	3,3-dimethyl-1-pentene	0.180	0.140	0.110	0.100
	3,3-dimethylpentane	0.160	0.250	0.280	0.270
	3,4-dimethyl-2-pentene	0.020	0.020	0.010	0.010
	4-methyl-trans-2-hexene	0.050	0.040	0.030	0.030
	4-methyl-1-hexene	0.020	0.020	0.010	0.010
	4,4-dimethyl-2-pentene	0.070	0.060	0.040	0.040
	5-methyl-cis-2-hexene	0.010	0.010	0.010	0.010
	5-methyl-1-hexene	0.010	0.010	0.010	0.010
8	c-1,2-dimethylcyclohexane	0.030	0.050	0.050	0.050
	cis-1,3-dimethylcyclohexane	0.070	0.110	0.120	0.120
	cis-2-octene	0.010	0.010	0.010	0.010
	c8 cycloparaffins	0.210	0.330	0.370	0.350
	ethylbenzene	2.150	1.270	1.640	1.560
	m-xylene	3.530	2.080	2.690	2.570
	n-octane	0.630	0.500	0.600	0.570
	o-xylene	2.100	1.240	1.600	1.530
	p-xylene	1.820	1.070	1.390	1.320
	propylcyclopentane	0.040	0.060	0.070	0.070
	t-1,2-dimethylcyclohexane	0.070	0.110	0.120	0.120
	t-2-ethylmethylcyclopentane	0.060	0.090	0.110	0.100
	trans-1,3-dimethylcyclohexane	0.020	0.030	0.030	0.030
	trans-1,4-dimethylcyclohexane	0.070	0.110	0.120	0.120
	trans-2-octene	0.030	0.020	0.020	0.020
	trans-4-octene	0.010	0.010	0.010	0.010
8	unidentified	2.670	2.130	2.540	2.430
	1,1-dimethylcyclohexane	0.010	0.020	0.020	0.020
	1,1-methylethylcyclopentane	0.010	0.020	0.020	0.020

CNUM	CHEMNAME	Liquid Gasoline			
		MTBE	Non-Oxy	EtOH 2%	EtOH3.5%
	1,1,2-trimethylcyclopentane	0.020	0.030	0.030	0.030
	1c,2c,3-trimethylcyclopentane	0.070	0.110	0.120	0.120
	1c,2t,3-trimethylcyclopentane	0.300	0.480	0.530	0.500
	1c,2t,4-trimethylcyclopentane	0.170	0.270	0.300	0.290
	1t,2c,3-trimethylcyclopentane	0.090	0.140	0.160	0.150
	2-methyl-3-ethylpentane	0.050	0.080	0.090	0.080
	2-methylheptane	0.690	1.090	1.220	1.160
	2,2-dimethylhexane	0.140	0.220	0.250	0.230
	2,2,3-trimethylpentane	0.130	0.210	0.230	0.220
	2,2,4-trimethylpentane	5.450	8.650	9.610	9.170
	2,3-dimethylhexane	0.600	0.950	1.060	1.010
	2,3,3-trimethylpentane	1.050	1.670	1.850	1.770
	2,3,4-trimethylpentane	1.420	2.250	2.500	2.390
	2,4-dimethylhexane	0.850	1.350	1.500	1.430
	2,5-dimethylhexane	0.620	0.980	1.090	1.040
	3-ethylhexane	0.060	0.090	0.110	0.100
	3-methyl-3-ethylpentane	0.080	0.130	0.140	0.130
	3-methylheptane	0.740	1.170	1.300	1.240
	3,3-dimethylhexane	0.050	0.080	0.090	0.080
	3,4-dimethylhexane	0.080	0.130	0.140	0.130
	4-methylheptane	0.290	0.460	0.510	0.490
9	c-1,c-3,5-trimethylcyclohexane	0.030	0.050	0.050	0.050
	cis-3-nonene	0.020	0.020	0.010	0.010
	c1,t2,t4-trimethylcyclohexane	0.020	0.030	0.030	0.030
	i-butylcyclopentane	0.140	0.220	0.250	0.230
	indan	0.170	0.100	0.130	0.120
	isopropylbenzene (cumene)	0.060	0.030	0.050	0.040
	isopropylcyclohexane	0.010	0.020	0.020	0.020
	n-butylcyclopentane	0.020	0.030	0.030	0.030
9	n-nonane	0.160	0.130	0.150	0.140
	n-propylbenzene	0.380	0.220	0.290	0.280
	trans-3-nonene	0.010	0.010	0.010	0.010
	trimethylcyclohexane	0.010	0.020	0.020	0.020
	1-methyl-2-ethylbenzene	0.370	0.220	0.280	0.270

CNUM	CHEMNAME	Liquid Gasoline			
		MTBE	Non-Oxy	EtOH 2%	EtOH3.5%
	1-methyl-3-ethylbenzene	1.340	0.790	1.020	0.970
	1-methyl-4-ethylbenzene	0.570	0.340	0.430	0.410
	1-nonene	0.010	0.010	0.010	0.010
	1,1-methylethylcyclohexane	0.030	0.050	0.050	0.050
	1,1,2-trimethylcyclohexane	0.010	0.020	0.020	0.020
	1,1,3-trimethylcyclohexane	0.010	0.020	0.020	0.020
	1,1,4-trimethylcyclohexane	0.100	0.160	0.180	0.170
	1,2,3-trimethylbenzene	0.320	0.190	0.240	0.230
	1,2,4-trimethylbenzene	1.870	1.100	1.430	1.360
	1,3,5-trimethylbenzene	0.680	0.400	0.520	0.490
	2-methyl-1-octene	0.010	0.010	0.010	0.010
	2-methyloctane	0.210	0.330	0.370	0.350
	2,2,3,trimethylhexane	0.070	0.110	0.120	0.120
	2,2,4-trimethylhexane	0.020	0.030	0.030	0.030
	2,2,5-trimethylhexane	0.690	1.090	1.220	1.160
	2,3-dimethylheptane	0.080	0.130	0.140	0.130
	2,3,4-trimethylhexane	0.110	0.170	0.190	0.180
	2,3,5-trimethylhexane	0.080	0.130	0.140	0.130
	2,4-dimethylheptane	0.010	0.020	0.020	0.020
	2,4,4-trimethylhexane	0.010	0.020	0.020	0.020
	2,5-dimethylheptane	0.150	0.240	0.260	0.250
	3-ethylheptane	0.050	0.080	0.090	0.080
	3-methyloctane	0.230	0.360	0.410	0.390
	3,3-dimethylheptane	0.050	0.080	0.090	0.080
	3,4-dimethylheptane	0.050	0.080	0.090	0.080
	3,5-dimethylheptane	0.020	0.030	0.030	0.030
	4-methyloctane	0.160	0.250	0.280	0.270
9	4,4-dimethylheptane	0.030	0.050	0.050	0.050
10	butylcyclohexane	0.010	0.010	0.010	0.010
	dihydronaphthalene	0.010	0.010	0.010	0.010
	isobutylbenzene	0.040	0.020	0.030	0.030
	n-butylbenzene	0.060	0.030	0.050	0.040
	n-decane	0.060	0.050	0.060	0.050
	naphthalene	0.180	0.110	0.140	0.130

CNUM	CHEMNAME	Liquid Gasoline			
		MTBE	Non-Oxy	EtOH 2%	EtOH3.5%
	sec-butylbenzene	**0.030**	**0.020**	**0.020**	**0.020**
	1-methyl-2-isopropylbenzene	**0.020**	**0.010**	**0.010**	**0.010**
	1-methyl-3-isopropylbenzene	**0.030**	**0.020**	**0.020**	**0.020**
	1-methyl-3n-propylbenzene	**0.240**	**0.140**	**0.180**	**0.170**
	1-methyl-4-isopropylbenzene	**0.010**	**0.010**	**0.010**	**0.010**
	1-methyl-4n-propylbenzene	**0.130**	**0.080**	**0.100**	**0.090**
	1,2-diethylbenzene (ortho)	**0.020**	**0.010**	**0.010**	**0.010**
	1,2-dimethyl-3-ethylbenzene	**0.050**	**0.030**	**0.040**	**0.040**
	1,2-dimethyl-4-ethylbenzene	**0.280**	**0.160**	**0.210**	**0.200**
	1,2,3,5-tetramethylbenzene	**0.150**	**0.090**	**0.110**	**0.110**
	1,2,4,5-tetramethylbenzene	**0.110**	**0.060**	**0.080**	**0.080**
	1,3-diethylbenzene (meta)	**0.110**	**0.060**	**0.080**	**0.080**
	1,3-dimethyl-2-ethylbenzene	**0.010**	**0.010**	**0.010**	**0.010**
	1,3-dimethyl-4-ethylbenzene	**0.140**	**0.080**	**0.110**	**0.100**
	1,3-dimethyl-5-ethylbenzene	**0.220**	**0.130**	**0.170**	**0.160**
	1,4-dimethyl-2-ethylbenzene	**0.150**	**0.090**	**0.110**	**0.110**
	2-methylindan	**0.130**	**0.080**	**0.100**	**0.090**
	2-methylnonane	**0.070**	**0.060**	**0.070**	**0.060**
	2,2-dimethyloctane	**0.010**	**0.010**	**0.010**	**0.010**
	2,3-dimethyl-2-octene	**0.010**	**0.010**	**0.010**	**0.010**
	2,4-dimethyloctane	**0.030**	**0.020**	**0.030**	**0.030**
	2,5-dimethyloctane	**0.050**	**0.040**	**0.050**	**0.040**
	2,6-dimethyloctane	**0.020**	**0.020**	**0.020**	**0.020**
	3-ethyloctane	**0.010**	**0.010**	**0.010**	**0.010**
	3-methylnonane	**0.070**	**0.060**	**0.070**	**0.060**
10	**3,3-dimethyloctane**	**0.040**	**0.030**	**0.040**	**0.040**
	3,6-dimethyloctane	**0.010**	**0.010**	**0.010**	**0.010**
	4-methylindan	**0.030**	**0.020**	**0.020**	**0.020**
	5-methylindan	**0.120**	**0.070**	**0.090**	**0.090**
	5-methylnonane	**0.030**	**0.020**	**0.030**	**0.030**
11	**c11 dialkyl benzenes**	**0.030**	**0.020**	**0.020**	**0.020**
	n-undecane	**0.030**	**0.020**	**0.030**	**0.030**
	pentamethylbenzene	**0.020**	**0.010**	**0.010**	**0.010**
	s-pentylbenzene	**0.030**	**0.020**	**0.020**	**0.020**

CNUM	CHEMNAME	Liquid Gasoline MTBE	Non-Oxy	EtOH 2%	EtOH3.5%
	1-ethyl-2n-propylbenzene	0.050	0.030	0.040	0.040
	1-methyl-4-t-butylbenzene	0.020	0.010	0.010	0.010
	1-methylnaphthalene	0.060	0.030	0.050	0.040
	2-methylnaphthalene	0.140	0.080	0.110	0.100
	3-ethylnonane	0.010	0.010	0.010	0.010
12	c12 dialkyl benzenes	0.010	0.010	0.010	0.010
	n-dodecane	0.030	0.020	0.030	0.030
	n-hexylbenzene	0.010	0.010	0.010	0.010
	1-methyl-4-n-pentylbenzene	0.040	0.020	0.030	0.030
	1,2-isodipropylbenzene	0.040	0.020	0.030	0.030
	1,2,4-triethylbenzene	0.010	0.010	0.010	0.010
	1,3-dipropylbenzene	0.040	0.020	0.030	0.030
	1,3-n-dipropylbenzene	0.030	0.020	0.020	0.020
	1,3,5-triethylbenzene	0.010	0.010	0.010	0.010
	Total	100.000	100.000	99.980	99.960

		Headspace Vapors			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
CNUM	CHEMNAME				
1	methyl alcohol	0.000	0.080	0.040	0.020
2	ethyl alcohol	0.000	0.000	9.350	9.560
3	n-propyl alcohol	0.000	0.030	0.010	0.010
	propane	0.280	0.000	0.000	0.000
4	cis-2-butene	0.340	0.070	0.060	0.060
	isobutane	1.300	1.740	2.920	2.920
	isobutene	0.160	0.000	0.000	0.000
	n-butane	6.290	7.420	10.310	10.360
	trans-2-butene	0.590	0.070	0.070	0.070
	1-butene	0.120	0.090	0.090	0.090
5	cis-2-pentene	0.300	0.470	0.470	0.450
	cyclopentane	0.980	0.320	0.220	0.210
	cyclopentene	0.090	0.120	0.120	0.110
	isopentane	34.880	46.780	32.030	32.170
	isoprene	0.000	0.020	0.020	0.020
	methyl t-butyl ether (MTBE)	16.830	0.000	0.000	0.000

CNUM	CHEMNAME	Headspace Vapors			
		MTBE	Non-Oxy	EtOH 2%	EtOH3.5%
	n-pentane	7.280	6.540	4.480	4.500
	trans-1,3-pentadiene	0.000	0.050	0.050	0.050
	trans-2-pentene	0.730	0.880	0.870	0.830
	1-pentene	0.220	0.330	0.320	0.310
	1,3-cyclopentadiene	0.000	0.020	0.020	0.020
	2-methyl-1-butene	0.410	0.600	0.590	0.570
	2-methyl-2-butene	1.020	1.240	1.230	1.170
	2,2-dimethylpropane	0.000	0.090	0.060	0.060
	3-methyl-1-butene	0.080	0.070	0.070	0.070
6	benzene	0.360	0.690	0.800	0.800
	cis-2-hexene	0.040	0.060	0.060	0.060
	cis-3-hexene	0.050	0.020	0.020	0.020
	cyclohexane	0.960	0.170	0.110	0.110
	cyclohexene	0.000	0.020	0.020	0.020
	methylcyclopentane	2.640	1.610	1.100	1.050
	n-hexane	1.440	1.380	0.940	0.950
6	t-amylmethylether (TAME)	0.010	0.000	0.000	0.000
	trans-2-hexene	0.090	0.120	0.120	0.120
	trans-3-hexene	0.000	0.070	0.060	0.060
	1-hexene	0.030	0.050	0.050	0.050
	1-methylcyclopentene	0.000	0.120	0.120	0.120
	2-ethyl-1-butene	0.020	0.000	0.000	0.000
	2-hexenes	0.030	0.000	0.000	0.000
	2-methyl-1-pentene	0.060	0.090	0.090	0.090
	2-methyl-2-pentene	0.180	0.140	0.140	0.130
	2-methylpentane	5.570	6.540	4.480	4.500
	2,2-dimethylbutane	1.550	0.550	0.380	0.380
	2,3-dimethyl-1-butene	0.000	0.010	0.010	0.010
	2,3-dimethylbutane	1.950	2.260	1.550	1.550
	3-methyl-cis-2-pentene	0.040	0.030	0.030	0.030
	3-methyl-trans-2-pentene	0.060	0.000	0.000	0.000
	3-methyl-1-pentene	0.000	0.020	0.020	0.020
	3-methylcyclopentene	0.000	0.080	0.080	0.080
	3-methylpentane	3.060	3.260	2.230	2.240

CNUM	CHEMNAME	Headspace Vapors			
		MTBE	Non-Oxy	EtOH 2%	EtOH3.5%
	4-methyl-cis-2-pentene	0.020	0.000	0.000	0.000
	4-methyl-trans-2-pentene	0.100	0.080	0.080	0.070
	4-methyl-1-pentene	0.030	0.030	0.030	0.020
7	cis-2-heptene	0.000	0.020	0.020	0.020
	dimethylcyclopentane	0.000	0.040	0.070	0.060
	ethylcyclopentane	0.000	0.080	0.130	0.120
	methylcyclohexane	0.380	0.340	0.530	0.500
	n-heptane	0.390	0.380	0.630	0.630
	toluene	1.590	0.860	1.310	1.240
	trans-2-heptene	0.000	0.020	0.020	0.020
	trans-3-heptene	0.000	0.040	0.040	0.030
	1-c-2-dimethylcyclopentane	0.000	0.080	0.120	0.120
	1-c-3-dimethylcyclopentane	0.000	0.290	0.460	0.430
	1-t-2-dimethylcyclopentane	0.000	0.220	0.350	0.330
7	1-t-3-dimethylcyclopentane	0.000	0.270	0.420	0.400
	2-methyl-trans-3-hexene	0.000	0.010	0.010	0.010
	2-methylhexane	0.670	1.670	2.610	2.620
	2,2-dimethylpentane	0.060	0.010	0.010	0.010
	2,2,3-trimethylbutane	0.000	0.040	0.060	0.060
	2,3-dimethylpentane	0.650	1.850	2.890	2.900
	2,4-dimethylpentane	0.510	1.600	2.490	2.510
	3-ethyl-2-pentene	0.000	0.010	0.010	0.010
	3-ethylpentane	0.040	0.160	0.250	0.250
	3-methyl-cis-2-hexene	0.000	0.040	0.040	0.040
	3-methyl-cis-3-hexene	0.000	0.010	0.010	0.010
	3-methyl-trans-2-hexene	0.000	0.040	0.040	0.040
	3-methyl-trans-3-hexene	0.000	0.010	0.010	0.010
	3-methylhexane	0.740	1.720	2.670	2.680
	3,3-dimethyl-1-pentene	0.000	0.050	0.050	0.050
	3,3-dimethylpentane	0.000	0.160	0.250	0.250
	3,4-dimethyl-2-pentene	0.000	0.010	0.010	0.010
	4-methyl-trans-2-hexene	0.000	0.010	0.010	0.010
	4-methyl-1-hexene	0.000	0.010	0.010	0.010
	4,4-dimethyl-2-pentene	0.000	0.020	0.020	0.020

CNUM	CHEMNAME	Headspace Vapors			
		MTBE	Non-Oxy	EtOH 2%	EtOH3.5%
8	c-1,2-dimethylcyclohexane	0.010	0.000	0.010	0.010
	cis-1,3-dimethylcyclohexane	0.000	0.020	0.020	0.020
	c8 cycloparaffins	0.000	0.030	0.050	0.050
	ethylbenzene	0.110	0.100	0.150	0.140
	ethylcyclohexane	0.070	0.000	0.000	0.000
	m-xylene	0.320	0.140	0.220	0.210
	n-octane	0.050	0.050	0.080	0.080
	o-xylene	0.120	0.070	0.110	0.100
	p-xylene	0.100	0.080	0.120	0.110
	propylcyclopentane	0.000	0.010	0.010	0.010
	t-1,2-dimethylcyclohexane	0.000	0.010	0.020	0.020
	t-2-ethylmethylcyclopentane	0.000	0.010	0.010	0.010
8	trans-1,3-dimethylcyclohexane	0.000	0.000	0.010	0.010
	trans-1,4-dimethylcyclohexane	0.000	0.020	0.030	0.020
	unidentified	1.160	0.000	0.000	0.000
	1,1,2-trimethylcyclopentane	0.000	0.010	0.010	0.010
	1c,2c,3-trimethylcyclopentane	0.000	0.010	0.020	0.020
	1c,2t,3-trimethylcyclopentane	0.000	0.050	0.070	0.070
	1c,2t,4-trimethylcyclopentane	0.000	0.060	0.090	0.080
	1t,2c,3-trimethylcyclopentane	0.000	0.010	0.020	0.020
	2-methyl-3-ethylpentane	0.090	0.010	0.020	0.020
	2-methylheptane	0.120	0.150	0.230	0.230
	2,2-dimethylhexane	0.010	0.050	0.080	0.080
	2,2,3-trimethylpentane	0.040	0.040	0.070	0.070
	2,2,4-trimethylpentane	1.210	2.640	4.110	4.130
	2,3-dimethylhexane	0.010	0.150	0.230	0.230
	2,3,3-trimethylpentane	0.310	0.290	0.450	0.450
	2,3,4-trimethylpentane	0.310	0.390	0.610	0.620
	2,4-dimethylhexane	0.130	0.260	0.410	0.410
	2,5-dimethylhexane	0.120	0.190	0.300	0.300
	3-ethylhexane	0.000	0.010	0.020	0.020
	3-methyl-3-ethylpentane	0.000	0.020	0.040	0.040
	3-methylheptane	0.120	0.150	0.240	0.240
	3,3-dimethylhexane	0.010	0.010	0.020	0.020

CNUM	CHEMNAME	Headspace Vapors			
		MTBE	Non-Oxy	EtOH 2%	EtOH3.5%
	3,4-dimethylhexane	0.000	0.020	0.030	0.030
	4-methylheptane	0.060	0.060	0.100	0.100
9	i-butylcyclopentane	0.000	0.010	0.010	0.010
	isopropylbenzene (cumene)	0.010	0.000	0.000	0.000
	m-ethyltoluene (99912)	0.040	0.000	0.000	0.000
	n-nonane	0.010	0.000	0.010	0.010
	n-propylbenzene	0.000	0.010	0.010	0.010
	o-ethyltoluene (99915)	0.010	0.000	0.000	0.000
	p-ethyltoluene (99914)	0.020	0.000	0.000	0.000
	1-methyl-2-ethylbenzene	0.000	0.010	0.010	0.010
9	1-methyl-3-ethylbenzene	0.000	0.020	0.030	0.030
	1-methyl-4-ethylbenzene	0.000	0.010	0.010	0.010
	1,1,4-trimethylcyclohexane	0.000	0.000	0.010	0.010
	1,2,3-trimethylbenzene	0.010	0.000	0.000	0.000
	1,2,4-trimethylbenzene	0.000	0.020	0.030	0.030
	1,3,5-trimethylbenzene	0.000	0.010	0.020	0.010
	2-methyloctane	0.000	0.020	0.020	0.020
	2,2,3,trimethylhexane	0.000	0.010	0.010	0.010
	2,2,4-trimethylhexane	0.000	0.000	0.000	0.010
	2,2,5-trimethylhexane	0.140	0.120	0.190	0.190
	2,3-dimethylheptane	0.000	0.010	0.010	0.010
	2,3,4-trimethylhexane	0.000	0.020	0.020	0.020
	2,3,5-trimethylhexane	0.000	0.010	0.020	0.020
	2,5-dimethylheptane	0.000	0.020	0.030	0.030
	3-ethylheptane	0.000	0.000	0.010	0.010
	3-methyloctane	0.000	0.020	0.030	0.030
	3,3-dimethylheptane	0.000	0.010	0.010	0.010
	3,4-dimethylheptane	0.000	0.010	0.010	0.010
	4-methyloctane	0.000	0.010	0.020	0.020
	4,4-dimethylheptane	0.000	0.000	0.010	0.010
12	1,2,4-triethylbenzene	0.040	0.000	0.000	0.000
	1,3,5-triethylbenzene	0.020	0.000	0.000	0.000

CNUM	CHEMNAME	Catalyst Start Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
1	formaldehyde	1.310	1.170	1.230	1.190
	methane	5.280	4.790	4.820	5.200
	methyl alcohol	1.230	0.000	0.000	0.280
2	acetaldehyde	0.400	0.380	0.510	0.910
	acetylene	4.130	3.740	3.770	4.070
	ethane	0.740	0.670	0.670	0.730
	ethyl alcohol	0.090	0.000	3.000	5.280
	ethylene	6.450	5.850	5.880	6.360
3	acetone	0.340	0.310	0.310	0.330
	acrolein (2-propenal)	0.110	0.100	0.100	0.110
	propane	0.070	0.060	0.060	0.070
	propionaldehyde	0.060	0.050	0.050	0.060
	propylene	3.250	2.950	2.960	3.200
	1-propyne	0.320	0.290	0.290	0.310
	1,2-propadiene	0.230	0.210	0.210	0.230
4	butyraldehyde	0.060	0.050	0.050	0.060
	cis-2-butene	0.220	0.200	0.200	0.220
	crotonaldehyde	0.050	0.040	0.050	0.050
	isobutane	0.020	0.020	0.020	0.020
	isobutene	2.860	1.370	1.380	2.820
	methyl ethyl ketone (MEK)	0.060	0.050	0.050	0.060
	n-butane	0.560	0.510	0.510	0.550
	trans-2-butene	0.240	0.220	0.220	0.240
	vinylacetylene	0.120	0.110	0.110	0.120
	1-butene	0.530	0.480	0.480	0.280
	1,2-butadiene	0.030	0.030	0.030	0.030
	1,3-butadiene	0.700	0.690	0.690	0.680
	1,3-butadiyne	0.020	0.020	0.020	0.020
	2-methyl-2-propenal	0.100	0.090	0.090	0.100
5	cis-2-pentene	0.120	0.110	0.110	0.120
	cyclopentane	0.410	0.370	0.370	0.400
	cyclopentene	0.220	0.200	0.200	0.220

CNUM	CHEMNAME	Catalyst Start Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
5	isopentane	5.360	5.360	4.890	5.280
	isoprene	0.210	0.190	0.190	0.210
	isovaleraldehyde	0.030	0.030	0.030	0.030
	methyl t-butyl ether (MTBE)	3.020	0.000	0.000	0.000
	n-pentane	2.380	2.380	2.170	2.350
	trans-1,3-pentadiene	0.030	0.030	0.030	0.030
	trans-2-pentene	0.260	0.240	0.240	0.260
	1-pentene	0.140	0.130	0.130	0.140
	2-methyl-1-butene	0.280	0.250	0.250	0.280
	2-methyl-2-butene	0.440	0.400	0.400	0.430
	3-methyl-1-butene	0.220	0.200	0.200	0.220
6	benzene	2.470	2.170	2.370	2.430
	cis-2-hexene	0.060	0.050	0.050	0.060
	cyclohexane	0.740	0.740	0.670	0.730
	cyclohexene	0.070	0.060	0.060	0.070
	c6 aldehydes	0.020	0.020	0.020	0.020
	methylcyclopentane	2.920	2.920	2.660	2.880
	n-hexane	1.740	1.740	1.590	1.710
	trans-2-hexene	0.180	0.160	0.160	0.180
	trans-3-hexene	0.070	0.060	0.060	0.070
	1-hexene	0.100	0.090	0.090	0.100
	2-methyl-1-pentene	0.060	0.050	0.050	0.060
	2-methyl-2-pentene	0.100	0.090	0.090	0.100
	2-methylpentane	3.680	3.680	3.360	3.630
	2,2-dimethylbutane	0.560	0.560	0.510	0.550
	2,3-dimethyl-1-butene	0.010	0.010	0.010	0.010
	2,3-dimethylbutane	0.980	0.980	0.890	0.970
	3-methyl-trans-2-pentene	0.010	0.010	0.010	0.010
	3-methyl-1-pentene	0.080	0.070	0.070	0.080
	3-methylcyclopentene	0.100	0.090	0.090	0.100
	3-methylpentane	2.230	2.230	2.030	2.200
	3,3-dimethyl-1-butene	0.020	0.020	0.020	0.020
6	4-methyl-trans-2-pentene	0.060	0.050	0.050	0.060
	4-methyl-1-pentene	0.030	0.030	0.030	0.030

CNUM	CHEMNAME	Catalyst Start Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
7	benzaldehyde	0.230	0.210	0.210	0.230
	cis-2-heptene	0.040	0.040	0.040	0.040
	ethylcyclopentane	0.220	0.400	0.370	0.220
	methylcyclohexane	0.790	1.430	1.320	0.780
	n-heptane	0.660	0.600	0.600	0.650
	toluene	7.250	6.570	6.610	7.140
	trans-2-heptene	0.040	0.040	0.040	0.040
	trans-3-heptene	0.060	0.050	0.050	0.060
	1-c-3-dimethylcyclopentane	0.300	0.540	0.500	0.300
	1-t-3-dimethylcyclopentane	0.330	0.600	0.550	0.320
	2-methyl-trans-3-hexene	0.010	0.010	0.010	0.010
	2-methyl-2-hexene	0.040	0.040	0.040	0.040
	2-methylhexane	0.030	0.050	0.050	0.030
	2,2,3-trimethylbutane	0.020	0.040	0.030	0.020
	2,3-dimethyl-2-pentene	0.020	0.020	0.020	0.020
	2,3-dimethylpentane	1.720	3.120	2.880	1.690
	2,4-dimethyl-1-pentene	0.010	0.010	0.010	0.010
	2,4-dimethyl-2-pentene	0.050	0.040	0.050	0.050
	2,4-dimethylpentane	0.540	0.980	0.910	0.530
	3-ethylpentane	0.330	0.600	0.550	0.320
	3-methyl-cis-2-hexene	0.040	0.040	0.040	0.040
	3-methyl-trans-3-hexene	0.010	0.010	0.010	0.010
	3-methylhexane	0.920	1.670	1.540	0.910
	3,3-dimethylpentane	0.020	0.040	0.030	0.020
	3,4-dimethyl-1-pentene	0.010	0.010	0.010	0.010
	4-methyl-trans-2-hexene	0.020	0.020	0.020	0.020
8	c-1-methyl-3-ethylcyclopentane	0.090	0.160	0.150	0.090
	c-1,2-dimethylcyclohexane	0.010	0.020	0.020	0.010
	cis-1,3-dimethylcyclohexane	0.050	0.090	0.080	0.050
	cis-2-octene	0.010	0.010	0.010	0.010
8	ethylbenzene	1.540	1.400	1.400	1.520
	ethylcyclohexane	0.020	0.040	0.030	0.020
	m-xylene	5.170	4.690	4.710	5.090
	n-octane	0.550	0.500	0.500	0.540

CNUM	CHEMNAME	Catalyst Start Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
	o-xylene	1.780	1.610	1.620	1.750
	styrene	0.250	0.230	0.230	0.250
	t-1-methyl-3-ethylcyclopentane	0.160	0.290	0.270	0.160
	tolualdehyde	0.200	0.180	0.180	0.200
	trans-1,3-dimethylcyclohexane	0.070	0.130	0.120	0.070
	trans-1,4-dimethylcyclohexane	0.140	0.250	0.230	0.140
	trans-2-octene	0.010	0.010	0.010	0.010
	unidentified	0.450	0.410	0.410	0.440
	1-octene	0.020	0.020	0.020	0.020
	1,2,4-trimethylcyclopentene	0.210	0.380	0.350	0.210
	1c,2t,3-trimethylcyclopentane	0.090	0.160	0.150	0.090
	2-methylheptane	0.480	0.870	0.800	0.470
	2,2-dimethylhexane	0.100	0.180	0.170	0.100
	2,2,4-trimethylpentane	1.920	3.480	3.220	1.890
	2,3-dimethylhexane	0.380	0.690	0.640	0.380
	2,3,4-trimethylpentane	0.770	1.400	1.290	0.760
	2,4-dimethylhexane	0.380	0.690	0.640	0.380
	2,5-dimethylhexane	0.430	0.780	0.720	0.420
	3-methylheptane	0.820	1.490	1.380	0.810
	3,3-dimethylhexane	0.010	0.020	0.020	0.010
	4-methylheptane	0.270	0.490	0.450	0.270
9	indan	0.150	0.140	0.140	0.150
	isopropylbenzene (cumene)	0.060	0.050	0.050	0.060
	n-nonane	0.290	0.260	0.260	0.290
	n-propylbenzene	0.380	0.340	0.350	0.380
	1-methyl-2-ethylbenzene	0.450	0.410	0.410	0.440
	1-methyl-3-ethylbenzene	1.230	1.110	1.120	1.210
	1-methyl-4-ethylbenzene	0.530	0.480	0.480	0.520
9	1-methyl-4-ethylcyclohexane	0.060	0.110	0.100	0.060
	1-nonene	0.060	0.050	0.050	0.060
	1,2,3-trimethylbenzene	0.290	0.260	0.260	0.290
	1,2,4-trimethylbenzene	1.520	1.380	1.390	1.500
	1,3,5-trimethylbenzene	0.610	0.550	0.560	0.600
	1,3,5-trimethylcyclohexane	0.110	0.200	0.180	0.110

CNUM	CHEMNAME	Catalyst Start Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
	2-methyloctane	0.050	0.090	0.080	0.050
	2,2,4-trimethylhexane	0.110	0.200	0.180	0.110
	2,2,5-trimethylhexane	0.390	0.710	0.650	0.380
	2,3-dimethylheptane	0.020	0.040	0.030	0.020
	2,3,5-trimethylhexane	0.060	0.110	0.100	0.060
	2,4-dimethylheptane	0.120	0.220	0.200	0.120
	2,4,4-trimethylhexane	0.020	0.040	0.030	0.020
	2,6-dimethylheptane	0.290	0.530	0.490	0.290
	3-methyloctane	0.400	0.720	0.670	0.390
	3,4-dimethylheptane	0.090	0.160	0.150	0.090
	3,5-dimethylheptane	0.220	0.400	0.370	0.220
	4-methyloctane	0.340	0.620	0.570	0.330
10	isobutylbenzene	0.030	0.030	0.030	0.030
	n-decane	0.130	0.120	0.120	0.130
	naphthalene	0.070	0.060	0.060	0.070
	1-methyl-2-isopropylbenzene	0.090	0.080	0.080	0.090
	1-methyl-2n-propylbenzene	0.060	0.050	0.050	0.060
	1-methyl-3-isopropylbenzene	0.070	0.060	0.060	0.070
	1-methyl-3n-propylbenzene	0.220	0.200	0.200	0.220
	1-methyl-4-isopropylbenzene	0.020	0.020	0.020	0.020
	1,2-diethylbenzene (ortho)	0.020	0.020	0.020	0.020
	1,2-dimethyl-3-ethylbenzene	0.040	0.040	0.040	0.040
	1,2-dimethyl-4-ethylbenzene	0.170	0.150	0.150	0.170
	1,2,3,4-tetramethylbenzene	0.050	0.040	0.050	0.050
	1,2,3,5-tetramethylbenzene	0.080	0.070	0.070	0.080
	1,2,4,5-tetramethylbenzene	0.060	0.050	0.050	0.060
10	1,3-diethylbenzene (meta)	0.110	0.100	0.100	0.110
	1,3-dimethyl-2-ethylbenzene	0.030	0.030	0.030	0.030
	1,3-dimethyl-4-ethylbenzene	0.130	0.120	0.120	0.130
	1,3-dimethyl-5-ethylbenzene	0.180	0.160	0.160	0.180
	1,4-diethylbenzene (para)	0.130	0.120	0.120	0.130
	1,4-dimethyl-2-ethylbenzene	0.120	0.110	0.110	0.120
	2-methylindan	0.080	0.070	0.070	0.080
	2-methylnonane	0.180	0.160	0.160	0.180

CNUM	CHEMNAME	Catalyst Start Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
	2,2-dimethyloctane	0.040	0.040	0.040	0.040
	2,2,4-trimethylheptane	0.120	0.110	0.110	0.120
	2,3-dimethyloctane	0.050	0.040	0.050	0.050
	2,4-dimethyloctane	0.060	0.050	0.050	0.060
	2,5-dimethyloctane	0.070	0.060	0.060	0.070
	2,6-dimethyloctane	0.090	0.080	0.080	0.090
	3,3-dimethyloctane	0.080	0.070	0.070	0.080
	4-methylindan	0.020	0.020	0.020	0.020
	5-methylindan	0.070	0.060	0.060	0.070
11	n-pentylbenzene	0.040	0.040	0.040	0.040
	n-undecane	0.070	0.060	0.060	0.070
	1-ethyl-2n-propylbenzene	0.020	0.020	0.020	0.020
	1-methyl-2-n-butylbenzene	0.030	0.030	0.030	0.030
	1-methyl-2-t-butylbenzene	0.010	0.010	0.010	0.010
12	n-dodecane	0.020	0.020	0.020	0.020
	t-1-butyl-3,5-dimethylbenzene	0.030	0.030	0.030	0.030
	1,3-dipropylbenzene	0.020	0.020	0.020	0.020
13	2,2,5-triethylheptane	0.160	0.140	0.150	0.160
0					
TOTAL		100.000	99.990	100.000	100.010

CNUM	CHEMNAME	Catalyst Stabilized Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
1	formaldehyde	1.76	1.57	1.65	1.62
	methane	15.82	14.57	14.75	15.85
	methyl alcohol	0.42	0	0	0.21
2	acetaldehyde	0.25	0.24	0.32	0.58
	acetylene	3.44	3.17	3.21	3.45
	ethane	1.09	1	1.02	1.09
	ethyl alcohol	0.07	0	2.01	3.58
	ethylene	6.73	6.2	6.28	6.74
3	acetone	0.17	0.16	0.16	0.17
	acrolein (2-propenal)	0.14	0.13	0.13	0.14

CNUM	CHEMNAME	Catalyst Stabilized Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
	propane	0.06	0.05	0.06	0.06
	propionaldehyde	0.04	0.04	0.04	0.04
	propylene	3.24	2.98	3.02	3.24
	1-propyne	0.24	0.22	0.22	0.24
	1,2-propadiene	0.15	0.14	0.14	0.15
4	butyraldehyde	0.02	0.02	0.02	0.02
	cis-2-butene	0.18	0.17	0.17	0.18
	crotonaldehyde	0.03	0.03	0.03	0.03
	isobutane	0.02	0.02	0.02	0.02
	isobutene	3.46	1.69	1.71	1.84
	methyl ethyl ketone (MEK)	0.02	0.02	0.02	0.02
	n-butane	0.81	0.75	0.76	0.81
	trans-2-butene	0.25	0.23	0.23	0.25
	vinylacetylene	0.07	0.06	0.07	0.07
	1-butene	0.44	0.4	0.41	0.44
	1,2-butadiene	0.01	0.01	0.01	0.01
	1,3-butadiene	0.57	0.56	0.56	0.56
	2-methyl-2-propenal	0.09	0.08	0.08	0.09
5	cis-2-pentene	0.12	0.11	0.11	0.12
	cyclopentane	0.37	0.34	0.35	0.37
	cyclopentene	0.2	0.18	0.19	0.2
	isopentane	7.08	7.08	6.6	7.09
5	isoprene	0.15	0.14	0.14	0.15
	isovaleraldehyde	0.04	0.04	0.04	0.04
	methyl t-butyl ether (MTBE)	2.01	0	0	0
	n-pentane	2.86	2.86	2.67	2.86
	trans-2-pentene	0.22	0.2	0.21	0.22
	1-pentene	0.14	0.13	0.13	0.14
	2-methyl-1-butene	0.3	0.28	0.28	0.3
	2-methyl-2-butene	0.43	0.4	0.4	0.43
	3-methyl-1-butene	0.24	0.22	0.22	0.24
6	benzene	2.73	2.4	2.62	2.73
	cis-2-hexene	0.04	0.04	0.04	0.04
	cyclohexane	0.63	0.63	0.59	0.63

CNUM	CHEMNAME	Catalyst Stabilized Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
	cyclohexene	0.09	0.08	0.08	0.09
	c6 aldehydes	0.02	0.02	0.02	0.02
	methylcyclopentane	2.86	2.86	2.67	2.86
	n-hexane	1.64	1.64	1.53	1.64
	trans-2-hexene	0.13	0.12	0.12	0.13
	trans-3-hexene	0.05	0.05	0.05	0.05
	1-hexene	0.05	0.05	0.05	0.05
	2-methyl-1-pentene	0.07	0.06	0.07	0.07
	2-methyl-2-pentene	0.08	0.07	0.07	0.08
	2-methylpentane	3.85	3.85	3.59	3.86
	2,2-dimethylbutane	0.66	0.66	0.62	0.66
	2,3-dimethyl-1-butene	0.01	0.01	0.01	0.01
	2,3-dimethylbutane	1.09	1.09	1.02	1.09
	3-methyl-1-pentene	0.11	0.1	0.1	0.11
	3-methylcyclopentene	0.07	0.06	0.07	0.07
	3-methylpentane	2.26	2.26	2.11	2.26
	4-methyl-trans-2-pentene	0.06	0.05	0.06	0.06
	4-methyl-1-pentene	0.01	0.01	0.01	0.01
7	benzaldehyde	0.17	0.16	0.16	0.17
	cis-2-heptene	0.01	0.01	0.01	0.01
7	ethylcyclopentane	0.15	0.28	0.26	0.15
	methylcyclohexane	0.63	1.16	1.07	0.63
	n-heptane	0.52	0.48	0.48	0.52
	toluene	6.09	5.61	5.68	6.1
	trans-2-heptene	0.01	0.01	0.01	0.01
	trans-3-heptene	0.05	0.05	0.05	0.05
	1-c-3-dimethylcyclopentane	0.24	0.44	0.41	0.24
	1-t-3-dimethylcyclopentane	0.27	0.5	0.46	0.27
	2-methyl-trans-3-hexene	0.04	0.04	0.04	0.04
	2,2,3-trimethylbutane	0.01	0.02	0.02	0.01
	2,3-dimethylpentane	1.49	2.74	2.54	1.49
	2,4-dimethyl-2-pentene	0.02	0.02	0.02	0.02
	2,4-dimethylpentane	0.45	0.83	0.77	0.45
	3-ethylpentane	0.27	0.5	0.46	0.27

CNUM	CHEMNAME	Catalyst Stabilized Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
	3-methyl-cis-2-hexene	0.01	0.01	0.01	0.01
	3-methylhexane	0.79	1.45	1.35	0.79
	3,3-dimethylpentane	0.01	0.02	0.02	0.01
8	c-1-methyl-3-ethylcyclopentane	0.07	0.13	0.12	0.07
	c-1,2-dimethylcyclohexane	0.03	0.05	0.05	0.03
	cis-1,3-dimethylcyclohexane	0.08	0.15	0.14	0.08
	ethylbenzene	1.11	1.02	1.04	1.11
	m-xylene	3.77	3.47	3.52	3.78
	n-octane	0.4	0.37	0.37	0.4
	o-xylene	1.31	1.21	1.22	1.31
	styrene	0.13	0.12	0.12	0.13
	t-1-methyl-3-ethylcyclopentane	0.11	0.2	0.19	0.11
	tolualdehyde	0.23	0.21	0.21	0.23
	trans-1,3-dimethylcyclohexane	0.04	0.07	0.07	0.04
	trans-1,4-dimethylcyclohexane	0.04	0.07	0.07	0.04
	1,2,4-trimethylcyclopentene	0.13	0.24	0.22	0.13
	1c,2t,3-trimethylcyclopentane	0.06	0.11	0.1	0.06
	2-methylheptane	0.35	0.64	0.6	0.35
8	2,2-dimethylhexane	0.07	0.13	0.12	0.07
	2,2,4-trimethylpentane	1.78	3.28	3.03	1.78
	2,3-dimethylhexane	0.25	0.46	0.43	0.25
	2,3,4-trimethylpentane	0.62	1.14	1.06	0.62
	2,4-dimethylhexane	0.28	0.52	0.48	0.28
	2,5-dimethylhexane	0.35	0.64	0.6	0.35
	3-methylheptane	0.62	1.14	1.06	0.62
	4-methylheptane	0.16	0.29	0.27	0.16
9	indan	0.09	0.08	0.08	0.09
	isopropylbenzene (cumene)	0.01	0.01	0.01	0.01
	n-nonane	0.18	0.17	0.17	0.18
	n-propylbenzene	0.24	0.22	0.22	0.24
	1-methyl-2-ethylbenzene	0.29	0.27	0.27	0.29
	1-methyl-3-ethylbenzene	0.84	0.77	0.78	0.84
	1-methyl-4-ethylbenzene	0.35	0.32	0.33	0.35
	1-methyl-4-ethylcyclohexane	0.01	0.02	0.02	0.01

CNUM	CHEMNAME	Catalyst Stabilized Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
	1,2,3-trimethylbenzene	0.18	0.17	0.17	0.18
	1,2,4-trimethylbenzene	1.02	0.94	0.95	1.02
	1,3,5-trimethylbenzene	0.41	0.38	0.38	0.41
	1,3,5-trimethylcyclohexane	0.07	0.13	0.12	0.07
	2-methyloctane	0.01	0.02	0.02	0.01
	2,2,4-trimethylhexane	0.08	0.15	0.14	0.08
	2,2,5-trimethylhexane	0.33	0.61	0.56	0.33
	2,3,5-trimethylhexane	0.02	0.04	0.03	0.02
	2,4-dimethylheptane	0.07	0.13	0.12	0.07
	2,6-dimethylheptane	0.18	0.33	0.31	0.18
	3-methyloctane	0.31	0.57	0.53	0.31
	3,4-dimethylheptane	0.04	0.07	0.07	0.04
	3,5-dimethylheptane	0.15	0.28	0.26	0.15
	4-methyloctane	0.24	0.44	0.41	0.24
10	n-decane	0.16	0.15	0.15	0.16
	naphthalene	0.05	0.05	0.05	0.05
10	1-methyl-2-isopropylbenzene	0.05	0.05	0.05	0.05
	1-methyl-2n-propylbenzene	0.01	0.01	0.01	0.01
	1-methyl-3-isopropylbenzene	0.03	0.03	0.03	0.03
	1-methyl-3n-propylbenzene	0.16	0.15	0.15	0.16
	1,2-dimethyl-3-ethylbenzene	0.01	0.01	0.01	0.01
	1,2-dimethyl-4-ethylbenzene	0.11	0.1	0.1	0.11
	1,2,3,4-tetramethylbenzene	0.02	0.02	0.02	0.02
	1,2,3,5-tetramethylbenzene	0.03	0.03	0.03	0.03
	1,2,4,5-tetramethylbenzene	0.02	0.02	0.02	0.02
	1,3-diethylbenzene (meta)	0.03	0.03	0.03	0.03
	1,3-dimethyl-4-ethylbenzene	0.05	0.05	0.05	0.05
	1,3-dimethyl-5-ethylbenzene	0.12	0.11	0.11	0.12
	1,4-diethylbenzene (para)	0.07	0.06	0.07	0.07
	1,4-dimethyl-2-ethylbenzene	0.05	0.05	0.05	0.05
	2-methylindan	0.02	0.02	0.02	0.02
	2-methylnonane	0.09	0.08	0.08	0.09
	2,2-dimethyloctane	0.01	0.01	0.01	0.01
	2,2,4-trimethylheptane	0.02	0.02	0.02	0.02

CNUM	CHEMNAME	Catalyst Stabilized Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
	2,3-dimethyloctane	0.01	0.01	0.01	0.01
	2,4-dimethyloctane	0.04	0.04	0.04	0.04
	2,5-dimethyloctane	0.04	0.04	0.04	0.04
	2,6-dimethyloctane	0.01	0.01	0.01	0.01
	3,3-dimethyloctane	0.04	0.04	0.04	0.04
	4-methylindan	0.01	0.01	0.01	0.01
	5-methylindan	0.02	0.02	0.02	0.02
11	n-pentylbenzene	0.01	0.01	0.01	0.01
	n-undecane	0.01	0.01	0.01	0.01
	1-methyl-2-n-butylbenzene	0.01	0.01	0.01	0.01
12	n-dodecane	0.01	0.01	0.01	0.01
	t-1-butyl-3,5-dimethylbenzene	0.01	0.01	0.01	0.01
	1,3-dipropylbenzene	0.01	0.01	0.01	0.01
13	2,2,5-triethylheptane	0.06	0.05	0.06	0.06
TOTAL		100	99.99	100	99.99

CNUM	CHEMNAME	Non-Catalyst Start Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
1	formaldehyde	1.460	1.300	1.370	1.340
	methane	6.530	5.940	5.960	6.520
	methyl alcohol	0.840	0.000	0.000	0.190
2	acetaldehyde	0.350	0.330	0.440	0.810
	acetylene	6.730	6.130	6.140	6.720
	ethane	0.740	0.670	0.670	0.740
	ethyl alcohol	0.060	0.000	3.000	5.280
	ethylene	8.060	7.340	7.350	8.040
3	acetone	0.280	0.250	0.250	0.280
	acrolein (2-propenal)	0.130	0.120	0.120	0.130
	propane	0.040	0.040	0.040	0.040
	propionaldehyde	0.070	0.060	0.060	0.070
	propylene	3.110	2.830	2.840	3.100
	1-propyne	0.370	0.340	0.340	0.370
	1,2-propadiene	0.310	0.280	0.280	0.310

CNUM	CHEMNAME	Non-Catalyst Start Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
4	butyraldehyde	0.070	0.060	0.060	0.070
	cis-2-butene	0.210	0.190	0.190	0.210
	crotonaldehyde	0.080	0.070	0.070	0.080
	isobutane	0.010	0.010	0.010	0.010
	isobutene	1.970	0.950	0.950	1.040
	methyl ethyl ketone (MEK)	0.100	0.090	0.090	0.100
	n-butane	0.480	0.440	0.440	0.480
	trans-2-butene	0.200	0.180	0.180	0.200
	vinylacetylene	0.160	0.150	0.150	0.160
	1-butene	0.440	0.400	0.400	0.440
	1,2-butadiene	0.020	0.020	0.020	0.020
	1,3-butadiene	0.780	0.760	0.760	0.770
	1,3-butadiyne	0.020	0.020	0.020	0.020
	2-methyl-2-propenal	0.100	0.090	0.090	0.100
5	cis-2-pentene	0.070	0.060	0.060	0.070
	cyclopentane	0.490	0.450	0.450	0.490
	cyclopentene	0.150	0.140	0.140	0.150
5	isopentane	4.550	4.550	4.150	4.540
	isoprene	0.250	0.230	0.230	0.250
	isovaleraldehyde	0.020	0.020	0.020	0.020
	methyl t-butyl ether (MTBE)	3.800	0.000	0.000	0.000
	n-pentane	1.960	1.960	1.790	1.960
	trans-1,3-pentadiene	0.040	0.040	0.040	0.040
	trans-2-pentene	0.330	0.300	0.300	0.330
	1-pentene	0.080	0.070	0.070	0.080
	2-methyl-1-butene	0.230	0.210	0.210	0.230
	2-methyl-2-butene	0.380	0.350	0.350	0.380
	3-methyl-1-butene	0.250	0.230	0.230	0.250
6	benzene	2.750	2.420	2.640	2.740
	cis-2-hexene	0.030	0.030	0.030	0.030
	cyclohexane	0.770	0.770	0.700	0.770
	cyclohexene	0.030	0.030	0.030	0.030
	c6 aldehydes	0.030	0.030	0.030	0.030
	methylcyclopentane	2.860	2.860	2.610	2.850

CNUM	CHEMNAME	Non-Catalyst Start Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
	n-hexane	1.690	1.690	1.540	1.690
	trans-2-hexene	0.170	0.150	0.150	0.170
	trans-3-hexene	0.040	0.040	0.040	0.040
	1-hexene	0.060	0.050	0.050	0.060
	2-methyl-1-pentene	0.040	0.040	0.040	0.040
	2-methyl-2-pentene	0.040	0.040	0.040	0.040
	2-methylpentane	3.500	3.500	3.190	3.490
	2,2-dimethylbutane	0.470	0.470	0.430	0.470
	2,3-dimethylbutane	0.940	0.940	0.860	0.940
	3-methyl-1-pentene	0.040	0.040	0.040	0.040
	3-methylcyclopentene	0.050	0.050	0.050	0.050
	3-methylpentane	2.160	2.160	1.970	2.160
	4-methyl-trans-2-pentene	0.040	0.040	0.040	0.040
	4-methyl-1-pentene	0.020	0.020	0.020	0.020
7	benzaldehyde	0.260	0.240	0.240	0.260
7	cis-2-heptene	0.020	0.020	0.020	0.020
	ethylcyclopentane	0.300	0.550	0.500	0.300
	methylcyclohexane	0.830	1.510	1.400	0.830
	n-heptane	0.720	0.650	0.660	0.720
	toluene	7.370	6.710	6.720	7.350
	trans-2-heptene	0.020	0.020	0.020	0.020
	trans-3-heptene	0.050	0.050	0.050	0.050
	1-c-3-dimethylcyclopentane	0.380	0.690	0.640	0.380
	1-t-3-dimethylcyclopentane	0.340	0.620	0.570	0.340
	2-methyl-2-hexene	0.020	0.020	0.020	0.020
	2,2,3-trimethylbutane	0.030	0.050	0.050	0.030
	2,3-dimethyl-2-pentene	0.020	0.020	0.020	0.020
	2,3-dimethylpentane	1.650	3.000	2.780	1.650
	2,4-dimethyl-2-pentene	0.020	0.020	0.020	0.020
	2,4-dimethylpentane	0.590	1.070	0.990	0.590
	3-ethylpentane	0.400	0.730	0.670	0.400
	3-methyl-cis-2-hexene	0.020	0.020	0.020	0.020
	3-methyl-trans-3-hexene	0.010	0.010	0.010	0.010
	3-methylhexane	0.950	1.730	1.600	0.950

CNUM	CHEMNAME	Non-Catalyst Start Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
	3,4-dimethyl-1-pentene	0.020	0.020	0.020	0.020
	4-methyl-trans-2-hexene	0.010	0.010	0.010	0.010
8	c-1-methyl-3-ethylcyclopentane	0.070	0.130	0.120	0.070
	c-1,2-dimethylcyclohexane	0.050	0.090	0.080	0.050
	cis-1,3-dimethylcyclohexane	0.180	0.330	0.300	0.180
	ethylbenzene	1.390	1.260	1.270	1.390
	m-xylene	4.750	4.320	4.330	4.740
	n-octane	0.480	0.440	0.440	0.480
	o-xylene	1.620	1.470	1.480	1.620
	styrene	0.140	0.130	0.130	0.140
	t-1-methyl-3-ethylcyclopentane	0.150	0.270	0.250	0.150
	tolualdehyde	0.260	0.240	0.240	0.260
	trans-1,3-dimethylcyclohexane	0.040	0.070	0.070	0.040
8	trans-1,4-dimethylcyclohexane	0.150	0.270	0.250	0.150
	trans-2-octene	0.010	0.010	0.010	0.010
	unidentified	1.630	1.480	1.490	1.630
	1-octene	0.010	0.010	0.010	0.010
	1,2,4-trimethylcyclopentene	0.290	0.530	0.490	0.290
	1c,2t,3-trimethylcyclopentane	0.050	0.090	0.080	0.050
	2-methylheptane	0.470	0.860	0.790	0.470
	2,2-dimethylhexane	0.050	0.090	0.080	0.050
	2,2,4-trimethylpentane	1.580	2.880	2.660	1.580
	2,3-dimethylhexane	0.420	0.760	0.710	0.420
	2,3,4-trimethylpentane	0.680	1.240	1.140	0.680
	2,4-dimethylhexane	0.430	0.780	0.720	0.430
	2,5-dimethylhexane	0.460	0.840	0.770	0.460
	3-methylheptane	0.700	1.270	1.180	0.700
	3,3-dimethylhexane	0.010	0.020	0.020	0.010
	4-methylheptane	0.340	0.620	0.570	0.340
9	indan	0.060	0.050	0.050	0.060
	isopropylbenzene (cumene)	0.030	0.030	0.030	0.030
	n-nonane	0.270	0.250	0.250	0.270
	n-propylbenzene	0.340	0.310	0.310	0.340
	1-methyl-2-ethylbenzene	0.290	0.260	0.260	0.290

CNUM	CHEMNAME	Non-Catalyst Start Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
	1-methyl-3-ethylbenzene	0.950	0.860	0.870	0.950
	1-methyl-4-ethylbenzene	0.400	0.360	0.360	0.400
	1-methyl-4-ethylcyclohexane	0.030	0.050	0.050	0.030
	1-nonene	0.020	0.020	0.020	0.020
	1,2,3-trimethylbenzene	0.220	0.200	0.200	0.220
	1,2,4-trimethylbenzene	1.100	1.000	1.000	1.100
	1,3,5-trimethylbenzene	0.480	0.440	0.440	0.480
	1,3,5-trimethylcyclohexane	0.070	0.130	0.120	0.070
	2-methyloctane	0.080	0.150	0.130	0.080
	2,2,4-trimethylhexane	0.060	0.110	0.100	0.060
	2,2,5-trimethylhexane	0.300	0.550	0.500	0.300
9	2,3-dimethylheptane	0.010	0.020	0.020	0.010
	2,3,5-trimethylhexane	0.030	0.050	0.050	0.030
	2,4-dimethylheptane	0.040	0.070	0.070	0.040
	2,4,4-trimethylhexane	0.010	0.020	0.020	0.010
	2,6-dimethylheptane	0.320	0.580	0.540	0.320
	3-methyloctane	0.570	1.040	0.960	0.570
	3,4-dimethylheptane	0.050	0.090	0.080	0.050
	3,5-dimethylheptane	0.210	0.380	0.350	0.210
	4-methyloctane	0.290	0.530	0.490	0.290
10	isobutylbenzene	0.010	0.010	0.010	0.010
	n-decane	0.060	0.050	0.050	0.060
	naphthalene	0.020	0.020	0.020	0.020
	1-methyl-2-isopropylbenzene	0.050	0.050	0.050	0.050
	1-methyl-2n-propylbenzene	0.020	0.020	0.020	0.020
	1-methyl-3-isopropylbenzene	0.050	0.050	0.050	0.050
	1-methyl-3n-propylbenzene	0.140	0.130	0.130	0.140
	1-methyl-4-isopropylbenzene	0.010	0.010	0.010	0.010
	1,2-dimethyl-3-ethylbenzene	0.010	0.010	0.010	0.010
	1,2-dimethyl-4-ethylbenzene	0.070	0.060	0.060	0.070
	1,2,3,4-tetramethylbenzene	0.020	0.020	0.020	0.020
	1,2,3,5-tetramethylbenzene	0.030	0.030	0.030	0.030
	1,2,4,5-tetramethylbenzene	0.020	0.020	0.020	0.020
	1,3-diethylbenzene (meta)	0.030	0.030	0.030	0.030

CNUM	CHEMNAME	Non-Catalyst Start Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
	1,3-dimethyl-2-ethylbenzene	0.010	0.010	0.010	0.010
	1,3-dimethyl-4-ethylbenzene	0.050	0.050	0.050	0.050
	1,3-dimethyl-5-ethylbenzene	0.070	0.060	0.060	0.070
	1,4-diethylbenzene (para)	0.050	0.050	0.050	0.050
	1,4-dimethyl-2-ethylbenzene	0.050	0.050	0.050	0.050
	2-methylindan	0.020	0.020	0.020	0.020
	2-methylnonane	0.120	0.110	0.110	0.120
	2,2-dimethyloctane	0.010	0.010	0.010	0.010
	2,2,4-trimethylheptane	0.040	0.040	0.040	0.040
10	2,3-dimethyloctane	0.040	0.040	0.040	0.040
	2,4-dimethyloctane	0.020	0.020	0.020	0.020
	2,5-dimethyloctane	0.030	0.030	0.030	0.030
	2,6-dimethyloctane	0.040	0.040	0.040	0.040
	3,3-dimethyloctane	0.040	0.040	0.040	0.040
	5-methylindan	0.020	0.020	0.020	0.020
11	n-pentylbenzene	0.010	0.010	0.010	0.010
	n-undecane	0.010	0.010	0.010	0.010
	1-ethyl-2n-propylbenzene	0.010	0.010	0.010	0.010
	1-methyl-2-n-butylbenzene	0.010	0.010	0.010	0.010
12	t-1-butyl-3,5-dimethylbenzene	0.010	0.010	0.010	0.010
13	2,2,5-triethylheptane	0.080	0.070	0.070	0.080
0					
TOTAL		100.000	99.990	99.990	100.000

CNUM	CHEMNAME	Non-Catalyst Stabilized Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
1	formaldehyde	3.12	2.78	2.93	2.88
	methane	5.58	5.16	5.19	5.59
	methyl alcohol	0.7	0	0	0.34
2	acetaldehyde	0.75	0.71	0.95	1.74
	acetylene	2.34	2.16	2.18	2.35
	ethane	1.77	1.64	1.65	1.77
	ethyl alcohol	0.01	0	1.86	3.24

CNUM	CHEMNAME	Non-Catalyst Stabilized Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
	ethylene	8.94	8.27	8.32	8.96
3	acetone	0.46	0.42	0.43	0.46
	acrolein (2-propenal)	0.18	0.17	0.17	0.18
	propane	0.09	0.08	0.08	0.09
	propionaldehyde	0.13	0.12	0.12	0.13
	propylene	4.9	4.53	4.56	4.91
	1-propyne	0.43	0.4	0.4	0.43
	1,2-propadiene	0.33	0.3	0.31	0.33
4	butyraldehyde	0.05	0.05	0.05	0.05
	cis-2-butene	0.25	0.23	0.23	0.25
	crotonaldehyde	0.13	0.12	0.12	0.13
	isobutane	0.02	0.02	0.02	0.02
	isobutene	3.95	1.94	1.95	2.1
	methyl ethyl ketone (MEK)	0.06	0.05	0.06	0.06
	n-butane	0.75	0.69	0.7	0.6
	trans-2-butene	0.35	0.32	0.33	0.35
	vinylacetylene	0.12	0.11	0.11	0.12
	1-butene	0.66	0.61	0.61	0.66
	1,2-butadiene	0.05	0.05	0.05	0.05
	1,3-butadiene	0.83	0.81	0.81	0.82
	1,3-butadiyne	0.01	0.01	0.01	0.01
	2-butyne	0.01	0.01	0.01	0.01
	2-methyl-2-propenal	0.2	0.18	0.19	0.2
5	cis-2-pentene	0.11	0.1	0.1	0.11
	cyclopentane	0.28	0.26	0.26	0.28
5	cyclopentene	0.18	0.17	0.17	0.18
	isopentane	6.56	6.56	6.11	6.58
	isoprene	0.14	0.13	0.13	0.14
	isovaleraldehyde	0.08	0.07	0.07	0.08
	methyl t-butyl ether (MTBE)	1.86	0	0	0
	n-pentane	2.19	2.19	2.04	2.2
	trans-1,3-pentadiene	0.03	0.03	0.03	0.03
	trans-2-pentene	0.19	0.18	0.18	0.19
	1-pentene	0.14	0.13	0.13	0.14

CNUM	CHEMNAME	Non-Catalyst Stabilized Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
	2-methyl-1-butene	0.32	0.3	0.3	0.32
	2-methyl-2-butene	0.39	0.36	0.36	0.39
	3-methyl-1-butene	0.25	0.23	0.23	0.25
6	benzene	3.44	3.03	3.3	3.45
	cis-2-hexene	0.04	0.04	0.04	0.04
	cyclohexane	0.45	0.45	0.42	0.45
	cyclohexene	0.07	0.06	0.06	0.07
	c6 aldehydes	0.06	0.05	0.06	0.06
	methylcyclopentane	2.2	2.2	2.05	2.21
	n-hexane	1.31	1.31	1.22	1.31
	trans-2-hexene	0.13	0.12	0.12	0.13
	trans-3-hexene	0.05	0.05	0.05	0.05
	1-hexene	0.08	0.07	0.07	0.08
	2-methyl-1-pentene	0.06	0.05	0.06	0.06
	2-methyl-2-pentene	0.07	0.06	0.06	0.07
	2-methylpentane	3.21	3.21	2.99	3.22
	2,2-dimethylbutane	0.51	0.51	0.47	0.51
	2,3-dimethyl-1-butene	0.02	0.02	0.02	0.02
	2,3-dimethylbutane	0.98	0.98	0.91	0.98
	3-methyl-trans-2-pentene	0.02	0.02	0.02	0.02
	3-methyl-1-pentene	0.1	0.09	0.09	0.1
	3-methylcyclopentene	0.07	0.06	0.06	0.07
	3-methylpentane	1.93	1.93	1.8	1.93
6	3,3-dimethyl-1-butene	0.01	0.01	0.01	0.01
	4-methyl-trans-2-pentene	0.06	0.05	0.06	0.06
	4-methyl-1-pentene	0.07	0.06	0.06	0.07
7	benzaldehyde	0.61	0.56	0.57	0.61
	cis-2-heptene	0.03	0.03	0.03	0.03
	ethylcyclopentane	0.13	0.24	0.22	0.13
	methylcyclohexane	0.5	0.92	0.85	0.5
	n-heptane	0.49	0.45	0.46	0.49
	toluene	6.79	6.28	6.32	6.81
	trans-2-heptene	0.03	0.03	0.03	0.03
	trans-3-heptene	0.04	0.04	0.04	0.04

CNUM	CHEMNAME	Non-Catalyst Stabilized Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
	1-c-3-dimethylcyclopentane	0.2	0.37	0.34	0.2
	1-t-3-dimethylcyclopentane	0.23	0.42	0.39	0.23
	2-methyl-trans-3-hexene	0.05	0.05	0.05	0.05
	2-methyl-2-hexene	0.02	0.02	0.02	0.02
	2,2,3-trimethylbutane	0.03	0.05	0.05	0.03
	2,3-dimethyl-2-pentene	0.01	0.01	0.01	0.01
	2,3-dimethylpentane	1.69	3.13	2.89	1.69
	2,4-dimethyl-1-pentene	0.01	0.01	0.01	0.01
	2,4-dimethyl-2-pentene	0.06	0.05	0.06	0.06
	2,4-dimethylpentane	0.53	0.98	0.91	0.53
	3-ethylpentane	0.24	0.44	0.41	0.24
	3-methyl-cis-2-hexene	0.03	0.03	0.03	0.03
	3-methyl-trans-3-hexene	0.01	0.01	0.01	0.01
	3-methylhexane	0.76	1.4	1.3	0.76
	3,3-dimethylpentane	0.02	0.04	0.03	0.02
	4-methyl-trans-2-hexene	0.01	0.01	0.01	0.01
8	c-1-methyl-3-ethylcyclopentane	0.07	0.13	0.12	0.07
	c-1,2-dimethylcyclohexane	0.01	0.02	0.02	0.01
	cis-1,3-dimethylcyclohexane	0.05	0.09	0.09	0.05
	cis-2-octene	0.01	0.01	0.01	0.01
	ethylbenzene	1.5	1.39	1.4	1.5
8	ethylcyclohexane	0.02	0.04	0.03	0.02
	m-xylene	4.45	4.11	4.14	4.46
	n-octane	0.35	0.32	0.33	0.35
	o-xylene	1.55	1.43	1.44	1.55
	styrene	0.13	0.12	0.12	0.13
	t-1-methyl-3-ethylcyclopentane	0.09	0.17	0.15	0.09
	tolualdehyde	0.6	0.55	0.56	0.6
	trans-1,3-dimethylcyclohexane	0.05	0.09	0.09	0.05
	trans-1,4-dimethylcyclohexane	0.05	0.09	0.09	0.05
	1,2,4-trimethylcyclopentene	0.11	0.2	0.19	0.11
	1c,2t,3-trimethylcyclopentane	0.07	0.13	0.12	0.07
	2-methylheptane	0.33	0.61	0.56	0.33
	2,2-dimethylhexane	0.08	0.15	0.14	0.08

CNUM	CHEMNAME	Non-Catalyst Stabilized Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
	2,2,4-trimethylpentane	1.99	3.68	3.4	1.99
	2,3-dimethylhexane	0.28	0.52	0.48	0.28
	2,3,4-trimethylpentane	0.63	1.16	1.08	0.63
	2,4-dimethylhexane	0.29	0.54	0.5	0.29
	2,5-dimethylhexane	0.33	0.61	0.56	0.33
	3-methylheptane	0.53	0.98	0.91	0.53
	3,3-dimethylhexane	0.01	0.02	0.02	0.01
	4-methylheptane	0.18	0.33	0.31	0.18
9	indan	0.12	0.11	0.11	0.12
	isopropylbenzene (cumene)	0.05	0.05	0.05	0.05
	n-nonane	0.18	0.17	0.17	0.18
	n-propylbenzene	0.28	0.26	0.26	0.28
	1-methyl-2-ethylbenzene	0.37	0.34	0.34	0.37
	1-methyl-3-ethylbenzene	1.07	0.99	1	1.07
	1-methyl-4-ethylbenzene	0.46	0.42	0.43	0.46
	1-methyl-4-ethylcyclohexane	0.04	0.07	0.07	0.04
	1-nonene	0.02	0.02	0.02	0.02
	1,2,3-trimethylbenzene	0.23	0.21	0.21	0.23
	1,2,4-trimethylbenzene	1.26	1.16	1.17	1.26
9	1,3,5-trimethylbenzene	0.5	0.46	0.46	0.5
	1,3,5-trimethylcyclohexane	0.08	0.15	0.14	0.08
	2-methyloctane	0.06	0.11	0.1	0.06
	2,2,4-trimethylhexane	0.08	0.15	0.14	0.08
	2,2,5-trimethylhexane	0.35	0.65	0.6	0.35
	2,3-dimethylheptane	0.01	0.02	0.02	0.01
	2,3,5-trimethylhexane	0.05	0.09	0.09	0.05
	2,4-dimethylheptane	0.08	0.15	0.14	0.08
	2,4,4-trimethylhexane	0.01	0.02	0.02	0.01
	2,6-dimethylheptane	0.16	0.3	0.27	0.16
	3-methyloctane	0.44	0.81	0.75	0.44
	3,4-dimethylheptane	0.05	0.09	0.09	0.05
	3,5-dimethylheptane	0.13	0.24	0.22	0.13
	4-methyloctane	0.18	0.33	0.31	0.18
10	isobutylbenzene	0.01	0.01	0.01	0.01

CNUM	CHEMNAME	Non-Catalyst Stabilized Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
	n-decane	0.1	0.09	0.09	0.1
	naphthalene	0.13	0.12	0.12	0.13
	1-methyl-2-isopropylbenzene	0.1	0.09	0.09	0.1
	1-methyl-2n-propylbenzene	0.05	0.05	0.05	0.05
	1-methyl-3-isopropylbenzene	0.01	0.01	0.01	0.01
	1-methyl-3n-propylbenzene	0.28	0.26	0.26	0.28
	1-methyl-4-isopropylbenzene	0.01	0.01	0.01	0.01
	1,2-diethylbenzene (ortho)	0.01	0.01	0.01	0.01
	1,2-dimethyl-3-ethylbenzene	0.04	0.04	0.04	0.04
	1,2-dimethyl-4-ethylbenzene	0.17	0.16	0.16	0.17
	1,2,3,4-tetramethylbenzene	0.05	0.05	0.05	0.05
	1,2,3,5-tetramethylbenzene	0.08	0.07	0.07	0.08
	1,2,4,5-tetramethylbenzene	0.06	0.05	0.06	0.06
	1,3-diethylbenzene (meta)	0.1	0.09	0.09	0.1
	1,3-dimethyl-2-ethylbenzene	0.02	0.02	0.02	0.02
	1,3-dimethyl-4-ethylbenzene	0.12	0.11	0.11	0.12
	1,3-dimethyl-5-ethylbenzene	0.17	0.16	0.16	0.17
10	1,4-diethylbenzene (para)	0.12	0.11	0.11	0.12
	1,4-dimethyl-2-ethylbenzene	0.11	0.1	0.1	0.11
	2-methylindan	0.08	0.07	0.07	0.08
	2-methylnonane	0.14	0.13	0.13	0.14
	2,2-dimethyloctane	0.02	0.02	0.02	0.02
	2,2,4-trimethylheptane	0.06	0.05	0.06	0.06
	2,3-dimethyloctane	0.04	0.04	0.04	0.04
	2,4-dimethyloctane	0.05	0.05	0.05	0.05
	2,5-dimethyloctane	0.03	0.03	0.03	0.03
	2,6-dimethyloctane	0.06	0.05	0.06	0.06
	3,3-dimethyloctane	0.05	0.05	0.05	0.05
	4-methylindan	0.02	0.02	0.02	0.02
	5-methylindan	0.07	0.06	0.06	0.07
11	n-pentylbenzene	0.03	0.03	0.03	0.03
	n-undecane	0.04	0.04	0.04	0.04
	1-ethyl-2n-propylbenzene	0.01	0.01	0.01	0.01
	1-methyl-2-n-butylbenzene	0.02	0.02	0.02	0.02

CNUM	CHEMNAME	Non-Catalyst Stabilized Exhaust			
		MTBE	Non-Oxy	EtOH 2%	EtOH 3.5%
12	n-dodecane	0.01	0.01	0.01	0.01
	t-1-butyl-3,5-dimethylbenzene	0.02	0.02	0.02	0.02
	1,3-dipropylbenzene	0.03	0.03	0.03	0.03
13	2,2,5-triethylheptane	0.11	0.1	0.1	0.11
0					
TOTAL		100	99.98	100	99.98

Attachment A3

Tables of Organic Gas Profiles From Emission Testing

List of Tables

Table 1 Liquid Gasoline Organic Gas Species Test Results

(MTBE, Weight Percent)

NAME	BARREL1
propane	0.01
butanes	1.14
pentanes	12.82
c6+ br-alkanes	37.83
c6+ n-alkanes	5.26
propene	0.00
c4+ alkenes	2.69
benzene	0.78
toluene	5.41
c8+ aromatics	19.88
MTBE	10.90
ethanol	0.00
isoprene	0.01
unidentified	3.29
Sum	100.00
MIR	2.42

Note: MIR means Maximum Incremental Reactivity (g ozone/g NMOG).

Table 2 Liquid Gasoline Organic Gas Species Test Results

(NonOxy, Weight Percent)

NAME	BARREL1	BARREL2	BARREL3	BARREL4	BARREL5	MEAN	COV
propane	0.00	0.00	0.00	0.00	0.00	0.00	n/a
butanes	0.98	0.95	0.89	0.89	1.02	0.94	6%
pentanes	15.18	14.51	15.61	15.61	15.52	15.29	3%
c6+ br-alkanes	47.15	45.37	44.60	44.59	45.80	45.50	2%
c6+ n-alkanes	4.28	4.24	4.17	4.17	4.28	4.23	1%
propene		0.00			0.00	0.00	20%
c4+ alkenes	2.75	2.76	2.69	2.70	2.83	2.75	2%
benzene	0.26	0.26	0.25	0.25	0.27	0.26	2%
toluene	8.60	8.48	8.65	8.64	8.44	8.56	1%
c8+ aromatics	18.13	20.67	20.65	20.69	19.56	19.94	6%
MTBE	0.07	0.07	0.06	0.06	0.05	0.06	11%
ethanol							
isoprene	0.00	0.00	0.00	0.00	0.00	0.00	8%
unidentified	2.63	2.69	2.47	2.43	2.25	2.49	7%
sum	100.03	100.00	100.04	100.04	100.01	100.03	
MIR	2.40	2.59	2.60	2.61	2.55	2.55	3%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).

Table 3 Liquid Gasoline Organic Gas Species Test Results

(Et2.0%, Weight Percent)

NAME	BARREL1	BARREL2	BARREL3	BARREL4	BARREL5	MEAN	COV
propane	0.00		0.00		0.00	0.00	7%
butanes	0.40	0.41	0.40	0.40	0.42	0.41	2%
pentanes	11.12	11.38	11.11	11.17	11.52	11.26	2%
c6+ br-alkanes	44.99	45.82	47.28	47.27	46.01	46.27	2%
c6+ n-alkanes	3.77	3.79	3.78	3.79	3.76	3.78	0%
propene		0.00		0.00		0.00	0%
c4+ alkenes	0.52	0.51	0.57	0.57	0.44	0.52	10%
benzene	0.56	0.57	0.57	0.56	0.58	0.57	1%
toluene	6.16	6.17	6.16	6.28	6.08	6.17	1%
c8+ aromatics	21.58	22.74	21.16	21.52	22.40	21.88	3%
MTBE	0.10	0.10	0.10	0.10	0.10	0.10	1%
ethanol	6.30	6.50	6.38	5.85	6.69	6.34	5%
isoprene		0.00	0.00	0.00		0.00	0%
unidentified	4.51	2.08	2.56	2.55	2.05	2.75	37%
Sum	100.00	100.06	100.07	100.07	100.04	100.05	
MIR	2.44	2.61	2.45	2.47	2.59	2.51	3%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).

Table 4 Liquid Gasoline Organic Gas Species Test Results

(MTBE, Weight Percent)

CNUM	CHEMNAME	BARREL1
2	ethane	0.00
2	ethylene	0.00
3	propane	0.01
3	propylene	0.00
4	1,3-butadiene	0.00
4	1-butene	0.03
4	cis-2-butene	0.05
4	isobutane	0.23
4	isobutylene	0.02
4	n-butane	0.91
4	trans-2-butene	0.05
5	1,3-cyclopentadiene	0.01
5	1-pentene	0.05
5	2,2-dimethylpropane	0.01
5	2-methyl-1-butene	0.09
5	2-methyl-2-butene	0.21
5	3-methyl-1-butene	0.01
5	cis-2-pentene	0.08
5	cyclopentadiene	0.00
5	cyclopentane	0.55
5	cyclopentene	0.03
5	isopentane	8.10
5	isoprene	0.01
5	methyl t-butyl ether (MTBE)	10.90
5	n-pentane	4.16
5	trans-1,3-pentadiene	0.01
5	trans-2-pentene	0.14

6	1,5-hexadiene	0.00
6	1-hexene	0.03
6	1-methylcyclopentene	0.12
6	2,2-dimethylbutane	0.09
6	2,3-dimethylbutane	1.04
6	2-methyl-1-pentene	0.04
6	2-methyl-2-pentene	0.10
6	2-methylpentane	4.11
6	3,3-dimethyl-1-butene	0.00
6	3-methyl-1-pentene	0.01
6	3-methyl-cis-2-pentene	0.05
6	3-methyl-trans-2-pentene	0.00
6	3-methylcyclopentene	0.01
6	3-methylpentane	2.56
6	4-methyl-1-pentene	0.01
6	4-methyl-trans-2-pentene	0.03
6	benzene	0.78
6	cis-2-hexene	0.04
6	cis-3-hexene	0.01
6	cyclohexane	1.17
6	methylcyclopentane	3.15
6	n-hexane	2.63
6	trans-2-hexene	0.07
6	trans-3-hexene	0.04
7	1-heptene	0.02
7	1-t-2-dimethylcyclopentane	0.96
7	1-t-3-dimethylcyclopentane	0.88
7	2,2,3-trimethylbutane	0.04
7	2,2-dimethylpentane	0.06
7	2,3-dimethylpentane	1.57
7	2,4-dimethyl-1-pentene	0.01
7	2,4-dimethylpentane	0.96
7	2-ethyl-3-methyl-1-butene	0.01
7	2-methyl-cis-3-hexene	0.01
7	2-methyl-trans-3-hexene	0.02
7	2-methylhexane	1.91
7	3,3-dimethyl-1-pentene	0.08
7	3,3-dimethylpentane	0.06
7	3,4-dimethyl-1-pentene	0.01
7	3,4-dimethyl-2-pentene	0.02
7	3-ethyl-2-pentene	0.03
7	3-ethylcyclopentene	0.00
7	3-ethylpentane	0.20
7	3-methyl-1-hexene	0.01
7	3-methyl-cis-2-hexene	0.13
7	3-methyl-cis-3-hexene	0.03
7	3-methyl-trans-2-hexene	0.13
7	3-methyl-trans-3-hexene	0.05
7	3-methylhexane	2.11

7	4,4-dimethyl-c-pentene-2	0.01
7	4-methyl-1-hexene	0.02
7	4-methyl-trans-2-hexene	0.04
7	cis-2-heptene	0.06
7	dimethylcyclopentane	0.14
7	ethylcyclopentane	0.35
7	methylcyclohexane	2.15
7	n-heptane	1.40
7	toluene	5.41
7	trans-2-heptene	0.06
7	trans-3-heptene	0.14
8	1,1,2-trimethylcyclopentane	0.02
8	1,1-dimethylcyclohexane	0.02
8	1,1-methylethylcyclopentane	0.01
8	1,3-octadiene	0.01
8	1c,2c,3-trimethylcyclopentan	0.04
8	1c,2c,4-trimethylcyclopentan	0.05
8	1c,2t,3-trimethylcyclopentan	0.34
8	1c,2t,4-trimethylcyclopentan	0.24
8	1t,2c,3-trimethylcyclopentan	0.19
8	2,2,3-trimethylpentane	0.11
8	2,2,4-trimethylpentane	2.33
8	2,2-dimethylhexane	0.19
8	2,3,3-trimethylpentane	0.99
8	2,3,4-trimethylpentane	1.05
8	2,3-dimethylhexane	0.46
8	2,4-dimethylhexane	0.53
8	2,5-dimethylhexane	0.48
8	2-methylheptane	0.71
8	3,3-dimethylhexane	0.04
8	3,4-dimethylhexane	0.07
8	3-ethylhexane	0.09
8	3-methyl-3-ethylpentane	0.06
8	3-methylheptane	0.67
8	3t-ethylmethylcyclopentane	0.14
8	4-methylheptane	0.27
8	unidentified	2.53
8	c-1-methyl-3-ethylcyclopenta	0.99
8	cis-1,3-dimethylcyclohexane	0.06
8	cis-1,4-dimethylcyclohexane	0.10
8	cis-2-octene	0.02
8	ethylbenzene	1.37
8	m-xylene	3.96
8	n-octane	0.70
8	n-propylcyclopentane	0.02
8	o-xylene	1.98
8	p-xylene	1.68
8	propylcyclopentane	0.08
8	t-1,2-dimethylcyclohexane	0.13

8	t-2-ethylmethylcyclopentane	0.12
8	trans-1,3-dimethylcyclohexan	0.09
8	trans-1,4-dimethylcyclohexan	0.11
8	trans-2-octene	0.04
8	trans-4-octene	0.04
8	unidentified	0.74
9	1,1,2-trimethylcyclohexane	0.03
9	1,1,3-trimethylcyclohexane	0.04
9	1,1,4-trimethylcyclohexane	0.18
9	1,2,3-trimethylbenzene	0.42
9	1,2,4-trimethylbenzene	2.31
9	1,3,5-trimethylbenzene	0.81
9	1-methyl-2-ethylbenzene	0.63
9	1-methyl-3-ethylbenzene	1.50
9	1-methyl-4-ethylbenzene	0.64
9	1c,2t,4c-trimethylcyclohexane	0.03
9	2,2,3,trimethylhexane	0.12
9	2,2,4-trimethylhexane	0.02
9	2,2,5-trimethylhexane	0.45
9	2,2-dimethylheptane	0.01
9	2,3,4-trimethylhexane	0.09
9	2,3-dimethylheptane	0.12
9	2,4-dimethylheptane	0.02
9	2,5-dimethylheptane	0.21
9	2,6-dimethylheptane	0.05
9	2-methyloctane	0.25
9	3,3-dimethylheptane	0.08
9	3,4-dimethylheptane	0.07
9	3-ethylheptane	0.08
9	3-methyloctane	0.30
9	4,4-dimethylheptane	0.14
9	4-ethylheptane	0.01
9	4-methyloctane	0.20
9	c-1,c-3,5-trimethylcyclohexa	0.09
9	c1,t2,c4-trimethylcyclohexan	0.03
9	ethylmethylcyclohexane	0.17
9	i-butylcyclopentane	0.03
9	indene	0.30
9	isopropylbenzene (cumene)	0.08
9	n-butylcyclopentane	0.03
9	n-nonane	0.29
9	n-propylbenzene	0.35
9	propylcyclohexane	0.02
9	trans-2-nonene	0.02
10	1,2,3,5-tetramethylbenzene	0.22
10	1,2,4,5-tetramethylbenzene	0.16
10	1,2-diethylbenzene (ortho)	0.03
10	1,2-dimethyl-3-ethylbenzene	0.09
10	1,2-dimethyl-4-ethylbenzene	0.42
10	1,2-methyl-n-propylbenzene	0.11
10	1,3-diethylbenzene (meta)	0.14
10	1,3-dimethyl-2-ethylbenzene	0.02
10	1,3-dimethyl-4-ethylbenzene	0.27

10	1,3-dimethyl-5-ethylbenzene	0.32
10	1,4-dimethyl-2-ethylbenzene	0.19
10	1-methyl-2-isopropylbenzene	0.04
10	1-methyl-2n-propylbenzene	0.07
10	1-methyl-3-isopropylbenzene	0.06
10	1-methyl-3n-propylbenzene	0.34
10	1-methyl-4-isopropylbenzene	0.02
10	1-methyl-4n-propylbenzene	0.18
10	2,2-dimethyloctane	0.05
10	2,4-dimethyloctane	0.02
10	2,5-dimethyloctane	0.07
10	2,6-dimethyloctane	0.06
10	2-methylindan	0.18
10	2-methylnonane	0.11
10	3,3-dimethyloctane	0.12
10	3,6-dimethyloctane	0.03
10	3-ethyloctane	0.03
10	3-methyl-5-ethylheptane	0.03
10	3-methylnonane	0.11
10	4-methylindan	0.04
10	5-methylindan	0.19
10	5-methylnonane	0.05
10	butylcyclohexane	0.02
10	dihydronaphthalene	0.01
10	isobutylbenzene	0.04
10	n-butylbenzene	0.10
10	n-decane	0.13
10	naphthalene	0.21
10	sec-butylbenzene	0.06
10	t-decahydronaphthalene	0.01
11	1-ethyl-2-isopropylbenzene	0.02
11	1-methyl-2-n-butylbenzene	0.01
11	1-methyl-2-t-butylbenzene	0.04
11	1-methyl-4-t-butylbenzene	0.03
11	1-methylnaphthalene	0.08
11	1-undecene	0.01
11	2-methylnaphthalene	0.16
11	3-ethylnonane	0.00
11	n-pentylbenzene	0.04
11	n-undecane	0.05
11	pentamethylbenzene	0.04
11	s-pentylbenzene	0.06
12	1,2,4-triethylbenzene	0.01
12	1,2-isodipropylbenzene	0.03
12	1,3-dipropylbenzene	0.04
12	1,3-isodipropylbenzene	0.06
12	1,4-di-i-propylbenzene	0.04
12	1-methyl-4-n-pentylbenzene	0.04
12	n-dodecane	0.01
12	n-hexylbenzene	0.01
13	n-tridecane	0.00
	sum	100.00
	MIR	2.42

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).

Table 5 Liquid Gasoline Organic Gas Species Test Results (NonOxy, Weight Percent)

CNUM	CHEMNAME	BARREL1	BARREL2	BARREL3	BARREL4	BARREL5	MEAN	COV
3	propylene		0.00			0.00	0.00	20%
4	1-butene	0.00	0.00			0.00	0.00	9%
4	cis-2-butene	0.00	0.00	0.00	0.00	0.00	0.00	6%
4	isobutane	0.06	0.06	0.06	0.06	0.07	0.06	6%
4	isobutylene	0.00	0.00			0.00	0.00	9%
4	n-butane	0.91	0.89	0.83	0.83	0.95	0.88	6%
4	trans-2-butene	0.00	0.00	0.00	0.00	0.00	0.00	13%
5	1,3-cyclopentadiene	0.01	0.01	0.01	0.01	0.01	0.01	4%
5	1-pentene	0.02	0.02	0.02	0.02	0.02	0.02	4%
5	2,2-dimethylpropane	0.01	0.01	0.01	0.01	0.01	0.01	5%
5	2-methyl-1-butene	0.06	0.06	0.06	0.06	0.06	0.06	5%
5	2-methyl-2-butene	0.21	0.20	0.20	0.20	0.22	0.21	4%
5	3-methyl-1-butene	0.00	0.00	0.00	0.00	0.00	0.00	6%
5	cis-2-pentene	0.06	0.06	0.06	0.05	0.06	0.06	4%
5	cyclopentadiene	0.00	0.00	0.00	0.00	0.00	0.00	8%
5	cyclopentane	0.64	0.62	0.61	0.61	0.66	0.63	4%
5	cyclopentene	0.03	0.03	0.03	0.03	0.03	0.03	4%
5	isopentane	10.18	9.67	10.92	10.92	10.40	10.42	5%
5	isoprene	0.00	0.00	0.00	0.00	0.00	0.00	8%
5	methyl t-butyl ether (MTBE)	0.07	0.07	0.06	0.06	0.05	0.06	11%
5	n-pentane	4.35	4.21	4.07	4.07	4.46	4.23	4%
5	trans-1,3-pentadiene	0.00	0.00	0.00	0.00	0.00	0.00	4%
5	trans-2-pentene	0.10	0.09	0.09	0.09	0.10	0.09	4%
6	1,4-hexadiene	0.00	0.00				0.00	16%
6	1,5-hexadiene	0.00	0.00	0.00	0.00	0.00	0.00	11%
6	1-hexene	0.05	0.05	0.05	0.05	0.05	0.05	3%
6	1-methylcyclopentene	0.14	0.13	0.13	0.13	0.14	0.13	2%
6	2,2-dimethylbutane	3.32	3.22	3.14	3.14	3.38	3.24	3%
6	2,3-dimethylbutane	2.54	2.47	2.42	2.42	2.58	2.48	3%
6	2-methyl-1-pentene	0.11	0.11	0.11	0.11	0.11	0.11	2%
6	2-methyl-2-pentene	0.21	0.21	0.21	0.21	0.22	0.21	3%
6	2-methylpentane	6.26	6.10	6.01	6.00	6.34	6.14	2%
6	3,3-dimethyl-1-butene	0.00	0.00	0.00	0.00	0.00	0.00	6%
6	3-methyl-1-pentene	0.03	0.03	0.03	0.03	0.03	0.03	2%
6	3-methyl-cis-2-pentene	0.11	0.11	0.11	0.11	0.12	0.11	2%
6	3-methyl-trans-2-pentene	0.00	0.00	0.00	0.00	0.00	0.00	6%
6	3-methylcyclopentene	0.02	0.02	0.02	0.02	0.02	0.02	6%
6	3-methylpentane	0.02				0.02	0.02	14%
6	3-methylpentane	3.72	3.62	3.56	3.56	3.76	3.64	2%
6	4-methyl-1-pentene	0.02	0.02	0.02	0.02	0.02	0.02	10%
6	4-methyl-cis-2-pentene					0.01	0.01	
6	4-methyl-trans-2-pentene	0.06	0.07	0.07	0.07	0.07	0.07	3%
6	benzene	0.26	0.26	0.25	0.25	0.27	0.26	2%
6	cis-2-hexene	0.08	0.08	0.07	0.07	0.08	0.08	2%
6	cis-3-hexene	0.02				0.02	0.02	1%
6	cyclohexane	2.25	2.21	2.19	2.18	2.26	2.22	2%
6	cyclohexene		0.03	0.03	0.03	0.03	0.03	2%

6	methylcyclopentane	2.95	2.88	2.85	2.84	2.98	2.90	2%
6	n-hexane	2.68	2.61	2.57	2.57	2.70	2.62	2%
6	trans-2-hexene	0.14	0.13	0.13	0.13	0.14	0.14	2%
6	trans-3-hexene	0.07	0.09	0.09	0.09	0.07	0.08	14%
7	1-c-2-dimethylcyclopentane	0.07				0.06	0.06	5%
7	1-t-2-dimethylcyclopentane	0.13	0.13	0.13	0.13	0.13	0.13	2%
7	1-t-3-dimethylcyclopentane	0.15	0.15	0.15	0.15	0.15	0.15	1%
7	2,2,3-trimethylbutane	0.07	0.07	0.07	0.07	0.07	0.07	1%
7	2,2-dimethylpentane	0.15	0.15	0.14	0.14	0.15	0.15	2%
7	2,3-dimethylpentane	1.48	1.46	1.45	1.44	1.47	1.46	1%
7	2,4-dimethyl-1-pentene	0.01	0.01	0.01	0.01	0.01	0.01	5%
7	2,4-dimethylpentane	0.99	0.98	0.96	0.96	1.00	0.98	2%
7	2-ethyl-3-methyl-1-butene	0.01	0.01	0.01	0.01	0.01	0.01	2%
7	2-methyl-cis-3-hexene	0.01	0.01	0.01	0.01	0.01	0.01	4%
7	2-methyl-trans-3-hexene	0.02	0.02	0.02	0.02	0.02	0.02	1%
7	2-methylhexane	1.37	1.36	1.34	1.34	1.37	1.36	1%
7	3,3-dimethyl-1-pentene	0.18	0.17	0.17	0.17	0.18	0.18	2%
7	3,3-dimethylpentane	0.13	0.13	0.13	0.13	0.13	0.13	1%
7	3,4-dimethyl-1-pentene	0.01	0.01	0.01	0.01	0.01	0.01	3%
7	3,4-dimethyl-2-pentene	0.02	0.02	0.02	0.02	0.02	0.02	2%
7	3-ethyl-2-pentene	0.03	0.03	0.03	0.03	0.03	0.03	4%
7	3-ethylcyclopentene	0.00				0.00	0.00	2%
7	3-ethylpentane	0.17	0.17	0.17	0.17	0.17	0.17	1%
7	3-methyl-1-hexene	0.01	0.01	0.01	0.01	0.01	0.01	2%
7	3-methyl-cis-2-hexene	0.12	0.12	0.12	0.12	0.12	0.12	1%
7	3-methyl-cis-3-hexene	0.03	0.03	0.03	0.03	0.03	0.03	1%
7	3-methyl-trans-2-hexene	0.10	0.10	0.10	0.10	0.10	0.10	1%
7	3-methyl-trans-3-hexene	0.05	0.05	0.05	0.05	0.05	0.05	2%
7	3-methylhexane	1.57	1.56	1.54	1.54	1.57	1.56	1%
7	4,4-dimethyl-c-pentene-2	0.01	0.01	0.01	0.01	0.01	0.01	2%
7	4-methyl-1-hexene	0.02	0.02	0.02	0.02	0.02	0.02	2%
7	4-methyl-trans-2-hexene	0.05	0.04	0.04	0.04	0.05	0.04	2%
7	cis-2-heptene	0.05	0.05	0.05	0.05	0.05	0.05	3%
7	dimethylcyclopentane	0.04	0.04	0.04	0.04	0.04	0.04	1%
7	ethylcyclopentane	0.09	0.09	0.09	0.09	0.09	0.09	1%
7	ethylpentene	0.01	0.01	0.01	0.01	0.01	0.01	10%
7	methylcyclohexane	0.59	0.65	0.64	0.64	0.59	0.62	5%
7	n-heptane	1.00	0.99	0.98	0.98	0.99	0.99	1%
7	toluene	8.60	8.48	8.65	8.64	8.44	8.56	1%
7	trans-2-heptene	0.04	0.04	0.04	0.04	0.04	0.04	2%
7	trans-3-heptene	0.09	0.09	0.09	0.09	0.09	0.09	1%
8	1,1,2-trimethylcyclopentane	0.02	0.02	0.02	0.02	0.02	0.02	8%
8	1,1-dimethylcyclohexane	0.03	0.03	0.03	0.03	0.03	0.03	2%
8	1,1-methylethylcyclopentane	0.02	0.02	0.02	0.02	0.02	0.02	5%
8	1,3-octadiene	0.00	0.00		0.00	0.00	0.00	45%
8	1c,2c,3-trimethylcyclopentan		0.01	0.02	0.01	0.01	0.01	26%
8	1c,2c,4-trimethylcyclopentan	0.02	0.02	0.02	0.02	0.02	0.02	8%
8	1c,2t,3-trimethylcyclopentan	0.28	0.29	0.29	0.29	0.28	0.29	2%
8	1c,2t,4-trimethylcyclopentan	0.06	0.06	0.06	0.06	0.06	0.06	1%

8	1c,4-dimethylcyclohexane				0.00	0.01	0.00	12%
8	1t,2c,3-trimethylcyclopentan	0.04	0.04	0.04	0.04	0.04	0.04	7%
8	2,2,3-trimethylpentane	0.24	0.23	0.24	0.25	0.23	0.24	3%
8	2,2,4-trimethylpentane	4.89	4.86	4.84	4.84	4.83	4.85	1%
8	2,2-dimethylhexane	0.07	0.07	0.07	0.07	0.07	0.07	1%
8	2,3,3-trimethylpentane	2.44	2.47	2.28	2.29	2.41	2.38	4%
8	2,3,4-trimethylpentane	2.18	2.18	2.17	2.17	2.13	2.16	1%
8	2,3-dimethylhexane	0.57	0.57	0.56	0.57	0.55	0.57	1%
8	2,4-dimethylhexane	0.63	0.63	0.63	0.63	0.62	0.63	1%
8	2,5-dimethylhexane	0.70	0.72	0.69	0.69	0.70	0.70	1%
8	2-methylheptane	0.37	0.37	0.36	0.37	0.36	0.37	2%
8	3,3-dimethylhexane	0.03	0.03	0.03	0.03	0.03	0.03	1%
8	3,4-dimethylhexane	0.07	0.07	0.07	0.07	0.07	0.07	3%
8	3-methyl-3-ethylpentane	0.07	0.07	0.07	0.07	0.06	0.07	2%
8	3-methylheptane	0.39	0.40	0.40	0.40	0.39	0.39	1%
8	3t-ethylmethylcyclopentane	0.04	0.06	0.06	0.06	0.06	0.05	17%
8	4-methylheptane	0.15	0.16	0.15	0.15	0.15	0.15	2%
8	unidentified	1.55	1.79	1.59	1.56	1.47	1.65	7%
8	c-1-methyl-3-ethylcyclopenta	0.17	0.16	0.16	0.16	0.17	0.16	1%
8	cis-1,3-dimethylcyclohexane	0.02	0.03	0.03	0.03	0.03	0.03	9%
8	cis-1,4-dimethylcyclohexane	0.06	0.06	0.06	0.06	0.06	0.06	3%
8	cis-2-octene	0.01	0.01	0.01	0.01	0.01	0.01	25%
8	ethylbenzene	1.59	1.62	1.61	1.62	1.56	1.60	1%
8	ethylcyclohexane	0.04					0.04	
8	m-xylene		4.40	4.40	4.42	4.24	4.36	2%
8	n-octane	0.36	0.38	0.38	0.37	0.36	0.37	2%
8	n-propylcyclopentane		0.02	0.02	0.02	0.02	0.02	3%
8	o-xylene	2.22	2.28	2.29	2.30	2.18	2.25	2%
8	p-xylene	4.33	1.82	1.83	1.83	1.74	2.31	49%
8	propylcyclopentane	0.03	0.03	0.03	0.03	0.03	0.03	2%
8	t-1,2-dimethylcyclohexane	0.09	0.09	0.09	0.09	0.09	0.09	2%
8	t-2-ethylmethylcyclopentane	0.03	0.04	0.04	0.04	0.04	0.04	5%
8	trans-1,3-dimethylcyclohexan	0.03	0.06	0.06	0.06	0.06	0.05	24%
8	trans-1,4-dimethylcyclohexan	0.08	0.09	0.09	0.09	0.09	0.09	4%
8	trans-2-octene	0.02	0.02	0.02	0.02	0.02	0.02	1%
8	trans-4-octene	0.02	0.02	0.02	0.02	0.02	0.02	4%
8	unidentified	1.06	0.89	0.87	0.86	0.76	0.89	12%
9	1,1,2-trimethylcyclohexane	0.06	0.07	0.06	0.07	0.06	0.06	7%
9	1,1,3-trimethylcyclohexane		0.02	0.01	0.01	0.01	0.01	4%
9	1,1,4-trimethylcyclohexane		0.08	0.08	0.08	0.08	0.08	2%
9	1,2,3-trimethylbenzene	0.43	0.45	0.45	0.46	0.42	0.44	4%
9	1,2,4-trimethylbenzene	2.39	2.48	2.50	2.51	2.32	2.44	3%
9	1,3,5-trimethylbenzene	0.81	0.85	0.85	0.85	0.80	0.83	3%
9	1-methyl-2-ethylbenzene	0.67	0.70	0.70	0.70	0.65	0.68	3%
9	1-methyl-3-ethylbenzene	1.54	1.60	1.60	1.61	1.50	1.57	3%
9	1-methyl-4-ethylbenzene	0.65	0.68	0.68	0.68	0.64	0.67	3%
9	1c,3c,5c-trimethylcyclohexane		0.08	0.08	0.08	0.08	0.08	5%
9	2,2,3,trimethylhexane		0.05	0.05	0.05	0.05	0.05	3%
9	2,2,4-trimethylhexane	0.01	0.01	0.01	0.01	0.01	0.01	7%

9	2,2,5-trimethylhexane	1.95	1.98	1.98	1.98	1.91	1.96	2%
9	2,2-dimethylheptane					0.00	0.00	
9	2,3,4-trimethylhexane	0.34	0.35	0.35	0.35	0.33	0.34	2%
9	2,3-dimethylheptane	1.92	0.09	0.09	0.09	0.09	0.46	179%
9	2,4-dimethylheptane	0.04	0.01	0.00	0.00	0.00	0.01	133%
9	2,5-dimethylheptane		0.16	0.15	0.15	0.15	0.15	2%
9	2,6-dimethylheptane		0.02	0.02	0.02	0.02	0.02	3%
9	2-methyloctane	0.05	0.14	0.14	0.14	0.13	0.12	33%
9	2-methyloctene-2	0.00					0.00	
9	3,3-dimethylheptane	0.14	0.03	0.03	0.03	0.03	0.05	91%
9	3,4-dimethylheptane	0.04	0.05	0.05	0.05	0.04	0.04	12%
9	3,5-dimethylheptane	0.02					0.02	
9	3-ethylheptane	0.04	0.04	0.04	0.04	0.04	0.04	4%
9	3-methyloctane	0.14	0.15	0.15	0.15	0.14	0.14	3%
9	4,4-dimethylheptane		0.05	0.04	0.05	0.04	0.05	4%
9	4-ethylheptane	0.00	0.01	0.01	0.01	0.01	0.01	32%
9	4-methyloctane	0.04	0.10	0.10	0.10	0.09	0.09	28%
9	c-1,c-3,5-trimethylcyclohexa	0.02					0.02	
9	c1,t2,c4-trimethylcyclohexan	0.01	0.01	0.01	0.01	0.01	0.01	13%
9	c9 internal alkenes	0.01					0.01	
9	ethylmethylcyclohexane	0.05	0.07	0.07	0.07	0.07	0.06	12%
9	i-butylcyclopentane	0.03	0.02	0.02	0.02	0.02	0.02	18%
9	indene	0.22	0.23	0.23	0.23	0.21	0.22	3%
9	isopropylbenzene (cumene)	0.06	0.06	0.06	0.06	0.06	0.06	3%
9	n-butylcyclopentane	0.01	0.01	0.01	0.01	0.01	0.01	4%
9	n-nonane	0.11	0.12	0.12	0.12	0.11	0.11	4%
9	n-propylbenzene	0.39	0.41	0.40	0.41	0.38	0.40	3%
9	propylcyclohexane	0.01	0.01	0.01	0.01	0.01	0.01	16%
9	trans-2-nonene	0.01	0.01	0.01	0.01	0.01	0.01	12%
10	1,2,3,5-tetramethylbenzene	0.19	0.21	0.21	0.21	0.19	0.20	5%
10	1,2,4,5-tetramethylbenzene	0.14	0.16	0.16	0.16	0.15	0.15	5%
10	1,2-diethylbenzene (ortho)	0.02	0.02	0.02	0.02	0.02	0.02	9%
10	1,2-dimethyl-3-ethylbenzene	0.06	0.08	0.07	0.07	0.07	0.07	7%
10	1,2-dimethyl-4-ethylbenzene	0.36	0.39	0.39	0.39	0.36	0.38	5%
10	1,2-methyl-n-propylbenzene	0.09	0.10	0.10	0.09	0.09	0.09	5%
10	1,3-diethylbenzene (meta)	0.12	0.13	0.13	0.12	0.11	0.12	5%
10	1,3-dimethyl-2-ethylbenzene	0.02	0.02	0.02	0.02	0.02	0.02	6%
10	1,3-dimethyl-4-ethylbenzene	0.21	0.23	0.23	0.23	0.27	0.23	8%
10	1,3-dimethyl-5-ethylbenzene	0.28	0.30	0.30	0.30	0.28	0.29	4%
10	1,4-dimethyl-2-ethylbenzene	0.17	0.18	0.18	0.18	0.17	0.18	4%
10	1-methyl-2-isopropylbenzene	0.02	0.02	0.01	0.01	0.01	0.02	13%
10	1-methyl-2n-propylbenzene	0.03	0.03	0.03	0.03	0.03	0.03	6%
10	1-methyl-3-isopropylbenzene	0.03	0.04	0.03	0.03	0.03	0.03	8%
10	1-methyl-3n-propylbenzene	0.36	0.38	0.38	0.38	0.35	0.37	5%
10	1-methyl-4-isopropylbenzene	0.01	0.02	0.01	0.01	0.01	0.01	13%
10	1-methyl-4n-propylbenzene	0.15	0.17	0.16	0.16	0.20	0.17	10%
10	2,2-dimethyloctane	0.02	0.02	0.02	0.02	0.02	0.02	4%
10	2,4-dimethyloctane	0.01	0.01	0.01	0.01	0.01	0.01	6%
10	2,5-dimethyloctane	0.03	0.04	0.03	0.03	0.03	0.03	3%

10	2,6-dimethyloctane	0.02	0.02	0.02	0.02	0.02	0.02	3%
10	2-methylindan	0.10	0.11	0.11	0.11	0.10	0.10	5%
10	2-methylnonane	0.07	0.08	0.07	0.07	0.07	0.07	4%
10	3,3-dimethyloctane	0.04	0.04	0.04	0.04	0.04	0.04	4%
10	3,6-dimethyloctane	0.01	0.01	0.01	0.01	0.01	0.01	10%
10	3-ethyloctane	0.01	0.01	0.01	0.01	0.01	0.01	18%
10	3-methyl-5-ethylheptane	0.01	0.01	0.01	0.01	0.01	0.01	21%
10	3-methylnonane	0.07	0.07	0.07	0.07	0.07	0.07	4%
10	4-methylindan	0.02	0.03	0.03	0.03	0.02	0.03	6%
10	5-methylindan	0.11	0.12	0.12	0.12	0.11	0.11	6%
10	5-methylnonane	0.02	0.03	0.03	0.02	0.03	0.03	10%
10	butylcyclohexane	0.01	0.01	0.01	0.01	0.01	0.01	16%
10	dihydronaphthalene	0.01	0.01	0.01	0.01	0.01	0.01	7%
10	isobutylbenzene	0.03	0.03	0.02	0.03	0.02	0.03	4%
10	n-butylbenzene	0.05	0.05	0.06	0.05		0.05	3%
10	n-decane	0.07	0.07	0.06	0.07	0.06	0.07	8%
10	naphthalene	0.14	0.15	0.15	0.15	0.14	0.15	5%
10	sec-butylbenzene	0.03	0.04	0.03	0.03	0.05	0.04	22%
10	sec-butylcyclohexane					0.01	0.01	
10	t-2,2,5,5-tetram-3-hexene	0.01	0.01	0.01	0.01	0.01	0.01	34%
10	t-decahydronaphthalene	0.01	0.01	0.01	0.01	0.01	0.01	10%
11	1-ethyl-2-isopropylbenzene	0.01	0.01	0.01	0.01	0.01	0.01	23%
11	1-methyl-2-n-butylbenzene	0.01	0.01	0.01	0.01	0.01	0.01	8%
11	1-methyl-2-t-butylbenzene	0.03	0.03	0.03	0.03	0.03	0.03	6%
11	1-methyl-4-t-butylbenzene	0.02	0.02	0.02	0.02	0.02	0.02	6%
11	1-methylnaphthalene	0.03	0.04	0.04	0.04	0.03	0.03	6%
11	1-undecene	0.01	0.02	0.02	0.01	0.01	0.02	12%
11	2-methylnaphthalene	0.07	0.08	0.08	0.08	0.07	0.07	6%
11	3-ethylnonane	0.00	0.00				0.00	19%
11	n-pentylbenzene	0.02	0.01	0.01	0.01	0.01	0.01	43%
11	n-undecane	0.04	0.05	0.05	0.05	0.05	0.05	7%
11	pentamethylbenzene	0.01	0.01	0.00	0.00	0.01	0.01	59%
11	s-pentylbenzene	0.02	0.02	0.02	0.02	0.02	0.02	7%
12	1,2,4-triethylbenzene	0.00		0.00	0.00	0.00	0.00	8%
12	1,2-isodipropylbenzene	0.01	0.01	0.01	0.01	0.01	0.01	7%
12	1,3,5-triethylbenzene			0.00	0.00	0.00	0.00	15%
12	1,3-dipropylbenzene	0.01	0.02	0.01	0.01	0.01	0.01	7%
12	1,3-isodipropylbenzene	0.05	0.05	0.05	0.05	0.05	0.05	5%
12	1,4-di-i-propylbenzene	0.02	0.02	0.02	0.02	0.02	0.02	6%
12	1-methyl-4-n-pentylbenzene	0.01	0.01			0.01	0.01	5%
12	n-dodecane	0.01	0.01	0.01	0.01	0.01	0.01	5%
13	c13 internal alkenes		0.00				0.00	
13	n-tridecane		0.00				0.00	
13	tridecene-1	0.00					0.00	
	sum	100.03	100.00	100.04	100.04	100.01	101.23	
	MIR	2.40	2.59	2.60	2.61	2.55	2.55	3%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).

Table 6 Liquid Gasoline Organic Gas Species Test Results
(Et2.0%, Weight Percent)

CNUM	CHEMNAME	BARREL1	BARREL2	BARREL3	BARREL4	BARREL5	MEAN	COV
2	ethyl alcohol	6.30	6.50	6.38	5.85	6.69	6.34	5%
3	acetone					0.00	0.00	
3	propane	0.00		0.00		0.00	0.00	7%
3	propylene		0.00		0.00		0.00	0%
4	1-butene	0.00	0.00	0.00	0.00	0.00	0.00	5%
4	cis-2-butene	0.00	0.00	0.00	0.00	0.00	0.00	5%
4	isobutane	0.03	0.03	0.03	0.03	0.03	0.03	3%
4	isobutylene	0.00	0.00	0.00	0.00	0.00	0.00	7%
4	n-butane	0.37	0.38	0.37	0.37	0.39	0.38	2%
4	trans-2-butene	0.00	0.00	0.00	0.00	0.00	0.00	5%
5	1-pentene	0.00	0.00	0.00	0.00	0.00	0.00	2%
5	2,2-dimethylpropane	0.01	0.01	0.01	0.01	0.01	0.01	2%
5	2-methyl-1-butene	0.01	0.01	0.01	0.01	0.01	0.01	2%
5	2-methyl-2-butene	0.01	0.01	0.01	0.01	0.01	0.01	2%
5	3-methyl-1-butene	0.04	0.03	0.06	0.05		0.04	30%
5	cis-2-pentene	0.00	0.00	0.00	0.00	0.00	0.00	2%
5	cyclopentane	0.80	0.82	0.81	0.80	0.83	0.81	2%
5	cyclopentene	0.00	0.00	0.00	0.00	0.00	0.00	3%
5	isopentane	8.06	8.24	8.00	8.06	8.32	8.14	2%
5	isoprene		0.00	0.00	0.00		0.00	0%
5	methyl t-butyl ether (MTBE)	0.10	0.10	0.10	0.10	0.10	0.10	1%
5	n-pentane	2.26	2.31	2.30	2.30	2.35	2.31	2%
5	trans-2-pentene	0.01	0.01	0.01	0.01	0.01	0.01	2%
6	1-hexene	0.00	0.00	0.00	0.00	0.00	0.00	13%
6	1-methylcyclopentene	0.00	0.01	0.01	0.00	0.00	0.00	2%
6	2,2-dimethylbutane	2.92	2.98	2.97	2.96	3.02	2.97	1%
6	2,3-dimethylbutane	2.39	2.44	2.43	2.42	2.47	2.43	1%
6	2-methyl-1-pentene	0.00	0.00	0.00	0.00	0.00	0.00	14%
6	2-methyl-2-pentene	0.01	0.01	0.01	0.01	0.01	0.01	3%
6	2-methylpentane	8.15	8.29	8.28	8.22	8.38	8.27	1%
6	3-methyl-1-pentene	0.00	0.00	0.00	0.00	0.00	0.00	5%
6	3-methyl-cis-2-pentene	0.00	0.00	0.00	0.00	0.00	0.00	3%
6	3-methyl-trans-2-pentene	0.00	0.00	0.00	0.00		0.00	12%
6	3-methylcyclopentene	0.00	0.00	0.00	0.00	0.00	0.00	13%
6	3-methylpentane	5.15	5.25	5.23	5.20	5.30	5.22	1%
6	4-methyl-1-pentene	0.00	0.00	0.00	0.00	0.00	0.00	5%
6	4-methyl-trans-2-pentene					0.00	0.00	
6	benzene	0.56	0.57	0.57	0.56	0.58	0.57	1%
6	cis-2-hexene	0.00	0.00	0.00	0.00	0.00	0.00	4%
6	cis-3-hexene	0.00	0.00			0.00	0.00	0%
6	cyclohexane	1.10	1.12	1.12	1.12	1.13	1.12	1%
6	cyclohexene					0.00	0.00	
6	methylcyclopentane	3.80	3.87	3.86	3.84	3.90	3.85	1%
6	n-hexane	1.25	1.27	1.26	1.27	1.28	1.27	1%
6	trans-2-hexene	0.00	0.00	0.00	0.00	0.00	0.00	2%
6	trans-3-hexene	0.00	0.00	0.00	0.00	0.00	0.00	17%

7	1-t-2-dimethylcyclopentane	0.46	0.47	0.46	0.46	0.47	0.46	1%
7	1-t-3-dimethylcyclopentane	0.43	0.44	0.44	0.43	0.44	0.44	1%
7	2,2,3-trimethylbutane	0.04	0.04	0.04	0.04	0.04	0.04	1%
7	2,2-dimethylpentane	0.15	0.15	0.15	0.15	0.16	0.15	2%
7	2,3-dimethylpentane	1.19	1.20	1.20	1.19	1.20	1.19	0%
7	2,4-dimethylpentane	0.69	0.70	0.70	0.69	0.70	0.70	1%
7	2-methyl-cis-3-hexene	0.00	0.00	0.00	0.00	0.00	0.00	3%
7	2-methyl-trans-3-hexene	0.00	0.00	0.00	0.00	0.00	0.00	4%
7	2-methylhexane	1.76	1.78	1.78	1.78	1.78	1.78	0%
7	3,3-dimethyl-1-pentene	0.00	0.01	0.01	0.01	0.01	0.01	2%
7	3,3-dimethylpentane	0.13	0.13	0.13	0.13	0.13	0.13	1%
7	3,4-dimethyl-2-pentene	0.00	0.00	0.00	0.00	0.00	0.00	17%
7	3-ethyl-2-pentene	0.00	0.00	0.00	0.00	0.00	0.00	9%
7	3-ethylpentane	0.17	0.17	0.17	0.17	0.17	0.17	1%
7	3-methyl-1-hexene	0.00	0.00	0.00	0.00	0.00	0.00	20%
7	3-methyl-cis-2-hexene	0.02	0.02	0.02	0.02	0.02	0.02	1%
7	3-methyl-cis-3-hexene	0.00	0.00	0.00	0.00	0.00	0.00	4%
7	3-methyl-trans-2-hexene	0.01	0.01	0.01	0.01	0.01	0.01	1%
7	3-methyl-trans-3-hexene	0.01	0.01	0.01	0.01	0.01	0.01	3%
7	3-methylhexane	1.98	2.00	2.00	2.00	2.00	2.00	0%
7	4,4-dimethyl-c-pentene-2	0.00	0.00	0.00	0.00	0.00	0.00	6%
7	4-methyl-1-hexene	0.00	0.00	0.00	0.00	0.00	0.00	5%
7	4-methyl-trans-2-hexene	0.01	0.01	0.01	0.01	0.01	0.01	3%
7	cis-2-heptene	0.01	0.01	0.01	0.01	0.01	0.01	3%
7	dimethylcyclopentane	0.08	0.09	0.09	0.09	0.09	0.09	1%
7	ethylcyclopentane	0.21	0.21	0.21	0.21	0.21	0.21	1%
7	methylcyclohexane	1.44	1.45	1.45	1.44	1.45	1.45	0%
7	n-heptane	1.44	1.45	1.45	1.45	1.45	1.45	0%
7	toluene	6.16	6.17	6.16	6.28	6.08	6.17	1%
7	trans-2-heptene	0.00	0.01	0.00	0.00	0.00	0.00	6%
7	trans-3-heptene	0.01	0.01	0.01	0.01	0.01	0.01	2%
8	1,1,2-trimethylcyclopentane	0.00	0.01	0.00	0.00	0.00	0.00	6%
8	1,1-dimethylcyclohexane	0.02	0.02	0.02	0.02	0.02	0.02	2%
8	1,1-methylethylcyclopentane	0.01	0.01	0.01	0.01	0.01	0.01	12%
8	1c,2c,3-trimethylcyclopentan	0.01	0.01	0.01	0.01	0.01	0.01	4%
8	1c,2c,4-trimethylcyclopentan	0.03	0.03		0.03	0.06	0.03	48%
8	1c,2t,3-trimethylcyclopentan	0.43	0.43	0.48	0.43	0.47	0.45	6%
8	1c,2t,4-trimethylcyclopentan	0.19	0.19	0.19	0.19	0.19	0.19	0%
8	1t,2c,3-trimethylcyclopentan	0.11	0.11	0.11	0.11	0.11	0.11	0%
8	2,2,4-trimethylpentane	2.60	2.61	2.61	2.64	2.60	2.61	1%
8	2,2-dimethylhexane	0.16	0.16	0.16	0.16	0.16	0.16	1%
8	2,3,3-trimethylpentane	0.80	0.79	0.83	0.81	0.85	0.82	3%
8	2,3,4-trimethylpentane	1.09	1.09	1.09	1.10	1.08	1.09	1%
8	2,3-dimethylhexane	0.46	0.46	0.46	0.46	0.46	0.46	1%
8	2,4-dimethylhexane	0.56	0.56	0.56	0.56	0.56	0.56	0%
8	2,5-dimethylhexane	0.54	0.55	0.54	0.55	0.54	0.54	1%
8	2-methylheptane	0.71	0.71	0.71	0.71	0.70	0.71	1%
8	3,3-dimethylhexane	0.07	0.07	0.07	0.07	0.07	0.07	1%
8	3,4-dimethylhexane	0.07	0.07	0.07	0.07	0.07	0.07	1%
8	3-ethylhexane	0.06	0.05		0.05		0.05	7%

9	3-methyloctane	0.27	0.27	0.27	0.27	0.26	0.27	2%
9	4,4-dimethylheptane	0.04	0.05			0.04	0.04	1%
9	4-ethylheptane	0.00	0.00	0.00	0.00	0.00	0.00	5%
9	4-methyloctane	0.20	0.19	0.19	0.20	0.19	0.19	2%
9	c-1,c-3,5-trimethylcyclohexa			0.02	0.02		0.02	3%
9	c1,t2,c4-trimethylcyclohexan	0.02	0.03	0.03	0.03	0.02	0.03	12%
9	c9 internal alkenes			0.03	0.03		0.03	1%
9	ethylmethylcyclohexane	0.12	0.12	0.12	0.12	0.12	0.12	1%
9	i-butylcyclopentane	0.02	0.02	0.02	0.02	0.02	0.02	2%
9	indene	0.27	0.26	0.26	0.27	0.25	0.26	2%
9	isopropylbenzene (cumene)	0.12	0.12	0.12	0.12	0.12	0.12	2%
9	n-butylcyclopentane	0.02	0.02	0.02	0.01	0.01	0.01	3%
9	n-nonane	0.23	0.23	0.23	0.23	0.22	0.23	2%
9	n-propylbenzene	0.52	0.50	0.51	0.52	0.50	0.51	2%
9	propylcyclohexane	0.02	0.02	0.02	0.02	0.02	0.02	3%
9	trans-2-methyl-3-octene		0.00	0.00	0.00	0.00	0.00	10%
9	trans-2-nonene	0.02	0.02	0.02	0.02	0.02	0.02	4%
10	1,2,3,5-tetramethylbenzene	0.32	0.29	0.30	0.31	0.29	0.30	4%
10	1,2,4,5-tetramethylbenzene	0.24	0.22	0.23	0.23	0.22	0.23	4%
10	1,2-diethylbenzene (ortho)	0.03	0.03	0.03	0.03	0.03	0.03	3%
10	1,2-dimethyl-3-ethylbenzene	0.11	0.10	0.10	0.10	0.10	0.10	3%
10	1,2-dimethyl-4-ethylbenzene	0.43	0.41	0.42	0.43	0.40	0.42	3%
10	1,2-methyl-n-propylbenzene	0.13	0.13	0.13	0.13	0.12	0.13	4%
10	1,3-diethylbenzene (meta)	0.15	0.15	0.15	0.15	0.14	0.15	3%
10	1,3-dimethyl-2-ethylbenzene	0.03	0.02	0.02	0.02	0.02	0.02	4%
10	1,3-dimethyl-4-ethylbenzene	0.28	0.26	0.27	0.27	0.25	0.27	3%
10	1,3-dimethyl-5-ethylbenzene	0.38	0.36	0.37	0.37	0.35	0.37	3%
10	1,4-dimethyl-2-ethylbenzene	0.23	0.21	0.22	0.22	0.21	0.22	3%
10	1-methyl-2-isopropylbenzen	0.02	0.02	0.02	0.02	0.02	0.02	7%
10	1-methyl-2n-propylbenzene	0.06	0.06	0.06	0.06	0.05	0.06	4%
10	1-methyl-3-isopropylbenzen	0.08	0.08	0.08	0.08	0.08	0.08	3%
10	1-methyl-3n-propylbenzene	0.43	0.41	0.42	0.43	0.40	0.42	3%
10	1-methyl-4-isopropylbenzen	0.02	0.03	0.02	0.02	0.02	0.02	10%
10	1-methyl-4n-propylbenzene	0.23	0.22	0.22	0.23	0.22	0.22	3%
10	2,2-dimethyloctane	0.04	0.04	0.04	0.04	0.04	0.04	7%
10	2,4-dimethyloctane	0.01		0.01	0.01		0.01	11%
10	2,5-dimethyloctane	0.06	0.06	0.06	0.06	0.06	0.06	3%
10	2,6-dimethyloctane	0.05	0.05	0.05	0.05	0.05	0.05	3%
10	2-methylindan	0.18	0.16	0.17	0.17	0.16	0.17	3%
10	2-methylnonane	0.08	0.08	0.08	0.08	0.08	0.08	2%
10	3,3-dimethyloctane	0.08	0.08	0.08	0.08	0.08	0.08	2%
10	3,6-dimethyloctane	0.02	0.02	0.02	0.02	0.02	0.02	3%
10	3-ethyloctane	0.02	0.02	0.02	0.02	0.02	0.02	7%
10	3-methyl-5-ethylheptane	0.02	0.02	0.02	0.02	0.02	0.02	5%
10	3-methylnonane	0.08	0.08	0.08	0.08	0.08	0.08	2%
10	4-methylindan	0.04	0.04	0.04	0.04	0.04	0.04	4%
10	5-methylindan	0.16	0.14	0.15	0.15	0.14	0.15	4%
10	5-methylnonane	0.03	0.03	0.03	0.03	0.03	0.03	2%
10	butylcyclohexane	0.02	0.02	0.02	0.02	0.02	0.02	5%

10	dihydronaphthalene	0.00	0.00	0.00	0.00	0.00	0.00	21%
10	isobutylbenzene	0.05	0.05	0.05	0.05	0.05	0.05	2%
10	n-butylbenzene	0.12	0.11	0.12	0.12	0.11	0.11	3%
10	n-decane	0.06	0.06	0.06	0.06	0.06	0.06	2%
10	naphthalene	0.25	0.23	0.24	0.25	0.23	0.24	3%
10	sec-butylbenzene	0.08	0.08	0.07	0.07	0.07	0.07	7%
10	sec-butylcyclohexane		0.01	0.01	0.01	0.01	0.01	15%
10	t-decahydronaphthalene	0.01	0.01	0.01	0.01	0.01	0.01	6%
10	t1-methyl-2n-propylcyclohex	0.01	0.01	0.01	0.01	0.01	0.01	10%
11	1-ethyl-2-isopropylbenzene	0.01	0.01	0.01	0.01	0.01	0.01	11%
11	1-methyl-2-n-butylbenzene	0.01	0.01	0.01	0.01	0.01	0.01	5%
11	1-methyl-2-t-butylbenzene	0.01	0.01	0.01	0.01	0.01	0.01	6%
11	1-methyl-4-t-butylbenzene	0.03	0.03	0.03	0.03	0.03	0.03	3%
11	1-methylnaphthalene	0.11	0.10	0.11	0.11	0.10	0.11	5%
11	1-undecene	0.01	0.01	0.01	0.01	0.00	0.01	7%
11	2-methylnaphthalene	0.23	0.22	0.22	0.23	0.21	0.22	4%
11	n-pentylbenzene	0.03	0.03	0.03	0.03	0.01	0.03	25%
11	n-undecane	0.01	0.01	0.01	0.01	0.01	0.01	5%
11	pentamethylbenzene	0.04	0.04	0.04	0.04	0.04	0.04	4%
11	s-pentylbenzene	0.04	0.04	0.04	0.04	0.04	0.04	4%
12	1,2,4-triethylbenzene	0.00	0.00	0.00	0.00	0.00	0.00	16%
12	1,2-isodipropylbenzene	0.03	0.03	0.03	0.03	0.03	0.03	5%
12	1,3,5-triethylbenzene			0.00	0.00	0.00	0.00	3%
12	1,3-dipropylbenzene	0.05	0.04	0.05	0.05	0.04	0.05	5%
12	1,3-isodipropylbenzene	0.09	0.08	0.09	0.09	0.08	0.09	4%
12	1,4-di-i-propylbenzene	0.03	0.03	0.03	0.03	0.03	0.03	4%
12	1-methyl-4-n-pentylbenzene	0.05	0.04	0.04	0.05	0.04	0.04	5%
12	n-dodecane	0.00	0.00	0.00	0.00	0.00	0.00	8%
12	n-hexylbenzene	0.00	0.00	0.00	0.00	0.00	0.00	39%
13	c13 internal alkenes	0.01						
	sum	100.00	100.06	100.07	100.07	100.04	103.23	
	MIR	2.44	2.61	2.45	2.47	2.59	2.51	3%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).

Table 7 Gasoline Headspace Organic Gas Species Test Results

(MTBE, Weight Percent)

NAME	BARREL1	BARREL2	MEAN	COV
ethane	0.17	0.13	0.15	18%
propane	0.36	0.24	0.30	28%
butanes	16.14	11.58	13.86	23%
pentanes	49.06	44.80	46.93	6%
c6+ br-alkanes	10.95	17.46	14.21	32%
c6+ n-alkanes	1.60	2.53	2.07	32%
ethene	0.04	0.03	0.04	17%
propene	0.09	0.06	0.08	28%
1,3-butadiene	0.05	0.00	0.02	141%
c4+ alkenes	4.05	3.95	4.00	2%
acetylene	0.00	0.00	0.00	n/a
benzene	0.34	0.56	0.45	35%
alkynes	0.00	0.00	0.00	n/a
toluene	0.34	0.87	0.60	62%
c8+ aromatics	0.15	0.30	0.22	46%
MTBE	16.71	17.44	17.08	3%
ethanol	0.00	0.00	0.00	n/a
ethers	0.00	0.00	0.00	n/a
styrenes	0.00	0.00	0.00	n/a
isoprene	0.00	0.03	0.01	141%
sum	100.06	100.00	100.03	
MIR	1.46	1.48	1.47	1%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).

Table 8 Gasoline Headspace Organic Gas Species Test Results

(NonOxy, Weight Percent)

NAME	BARREL1	BARREL2	BARREL3	BARREL4	BARREL5	BARREL6	MEAN	COV
ethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
propane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
butanes	12.53	10.37	12.13	9.88	10.14	8.50	11.01	0.11
pentanes	63.22	59.57	61.96	57.62	59.56	54.09	60.39	0.04
c6+ br-alkanes	20.00	24.24	20.99	25.88	24.64	29.35	23.15	0.11
c6+ n-alkanes	1.45	1.93	1.59	2.12	2.00	2.57	1.82	0.16
ethene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
propene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
1,3-butadiene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
c4+ alkenes	1.96	2.14	1.97	2.19	2.15	2.36	2.08	5%
acetylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
benzene	0.15	0.20	0.17	0.23	0.22	0.27	0.19	16%
alkynes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
toluene	0.54	1.10	0.89	1.50	1.01	2.11	1.01	34%
c8+ aromatics	0.20	0.66	0.36	0.65	0.28	0.81	0.43	50%
MTBE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
ethanol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
ethers	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
styrenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
isoprene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
sum	100.05	100.20	100.07	100.07	100.00	100.06	100.08	
MIR	1.40	1.45	1.42	1.47	1.44	1.51	1.45	3%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).

Table 9 Gasoline Headspace Organic Gas Species Test Results
(Et2.0%, Weight Percent)

NAME	BARREL1	BARREL2	BARREL3	BARREL4	BARREL5	BARREL6	MEAN	COV
ethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
propane	0.05	0.05	0.04	0.04	0.05	0.04	0.05	0.08
butanes	4.41	4.55	4.09	3.99	4.70	3.90	4.35	0.07
pentanes	45.09	45.63	42.38	42.01	47.27	41.47	44.48	0.05
c6+ br-alkanes	35.83	35.37	36.46	36.93	35.01	37.25	35.92	0.02
c6+ n-alkanes	1.55	1.51	1.68	1.70	1.50	1.78	1.59	0.06
ethene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
propene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
1,3-butadiene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
c4+ alkenes	0.23	0.25	0.27	0.28	0.25	0.29	0.26	8%
acetylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
benzene	0.37	0.36	0.41	0.41	0.37	0.43	0.39	6%
alkynes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
toluene	1.13	1.09	1.37	1.38	0.91	1.52	1.18	17%
c8+ aromatics	0.61	0.55	1.06	0.75	0.41	0.88	0.67	37%
MTBE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
ethanol	10.80	10.68	12.35	12.56	9.55	12.50	11.19	11%
ethers	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
styrenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
isoprene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
sum	100.06	100.05	100.10	100.05	100.02	100.07	100.06	
MIR	1.42	1.42	1.45	1.44	1.41	1.45	1.43	1%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).

Table 10 Gasoline Headspace Organic Gas Species Test Results

(MTBE, Weight Percent)

CNUM	CHEMNAME	BARREL1	BARREL2	MEAN	COV
2	ethane	0.17	0.13	0.15	18%
2	ethylene	0.04	0.03	0.04	17%
3	propane	0.36	0.24	0.30	28%
3	propylene	0.09	0.06	0.08	28%
4	1,3-butadiene	0.05	0.00	0.02	141%
4	1-butene	0.32	0.22	0.27	26%
4	cis-2-butene	0.53	0.38	0.45	23%
4	isobutane	4.41	3.06	3.74	26%
4	isobutylene	0.56	0.58	0.57	3%
4	n-butane	11.73	8.53	10.13	22%
4	trans-2-butene	0.61	0.43	0.52	23%
5	1-pentene	0.21	0.17	0.19	13%
5	2,2-dimethylpropane	0.07	0.05	0.06	25%
5	2-methyl-1-butene	0.30	0.07	0.19	87%
5	2-methyl-2-butene	0.53	0.74	0.63	23%
5	3-methyl-1-butene	0.09	0.07	0.08	11%
5	cis-2-pentene	0.21	0.20	0.21	4%
5	cyclopentane	0.00	0.96	0.48	141%
5	cyclopentene	0.07	0.07	0.07	4%
5	isopentane	35.97	31.80	33.88	9%
5	isoprene	0.00	0.03	0.01	141%
5	methyl t-butyl ether (MTBE)	16.71	17.44	17.08	3%
5	n-pentane	13.03	12.00	12.51	6%
5	trans-1,3-pentadiene	0.00	0.02	0.00	141%
5	trans-2-pentene	0.39	0.37	0.38	3%
6	1-hexene	0.00	0.03	0.01	141%
6	2,2-dimethylbutane	0.16	0.19	0.17	12%
6	2,3-dimethylbutane	0.86	1.41	1.14	34%
6	2-methyl-1-pentene	0.04	0.05	0.04	20%
6	2-methyl-2-pentene	0.06	0.09	0.08	25%
6	2-methylpentane	3.89	4.96	4.43	17%
6	3-methyl-1-pentene	0.00	0.04	0.02	141%
6	3-methylcyclopentene	0.04	0.05	0.04	26%
6	3-methylpentane	2.01	2.73	2.37	22%
6	4-methyl-trans-2-pentene	0.03	0.04	0.04	12%
6	benzene	0.34	0.56	0.45	35%
6	cis-2-hexene	0.00	0.03	0.02	141%
6	cyclohexane	0.35	0.65	0.50	41%
6	cyclohexene	0.03	0.06	0.04	41%
6	methylcyclopentane	1.54	2.39	1.96	31%
6	n-hexane	1.47	2.19	1.83	28%
6	trans-2-hexene	0.04	0.06	0.05	26%
6	trans-3-hexene	0.00	0.04	0.02	141%

7	1-c-3-dimethylcyclopentane	0.14	0.29	0.21	50%
7	1-t-3-dimethylcyclopentane	0.16	0.33	0.25	51%
7	2,2,3-trimethylbutane	0.00	0.02	0.00	141%
7	2,3-dimethylpentane	0.26	0.54	0.40	50%
7	2,4-dimethyl-2-pentene	0.00	0.02	0.01	141%
7	2,4-dimethylpentane	0.29	0.52	0.41	41%
7	2-methyl-2-hexene	0.00	0.03	0.01	141%
7	2-methylhexane	0.30	0.66	0.48	53%
7	3-ethylpentane	0.15	0.37	0.26	61%
7	3-methyl-cis-2-hexene	0.00	0.03	0.02	141%
7	3-methylhexane	0.30	0.65	0.47	53%
7	ethylcyclopentane	0.00	0.07	0.03	141%
7	methylcyclohexane	0.19	0.47	0.33	60%
7	n-heptane	0.13	0.31	0.22	59%
7	toluene	0.34	0.87	0.60	62%
7	trans-3-heptene	0.00	0.04	0.02	141%
8	1,2,4-trimethylcyclopentene	0.00	0.04	0.02	141%
8	1c,2t,3-trimethylcyclopentan	0.00	0.02	0.01	141%
8	2,2,4-trimethylpentane	0.24	0.57	0.40	58%
8	2,2-dimethylhexane	0.00	0.04	0.02	141%
8	2,3,4-trimethylpentane	0.05	0.14	0.09	67%
8	2,3-dimethylhexane	0.00	0.04	0.02	141%
8	2,4-dimethylhexane	0.04	0.09	0.06	63%
8	2,5-dimethylhexane	0.05	0.07	0.06	23%
8	2-methylheptane	0.00	0.06	0.03	141%
8	3-methylheptane	0.00	0.06	0.03	141%
8	4-methylheptane	0.00	0.02	0.01	141%
8	cis-1,3-dimethylcyclohexane	0.00	0.03	0.01	141%
8	ethylbenzene	0.00	0.05	0.03	141%
8	m-xylene	0.04	0.18	0.11	87%
8	n-octane	0.00	0.03	0.01	141%
8	o-xylene	0.00	0.05	0.03	141%
9	1,2,4-trimethylbenzene	0.00	0.02	0.00	141%
9	1-methyl-4-ethylbenzene	0.06	0.00	0.03	141%
9	2,2,5-trimethylhexane	0.00	0.03	0.02	141%
9	p-ethyltoluene (99914)	0.06	0.00	0.03	141%
	sum	100.11	99.98	99.99	
	MIR	1.46	1.48	1.47	1%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).

Table 11 Gasoline Headspace Organic Gas Species Test Results

(NonOxy, Weight Percent)

CNUM	CHEMNAME	BARREL1	BARREL2	BARREL3	BARREL4	BARREL5	BARREL6	MEAN	COV
4	cis-2-butene	0.00	0.02	0.00	0.00	0.00	0.00	0.00	245%
4	isobutane	1.20	0.97	1.16	0.93	0.94	0.78	1.00	16%
4	n-butane	11.33	9.40	10.96	8.95	9.20	7.72	9.59	14%
4	trans-2-butene	0.00	0.02	0.00	0.02	0.00	0.02	0.01	110%
5	1-pentene	0.10	0.10	0.09	0.08	0.09	0.08	0.09	10%
5	2,2-dimethylpropane	0.09	0.08	0.10	0.08	0.08	0.07	0.08	13%
5	2-methyl-1-butene	0.18	0.18	0.22	0.20	0.05	0.05	0.15	51%
5	2-methyl-2-butene	0.53	0.51	0.52	0.51	0.64	0.61	0.55	11%
5	3-methyl-1-butene	0.00	0.00	0.00	0.00	0.00	0.02	0.00	245%
5	cis-2-pentene	0.16	0.16	0.16	0.15	0.15	0.15	0.15	4%
5	cyclopentane	0.95	1.00	0.97	1.04	1.05	1.06	1.01	4%
5	cyclopentene	0.05	0.05	0.05	0.05	0.05	0.05	0.05	2%
5	isopentane	49.04	45.81	48.33	44.30	46.06	41.41	45.82	6%
5	n-pentane	13.14	12.69	12.57	12.21	12.37	11.54	12.42	4%
5	trans-2-pentene	0.27	0.26	0.27	0.26	0.26	0.25	0.26	3%
6	1-hexene	0.03	0.04	0.03	0.04	0.04	0.05	0.04	16%
6	2,2-dimethylbutane	5.45	5.71	5.36	5.77	5.80	5.82	5.65	3%
6	2,3-dimethyl-1-butene	0.06	0.07	0.06	0.06	0.04	0.05	0.06	17%
6	2,3-dimethylbutane	2.60	2.93	2.62	3.04	3.04	3.27	2.91	9%
6	2-methyl-1-pentene	0.08	0.10	0.09	0.11	0.11	0.12	0.10	13%
6	2-methyl-2-pentene	0.12	0.15	0.13	0.16	0.16	0.19	0.15	17%
6	2-methylpentane	5.62	6.55	5.64	6.74	6.68	7.39	6.44	11%
6	3-methyl-1-pentene	0.06	0.06	0.00	0.00	0.07	0.07	0.04	78%
6	3-methylcyclopentene	0.07	0.09	0.08	0.10	0.09	0.11	0.09	17%
6	3-methylpentane	2.77	3.32	2.84	3.49	3.43	3.91	3.29	13%
6	4-methyl-trans-2-pentene	0.05	0.06	0.06	0.07	0.07	0.08	0.07	15%
6	benzene	0.15	0.20	0.17	0.23	0.22	0.27	0.21	21%
6	cis-2-hexene	0.04	0.05	0.04	0.06	0.05	0.06	0.05	18%
6	cyclohexane	0.64	0.92	0.73	1.03	0.95	1.31	0.93	26%
6	cyclohexene	0.00	0.00	0.00	0.00	0.00	0.02	0.00	245%
6	methylcyclopentane	1.38	1.82	1.48	1.97	1.89	2.35	1.82	19%
6	n-hexane	1.37	1.78	1.47	1.92	1.86	2.27	1.78	18%
6	trans-2-hexene	0.07	0.09	0.08	0.10	0.10	0.12	0.09	18%
6	trans-3-hexene	0.05	0.07	0.06	0.07	0.07	0.09	0.07	18%
7	1-c-3-dimethylcyclopentane	0.00	0.03	0.03	0.04	0.03	0.06	0.03	58%
7	1-t-2-dimethylcyclopentane	0.00	0.03	0.03	0.04	0.00	0.00	0.02	113%
7	1-t-3-dimethylcyclopentane	0.00	0.04	0.03	0.05	0.04	0.06	0.04	58%
7	2,2,3-trimethylbutane	0.00	0.03	0.00	0.03	0.03	0.04	0.02	80%
7	2,3-dimethylpentane	0.22	0.36	0.28	0.43	0.37	0.59	0.37	34%
7	2,4-dimethyl-2-pentene	0.03	0.04	0.04	0.05	0.04	0.06	0.04	25%
7	2,4-dimethylpentane	0.28	0.40	0.32	0.45	0.42	0.58	0.41	26%
7	2-methyl-2-hexene	0.00	0.02	0.00	0.03	0.02	0.04	0.02	84%
7	2-methylhexane	0.19	0.33	0.25	0.39	0.32	0.53	0.34	35%
7	3-ethylpentane	0.00	0.03	0.00	0.03	0.06	0.11	0.04	105%
7	3-methyl-cis-2-hexene	0.00	0.00	0.00	0.02	0.00	0.03	0.00	158%
7	3-methylhexane	0.19	0.34	0.26	0.41	0.33	0.57	0.35	37%
7	4-methyl-trans-2-hexene	0.00	0.00	0.00	0.00	0.00	0.02	0.00	245%

7	ethylcyclopentane	0.00	0.00	0.00	0.00	0.00	0.02	0.00	245%
7	methylcyclohexane	0.05	0.10	0.08	0.13	0.10	0.18	0.11	42%
7	n-heptane	0.08	0.15	0.12	0.20	0.14	0.27	0.16	42%
7	toluene	0.54	1.10	0.89	1.50	1.01	2.11	1.19	46%
7	trans-3-heptene	0.00	0.00	0.00	0.02	0.02	0.03	0.01	115%
8	2,2,4-trimethylpentane	0.43	0.80	0.64	1.01	0.76	1.41	0.84	40%
8	2,2-dimethylhexane	0.00	0.00	0.00	0.00	0.00	0.02	0.00	245%
8	2,3,4-trimethylpentane	0.08	0.17	0.15	0.27	0.15	0.37	0.20	52%
8	2,3-dimethylhexane	0.00	0.04	0.03	0.06	0.04	0.09	0.04	71%
8	2,4-dimethylhexane	0.04	0.09	0.07	0.12	0.06	0.14	0.09	42%
8	2,5-dimethylhexane	0.03	0.07	0.06	0.10	0.06	0.14	0.08	50%
8	2-methylheptane	0.00	0.02	0.00	0.04	0.00	0.05	0.02	117%
8	3,4-dimethylhexane	0.00	0.00	0.00	0.00	0.00	0.02	0.00	245%
8	3-methylheptane	0.00	0.02	0.00	0.05	0.00	0.06	0.02	120%
8	4-methylheptane	0.00	0.00	0.00	0.00	0.00	0.02	0.00	245%
8	cis-1,3-dimethylcyclohexane	0.00	0.00	0.00	0.02	0.00	0.03	0.00	156%
8	ethylbenzene	0.00	0.05	0.04	0.09	0.05	0.12	0.06	72%
8	m-xylene	0.06	0.15	0.14	0.27	0.16	0.39	0.19	61%
8	n-octane	0.00	0.00	0.00	0.00	0.00	0.03	0.00	245%
8	o-xylene	0.00	0.04	0.04	0.09	0.05	0.12	0.06	73%
9	1,2,4-trimethylbenzene	0.00	0.00	0.00	0.05	0.02	0.05	0.02	119%
9	1,3,5-trimethylbenzene	0.00	0.00	0.00	0.02	0.00	0.02	0.00	155%
9	1-methyl-3-ethylbenzene	0.00	0.10	0.00	0.02	0.00	0.04	0.03	143%
9	1-methyl-4-ethylbenzene	0.05	0.10	0.07	0.05	0.00	0.02	0.05	77%
9	2,2,5-trimethylhexane	0.04	0.09	0.08	0.15	0.08	0.21	0.11	58%
9	2,3,5-trimethylhexane	0.00	0.00	0.00	0.00	0.00	0.03	0.00	245%
9	m-ethyltoluene (99912)	0.00	0.10	0.00	0.02	0.00	0.04	0.03	143%
9	p-ethyltoluene (99914)	0.05	0.10	0.07	0.05	0.00	0.02	0.05	77%
10	naphthalene	0.04	0.03	0.00	0.00	0.00	0.00	0.01	160%
	sum	100.05	100.23	100.06	100.04	99.97	100.10	100.02	
	MIR	1.40	1.45	1.42	1.47	1.44	1.51	1.45	3%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).

The COVs were calculated before the mean and standard deviation were rounded.

MIR means Maximum Incremental Reactivity (g ozone/g NMOG).

Table 12 Gasoline Headspace Organic Gas Species Test Results
(Et2.0%, Weight Percent)

CNUM	CHEMNAME	BARREL1	BARREL2	BARREL3	BARREL4	BARREL5	BARREL6	MEAN	COV
2	ethyl alcohol	10.80	10.68	12.35	12.56	9.55	12.50	11.41	11%
3	propane	0.05	0.05	0.04	0.04	0.05	0.04	0.05	9%
4	isobutane	0.48	0.50	0.44	0.42	0.51	0.42	0.46	8%
4	n-butane	3.93	4.06	3.64	3.56	4.19	3.48	3.81	8%
5	2,2-dimethylpropane	0.06	0.06	0.06	0.06	0.06	0.05	0.06	5%
5	2-methyl-1-butene	0.00	0.00	0.02	0.02	0.00	0.00	0.00	155%
5	2-methyl-2-butene	0.03	0.03	0.03	0.03	0.04	0.04	0.03	22%
5	cyclopentane	1.52	1.51	1.49	1.48	1.56	1.47	1.51	2%
5	isopentane	35.91	36.42	33.82	33.47	38.10	33.20	35.15	6%
5	n-pentane	7.61	7.64	7.01	7.00	7.55	6.74	7.26	5%
5	trans-2-pentene	0.03	0.03	0.03	0.03	0.03	0.03	0.03	3%
6	2,2-dimethylbutane	6.20	6.20	5.97	6.01	6.21	5.84	6.07	3%
6	2,3-dimethyl-1-butene	0.07	0.07	0.08	0.09	0.08	0.11	0.08	18%
6	2,3-dimethylbutane	3.60	3.57	3.55	3.59	3.59	3.56	3.58	0%
6	2-methylpentane	11.24	11.13	11.02	11.12	11.05	11.13	11.12	0%
6	3-methylpentane	6.22	6.15	6.20	6.27	6.13	6.30	6.21	1%
6	benzene	0.37	0.36	0.41	0.41	0.37	0.43	0.39	7%
6	cyclohexane	0.65	0.64	0.72	0.74	0.64	0.76	0.69	8%
6	cyclohexene	0.04	0.04	0.04	0.04	0.03	0.05	0.04	10%
6	methylcyclopentane	3.24	3.19	3.37	3.43	3.18	3.51	3.32	4%
6	n-hexane	1.15	1.13	1.19	1.22	1.15	1.25	1.18	4%
7	1-c-3-dimethylcyclopentane	0.16	0.16	0.19	0.19	0.15	0.20	0.17	12%
7	1-t-2-dimethylcyclopentane	0.05	0.05	0.06	0.06	0.00	0.00	0.04	79%
7	1-t-3-dimethylcyclopentane	0.19	0.18	0.21	0.22	0.18	0.23	0.20	12%
7	2,2,3-trimethylbutane	0.02	0.02	0.02	0.02	0.02	0.03	0.02	9%
7	2,3-dimethylpentane	0.46	0.44	0.52	0.54	0.41	0.54	0.49	11%
7	2,4-dimethyl-2-pentene	0.06	0.06	0.07	0.07	0.06	0.07	0.07	10%
7	2,4-dimethylpentane	0.40	0.39	0.45	0.46	0.40	0.48	0.43	8%
7	2-methylhexane	0.67	0.65	0.77	0.79	0.64	0.86	0.73	12%
7	3-ethylpentane	0.16	0.16	0.19	0.20	0.21	0.28	0.20	22%
7	3-methylhexane	0.69	0.67	0.79	0.82	0.64	0.87	0.75	13%
7	ethylcyclopentane	0.00	0.00	0.00	0.00	0.04	0.06	0.02	161%
7	methylcyclohexane	0.36	0.35	0.43	0.44	0.32	0.48	0.40	15%
7	n-heptane	0.36	0.34	0.43	0.44	0.32	0.48	0.39	16%
7	toluene	1.13	1.09	1.37	1.38	0.91	1.52	1.23	18%
7	trans-3-heptene	0.00	0.03	0.00	0.00	0.00	0.00	0.00	245%
8	1,1-methylethylcyclopentane	0.00	0.00	0.00	0.00	0.00	0.02	0.00	245%
8	1,2,4-trimethylcyclopentene	0.04	0.04	0.05	0.06	0.03	0.05	0.05	23%
8	1c,2t,3-trimethylcyclopentan	0.02	0.00	0.02	0.02	0.00	0.02	0.01	79%
8	2,2,4-trimethylpentane	0.71	0.69	0.85	0.89	0.64	0.93	0.79	15%
8	2,2-dimethylhexane	0.02	0.02	0.03	0.03	0.03	0.05	0.03	30%
8	2,3,4-trimethylpentane	0.16	0.15	0.20	0.20	0.13	0.22	0.18	21%
8	2,3-dimethylhexane	0.05	0.05	0.07	0.07	0.04	0.08	0.06	22%
8	2,4-dimethylhexane	0.11	0.11	0.14	0.14	0.08	0.15	0.12	20%
8	2,5-dimethylhexane	0.12	0.11	0.15	0.15	0.07	0.11	0.12	26%
8	2-methylheptane	0.07	0.07	0.10	0.10	0.06	0.11	0.09	24%
8	3,4-dimethylhexane	0.02	0.00	0.02	0.02	0.00	0.02	0.01	79%

8	3-methylheptane	0.09	0.08	0.14	0.14	0.07	0.13	0.11	29%
8	4-methylheptane	0.04	0.03	0.04	0.04	0.03	0.05	0.04	22%
8	c-1-methyl-3-ethylcyclopenta	0.00	0.00	0.00	0.00	0.00	0.02	0.00	245%
8	cis-1,3-dimethylcyclohexane	0.04	0.04	0.05	0.05	0.03	0.06	0.04	22%
8	ethylbenzene	0.09	0.08	0.13	0.11	0.06	0.13	0.10	28%
8	m-xylene	0.29	0.26	0.44	0.35	0.20	0.44	0.33	29%
8	n-octane	0.04	0.04	0.05	0.05	0.03	0.06	0.04	25%
8	o-xylene	0.08	0.08	0.14	0.11	0.06	0.13	0.10	31%
8	t-1-methyl-3-ethylcyclopenta	0.00	0.00	0.02	0.02	0.00	0.02	0.00	110%
8	trans-1,3-dimethylcyclohexan	0.00	0.00	0.02	0.02	0.00	0.03	0.01	110%
8	trans-1,4-dimethylcyclohexan	0.00	0.00	0.02	0.02	0.00	0.02	0.01	110%
9	1,2,4-trimethylbenzene	0.03	0.02	0.06	0.03	0.03	0.04	0.04	44%
9	1,3,5-trimethylbenzene	0.00	0.00	0.03	0.00	0.00	0.02	0.00	155%
9	1-methyl-3-ethylbenzene	0.03	0.02	0.05	0.03	0.02	0.04	0.03	36%
9	1-methyl-4-ethylbenzene	0.03	0.03	0.03	0.02	0.00	0.02	0.02	57%
9	2,2,5-trimethylhexane	0.03	0.02	0.04	0.04	0.00	0.04	0.03	54%
9	3,5-dimethylheptane	0.00	0.00	0.00	0.00	0.00	0.02	0.00	245%
9	4-methyloctane	0.00	0.00	0.03	0.02	0.00	0.00	0.00	158%
9	m-ethyltoluene (99912)	0.03	0.02	0.05	0.03	0.02	0.04	0.03	36%
9	n-propylbenzene	0.00	0.00	0.02	0.00	0.00	0.00	0.00	245%
9	p-ethyltoluene (99914)	0.03	0.03	0.03	0.02	0.00	0.02	0.02	57%
9	propylbenzene	0.00	0.00	0.02	0.00	0.00	0.00	0.00	245%
10	1,3-dimethyl-2-ethylbenzene	0.00	0.00	0.02	0.03	0.00	0.00	0.00	157%
10	naphthalene	0.00	0.00	0.03	0.02	0.00	0.00	0.00	157%
	sum	100.08	100.04	100.07	100.05	100.00	100.10	100.00	
	MIR	1.42	1.42	1.45	1.44	1.41	1.45	1.43	1%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).

The COVs were calculated before the mean and standard deviation were rounded.

MIR means Maximum Incremental Reactivity (g ozone/g NMOG).

Table 13 Exhaust Gasoline Organic Gas Species Test Results

(MTBE, Hot Stabilized Emissions, Weight Percent)

NAME	VEH1	VEH2	VEH3	VEH4	VEH5	MEAN	COV
ethane	2.18	1.55	7.52	4.81	1.03	3.42	79%
propane	0.12	0.06	0.00	0.17	0.07	0.08	76%
butanes	0.74	0.65	0.00	1.01	0.89	0.66	60%
pentanes	7.92	7.50	8.99	7.34	10.77	8.50	17%
c6+ br-alkanes	21.36	19.55	22.11	18.12	35.09	23.25	29%
c6+ n-alkanes	2.92	2.40	2.39	2.55	4.88	3.03	35%
ethene	15.23	13.53	3.94	22.26	6.38	12.27	60%
propene	5.99	5.21	2.11	8.43	3.00	4.95	51%
1,3-butadiene	0.22	0.28	0.00	0.24	0.06	0.16	77%
c4+ alkenes	7.49	7.46	0.37	4.00	5.66	5.00	59%
acetylene	4.09	2.86	0.00	1.27	1.82	2.01	77%
alkynes	0.12	0.50	0.00	0.30	0.13	0.21	91%
benzene	7.34	2.64	9.91	7.08	4.40	6.27	45%
toluene	7.59	4.67	6.70	7.60	7.11	6.74	18%
c8+ aromatics	14.76	13.10	33.94	12.87	18.06	18.55	48%
formaldehyde	0.64	9.07	1.01	0.15	0.10	2.19	176%
acetaldehyde	0.18	2.46	0.00	0.45	0.03	0.62	167%
c3+aldehydes	0.12	2.78	0.00	0.76	0.04	0.74	160%
MTBE	0.35	0.37	0.64	0.32	0.35	0.41	32%
ethanol							
c3+ alcohols	0.36	2.73	0.00	0.00	0.00	0.62	192%
ketones	0.14	0.55	0.37	0.20	0.04	0.26	79%
styrenes	0.10	0.05	0.00	0.07	0.09	0.06	62%
isoprene	0.03	0.00	0.00	0.00	0.00	0.01	224%
sum	100.00	100.00	100.00	100.00	100.00	100.00	
Mass (mg/mi)	897.00	408.00	11.00	301.00	1230.00	570.00	86%
MIR	4.01	4.34	3.90	4.37	3.28	3.98	11%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).
Hot stabilized emissions are represented by Bag 2 of Unified Cycle.

Table 14 Exhaust Gasoline Organic Gas Species Test Results

(NonOxy, Hot Stabilized Emissions, Weight Percent)

NAME	VEH1	VEH2	VEH3	VEH4	VEH5	VEH6	VEH7	MEAN	COV
ethane	2.06	0.82	6.12	2.17	1.20	3.13	2.39	2.56	68%
propane	0.10	0.04	1.06	0.12	0.07	0.00	0.12	0.22	173%
butanes	0.51	0.81	0.18	0.69	0.81	0.46	0.74	0.60	39%
pentanes	8.59	13.51	9.16	10.29	11.87	8.06	10.17	10.24	19%
c6+ br-alkanes	21.69	31.82	29.25	28.32	35.52	22.50	29.00	28.30	17%
c6+ n-alkanes	2.12	2.88	1.92	2.67	3.29	2.05	2.84	2.54	20%
ethene	16.08	6.50	4.50	11.97	7.18	4.67	9.48	8.63	49%
propene	6.50	4.45	3.11	5.92	3.52	2.67	4.76	4.42	32%
1,3-butadiene	0.26	0.14	0.00	0.88	0.06	0.00	0.27	0.23	134%
c4+ alkenes	5.58	6.24	0.58	5.65	2.99	4.78	3.67	4.21	47%
acetylene	4.33	0.87	0.00	0.55	1.81	0.10	0.77	1.20	125%
alkynes	0.14	0.06	0.00	0.07	0.14	0.00	0.07	0.07	85%
benzene	5.96	1.12	9.67	5.75	4.40	6.27	5.70	5.55	46%
toluene	10.44	9.16	9.21	10.74	10.12	11.97	10.95	10.37	10%
c8+ aromatics	15.38	14.40	23.56	13.64	16.14	29.69	18.97	18.82	31%
formaldehyde	0.02	3.50	0.66	0.01	0.25	0.51	0.01	0.71	177%
acetaldehyde	0.01	1.08	0.15	0.00	0.12	0.36	0.00	0.24	159%
c3+aldehydes	0.00	1.84	0.35	0.00	0.33	2.62	0.01	0.74	143%
MTBE	0.05	0.04	0.40	0.04	0.04	0.00	0.01	0.08	171%
ethanol									
c3+ alcohols	0.00	0.40	0.00	0.00	0.00	0.00	0.00	0.06	265%
ketones	0.02	0.28	0.10	0.02	0.11	0.15	0.01	0.10	101%
styrenes	0.14	0.02	0.00	0.44	0.04	0.00	0.06	0.10	160%
isoprene	0.03	0.02	0.00	0.09	0.00	0.00	0.01	0.02	145%
sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	
Mass (mg/mi)	1194.00	1908.00	20.00	1058.00	1074.00	19.00	1334.00	943.86	73%
MIR	4.05	3.63	3.23	3.74	3.21	3.92	3.65	3.63	9%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).
Hot stabilized emissions are represented by Bag 2 of Unified Cycle.

Table 15 Exhaust Gasoline Organic Gas Species Test Results

(Et2.0%, Hot Stabilized Emissions, Weight Percent)

NAME	VEH1	VEH3	VEH4	VEH5	VEH6	VEH7	MEAN	COV
ethane	1.91	4.49	3.61	1.70	3.05	1.99	2.79	40%
propane	0.09	1.27	0.16	0.22	0.27	0.08	0.35	131%
butanes	0.33	0.26	0.51	0.57	0.36	0.31	0.39	31%
pentanes	6.85	5.45	7.87	9.84	7.11	7.42	7.42	19%
c6+br-alkanes	31.22	22.16	28.91	37.25	25.06	33.84	29.74	19%
c6+n-alkanes	2.08	2.33	2.27	3.09	3.64	2.62	2.67	22%
ethene	12.91	3.23	15.19	8.43	5.01	8.85	8.94	51%
propene	4.58	2.27	6.90	4.11	3.01	3.74	4.10	39%
1,3-butadiene	0.09	0.00	0.46	0.00	0.00	0.31	0.14	136%
c4+alkenes	3.72	0.00	3.41	1.93	0.00	3.60	2.11	83%
acetylene	2.63	0.00	0.72	1.73	0.18	1.05	1.05	94%
alkynes	0.35	0.00	0.13	0.15	0.00	0.03	0.11	123%
benzene	6.49	8.46	5.75	4.19	12.89	5.40	7.20	43%
toluene	6.93	8.04	8.22	7.24	7.88	8.44	7.79	8%
c8+aromatics	11.79	36.44	15.49	19.41	29.98	20.89	22.33	41%
formaldehyde	3.23	2.01	0.04	0.02	0.50	0.08	0.98	137%
acetaldehyde	1.62	0.26	0.01	0.01	0.00	0.37	0.38	166%
c3+aldehydes	1.55	2.59	0.01	0.00	0.18	0.29	0.77	138%
MTBE	0.00	0.74	0.06	0.07	0.55	0.00	0.24	137%
ethanol	0.63	0.00	0.00	0.00	0.00	0.27	0.15	173%
c3+ alcohols	0.42	0.00	0.00	0.00	0.00	0.16	0.10	176%
ketones	0.53	0.00	0.00	0.01	0.32	0.20	0.18	122%
styrenes	0.04	0.00	0.29	0.04	0.00	0.06	0.07	157%
isoprene								
sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	
Mass (mg/mi)	788	19	461	498	22	1415	533.83	98%
MIR	3.57	3.86	3.97	3.45	3.72	3.72	3.72	5%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).
Hot stabilized emissions are represented by Bag 2 of Unified Cycle.

Table 16 Exhaust Gasoline Organic Gas Species Test Results

(MTBE, Hot Stabilized Emissions, Weight Percent)

CNUM	CHEMNAME	VEH1	VEH2	VEH3	VEH4	VEH5	MEAN	COV
1	formaldehyde	0.64	9.07	1.01	0.15	0.10	2.19	176%
1	methyl alcohol	0.36	2.73	0.00	0.00	0.00	0.62	192%
2	acetaldehyde	0.18	2.46	0.00	0.45	0.03	0.62	168%
2	acetylene	4.09	2.86	0.00	1.27	1.82	2.01	78%
2	ethane	2.18	1.55	7.52	4.81	1.03	3.42	80%
2	ethylene	15.23	13.53	3.94	22.26	6.38	12.27	60%
3	1,2-propadiene	0.27	0.21	0.00	0.00	0.00	0.10	130%
3	1-propyne	0.00	0.37	0.00	0.23	0.11	0.14	114%
3	acetone	0.11	0.55	0.28	0.20	0.03	0.23	87%
3	acrolein (2-propenal)	0.00	0.54	0.00	0.00	0.00	0.11	218%
3	propane	0.12	0.06	0.00	0.17	0.07	0.08	75%
3	propionaldehyde	0.03	0.24	0.00	0.16	0.01	0.09	122%
3	propylene	5.99	5.21	2.11	8.43	3.00	4.95	51%
4	1,3-butadiene	0.22	0.28	0.00	0.24	0.06	0.16	75%
4	1-butene	0.62	0.74	0.00	0.79	0.37	0.51	63%
4	1-butyne (ethylacetylene)	0.02	0.00	0.00	0.00	0.00	0.00	n/a
4	2-methyl-2-propenal	0.00	0.31	0.00	0.11	0.01	0.08	163%
4	butyraldehyde	0.00	0.00	0.00	0.03	0.00	0.01	100%
4	cis-2-butene	0.30	0.31	0.00	0.29	0.17	0.22	59%
4	crotonaldehyde	0.00	0.05	0.00	0.06	0.01	0.03	100%
4	isobutane	0.18	0.20	0.00	0.20	0.00	0.11	91%
4	isobutene	4.36	3.54	0.37	1.80	3.47	2.71	59%
4	methyl ethyl ketone (MEK)	0.03	0.00	0.09	0.00	0.01	0.03	133%
4	n-butane	0.56	0.46	0.00	0.81	0.89	0.54	65%
4	trans-2-butene	0.39	0.44	0.00	0.43	0.24	0.30	63%
4	vinylacetylene	0.10	0.12	0.00	0.07	0.03	0.06	83%
5	1-pentene	0.11	0.17	0.00	0.13	0.10	0.10	60%
5	2-methyl-1-butene	0.07	0.17	0.00	0.00	0.00	0.05	140%
5	2-methyl-2-butene	0.03	0.08	0.00	0.00	0.17	0.06	117%
5	3-methyl-1-butene	0.10	0.16	0.00	0.10	0.07	0.09	67%
5	cis-2-pentene	0.08	0.11	0.00	0.07	0.05	0.06	67%
5	cyclopentane	0.30	0.46	0.00	0.31	0.44	0.30	60%
5	cyclopentene	0.11	0.00	0.00	0.00	0.05	0.03	167%
5	isopentane	5.24	4.70	5.50	4.86	7.02	5.47	17%
5	isoprene	0.03	0.00	0.00	0.00	0.00	0.01	100%
5	isovaleraldehyde	0.00	0.18	0.00	0.04	0.00	0.04	200%
5	methyl t-butyl ether (MTBE)	0.35	0.37	0.64	0.32	0.35	0.41	32%
5	n-pentane	2.38	2.34	3.49	2.18	3.31	2.74	22%
5	trans-2-pentene	0.15	0.20	0.00	0.14	0.13	0.12	58%
6	1-hexene	0.05	0.08	0.00	0.00	0.06	0.04	100%
6	2,2-dimethylbutane	0.07	0.17	0.00	0.08	0.11	0.09	67%
6	2,3-dimethylbutane	0.60	0.65	0.00	0.56	0.91	0.54	61%
6	2-methyl-2-pentene	0.07	0.00	0.00	0.00	0.03	0.02	150%
6	2-methylpentane	2.40	2.31	2.20	2.11	3.49	2.50	22%
6	3-methyl-1-pentene	0.04	0.32	0.00	0.00	0.05	0.08	163%
6	3-methylcyclopentene	0.05	0.00	0.00	0.00	0.02	0.01	200%

6	3-methylpentane	1.46	1.44	2.75	1.29	2.20	1.83	34%
6	4-methyl-1-pentene	0.12	0.00	0.00	0.15	0.06	0.07	100%
6	4-methyl-trans-2-pentene	0.03	0.10	0.00	0.00	0.04	0.03	133%
6	benzene	7.34	2.64	9.91	7.08	4.40	6.27	45%
6	cis-2-hexene	0.03	0.00	0.00	0.00	0.03	0.01	100%
6	cyclohexane	0.64	0.54	0.00	0.57	1.01	0.55	65%
6	cyclohexene	0.07	0.04	0.00	0.09	0.04	0.05	60%
6	hexaldehyde	0.00	0.00	0.00	0.02	0.00	0.00	n/a
6	methylcyclopentane	1.79	1.63	2.29	1.58	2.69	1.99	24%
6	n-hexane	1.47	1.35	2.39	1.34	2.24	1.76	29%
6	trans-2-hexene	0.05	0.00	0.00	0.00	0.05	0.02	150%
6	trans-3-hexene	0.03	0.10	0.00	0.00	0.03	0.03	133%
7	1-c-3-dimethylcyclopentane	0.50	0.47	0.00	0.46	0.82	0.45	64%
7	1-t-2-dimethylcyclopentane	0.00	0.08	0.00	0.00	0.00	0.02	200%
7	1-t-3-dimethylcyclopentane	0.54	0.50	0.00	0.48	0.88	0.48	65%
7	2,2,3-trimethylbutane	0.00	0.00	0.00	0.00	0.03	0.01	200%
7	2,3-dimethylpentane	0.85	0.85	1.74	0.73	1.40	1.12	39%
7	2,4-dimethyl-1-pentene	0.00	0.00	0.00	0.00	0.02	0.00	n/a
7	2,4-dimethyl-2-pentene	0.05	0.07	0.00	0.00	0.07	0.04	75%
7	2,4-dimethylpentane	0.56	0.53	0.00	0.50	0.88	0.49	63%
7	2-methyl-2-hexene	0.09	0.00	0.00	0.00	0.02	0.02	200%
7	2-methylhexane	1.13	1.03	1.74	1.02	1.91	1.37	31%
7	3,3-dimethylpentane	0.02	0.00	0.00	0.07	0.03	0.02	150%
7	3,4-dimethyl-1-pentene	0.02	0.00	0.00	0.00	0.00	0.00	n/a
7	3-ethylpentane	0.66	0.51	0.00	0.60	1.06	0.57	67%
7	3-methylhexane	1.21	1.12	2.39	1.09	2.02	1.56	38%
7	4-methyl-trans-2-hexene	0.00	0.00	0.00	0.00	0.02	0.00	n/a
7	benzaldehyde	0.09	0.96	0.00	0.24	0.01	0.26	154%
7	cis-2-heptene	0.02	0.00	0.00	0.00	0.03	0.01	100%
7	ethylcyclopentane	0.20	0.00	0.00	0.17	0.34	0.14	107%
7	methylcyclohexane	1.18	1.00	1.74	1.05	2.02	1.40	33%
7	n-heptane	0.76	0.65	0.00	0.67	1.32	0.68	69%
7	toluene	7.59	4.67	6.70	7.60	7.11	6.74	18%
7	trans-2-heptene	0.00	0.15	0.00	0.00	0.04	0.04	175%
7	trans-3-heptene	0.03	0.00	0.00	0.00	0.03	0.01	200%
8	1,1-methylethylcyclopentane	0.09	0.00	0.00	0.10	0.16	0.07	100%
8	1,2,4-trimethylcyclopentene	0.15	0.15	0.00	0.13	0.26	0.14	64%
8	1-octene	0.07	0.26	0.00	0.00	0.11	0.09	122%
8	1c,2t,3-trimethylcyclopentan	0.10	0.09	0.00	0.09	0.17	0.09	67%
8	2,2,4-trimethylpentane	1.47	1.46	2.84	1.28	2.49	1.91	37%
8	2,2-dimethylhexane	0.13	0.16	0.00	0.12	0.22	0.13	62%
8	2,3,4-trimethylpentane	0.57	0.57	2.02	0.45	1.10	0.94	69%
8	2,3-dimethylhexane	0.24	0.05	0.00	0.25	0.44	0.20	90%
8	2,4-dimethylhexane	0.40	0.40	0.00	0.30	0.65	0.35	69%
8	2,5-dimethylhexane	0.29	0.45	0.00	0.26	0.54	0.31	68%
8	2-methylheptane	0.43	0.48	0.00	0.36	0.77	0.41	68%
8	3,3-dimethylhexane	0.02	0.00	0.00	0.00	0.04	0.01	200%
8	3,4-dimethylhexane	0.07	0.07	0.00	0.00	0.13	0.06	100%
8	3-methylheptane	0.45	0.54	0.00	0.38	0.85	0.44	70%

8	4-methylheptane	0.16	0.00	0.00	0.14	0.29	0.12	100%
8	c-1,2-dimethylcyclohexane	0.04	0.07	0.00	0.00	0.08	0.04	100%
8	cis-1,3-dimethylcyclohexane	0.19	0.10	0.00	0.18	0.34	0.16	81%
8	cis-2-octene	0.05	0.08	0.00	0.00	0.00	0.02	200%
8	ethylbenzene	1.17	1.01	2.75	1.29	1.40	1.52	46%
8	ethylcyclohexane	0.07	0.13	0.00	0.00	0.12	0.06	100%
8	m-xylene	4.99	3.43	8.26	4.54	5.25	5.29	34%
8	n-octane	0.28	0.00	0.00	0.25	0.52	0.21	105%
8	o-xylene	1.63	1.20	4.59	1.62	1.87	2.18	63%
8	styrene	0.10	0.05	0.00	0.07	0.09	0.06	67%
8	t-1-methyl-3-ethylcyclopenta	0.15	0.07	0.00	0.15	0.20	0.11	73%
8	tolualdehyde	0.00	0.51	0.00	0.11	0.00	0.12	183%
8	trans-1,3-dimethylcyclohexan	0.11	0.05	0.00	0.10	0.20	0.09	89%
8	trans-1,4-dimethylcyclohexan	0.06	0.08	0.00	0.00	0.12	0.05	100%
8	trans-2-octene	0.03	0.00	0.00	0.00	0.05	0.02	100%
8	trans-4-octene	0.00	0.13	0.00	0.00	0.00	0.03	200%
9	1,2,3-trimethylbenzene	0.33	0.36	0.00	0.26	0.42	0.28	57%
9	1,2,4-trimethylbenzene	1.52	1.15	7.16	1.21	1.83	2.57	100%
9	1,3,5-trimethylbenzene	0.57	0.48	2.11	0.48	0.71	0.87	80%
9	1,3,5-trimethylcyclohexane	0.05	0.05	0.00	0.00	0.10	0.04	100%
9	1-methyl-3-ethylbenzene	1.08	0.91	4.04	0.99	1.37	1.68	79%
9	1-methyl-4-ethylbenzene	0.45	0.35	1.74	0.41	0.57	0.71	83%
9	1-methyl-4-ethylcyclohexane	0.03	0.00	0.00	0.00	0.07	0.02	150%
9	1-nonene	0.00	0.00	0.00	0.00	0.04	0.01	200%
9	2,2,4-trimethylhexane	0.06	0.05	0.00	0.06	0.10	0.05	80%
9	2,2,5-trimethylhexane	0.31	0.07	2.39	0.29	0.55	0.72	132%
9	2,3,5-trimethylhexane	0.06	0.17	0.00	0.00	0.12	0.07	114%
9	2,4,4-trimethylhexane	0.00	0.00	0.00	0.00	0.07	0.01	300%
9	2,4-dimethylheptane	0.12	0.06	0.00	0.11	0.13	0.08	75%
9	2,6-dimethylheptane	0.13	0.00	0.00	0.11	0.25	0.10	100%
9	2-methyloctane	0.00	0.00	0.00	0.16	0.00	0.03	233%
9	3,5-dimethylheptane	0.22	0.00	0.00	0.19	0.42	0.16	106%
9	3-methyloctane	0.22	0.21	0.00	0.18	0.44	0.21	76%
9	4-methyloctane	0.30	0.26	0.00	0.10	0.36	0.20	75%
9	indan	0.18	0.17	0.00	0.13	0.26	0.15	67%
9	isopropylbenzene (cumene)	0.06	0.08	0.00	0.00	0.11	0.05	100%
9	n-nonane	0.19	0.20	0.00	0.16	0.39	0.19	74%
9	n-propylbenzene	0.22	0.25	0.00	0.20	0.36	0.21	62%
9	o-ethyltoluene	0.34	0.35	0.00	0.33	0.46	0.29	59%
10	1,2,3,4-tetramethylbenzene	0.03	0.12	0.00	0.00	0.06	0.04	125%
10	1,2,3,5-tetramethylbenzene	0.11	0.11	0.00	0.09	0.15	0.09	67%
10	1,2,4,5-tetramethylbenzene	0.09	0.00	0.00	0.07	0.12	0.06	83%
10	1,2-diethylbenzene (ortho)	0.03	0.09	0.00	0.00	0.03	0.03	133%
10	1,2-dimethyl-3-ethylbenzene	0.05	0.10	0.00	0.00	0.09	0.05	100%
10	1,2-dimethyl-4-ethylbenzene	0.23	0.19	1.65	0.16	0.32	0.51	125%
10	1,3-diethylbenzene (meta)	0.10	0.16	0.00	0.08	0.13	0.09	67%
10	1,3-dimethyl-2-ethylbenzene	0.05	0.11	0.00	0.06	0.11	0.07	57%
10	1,3-dimethyl-4-ethylbenzene	0.13	0.15	0.00	0.09	0.16	0.11	64%
10	1,3-dimethyl-5-ethylbenzene	0.28	0.33	1.65	0.21	0.38	0.57	107%

10	1,4-diethylbenzene (para)	0.11	0.13	0.00	0.08	0.19	0.10	70%
10	1,4-dimethyl-2-ethylbenzene	0.15	0.17	0.00	0.11	0.21	0.13	62%
10	1-methyl-2-isopropylbenzene	0.05	0.12	0.00	0.00	0.14	0.06	100%
10	1-methyl-2n-propylbenzene	0.07	0.10	0.00	0.06	0.14	0.08	63%
10	1-methyl-3-isopropylbenzene	0.03	0.09	0.00	0.00	0.05	0.03	133%
10	1-methyl-3n-propylbenzene	0.28	0.46	0.00	0.25	0.40	0.28	64%
10	1-methyl-4-isopropylbenzene	0.03	0.06	0.00	0.00	0.08	0.03	100%
10	2,2,4-trimethylheptane	0.02	0.00	0.00	0.00	0.05	0.02	100%
10	2,2-dimethyloctane	0.07	0.05	0.00	0.00	0.15	0.05	120%
10	2,3-dimethyloctane	0.03	0.06	0.00	0.00	0.05	0.03	100%
10	2,4-dimethyloctane	0.20	0.33	0.00	0.00	0.16	0.14	100%
10	2,5-dimethyloctane	0.05	0.05	0.00	0.00	0.12	0.04	125%
10	2,6-dimethyloctane	0.07	0.08	0.00	0.00	0.15	0.06	100%
10	2-methylindan	0.08	0.00	0.00	0.00	0.11	0.04	125%
10	2-methylnonane	0.26	0.19	0.00	0.21	0.54	0.24	79%
10	3,3-dimethyloctane	0.04	0.05	0.00	0.00	0.08	0.03	100%
10	4-methylindan	0.03	0.11	0.00	0.00	0.04	0.04	125%
10	5-methylindan	0.06	0.07	0.00	0.00	0.10	0.05	100%
10	isobutylbenzene	0.00	0.05	0.00	0.00	0.05	0.02	150%
10	n-decane	0.16	0.15	0.00	0.13	0.24	0.14	64%
10	naphthalene	0.13	0.15	0.00	0.16	0.16	0.12	58%
11	1-ethyl-2n-propylbenzene	0.03	0.05	0.00	0.00	0.06	0.03	100%
11	1-methyl-2-n-butylbenzene	0.05	0.08	0.00	0.00	0.07	0.04	100%
11	1-methyl-2-tert-butylbenzene	0.00	0.15	0.00	0.00	0.03	0.04	175%
11	n-pentylbenzene	0.02	0.05	0.00	0.00	0.04	0.02	100%
11	n-undecane	0.04	0.00	0.00	0.00	0.09	0.02	200%
12	1,3-dipropylbenzene	0.03	0.06	0.00	0.00	0.04	0.02	150%
12	1-(1,1-dme)-3,5-dmbenzene	0.00	0.15	0.00	0.00	0.03	0.04	150%
12	n-dodecane	0.00	0.00	0.00	0.00	0.04	0.01	200%
13	2,2,5-triethylheptane	0.11	0.14	0.00	0.10	0.22	0.11	73%
	sum	99.99	100.00	100.00	100.06	100.02	100.00	
	Mass (mg/mi)	897.00	408.00	11.00	301.00	1230.00	570.00	86%
	MIR	4.01	4.34	3.90	4.37	3.28	3.98	11%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).
Hot stabilized emissions are represented by Bag 2 of Unified Cycle.

Table 17 Exhaust Gasoline Organic Gas Species Test Results

(NonOxy, Hot Stabilized Emissions, Weight Percent)

CNUM	CHEMNAME	VEH1	VEH2	VEH3	VEH4	VEH5	VEH6	VEH7	MEAN	COV
1	formaldehyde	0.02	3.50	0.66	0.01	0.25	0.51	0.01	0.71	177%
1	methyl	0.00	0.40	0.00	0.00	0.00	0.00	0.00	0.06	250%
2	acetaldehyde	0.01	1.08	0.15	0.00	0.12	0.36	0.00	0.24	163%
2	acetylene	4.33	0.87	0.00	0.55	1.81	0.10	0.77	1.20	125%
2	ethane	2.06	0.82	6.12	2.17	1.20	3.13	2.39	2.56	68%
2	ethylene	16.08	6.50	4.50	11.97	7.18	4.67	9.48	8.63	49%
3	1,2-propadiene	0.24	0.10	0.00	0.03	0.00	0.00	0.00	0.05	180%
3	1-propyne	0.00	0.00	0.00	0.05	0.12	0.00	0.05	0.03	133%
3	acetone	0.01	0.28	0.05	0.01	0.10	0.15	0.01	0.09	111%
3	acrolein (2-propenal)	0.00	0.30	0.00	0.00	0.00	0.00	0.00	0.04	300%
3	propane	0.10	0.04	1.06	0.12	0.07	0.00	0.12	0.22	173%
3	propionaldehyde	0.00	0.22	0.03	0.00	0.06	0.05	0.00	0.05	160%
3	propylene	6.50	4.45	3.11	5.92	3.52	2.67	4.76	4.42	32%
4	1,2-butadiene	0.00	0.00	0.00	0.10	0.00	0.00	0.00	0.01	400%
4	1,3-butadiene	0.26	0.14	0.00	0.88	0.06	0.00	0.27	0.23	135%
4	1,3-butadiyne	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
4	1-butene	0.60	0.74	0.00	0.51	0.37	0.00	0.48	0.39	74%
4	1-butyne (ethylacetylene)	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n/a
4	2-butyne	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	n/a
4	2-methyl-2-propenal	0.00	0.22	0.00	0.00	0.04	0.00	0.00	0.04	200%
4	butyraldehyde	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.01	300%
4	cis-2-butene	0.33	0.36	0.00	0.28	0.19	0.00	0.25	0.20	75%
4	crotonaldehyde	0.00	0.11	0.00	0.00	0.03	0.00	0.00	0.02	200%
4	isobutane	0.06	0.06	0.00	0.06	0.03	0.00	0.06	0.04	75%
4	isobutene	2.38	1.70	0.58	2.58	0.84	1.18	1.31	1.51	50%
4	methyl ethyl ketone (MEK)	0.01	0.00	0.05	0.00	0.01	0.00	0.00	0.01	200%
4	n-butane	0.45	0.75	0.18	0.62	0.78	0.46	0.68	0.56	38%
4	trans-2-butene	0.44	0.54	0.00	0.38	0.27	0.00	0.34	0.28	75%
4	vinylacetylene	0.09	0.05	0.00	0.02	0.03	0.00	0.02	0.03	100%
5	1-pentene	0.08	0.17	0.00	0.09	0.08	0.00	0.09	0.07	86%
5	2,2-dimethylpropane	0.09	0.01	0.00	0.01	0.00	0.00	0.01	0.02	150%
5	2-methyl-1-butene	0.09	0.29	0.00	0.14	0.02	0.00	0.02	0.08	138%
5	2-methyl-2-butene	0.20	0.29	0.00	0.31	0.24	0.00	0.16	0.17	76%
5	3-methyl-1-butene	0.11	0.20	0.00	0.11	0.05	0.00	0.08	0.08	88%
5	cis-2-pentene	0.08	0.13	0.00	0.07	0.06	0.00	0.06	0.06	83%
5	cyclopentane	0.30	0.44	0.00	0.37	0.43	0.00	0.37	0.27	70%
5	cyclopentene	0.09	0.13	0.00	0.08	0.05	0.00	0.04	0.06	83%
5	isopentane	6.11	10.08	6.53	7.24	8.51	6.01	7.46	7.42	20%
5	isoprene	0.03	0.02	0.00	0.09	0.00	0.00	0.01	0.02	150%
5	isovaleraldehyde	0.00	0.13	0.00	0.00	0.01	0.00	0.00	0.02	250%
5	methyl t-butyl ether (MTBE)	0.05	0.04	0.40	0.04	0.04	0.00	0.01	0.08	175%
5	n-pentane	2.08	2.98	2.63	2.67	2.93	2.05	2.34	2.53	15%
5	trans-2-pentene	0.13	0.24	0.00	0.12	0.12	0.00	0.12	0.11	73%
6	1-hexene	0.04	0.07	0.00	0.05	0.06	0.00	0.07	0.04	75%
6	2,2-dimethylbutane	1.83	2.70	2.81	2.36	2.65	2.26	2.16	2.39	15%
6	2,3-dimethyl-1-butene	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.01	100%

6	2,3-dimethylbutane	1.20	1.89	1.77	1.56	1.85	2.47	1.51	1.75	22%
6	2-methyl-1-pentene	0.03	0.00	0.00	0.03	0.00	0.00	0.00	0.01	200%
6	2-methyl-2-pentene	0.04	0.06	0.00	0.08	0.02	0.00	0.02	0.03	100%
6	2-methylpentane	3.07	4.52	3.19	3.94	4.50	3.18	3.83	3.75	17%
6	3,3-dimethyl-1-butene	0.03	0.06	0.00	0.03	0.03	0.00	0.03	0.03	67%
6	3-methyl-1-pentene	0.04	0.07	0.00	0.05	0.06	0.00	0.04	0.04	75%
6	3-methylcyclopentene	0.03	0.04	0.00	0.05	0.02	0.00	0.02	0.02	100%
6	3-methylpentane	1.78	2.68	2.63	2.31	2.68	2.67	2.28	2.43	14%
6	4-methyl-1-pentene	0.08	0.16	0.00	0.02	0.04	0.00	0.03	0.05	120%
6	4-methyl-trans-2-pentene	0.04	0.07	0.00	0.05	0.05	0.00	0.04	0.04	75%
6	benzene	5.96	1.12	9.67	5.75	4.40	6.27	5.70	5.55	46%
6	cis-2-hexene	0.03	0.05	0.00	0.03	0.03	0.00	0.02	0.02	100%
6	cyclohexane	1.02	1.44	1.32	1.32	1.59	1.23	1.38	1.33	14%
6	cyclohexene	0.07	0.11	0.00	0.07	0.04	1.34	0.01	0.23	213%
6	hexaldehyde	0.00	0.04	0.23	0.00	0.00	0.00	0.00	0.04	200%
6	methylcyclopentane	1.45	2.13	2.07	1.88	2.19	2.26	1.92	1.99	14%
6	n-hexane	1.25	1.81	1.92	1.62	1.90	2.05	1.63	1.74	16%
6	trans-2-hexene	0.05	0.08	0.00	0.05	0.06	0.00	0.04	0.04	75%
6	trans-3-hexene	0.03	0.06	0.00	0.03	0.04	0.00	0.03	0.03	67%
7	1-c-3-dimethylcyclopentane	0.09	0.11	0.00	0.10	0.13	0.00	0.11	0.08	63%
7	1-t-2-dimethylcyclopentane	0.08	0.09	0.00	0.08	0.11	0.00	0.20	0.08	88%
7	1-t-3-dimethylcyclopentane	0.08	0.12	0.00	0.11	0.14	0.00	0.12	0.08	75%
7	2,2,3-trimethylbutane	0.00	0.00	0.00	0.02	0.06	0.00	0.05	0.02	150%
7	2,3-dimethylpentane	0.68	1.05	1.29	0.94	1.16	0.00	0.94	0.86	50%
7	2,4-dimethyl-1-pentene	0.02	0.04	0.00	0.00	0.02	0.00	0.02	0.01	200%
7	2,4-dimethyl-2-pentene	0.08	0.13	0.00	0.11	0.12	0.00	0.11	0.08	75%
7	2,4-dimethylpentane	0.48	0.70	0.00	0.68	0.77	0.00	0.65	0.47	70%
7	2-methyl-2-hexene	0.04	0.01	0.00	0.03	0.01	0.00	0.02	0.02	100%
7	2-methyl-trans-3-hexene	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	n/a
7	2-methylhexane	0.68	0.99	1.14	0.90	1.16	1.28	0.98	1.02	20%
7	3,3-dimethylpentane	0.02	0.03	0.00	0.00	0.02	0.00	0.03	0.01	100%
7	3,4-dimethyl-1-pentene	0.04	0.06	0.00	0.03	0.00	0.00	0.00	0.02	100%
7	3-ethylpentane	0.08	0.10	0.00	0.10	0.12	3.54	0.00	0.56	234%
7	3-methyl-cis-2-hexene	0.00	0.01	0.00	0.03	0.00	0.00	0.00	0.00	n/a
7	3-methylhexane	0.76	1.12	1.29	1.02	1.30	0.00	1.09	0.94	48%
7	4-methyl-trans-2-hexene	0.02	0.02	0.00	0.00	0.02	1.23	0.02	0.19	242%
7	benzaldehyde	0.00	0.54	0.10	0.00	0.14	1.75	0.00	0.36	178%
7	cis-2-heptene	0.02	0.04	0.00	0.03	0.02	0.00	0.02	0.02	50%
7	ethylcyclopentane	0.00	0.05	0.00	0.03	0.07	0.00	0.07	0.03	100%
7	methylcyclohexane	0.31	0.45	0.00	0.41	0.55	0.00	0.47	0.31	74%
7	n-heptane	0.46	0.65	0.00	0.63	0.81	0.00	0.68	0.46	72%
7	toluene	10.44	9.16	9.21	10.74	10.12	11.97	10.95	10.37	10%
7	trans-2-heptene	0.02	0.02	0.00	0.01	0.02	0.00	0.02	0.01	100%
7	trans-3-heptene	0.02	0.03	0.00	0.02	0.02	1.03	0.02	0.16	238%
8	1,1-methylethylcyclopentane	0.05	0.09	0.00	0.03	0.04	0.00	0.06	0.04	75%
8	1,2,4-trimethylcyclopentene	0.04	0.05	0.00	0.06	0.07	0.00	0.05	0.04	75%
8	1-octene	0.03	0.03	0.00	0.01	0.01	0.00	0.02	0.02	50%
8	1c,2t,3-trimethylcyclopentan	0.02	0.02	0.00	0.03	0.03	1.54	0.03	0.24	238%
8	2,2,4-trimethylpentane	2.56	3.83	4.00	3.53	4.47	0.00	3.52	3.13	48%

8	2,2-dimethylhexane	0.05	0.07	0.00	0.04	0.07	0.00	0.07	0.04	75%
8	2,3,4-trimethylpentane	0.98	1.55	2.05	1.33	1.92	0.00	1.42	1.32	52%
8	2,3-dimethylhexane	0.26	0.39	0.00	0.37	0.55	0.00	0.44	0.29	76%
8	2,4,4-trimethyl-2-pentene	0.00	0.02	0.00	0.00	0.00	0.00	0.02	0.01	100%
8	2,4-dimethylhexane	0.44	0.66	0.00	0.59	0.77	0.00	0.54	0.43	72%
8	2,5-dimethylhexane	0.39	0.50	0.00	0.51	0.67	0.00	0.62	0.38	74%
8	2-methylheptane	0.19	0.25	0.00	0.27	0.35	0.00	0.29	0.19	74%
8	3,3-dimethylhexane	0.02	0.03	0.00	0.00	0.03	0.00	0.02	0.01	100%
8	3,4-dimethylhexane	0.08	0.10	0.00	0.10	0.13	0.00	0.10	0.07	71%
8	3-methylheptane	0.24	0.33	0.00	0.34	0.42	0.00	0.37	0.24	75%
8	4-methylheptane	0.09	0.11	0.00	0.10	0.14	0.00	0.12	0.08	75%
8	c-1,2-dimethylcyclohexane	0.02	0.03	0.00	0.01	0.02	0.00	0.03	0.02	50%
8	cis-1,3-dimethylcyclohexane	0.14	0.18	0.00	0.15	0.20	0.00	0.18	0.12	75%
8	cis-2-octene	0.00	0.02	0.00	0.00	0.00	0.00	0.05	0.01	200%
8	ethylbenzene	1.31	1.41	2.07	1.35	1.44	3.03	1.56	1.74	36%
8	ethylcyclohexane	0.03	0.04	0.00	0.04	0.05	0.00	0.04	0.03	67%
8	m-xylene	5.14	4.72	3.31	4.79	5.03	10.32	5.83	5.59	40%
8	n-octane	0.15	0.17	0.00	0.19	0.24	0.00	0.22	0.14	71%
8	o-xylene	1.76	1.74	2.86	1.80	1.94	4.11	2.17	2.34	37%
8	styrene	0.14	0.02	0.00	0.44	0.04	0.00	0.06	0.10	160%
8	t-1-methyl-3-ethylcyclopenta	0.08	0.11	0.00	0.04	0.07	0.00	0.08	0.05	80%
8	tolualdehyde	0.00	0.21	0.00	0.00	0.05	0.82	0.00	0.16	188%
8	trans-1,3-dimethylcyclohexan	0.06	0.08	0.00	0.07	0.10	0.00	0.10	0.06	67%
8	trans-1,4-dimethylcyclohexan	0.08	0.11	0.00	0.07	0.09	0.00	0.08	0.06	67%
8	trans-2-octene	0.00	0.03	0.00	0.01	0.00	0.00	0.00	0.01	100%
8	trans-4-octene	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	n/a
9	1,2,3-trimethylbenzene	0.32	0.29	1.09	0.28	0.35	0.98	0.43	0.53	66%
9	1,2,4-trimethylbenzene	1.59	1.42	5.04	1.37	1.61	5.19	2.09	2.61	66%
9	1,3,5-trimethylbenzene	0.57	0.52	1.52	0.47	0.61	1.75	0.75	0.88	59%
9	1,3,5-trimethylcyclohexane	0.04	0.04	0.00	0.05	0.03	0.00	0.05	0.03	67%
9	1-methyl-3-ethylbenzene	1.08	1.13	2.68	0.98	1.25	1.03	1.38	1.36	44%
9	1-methyl-4-ethylbenzene	0.43	0.47	0.15	0.40	0.51	0.00	0.59	0.37	57%
9	1-methyl-4-ethylcyclohexane	0.00	0.01	0.00	0.00	0.01	0.00	0.02	0.01	100%
9	1-nonene	0.00	0.01	0.00	0.00	0.00	0.00	0.03	0.01	100%
9	2,2,4-trimethylhexane	0.04	0.05	0.00	0.03	0.05	0.00	0.05	0.03	67%
9	2,2,5-trimethylhexane	1.13	1.61	2.38	1.51	2.09	2.05	1.58	1.77	24%
9	2,3,5-trimethylhexane	0.18	0.27	0.00	0.13	0.35	0.00	0.27	0.17	82%
9	2,3-dimethylheptane	0.00	0.00	3.31	0.00	0.03	0.00	0.00	0.48	260%
9	2,4,4-trimethylhexane	0.03	0.08	0.00	0.02	0.06	0.00	0.00	0.03	100%
9	2,4-dimethylheptane	0.06	0.10	0.00	0.04	0.09	0.00	0.09	0.05	80%
9	2,6-dimethylheptane	0.05	0.07	0.00	0.07	0.09	0.00	0.08	0.05	80%
9	2-methyloctane	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.01	200%
9	3,5-dimethylheptane	0.10	0.13	0.00	0.12	0.19	0.00	0.15	0.10	70%
9	3-methyloctane	0.09	0.11	0.00	0.13	0.17	0.00	0.14	0.09	78%
9	4-methyloctane	0.14	0.17	0.00	0.14	0.27	0.00	0.22	0.13	77%
9	indan	0.13	0.13	0.00	0.09	0.16	0.00	0.17	0.10	70%
9	isopropylbenzene (cumene)	0.05	0.06	0.00	0.06	0.07	0.00	0.06	0.04	75%
9	n-nonane	0.09	0.10	0.00	0.10	0.18	0.00	0.15	0.09	78%
9	n-propylbenzene	0.21	0.28	0.00	0.24	0.32	0.00	0.31	0.20	70%

9	o-ethyltoluene	0.34	0.36	0.51	0.34	0.41	1.18	0.68	0.55	56%
10	1,2,3,4-tetramethylbenzene	0.05	0.02	0.00	0.02	0.05	0.00	0.06	0.03	67%
10	1,2,3,5-tetramethylbenzene	0.16	0.08	0.48	0.08	0.12	0.00	0.14	0.15	100%
10	1,2,4,5-tetramethylbenzene	0.12	0.07	0.00	0.06	0.10	0.00	0.00	0.05	100%
10	1,2-diethylbenzene (ortho)	0.02	0.02	0.00	0.01	0.02	0.00	0.03	0.01	100%
10	1,2-dimethyl-3-ethylbenzene	0.05	0.03	0.00	0.03	0.03	0.00	0.05	0.03	67%
10	1,2-dimethyl-4-ethylbenzene	0.25	0.18	0.48	0.13	0.24	1.13	0.29	0.39	90%
10	1,3-diethylbenzene (meta)	0.09	0.08	0.00	0.07	0.10	0.00	0.12	0.07	71%
10	1,3-dimethyl-2-ethylbenzene	0.07	0.06	0.00	0.06	0.10	0.00	0.09	0.05	80%
10	1,3-dimethyl-4-ethylbenzene	0.14	0.10	0.00	0.10	0.12	0.00	0.17	0.09	78%
10	1,3-dimethyl-5-ethylbenzene	0.26	0.22	0.71	0.18	0.27	0.00	0.32	0.28	79%
10	1,4-diethylbenzene (para)	0.11	0.11	0.00	0.08	0.15	0.98	0.15	0.22	155%
10	1,4-dimethyl-2-ethylbenzene	0.18	0.14	0.00	0.13	0.20	0.00	0.22	0.12	75%
10	1-methyl-2-isopropylbenzene	0.06	0.06	0.00	0.05	0.07	0.00	0.11	0.05	80%
10	1-methyl-2n-propylbenzene	0.07	0.07	0.00	0.06	0.12	0.00	0.10	0.06	83%
10	1-methyl-3-isopropylbenzene	0.02	0.02	0.00	0.00	0.03	0.00	0.03	0.01	100%
10	1-methyl-3n-propylbenzene	0.30	0.34	1.64	0.24	0.39	0.00	0.35	0.47	115%
10	1-methyl-4-isopropylbenzene	0.02	0.02	0.00	0.02	0.03	0.00	0.04	0.02	50%
10	2,2,4-trimethylheptane	0.02	0.02	0.00	0.02	0.00	0.00	0.00	0.01	100%
10	2,2-dimethyloctane	0.02	0.03	0.00	0.01	0.05	0.00	0.04	0.02	100%
10	2,3-dimethyloctane	0.02	0.03	0.00	0.05	0.02	0.00	0.04	0.02	100%
10	2,4-dimethyloctane	0.02	0.03	0.00	0.03	0.05	0.00	0.04	0.02	100%
10	2,5-dimethyloctane	0.02	0.03	0.00	0.03	0.05	0.00	0.04	0.02	100%
10	2,6-dimethyloctane	0.02	0.03	0.00	0.03	0.06	0.00	0.05	0.03	67%
10	2-methylindan	0.09	0.03	0.00	0.04	0.05	0.00	0.07	0.04	75%
10	2-methylnonane	0.21	0.23	0.00	0.26	0.41	0.00	0.05	0.17	88%
10	3,3-dimethyloctane	0.02	0.02	0.00	0.03	0.03	0.00	0.03	0.02	50%
10	4-methylindan	0.03	0.02	0.00	0.00	0.03	0.00	0.04	0.02	100%
10	5-methylindan	0.07	0.03	0.00	0.03	0.07	0.00	0.03	0.03	100%
10	isobutylbenzene	0.02	0.02	0.00	0.02	0.02	0.00	0.04	0.02	50%
10	n-decane	0.09	0.10	0.00	0.09	0.07	0.00	0.15	0.07	71%
10	naphthalene	0.16	0.06	1.01	0.05	0.08	0.00	0.15	0.22	164%
11	1-ethyl-2n-propylbenzene	0.03	0.01	0.00	0.00	0.01	0.00	0.03	0.01	100%
11	1-methyl-2-n-butylbenzene	0.05	0.03	0.00	0.00	0.02	0.00	0.05	0.02	100%
11	1-methyl-2-tert-butylbenzene	0.00	0.01	0.00	0.00	0.01	0.00	0.18	0.03	233%
11	n-pentylbenzene	0.03	0.01	0.00	0.00	0.01	0.00	0.00	0.01	100%
11	n-undecane	0.04	0.03	0.00	0.05	0.06	0.00	0.00	0.03	100%
12	1,3-dipropylbenzene	0.02	0.01	0.00	0.00	0.02	0.00	0.04	0.01	100%
12	1-(1,1-dme)-3,5-dmbenzene	0.03	0.01	0.00	0.00	0.01	0.00	0.02	0.01	100%
12	n-dodecane	0.02	0.00	0.00	0.00	0.01	0.00	0.02	0.01	100%
13	2,2,5-triethylheptane	0.07	0.09	0.00	0.12	0.15	0.00	0.12	0.08	75%
	sum	100.04	100.01	99.98	99.97	100.00	99.98	99.98	100.01	
	Mass (mg/mi)	1194	1908	20	1058	1074	19	1334	944	73%
	MIR	4.05	3.63	3.23	3.74	3.21	3.92	3.65	3.63	9%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).
Hot stabilized emissions are represented by Bag 2 of Unified Cycle.

Table 18 Exhaust Gasoline Organic Gas Species Test Results

(Et2.0%, Hot Stabilized Emissions, Weight Percent)

CNUM	CHEMNAME	VEH1	VEH3	VEH4	VEH5	VEH6	VEH7	MEAN	COV
1	formaldehyde	3.23	2.01	0.04	0.02	0.50	0.08	0.98	137%
1	methyl alcohol	0.42	0.00	0.00	0.00	0.00	0.16	0.10	177%
2	acetaldehyde	1.62	0.26	0.01	0.01	0.00	0.37	0.38	166%
2	acetylene	2.63	0.00	0.72	1.73	0.18	1.05	1.05	94%
2	ethane	1.91	4.49	3.61	1.70	3.05	1.99	2.79	40%
2	ethyl alcohol	0.63	0.00	0.00	0.00	0.00	0.27	0.15	173%
2	ethylene	12.91	3.23	15.19	8.43	5.01	8.85	8.94	51%
3	1,2-propadiene	0.15	0.00	0.00	0.00	0.00	0.08	0.04	165%
3	1-propyne	0.29	0.00	0.13	0.11	0.00	0.00	0.09	130%
3	acetone	0.50	0.00	0.00	0.01	0.18	0.17	0.14	135%
3	propane	0.09	1.27	0.16	0.22	0.27	0.08	0.35	131%
3	propionaldehyde	0.15	0.26	0.00	0.00	0.18	0.05	0.11	100%
3	propylene	4.58	2.27	6.90	4.11	3.01	3.74	4.10	39%
4	1,2-butadiene	0.00	0.00	0.00	0.00	0.00	0.18	0.03	245%
4	1,3-butadiene	0.09	0.00	0.46	0.00	0.00	0.31	0.14	137%
4	1-butene	0.45	0.00	0.61	0.47	0.00	0.42	0.33	80%
4	2-methyl-2-propenal	0.10	0.00	0.00	0.00	0.00	0.02	0.02	200%
4	butyraldehyde	0.01	0.00	0.00	0.00	0.00	0.00	0.00	245%
4	cis-2-butene	0.23	0.00	0.27	0.17	0.00	0.21	0.15	81%
4	crotonaldehyde	0.07	0.00	0.00	0.00	0.00	0.03	0.02	173%
4	isobutane	0.09	0.00	0.08	0.06	0.00	0.05	0.05	83%
4	isobutene	1.47	0.00	1.22	0.10	0.00	1.35	0.69	105%
4	methyl ethyl ketone (MEK)	0.03	0.00	0.00	0.00	0.14	0.02	0.03	172%
4	n-butane	0.25	0.26	0.43	0.51	0.36	0.26	0.35	31%
4	trans-2-butene	0.32	0.00	0.39	0.27	0.00	0.28	0.21	80%
4	vinylacetylene	0.07	0.00	0.00	0.04	0.00	0.03	0.02	123%
5	1-pentene	0.08	0.00	0.10	0.10	0.00	0.14	0.07	82%
5	2-methyl-1-butene	0.16	0.00	0.00	0.00	0.00	0.17	0.06	155%
5	2-methyl-2-butene	0.11	0.00	0.09	0.12	0.00	0.00	0.05	111%
5	3-methyl-1-butene	0.09	0.00	0.10	0.00	0.00	0.08	0.05	110%
5	cis-2-pentene	0.06	0.00	0.07	0.06	0.00	0.06	0.04	78%
5	cyclopentane	0.49	0.00	0.53	0.58	0.00	0.54	0.36	78%
5	cyclopentene	0.03	0.00	0.08	0.04	0.00	0.04	0.03	95%
5	isopentane	5.01	4.18	5.81	7.40	5.51	5.36	5.55	19%
5	isovaleraldehyde	0.03	0.00	0.01	0.00	0.00	0.00	0.01	182%
5	methyl t-butyl ether (MTBE)	0.00	0.74	0.06	0.07	0.55	0.00	0.24	137%
5	n-pentane	1.35	1.27	1.53	1.85	1.59	1.52	1.52	13%
5	trans-2-pentene	0.12	0.00	0.13	0.12	0.00	0.10	0.08	78%
6	1-hexene	0.04	0.00	0.06	0.04	0.00	0.05	0.03	81%
6	2,2-dimethylbutane	2.07	2.33	2.27	2.79	2.60	2.28	2.39	11%
6	2,3-dimethylbutane	1.43	1.59	1.54	1.95	1.91	1.62	1.67	13%
6	2-methyl-2-pentene	0.00	0.00	0.00	0.00	0.00	0.02	0.00	245%
6	2-methylpentane	4.76	3.86	5.25	6.48	4.78	5.67	5.13	17%
6	3-methyl-1-pentene	0.06	0.00	0.04	0.06	0.00	0.03	0.03	86%
6	3-methylcyclopentene	0.00	0.00	0.00	0.00	0.00	0.02	0.00	245%
6	3-methylpentane	3.00	3.12	3.26	4.11	2.87	3.54	3.32	14%

6	4-methyl-1-pentene	0.00	0.00	0.05	0.08	0.00	0.02	0.03	133%
6	4-methyl-trans-2-pentene	0.02	0.00	0.00	0.05	0.00	0.02	0.02	132%
6	benzene	6.49	8.46	5.75	4.19	12.89	5.40	7.20	43%
6	cis-2-hexene	0.00	0.00	0.00	0.00	0.00	0.01	0.00	245%
6	cyclohexane	0.59	0.00	0.70	0.83	0.91	0.76	0.63	52%
6	cyclohexene	0.04	0.00	0.05	0.08	0.00	0.04	0.04	88%
6	hexaldehyde	0.07	0.00	0.00	0.00	0.00	0.00	0.01	245%
6	methylcyclopentane	2.19	2.33	2.46	2.96	2.82	2.69	2.58	12%
6	n-hexane	0.70	1.32	0.82	1.04	1.46	0.86	1.03	29%
6	trans-2-hexene	0.00	0.00	0.00	0.00	0.00	0.02	0.00	245%
6	trans-3-hexene	0.04	0.00	0.00	0.00	0.00	0.02	0.01	167%
7	1-c-3-dimethylcyclopentane	0.00	0.00	0.29	0.37	0.00	0.32	0.16	111%
7	1-t-2-dimethylcyclopentane	0.28	0.00	0.00	0.00	0.00	0.10	0.06	179%
7	1-t-3-dimethylcyclopentane	0.28	0.00	0.31	0.39	0.00	0.34	0.22	79%
7	2,2,3-trimethylbutane	0.00	0.00	0.00	0.00	0.00	0.03	0.01	245%
7	2,3-dimethylpentane	1.05	1.59	0.68	0.94	1.23	0.82	1.05	31%
7	2,4-dimethyl-2-pentene	0.11	0.00	0.10	0.13	0.00	0.10	0.07	79%
7	2,4-dimethylpentane	0.41	0.00	0.47	0.62	0.00	0.51	0.34	80%
7	2-methyl-2-hexene	0.00	0.00	0.00	0.04	0.00	0.00	0.01	245%
7	2-methylhexane	0.00	1.27	1.19	1.58	1.55	1.30	1.15	51%
7	3,3-dimethylpentane	0.03	0.00	0.00	0.00	0.00	0.00	0.01	245%
7	3,4-dimethyl-1-pentene	0.03	0.00	0.00	0.00	0.00	0.00	0.01	245%
7	3-ethylpentane	0.09	0.00	0.42	0.53	0.00	0.33	0.23	100%
7	3-methylhexane	1.16	1.43	1.26	1.67	2.19	1.43	1.52	24%
7	benzaldehyde	0.70	1.37	0.00	0.00	0.00	0.12	0.37	154%
7	cis-2-heptene	0.00	0.00	0.00	0.00	0.00	0.01	0.00	245%
7	ethylcyclopentane	0.00	0.00	0.13	0.17	0.00	0.00	0.05	157%
7	methylcyclohexane	0.80	1.22	0.91	1.16	1.23	1.02	1.06	17%
7	n-heptane	0.83	1.00	0.91	1.20	1.18	1.05	1.03	14%
7	toluene	6.93	8.04	8.22	7.24	7.88	8.44	7.79	8%
7	trans-2-heptene	0.00	0.00	0.00	0.00	0.00	0.03	0.01	245%
8	1,1-methylethylcyclopentane	0.07	0.00	0.10	0.07	0.00	0.09	0.06	80%
8	1,2,4-trimethylcyclopentene	0.18	0.00	0.13	0.17	0.00	0.20	0.11	80%
8	1-octene	0.05	0.00	0.05	0.00	0.00	0.06	0.03	110%
8	1c,2t,3-trimethylcyclopentane	0.07	0.00	0.08	0.10	0.00	0.09	0.06	79%
8	2,2,4-trimethylpentane	1.72	2.33	1.76	2.52	1.73	2.12	2.03	17%
8	2,2-dimethylhexane	0.05	0.00	0.12	0.17	0.00	0.08	0.07	96%
8	2,3,4-trimethylpentane	0.63	1.11	0.62	0.95	1.23	0.79	0.89	28%
8	2,3-dimethylhexane	0.28	0.00	0.29	0.47	0.00	0.33	0.23	83%
8	2,4-dimethylhexane	0.43	0.00	0.42	0.57	0.00	0.53	0.33	79%
8	2,5-dimethylhexane	0.40	0.00	0.32	0.46	0.00	0.50	0.28	80%
8	2-methylheptane	0.43	0.00	0.46	0.65	0.00	0.56	0.35	81%
8	3,3-dimethylhexane	0.00	0.00	0.04	0.07	0.00	0.00	0.02	163%
8	3,4-dimethylhexane	0.10	0.00	0.09	0.13	0.00	0.11	0.07	80%
8	3-methylheptane	0.61	0.00	0.57	0.79	0.00	0.70	0.45	79%
8	4-methylheptane	0.20	0.00	0.20	0.28	0.00	0.24	0.15	80%
8	c-1,2-dimethylcyclohexane	0.05	0.00	0.04	0.00	0.00	0.00	0.02	156%
8	cis-1,3-dimethylcyclohexane	0.21	0.00	0.23	0.30	0.00	0.26	0.17	80%
8	cis-2-octene	0.04	0.00	0.00	0.00	0.00	0.00	0.01	245%

8	ethylbenzene	1.22	2.49	1.45	1.53	1.59	0.03	1.39	57%
8	ethylcyclohexane	0.08	0.00	0.07	0.10	0.00	0.11	0.06	81%
8	m-xylene	0.03	7.99	5.32	5.83	7.43	6.80	5.57	52%
8	n-octane	0.31	0.00	0.34	0.48	1.00	0.41	0.42	77%
8	o-xylene	1.72	3.54	1.92	2.09	3.55	2.38	2.53	32%
8	styrene	0.04	0.00	0.29	0.04	0.00	0.06	0.07	153%
8	t-1-methyl-3-ethylcyclopentane	0.08	0.00	0.14	0.12	0.00	0.11	0.08	82%
8	tolualdehyde	0.41	0.95	0.00	0.00	0.00	0.07	0.24	161%
8	trans-1,3-dimethylcyclohexane	0.12	0.00	0.13	0.18	0.00	0.15	0.10	80%
8	trans-1,4-dimethylcyclohexane	0.09	0.00	0.09	0.12	0.00	0.11	0.07	79%
8	trans-2-octene	0.03	0.00	0.00	0.00	0.00	0.04	0.01	157%
9	1,2,3-trimethylbenzene	0.44	1.32	0.33	0.50	0.00	0.38	0.50	89%
9	1,2,4-trimethylbenzene	1.84	6.03	1.61	2.12	5.56	2.79	3.33	59%
9	1,3,5-trimethylbenzene	0.68	1.85	0.61	0.79	2.00	0.96	1.15	54%
9	1,3,5-trimethylcyclohexane	0.08	0.00	0.08	0.11	0.00	1.77	0.34	206%
9	1-methyl-3-ethylbenzene	1.19	3.12	1.18	1.49	2.82	1.68	1.91	44%
9	1-methyl-4-ethylbenzene	0.52	1.80	0.51	0.66	1.32	0.71	0.92	57%
9	1-methyl-4-ethylcyclohexane	0.03	0.00	0.00	0.05	0.00	0.03	0.02	117%
9	2,2,4-trimethylhexane	0.00	0.00	0.00	0.00	0.00	0.03	0.01	245%
9	2,2,5-trimethylhexane	0.24	0.00	0.25	0.37	0.00	0.33	0.20	81%
9	2,3,5-trimethylhexane	0.05	0.00	0.05	0.08	0.00	0.06	0.04	82%
9	2,3-dimethylheptane	5.32	0.00	0.00	0.00	0.00	0.00	0.89	245%
9	2,4,4-trimethylhexane	0.02	0.00	0.00	0.07	0.00	0.04	0.02	132%
9	2,4-dimethylheptane	0.06	0.00	0.08	0.12	0.00	0.07	0.06	86%
9	2,6-dimethylheptane	0.10	0.00	0.10	0.14	0.00	0.06	0.07	86%
9	2-methyloctane	0.00	0.00	0.18	0.00	0.00	0.00	0.03	245%
9	3,5-dimethylheptane	0.14	0.00	0.18	0.24	0.00	0.10	0.11	88%
9	3-methyloctane	0.23	0.00	0.23	0.33	0.00	0.29	0.18	80%
9	4-methyloctane	0.30	0.00	0.14	0.24	0.00	0.38	0.18	89%
9	indan	0.15	0.00	0.12	0.20	0.00	0.19	0.11	82%
9	isopropylbenzene (cumene)	0.09	0.00	0.09	0.11	0.00	0.12	0.07	79%
9	n-nonane	0.15	0.00	0.15	0.21	0.00	0.19	0.12	80%
9	n-propylbenzene	0.33	0.00	0.30	0.44	0.00	0.43	0.25	80%
9	o-ethyltoluene	0.43	1.32	0.42	0.73	1.32	0.60	0.80	52%
10	1,2,3,4-tetramethylbenzene	0.11	0.00	0.04	0.08	0.00	0.07	0.05	89%
10	1,2,3,5-tetramethylbenzene	0.15	1.00	0.11	0.18	0.96	0.28	0.45	93%
10	1,2,4,5-tetramethylbenzene	0.00	1.16	0.08	0.14	0.00	0.22	0.27	167%
10	1,2-diethylbenzene (ortho)	0.04	0.00	0.00	0.00	0.00	0.04	0.01	155%
10	1,2-dimethyl-3-ethylbenzene	0.09	0.00	0.05	0.08	0.00	0.10	0.05	84%
10	1,2-dimethyl-4-ethylbenzene	0.26	1.16	0.19	0.30	1.09	0.36	0.56	79%
10	1,3-diethylbenzene (meta)	0.14	0.00	0.09	0.13	0.00	0.16	0.09	82%
10	1,3-dimethyl-2-ethylbenzene	0.07	0.00	0.05	0.08	0.00	0.11	0.05	86%
10	1,3-dimethyl-4-ethylbenzene	0.17	0.00	0.11	0.17	0.00	0.24	0.12	85%
10	1,3-dimethyl-5-ethylbenzene	0.35	1.27	0.26	0.38	1.05	0.49	0.63	66%
10	1,4-diethylbenzene (para)	0.14	0.00	0.11	0.21	0.00	0.19	0.11	84%
10	1,4-dimethyl-2-ethylbenzene	0.20	0.00	0.14	0.20	0.00	0.27	0.14	83%
10	1-methyl-2-isopropylbenzene	0.07	0.00	0.00	0.09	0.00	0.08	0.04	111%
10	1-methyl-2n-propylbenzene	0.10	0.00	0.07	0.12	0.00	0.12	0.07	82%
10	1-methyl-3-isopropylbenzene	0.06	0.00	0.00	0.14	0.00	0.07	0.05	126%

10	1-methyl-3n-propylbenzene	0.40	1.32	0.25	0.43	1.28	0.48	0.69	69%
10	1-methyl-4-isopropylbenzene	0.04	0.00	0.00	0.04	0.00	0.04	0.02	110%
10	2,2,4-trimethylheptane	0.03	0.00	0.00	0.05	0.00	0.04	0.02	114%
10	2,2-dimethyloctane	0.04	0.00	0.07	0.10	0.00	0.01	0.04	113%
10	2,3-dimethyloctane	0.03	0.00	0.00	0.00	0.00	0.05	0.01	162%
10	2,4-dimethyloctane	0.21	0.00	0.00	0.06	0.00	0.19	0.08	129%
10	2,5-dimethyloctane	0.04	0.00	0.05	0.07	0.00	0.05	0.04	82%
10	2,6-dimethyloctane	0.06	0.00	0.06	0.09	0.00	0.07	0.05	81%
10	2-methylindan	0.00	0.00	0.04	0.08	0.00	0.14	0.04	132%
10	2-methylnonane	0.18	0.00	0.23	0.13	0.00	0.30	0.14	87%
10	3,3-dimethyloctane	0.05	0.00	0.05	0.07	0.00	0.06	0.04	80%
10	4-methylindan	0.09	0.00	0.00	0.00	0.00	0.00	0.02	245%
10	5-methylindan	0.04	0.00	0.00	0.06	0.00	0.12	0.04	131%
10	isobutylbenzene	0.02	0.00	0.00	0.00	0.00	0.03	0.01	159%
10	n-decane	0.04	0.00	0.05	0.15	0.00	0.07	0.05	108%
10	naphthalene	0.04	1.06	0.05	0.00	0.00	0.04	0.20	213%
10	sec-butylbenzene	0.00	0.00	0.00	0.00	0.00	0.05	0.01	245%
11	1-ethyl-2n-propylbenzene	0.04	0.00	0.00	0.00	0.00	0.00	0.01	245%
11	1-methyl-2-n-butylbenzene	0.07	0.00	0.00	0.00	0.00	0.08	0.03	155%
11	1-methyl-2-tert-butylbenzene	0.21	0.00	0.00	0.00	0.00	0.00	0.04	245%
11	n-pentylbenzene	0.05	0.00	0.00	0.00	0.00	0.00	0.01	245%
11	n-undecane	0.00	0.00	0.00	0.00	0.00	0.02	0.00	245%
12	1,3-dipropylbenzene	0.04	0.00	0.00	0.00	0.00	0.05	0.02	156%
12	1-(1,1-dme)-3,5-dmbenzene	0.21	0.00	0.00	0.00	0.00	0.00	0.04	245%
12	n-dodecane	0.00	0.00	0.00	0.00	0.00	0.03	0.01	245%
13	2,2,5-triethylheptane	0.04	0.00	0.11	0.15	0.00	0.09	0.07	95%
	sum	99.98	99.99	100.01	99.97	99.96	100.03	99.99	
	Mass (mg/mi)	788	19	461	498	22	1415	533.83	98%
	MIR	3.57	3.86	3.97	3.45	3.72	3.72	3.72	5%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).
Hot stabilized emissions are represented by Bag 2 of Unified Cycle.

Table 19 Exhaust Gasoline Organic Gas Species Test Results

(MTBE, Start Emissions, Weight Percent)

NAME	VEH1	VEH2	VEH3	VEH4	VEH5	MEAN	COV
ethane	0.73	1.98	0.88	0.77	0.12	0.90	75%
propane	0.03	0.17	0.06	0.06	0.01	0.07	92%
butanes	0.30	0.14	0.56	0.79	0.65	0.49	54%
pentanes	5.88	0.00	6.85	9.42	9.26	6.28	61%
c6+ br-alkanes	31.19	10.87	25.83	37.25	37.80	28.59	39%
c6+ n-alkanes	3.96	1.65	3.39	4.97	5.07	3.81	37%
ethene	8.30	14.54	8.22	5.38	1.66	7.62	62%
propene	3.33	6.39	3.89	2.65	0.91	3.43	58%
1,3-butadiene	0.66	1.09	0.47	0.47	0.23	0.59	55%
c4+ alkenes	5.75	5.89	7.67	6.32	3.16	5.76	28%
acetylene	9.65	13.49	2.43	2.37	2.32	6.05	86%
alkynes	0.22	0.94	0.16	0.26	0.22	0.36	91%
benzene	1.72	5.46	2.76	2.73	1.26	2.79	58%
toluene	6.89	9.04	7.34	6.57	6.67	7.30	14%
c8+ aromatics	10.33	22.14	20.85	15.28	17.98	17.32	27%
formaldehyde	0.86	0.00	1.32	0.74	0.32	0.65	78%
acetaldehyde	0.37	0.00	0.50	0.36	0.16	0.28	71%
c3+aldehydes	0.75	0.38	0.74	0.24	0.23	0.47	55%
MTBE	7.09	4.62	3.16	1.85	10.73	5.49	64%
ethanol							
c3+ alcohols	1.65	0.97	2.16	0.98	0.90	1.33	42%
ketones	0.15	0.06	0.48	0.28	0.24	0.24	65%
styrenes	0.19	0.18	0.17	0.22	0.06	0.16	39%
isoprene	0.00	0.00	0.10	0.05	0.03	0.04	118%
sum	100.00	100.00	100.00	100.00	100.00	100.00	
Mass (mg/mi)	3399	1714	1564	3773	6320	3354	57%
MIR	3.12	4.36	3.92	3.17	2.74	3.47	19%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).
Start emissions are represented by Bag 1 minus Bag 3 of Unified Cycle.

Table 20 Exhaust Gasoline Organic Gas Species Test Results

(NonOxy, Start Emissions, Weight Percent)

NAME	VEH1	VEH2	VEH3	VEH4	VEH5	VEH6	VEH7	MEAN	COV
ethane	0.59	1.40	0.78	0.62	0.20	0.79	0.68	0.72	49%
propane	0.05	0.07	0.02	0.05	0.01	0.07	0.08	0.05	52%
butanes	0.37	0.10	0.51	0.60	0.72	0.67	0.88	0.55	47%
pentanes	8.27	6.69	8.57	10.40	10.48	11.31	7.00	8.96	20%
c6+ br-alkanes	32.33	22.30	31.39	40.47	40.13	31.33	23.85	31.69	22%
c6+ n-alkanes	3.21	2.25	2.66	3.78	3.89	2.68	2.40	2.98	22%
ethene	8.15	10.08	8.07	5.77	2.49	6.80	7.99	7.05	34%
propene	2.74	4.75	4.40	2.78	1.22	4.70	4.70	3.61	38%
1,3-butadiene	0.48	0.63	0.23	0.43	0.18	0.78	0.71	0.49	47%
c4+ alkenes	5.46	5.02	5.43	4.10	1.99	6.23	6.00	4.89	30%
acetylene	10.64	11.17	2.51	2.29	3.60	3.65	13.41	6.75	71%
alkynes	0.18	0.36	0.26	0.10	0.25	0.11	0.80	0.30	82%
benzene	1.82	4.03	2.40	2.94	1.16	1.83	2.06	2.32	40%
toluene	9.98	11.34	11.00	10.07	10.69	10.37	9.06	10.36	7%
c8+ aromatics	12.97	19.23	18.94	13.99	21.96	14.75	17.21	17.01	19%
formaldehyde	0.88	0.00	1.04	0.34	0.22	1.46	0.78	0.67	76%
acetaldehyde	0.47	0.00	0.51	0.21	0.12	0.70	0.59	0.37	70%
c3+aldehydes	0.61	0.22	0.67	0.25	0.14	0.97	0.56	0.49	61%
MTBE	0.21	0.01	0.07	0.08	0.11	0.07	0.12	0.10	67%
Ethanol	0.00	0.00	0.00	0.00	0.00	0.00	0.31	0.04	265%
c3+ alcohols	0.00	0.20	0.00	0.14	0.24	0.00	0.00	0.08	130%
ketones	0.29	0.00	0.39	0.17	0.09	0.48	0.44	0.27	69%
styrenes	0.22	0.12	0.15	0.26	0.10	0.26	0.25	0.19	36%
isoprene	0.08	0.02	0.00	0.15	0.01	0.00	0.11	0.05	113%
sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	
Mass (mg/mi)	5662	3042	1487	6720	5774	1574	6432	4384	52%
MIR	3.22	3.82	3.74	3.05	3.07	3.56	3.66	3.45	9%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).
Start emissions are represented by Bag 1 minus Bag 3 of Unified Cycle.

Table 21 Exhaust Gasoline Organic Gas Species Test Results (Et2.0%, Start Emissions, Weight Percent)

NAME	VEH1	VEH3	VEH4	VEH5	VEH6	VEH7	MEAN	COV
ethane	0.79	0.84	0.74	0.31	0.88	0.64	0.70	30%
propane	0.06	0.07	0.07	0.00	0.08	0.05	0.06	52%
butanes	0.19	0.25	0.33	0.38	0.53	0.24	0.32	38%
pentanes	4.11	6.29	6.55	6.43	5.57	5.69	5.77	16%
c6+br-alkanes	34.27	27.85	43.14	35.54	25.71	30.41	32.82	19%
c6+n-alkanes	2.33	2.50	3.82	3.32	2.18	2.60	2.79	23%
ethene	10.94	8.24	5.81	3.93	10.42	8.43	7.96	34%
propene	4.03	4.37	2.79	1.99	5.36	3.88	3.74	32%
1,3-butadiene	0.73	0.09	0.32	0.18	0.75	1.17	0.54	77%
c4+alkenes	4.53	3.46	2.63	1.95	4.32	5.06	3.66	33%
acetylene	9.33	3.33	1.79	3.52	6.04	9.18	5.53	58%
alkynes	0.81	0.13	0.21	0.30	0.50	0.22	0.36	69%
benzene	2.52	2.81	3.37	1.56	3.34	2.10	2.62	27%
toluene	7.57	8.32	8.51	8.32	8.11	7.30	8.02	6%
c8+aromatics	11.96	25.14	16.74	26.03	22.07	18.95	20.15	27%
formaldehyde	0.66	1.10	0.48	0.90	1.24	0.64	0.84	35%
acetaldehyde	0.85	0.96	0.53	0.80	1.16	0.46	0.79	33%
c3+aldehydes	0.67	0.65	0.30	0.50	0.94	0.28	0.56	45%
MTBE	0.05	0.05	0.16	0.18	0.05	0.09	0.10	61%
ethanol	2.61	3.00	0.99	3.11	0.00	1.61	1.89	66%
c3+ alcohols	0.45	0.00	0.27	0.37	0.00	0.22	0.22	85%
ketones	0.29	0.31	0.22	0.27	0.38	0.10	0.26	37%
styrenes	0.23	0.19	0.21	0.04	0.36	0.43	0.24	56%
isoprene	0.02	0.03	0.02	0.04	0.06	0.25	0.07	125%
sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	
Mass (mg/mi)	788	19	461	498	22	1415	533.83	98%
MIR	3.57	3.86	3.97	3.45	3.72	3.72	3.72	5%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).
Start emissions are represented by Bag 1 minus Bag 3 of Unified Cycle.

Table 22 Exhaust Gasoline Organic Gas Species Test Results
(MTBE, Start Emissions, Weight Percent)

CNUM	CHEMNAME	VEH1	VEH2	VEH3	VEH4	VEH5	MEAN	COV
1	formaldehyde	0.86	0.00	1.32	0.74	0.32	0.65	78%
1	methyl alcohol	1.65	0.97	2.16	0.98	0.90	1.33	42%
2	acetaldehyde	0.37	0.00	0.50	0.36	0.16	0.28	71%
2	acetylene	9.65	13.49	2.43	2.37	2.32	6.05	86%
2	ethane	0.73	1.98	0.88	0.77	0.12	0.90	74%
2	ethylene	8.30	14.54	8.22	5.38	1.66	7.62	62%
3	1,2-propadiene	0.45	0.54	0.28	0.00	0.00	0.25	100%
3	1-propyne	0.00	0.70	0.00	0.18	0.14	0.20	145%
3	acetone	0.11	0.06	0.45	0.26	0.16	0.21	71%
3	acrolein (2-propenal)	0.13	0.00	0.00	0.00	0.00	0.03	200%
3	propane	0.03	0.17	0.06	0.06	0.01	0.07	86%
3	propionaldehyde	0.10	0.07	0.21	0.10	0.07	0.11	55%
3	propylene	3.33	6.39	3.89	2.65	0.91	3.43	58%
4	1,2-butadiene	0.00	0.00	0.00	0.03	0.02	0.01	200%
4	1,3-butadiene	0.66	1.09	0.47	0.47	0.23	0.59	54%
4	1,3-butadiyne	0.00	0.06	0.00	0.02	0.02	0.02	150%
4	1-butene	0.71	0.76	1.06	0.37	0.20	0.62	55%
4	2-butyne	0.00	0.00	0.09	0.00	0.01	0.02	200%
4	2-methyl-2-propenal	0.09	0.00	0.09	0.07	0.03	0.06	67%
4	butyraldehyde	0.00	0.00	0.02	0.00	0.00	0.00	n/a
4	cis-2-butene	0.16	0.27	0.50	0.14	0.07	0.23	74%
4	crotonaldehyde	0.08	0.04	0.08	0.05	0.04	0.06	33%
4	isobutane	0.06	0.14	0.13	0.00	0.00	0.07	100%
4	isobutene	2.10	2.77	3.24	3.82	0.95	2.58	43%
4	methyl ethyl ketone (MEK)	0.04	0.00	0.04	0.02	0.08	0.04	75%
4	n-butane	0.24	0.00	0.43	0.79	0.65	0.42	76%
4	trans-2-butene	0.21	0.35	0.46	0.19	0.09	0.26	54%
4	vinylacetylene	0.22	0.18	0.07	0.07	0.06	0.12	58%
5	1-pentene	0.10	0.09	0.16	0.09	0.07	0.10	30%
5	2,2-dimethylpropane	0.00	0.00	0.00	0.00	0.01	0.00	n/a
5	2-methyl-1-butene	0.23	0.22	0.18	0.02	0.03	0.14	71%
5	2-methyl-2-butene	0.27	0.00	0.12	0.22	0.25	0.17	65%
5	3-methyl-1-butene	0.08	0.07	0.12	0.05	0.03	0.07	43%
5	cis-2-pentene	0.07	0.05	0.11	0.07	0.07	0.07	29%
5	cyclopentane	0.31	0.00	0.31	0.41	0.43	0.29	59%
5	cyclopentene	0.10	0.09	0.17	0.06	0.06	0.09	44%
5	isopentane	3.86	0.00	4.50	6.22	5.94	4.10	61%
5	isoprene	0.00	0.00	0.10	0.05	0.03	0.04	100%
5	isovaleraldehyde	0.00	0.00	0.00	0.00	0.03	0.01	200%
5	methyl t-butyl ether (MTBE)	7.09	4.62	3.16	1.85	10.73	5.49	64%
5	n-pentane	1.72	0.00	2.04	2.79	2.89	1.89	62%
5	trans-1,3-pentadiene	0.09	0.00	0.00	0.00	0.00	0.02	200%
5	trans-2-pentene	0.12	0.08	0.17	0.11	0.15	0.13	23%
6	1-hexene	0.07	0.05	0.11	0.06	0.05	0.07	29%
6	2,2-dimethylbutane	0.07	0.00	0.07	0.08	0.10	0.06	67%
6	2,3-dimethylbutane	0.66	0.00	0.58	0.85	0.92	0.60	60%

6	2-methyl-1-pentene	0.00	0.00	0.00	0.03	0.02	0.01	200%
6	2-methyl-2-pentene	0.13	0.06	0.08	0.06	0.05	0.07	43%
6	2-methylpentane	2.72	0.34	2.31	3.32	3.67	2.47	53%
6	3,3-dimethyl-1-butene	0.00	0.01	0.00	0.00	0.01	0.00	n/a
6	3-methyl-1-pentene	0.00	0.00	0.07	0.04	0.03	0.03	100%
6	3-methylcyclopentene	0.08	0.05	0.06	0.04	0.03	0.05	40%
6	3-methylpentane	1.76	0.24	1.46	2.10	2.30	1.57	52%
6	4-methyl-1-pentene	0.10	0.00	0.08	0.05	0.03	0.05	80%
6	4-methyl-cis-2-pentene	0.00	0.00	0.03	0.00	0.00	0.01	100%
6	4-methyl-trans-2-pentene	0.00	0.01	0.03	0.03	0.03	0.02	100%
6	benzene	1.72	5.46	2.76	2.73	1.26	2.79	58%
6	cis-2-hexene	0.00	0.02	0.04	0.03	0.04	0.03	67%
6	cyclohexane	1.01	0.32	0.76	1.07	1.13	0.86	38%
6	cyclohexene	0.07	0.07	0.07	0.04	0.05	0.06	17%
6	methylcyclopentane	2.52	0.74	1.93	2.73	2.92	2.17	41%
6	n-hexane	1.87	0.45	1.54	2.20	2.46	1.70	46%
6	trans-2-hexene	0.07	0.03	0.06	0.05	0.08	0.06	33%
6	trans-3-hexene	0.00	0.00	0.04	0.03	0.05	0.03	67%
7	1-c-3-dimethylcyclopentane	0.86	0.34	0.61	0.88	0.90	0.72	33%
7	1-t-2-dimethylcyclopentane	0.00	0.04	0.00	0.00	0.00	0.01	200%
7	1-t-3-dimethylcyclopentane	0.95	0.34	0.66	0.95	1.01	0.78	36%
7	2,2,3-trimethylbutane	0.00	0.00	0.00	0.04	0.05	0.02	150%
7	2,3-dimethylpentane	1.49	0.33	0.99	1.45	1.49	1.15	44%
7	2,4-dimethyl-1-pentene	0.00	0.00	0.02	0.01	0.02	0.01	100%
7	2,4-dimethyl-2-pentene	0.00	0.01	0.06	0.06	0.06	0.04	75%
7	2,4-dimethylpentane	0.84	0.20	0.62	0.90	1.00	0.71	45%
7	2-methyl-2-hexene	0.08	0.04	0.03	0.03	0.01	0.04	50%
7	2-methyl-trans-3-hexene	0.00	0.01	0.00	0.00	0.00	0.00	n/a
7	2-methylhexane	1.86	0.58	1.32	2.01	2.25	1.60	42%
7	3,3-dimethylpentane	0.00	0.01	0.00	0.02	0.01	0.01	100%
7	3,4-dimethyl-1-pentene	0.00	0.00	0.02	0.00	0.00	0.01	100%
7	3-ethyl-2-pentene	0.00	0.04	0.00	0.01	0.00	0.01	200%
7	3-ethylpentane	1.17	0.36	0.80	1.16	1.19	0.94	38%
7	3-methyl-cis-2-hexene	0.14	0.00	0.00	0.05	0.03	0.04	150%
7	3-methyl-trans-3-hexene	0.00	0.00	0.00	0.02	0.01	0.01	100%
7	3-methylhexane	2.06	0.62	1.43	2.11	2.24	1.69	40%
7	4-methyl-trans-2-hexene	0.00	0.00	0.00	0.03	0.04	0.01	200%
7	benzaldehyde	0.35	0.26	0.33	0.01	0.06	0.20	80%
7	cis-2-heptene	0.00	0.02	0.04	0.04	0.06	0.03	67%
7	ethylcyclopentane	0.35	0.00	0.26	0.37	0.38	0.27	59%
7	methylcyclohexane	2.18	0.88	1.54	2.22	2.27	1.82	33%
7	n-heptane	1.36	0.51	0.95	1.41	1.48	1.14	36%
7	toluene	6.89	9.04	7.34	6.57	6.67	7.30	14%
7	trans-2-heptene	0.00	0.00	0.04	0.05	0.07	0.03	100%
7	trans-3-heptene	0.16	0.02	0.04	0.07	0.08	0.07	71%
8	1,1-methylethylcyclopentane	0.15	0.07	0.14	0.18	0.18	0.15	33%
8	1,2,4-trimethylcyclopentene	0.26	0.13	0.19	0.28	0.29	0.23	30%
8	1-octene	0.12	0.06	0.10	0.14	0.13	0.11	27%
8	1c,2t,3-trimethylcyclopentan	0.19	0.08	0.14	0.21	0.21	0.17	29%

8	2,2,4-trimethylpentane	2.44	0.62	1.72	2.56	2.60	1.99	42%
8	2,2-dimethylhexane	0.21	0.09	0.16	0.22	0.22	0.18	33%
8	2,3,4-trimethylpentane	1.11	0.30	0.87	1.28	1.26	0.96	43%
8	2,3-dimethylhexane	0.43	0.15	0.37	0.49	0.48	0.38	37%
8	2,4,4-trimethyl-2-pentene	0.00	0.00	0.00	0.01	0.01	0.00	n/a
8	2,4-dimethylhexane	0.70	0.26	0.52	0.69	0.64	0.56	32%
8	2,5-dimethylhexane	0.48	0.34	0.36	0.61	0.63	0.48	29%
8	2-methylheptane	0.67	0.34	0.57	0.86	0.81	0.65	32%
8	3,3-dimethylhexane	0.00	0.00	0.03	0.05	0.04	0.02	100%
8	3,4-dimethylhexane	0.12	0.06	0.12	0.15	0.14	0.12	33%
8	3-methylheptane	0.72	0.40	0.63	0.95	0.92	0.72	31%
8	4-methylheptane	0.25	0.12	0.22	0.32	0.31	0.24	33%
8	c-1,2-dimethylcyclohexane	0.00	0.04	0.06	0.10	0.10	0.06	67%
8	cis-1,3-dimethylcyclohexane	0.31	0.17	0.27	0.38	0.37	0.30	30%
8	cis-2-octene	0.07	0.04	0.00	0.01	0.02	0.03	100%
8	ethylbenzene	1.26	1.80	1.81	1.31	1.51	1.54	17%
8	ethylcyclohexane	0.10	0.07	0.10	0.14	0.13	0.11	27%
8	m-xylene	4.20	7.44	6.44	4.96	6.01	5.81	22%
8	n-octane	0.40	0.26	0.40	0.60	0.56	0.44	32%
8	o-xylene	1.38	2.39	2.25	1.78	2.02	1.96	20%
8	styrene	0.19	0.18	0.17	0.22	0.06	0.16	38%
8	t-1-methyl-3-ethylcyclopenta	0.15	0.09	0.26	0.20	0.21	0.18	33%
8	tolualdehyde	0.00	0.00	0.00	0.00	0.00	0.00	n/a
8	trans-1,3-dimethylcyclohexan	0.17	0.09	0.16	0.22	0.22	0.18	28%
8	trans-1,4-dimethylcyclohexan	0.11	0.05	0.09	0.13	0.13	0.10	30%
8	trans-2-octene	0.00	0.04	0.05	0.06	0.06	0.04	75%
8	trans-4-octene	0.00	0.00	0.00	0.00	0.07	0.01	300%
9	1,2,3-trimethylbenzene	0.14	0.49	0.47	0.32	0.37	0.36	39%
9	1,2,4-trimethylbenzene	0.85	2.41	2.28	1.52	1.92	1.80	35%
9	1,3,5-trimethylbenzene	0.33	0.89	0.84	0.57	0.71	0.67	33%
9	1,3,5-trimethylcyclohexane	0.00	0.06	0.07	0.11	0.09	0.07	57%
9	1-methyl-3-ethylbenzene	0.78	1.72	1.75	1.12	1.33	1.34	31%
9	1-methyl-4-ethylbenzene	0.34	0.74	0.74	0.47	0.59	0.58	31%
9	1-methyl-4-ethylcyclohexane	0.00	0.05	0.05	0.09	0.07	0.05	60%
9	1-nonene	0.00	0.00	0.03	0.05	0.04	0.02	100%
9	2,2,4-trimethylhexane	0.00	0.04	0.07	0.03	0.11	0.05	80%
9	2,2,5-trimethylhexane	0.47	0.24	0.58	0.64	0.56	0.50	32%
9	2,3,5-trimethylhexane	0.09	0.05	0.14	0.14	0.12	0.11	36%
9	2,3-dimethylheptane	0.00	0.00	0.00	0.02	0.02	0.01	100%
9	2,4,4-trimethylhexane	0.00	0.02	0.06	0.06	0.07	0.04	75%
9	2,4-dimethylheptane	0.26	0.05	0.09	0.13	0.11	0.13	62%
9	2,6-dimethylheptane	0.16	0.12	0.19	0.29	0.24	0.20	35%
9	2-methyloctane	0.00	0.00	0.00	0.41	0.45	0.17	141%
9	3,5-dimethylheptane	0.27	0.12	0.33	0.50	0.40	0.32	44%
9	3-methyloctane	0.21	0.22	0.33	0.52	0.41	0.34	38%
9	4-methyloctane	0.33	0.29	0.45	0.30	0.12	0.30	40%
9	indan	0.09	0.24	0.30	0.20	0.24	0.21	38%
9	isopropylbenzene (cumene)	0.06	0.08	0.11	0.12	0.11	0.09	22%
9	n-nonane	0.15	0.21	0.28	0.44	0.33	0.28	39%

9	n-propylbenzene	0.19	0.31	0.37	0.33	0.36	0.31	23%
9	o-ethyltoluene	0.24	0.53	0.54	0.39	0.41	0.42	29%
10	1,2,3,4-tetramethylbenzene	0.00	0.13	0.04	0.03	0.01	0.04	125%
10	1,2,3,5-tetramethylbenzene	0.00	0.14	0.15	0.09	0.11	0.10	60%
10	1,2,4,5-tetramethylbenzene	0.00	0.03	0.12	0.07	0.15	0.07	86%
10	1,2-diethylbenzene (ortho)	0.00	0.04	0.04	0.02	0.03	0.03	67%
10	1,2-dimethyl-3-ethylbenzene	0.00	0.10	0.07	0.06	0.06	0.06	67%
10	1,2-dimethyl-4-ethylbenzene	0.08	0.27	0.34	0.19	0.25	0.23	43%
10	1,3-diethylbenzene (meta)	0.04	0.16	0.15	0.09	0.10	0.11	45%
10	1,3-dimethyl-2-ethylbenzene	0.00	0.07	0.07	0.08	0.06	0.06	50%
10	1,3-dimethyl-4-ethylbenzene	0.04	0.20	0.18	0.10	0.12	0.13	46%
10	1,3-dimethyl-5-ethylbenzene	0.12	0.41	0.40	0.22	0.28	0.29	41%
10	1,4-diethylbenzene (para)	0.05	0.14	0.17	0.14	0.16	0.13	38%
10	1,4-dimethyl-2-ethylbenzene	0.05	0.21	0.21	0.14	0.15	0.15	47%
10	1-methyl-2-isopropylbenzene	0.00	0.06	0.06	0.07	0.04	0.05	60%
10	1-methyl-2n-propylbenzene	0.00	0.08	0.11	0.11	0.09	0.08	63%
10	1-methyl-3-isopropylbenzene	0.00	0.05	0.05	0.05	0.05	0.04	50%
10	1-methyl-3n-propylbenzene	0.08	0.33	0.32	0.28	0.28	0.26	38%
10	1-methyl-4-isopropylbenzene	0.00	0.04	0.05	0.07	0.05	0.04	75%
10	2,2,4-trimethylheptane	0.00	0.03	0.04	0.07	0.05	0.04	75%
10	2,2-dimethyloctane	0.06	0.05	0.11	0.18	0.19	0.12	50%
10	2,3-dimethyloctane	0.00	0.03	0.04	0.06	0.00	0.03	100%
10	2,4-dimethyloctane	0.00	0.19	0.14	0.16	0.13	0.12	58%
10	2,5-dimethyloctane	0.00	0.04	0.09	0.15	0.11	0.08	75%
10	2,6-dimethyloctane	0.00	0.09	0.10	0.17	0.12	0.10	60%
10	2-methylindan	0.00	0.03	0.10	0.06	0.08	0.05	80%
10	2-methylnonane	0.17	0.18	0.36	0.57	0.39	0.33	52%
10	3,3-dimethyloctane	0.00	0.05	0.06	0.09	0.08	0.06	67%
10	4-methylindan	0.00	0.12	0.04	0.02	0.02	0.04	125%
10	5-methylindan	0.00	0.06	0.09	0.07	0.07	0.06	50%
10	isobutylbenzene	0.00	0.01	0.03	0.05	0.04	0.03	67%
10	n-decane	0.19	0.14	0.13	0.21	0.16	0.17	18%
10	naphthalene	0.00	0.01	0.06	0.07	0.06	0.04	75%
11	1-ethyl-2n-propylbenzene	0.00	0.04	0.04	0.03	0.03	0.03	67%
11	1-methyl-2-n-butylbenzene	0.00	0.07	0.02	0.02	0.07	0.04	75%
11	1-methyl-2-tert-butylbenzene	0.00	0.15	0.00	0.02	0.02	0.04	175%
11	n-pentylbenzene	0.00	0.03	0.03	0.00	0.02	0.02	50%
11	n-undecane	0.00	0.03	0.05	0.06	0.04	0.04	50%
12	1,3-dipropylbenzene	0.00	0.02	0.03	0.02	0.02	0.02	50%
12	1-(1,1-dme)-3,5-dmbenzene	0.00	0.13	0.00	0.02	0.01	0.03	200%
12	n-dodecane	0.00	0.03	0.00	0.03	0.02	0.02	100%
13	2,2,5-triethylheptane	0.12	0.10	0.19	0.26	0.20	0.17	41%
	sum	100.06	99.94	99.95	99.92	99.99	100.01	
	Mass (mg/mi)	3399	1714	1564	3773	6320	3354	57%
	MIR	3.12	4.36	3.92	3.17	2.74	3.47	19%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).
Start emissions are represented by Bag 1 minus Bag 3 of Unified Cycle.

Table 23 Exhaust Gasoline Organic Gas Species Test Results
(NonOxy, Start Emissions, Weight Percent)

CNUM	CHEMNAME	VEH1	VEH2	VEH3	VEH4	VEH5	VEH6	VEH7	MEAN	COV
1	formaldehyde	0.88	0.00	1.04	0.34	0.22	1.46	0.78	0.67	76%
1	methyl alcohol	0.00	0.20	0.00	0.14	0.24	0.00	0.00	0.08	130%
2	acetaldehyde	0.47	0.00	0.51	0.21	0.12	0.70	0.59	0.37	70%
2	acetylene	10.64	11.17	2.51	2.29	3.60	3.65	13.41	6.75	71%
2	ethane	0.59	1.40	0.78	0.62	0.20	0.79	0.68	0.72	49%
2	ethyl alcohol	0.00	0.00	0.00	0.00	0.00	0.00	0.31	0.04	265%
2	ethylene	8.15	10.08	8.07	5.77	2.49	6.80	7.99	7.05	34%
3	1,2-propadiene	0.25	0.42	0.22	0.05	0.00	0.30	0.00	0.18	92%
3	1-propyne	0.00	0.00	0.13	0.05	0.18	0.00	0.55	0.13	153%
3	acetone	0.25	0.00	0.35	0.16	0.07	0.40	0.40	0.23	69%
3	acrolein (2-propenal)	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.01	265%
3	propane	0.05	0.07	0.02	0.05	0.01	0.07	0.08	0.05	52%
3	propionaldehyde	0.17	0.13	0.18	0.08	0.06	0.34	0.22	0.17	56%
3	propylene	2.74	4.75	4.40	2.78	1.22	4.70	4.70	3.61	38%
4	1,2-butadiene	0.00	0.00	0.00	0.16	0.01	0.51	0.05	0.1	182%
4	1,3-butadiene	0.48	0.63	0.23	0.43	0.18	0.78	0.71	0.49	47%
4	1,3-butadiyne	0.06	0.08	0.00	0.00	0.01	0.00	0.07	0.03	114%
4	1-butene	0.47	0.60	1.03	0.32	0.13	0.70	0.75	0.57	52%
4	1-butyne (athylacetylene)	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.01	265%
4	2-butyne	0.00	0.02	0.08	0.00	0.00	0.11	0.00	0.03	150%
4	2-methyl-2-propenal	0.08	0.00	0.08	0.03	0.01	0.13	0.10	0.06	76%
4	butyraldehyde	0.04	0.05	0.03	0.00	0.02	0.02	0.06	0.03	67%
4	cis-2-butene	0.16	0.26	0.56	0.14	0.06	0.26	0.22	0.24	67%
4	crotonaldehyde	0.08	0.04	0.08	0.03	0.02	0.12	0.06	0.06	54%
4	isobutane	0.04	0.02	0.06	0.05	0.02	0.09	0.00	0.04	75%
4	isobutene	1.42	1.80	1.15	1.28	0.41	2.17	1.76	1.43	40%
4	methyl ethyl ketone (MEK)	0.05	0.00	0.04	0.02	0.02	0.07	0.05	0.04	72%
4	n-butane	0.33	0.08	0.45	0.55	0.70	0.58	0.88	0.51	51%
4	trans-2-butene	0.22	0.36	0.51	0.19	0.16	0.38	0.31	0.3	41%
4	vinylacetylene	0.12	0.22	0.05	0.05	0.06	0.00	0.18	0.1	80%
5	1-pentene	0.07	0.08	0.13	0.06	0.05	0.13	0.16	0.1	43%
5	2,2-dimethylpropane	0.05	0.00	0.00	0.01	0.01	0.00	0.00	0.01	207%
5	2-methyl-1-butene	0.10	0.22	0.18	0.11	0.01	0.33	0.06	0.14	75%
5	2-methyl-2-butene	0.49	0.16	0.28	0.29	0.23	0.00	0.55	0.28	66%
5	3-methyl-1-butene	0.07	0.08	0.15	0.07	0.01	0.16	0.13	0.1	55%
5	cis-2-pentene	0.06	0.08	0.10	0.05	0.04	0.11	0.08	0.07	31%
5	cyclopentane	0.36	0.30	0.37	0.43	0.44	0.47	0.31	0.38	17%
5	cyclopentene	0.08	0.07	0.15	0.05	0.03	0.09	0.13	0.09	48%
5	isopentane	5.73	4.77	5.95	7.26	7.34	7.84	4.63	6.22	21%
5	isoprene	0.08	0.02	0.00	0.15	0.01	0.00	0.11	0.05	113%
5	isovaleraldehyde	0.02	0.00	0.00	0.00	0.01	0.09	0.02	0.02	149%
5	methyl t-butyl ether (MTBE)	0.21	0.01	0.07	0.08	0.11	0.07	0.12	0.0957	67%
5	n-pentane	2.12	1.62	2.24	2.70	2.70	3.00	2.06	2.35	20%
5	trans-1,3-pentadiene	0.37	0.00	0.00	0.01	0.00	0.00	0.00	0.05	256%
5	trans-2-pentene	0.11	0.13	0.16	0.09	0.08	0.19	0.14	0.13	30%
6	1-hexene	0.05	0.06	0.10	0.05	0.06	0.08	0.17	0.08	52%

6	2,2-dimethylbutane	2.01	1.42	1.96	2.34	2.25	2.62	1.39	2	23%
6	2,3-dimethyl-1-butene	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0	265%
6	2,3-dimethylbutane	1.63	1.15	1.38	1.84	1.80	1.84	1.08	1.53	21%
6	2-methyl-1-pentene	0.08	0.00	0.00	0.06	0.03	0.00	0.06	0.03	102%
6	2-methyl-2-pentene	0.18	0.03	0.05	0.11	0.04	0.06	0.09	0.08	64%
6	2-methylpentane	4.29	3.08	3.49	4.68	4.54	4.70	2.97	3.96	19%
6	3,3-dimethyl-1-butene	0.00	0.01	0.03	0.01	0.00	0.04	0.00	0.01	112%
6	3-methyl-1-pentene	0.05	0.04	0.06	0.05	0.04	0.06	0.07	0.05	24%
6	3-methylcyclopentene	0.12	0.02	0.04	0.07	0.01	0.05	0.05	0.05	73%
6	3-methylpentane	2.58	1.82	2.09	2.82	2.75	2.75	1.74	2.36	20%
6	4-methyl-1-pentene	0.05	0.02	0.00	0.01	0.00	0.00	0.08	0.02	132%
6	4-methyl-trans-2-pentene	0.06	0.04	0.05	0.04	0.05	0.06	0.06	0.05	22%
6	benzene	1.82	4.03	2.40	2.94	1.16	1.83	2.06	2.32	40%
6	cis-2-hexene	0.06	0.04	0.06	0.02	0.05	0.05	0.04	0.05	30%
6	cyclohexane	1.77	1.26	1.33	1.91	1.92	1.46	1.15	1.54	21%
6	cyclohexene	0.06	0.05	0.05	0.06	0.03	0.09	0.10	0.06	37%
6	hexaldehyde	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0	265%
6	methylcyclopentane	2.35	1.71	1.78	2.48	2.48	2.22	1.52	2.08	19%
6	n-hexane	1.98	1.37	1.50	2.08	2.05	1.79	1.37	1.74	18%
6	trans-2-hexene	0.11	0.07	0.08	0.07	0.08	0.09	0.08	0.08	15%
6	trans-3-hexene	0.08	0.04	0.05	0.04	0.06	0.06	0.06	0.06	20%
7	1-c-3-dimethylcyclopentane	0.14	0.09	0.11	0.15	0.16	0.12	0.09	0.12	22%
7	1-t-2-dimethylcyclopentane	0.15	0.07	0.09	0.06	0.06	0.10	0.00	0.08	61%
7	1-t-3-dimethylcyclopentane	0.15	0.10	0.12	0.17	0.17	0.13	0.10	0.13	23%
7	2,2,3-trimethylbutane	0.00	0.00	0.02	0.03	0.06	0.05	0.05	0.03	81%
7	2,3-dimethylpentane	1.24	0.73	0.91	1.42	1.34	1.05	0.73	1.06	27%
7	2,4-dimethyl-1-pentene	0.00	0.01	0.00	0.01	0.01	0.00	0.05	0.01	167%
7	2,4-dimethyl-2-pentene	0.10	0.06	0.11	0.15	0.12	0.13	0.08	0.11	27%
7	2,4-dimethylpentane	0.84	0.52	0.59	0.91	0.85	0.73	0.50	0.71	24%
7	2-methyl-2-hexene	0.08	0.00	0.01	0.03	0.01	0.00	0.06	0.03	114%
7	2-methyl-trans-3-hexene	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0	265%
7	2-methylhexane	1.20	0.79	0.89	1.38	1.36	0.99	1.30	1.13	21%
7	3,3-dimethylpentane	0.00	0.01	0.00	0.01	0.01	0.00	0.04	0.01	143%
7	3,4-dimethyl-1-pentene	0.05	0.03	0.02	0.03	0.00	0.00	0.00	0.02	106%
7	3-ethyl-2-pentene	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0	265%
7	3-ethylpentane	0.12	0.08	0.09	0.23	0.24	0.00	0.18	0.14	65%
7	3-methyl-cis-2-hexene	0.09	0.00	0.00	0.08	0.00	0.00	0.06	0.03	124%
7	3-methyl-trans-3-hexene	0.24	0.00	0.00	0.04	0.00	0.00	0.00	0.04	225%
7	3-methylhexane	1.35	0.87	1.02	1.56	1.53	1.11	0.87	1.19	25%
7	4-methyl-trans-2-hexene	0.00	0.03	0.00	0.01	0.02	0.00	0.00	0.01	136%
7	benzaldehyde	0.18	0.00	0.29	0.09	0.02	0.24	0.09	0.13	85%
7	cis-2-heptene	0.05	0.03	0.04	0.06	0.02	0.04	0.04	0.04	35%
7	ethylcyclopentane	0.00	0.04	0.00	0.05	0.10	0.00	0.09	0.04	108%
7	methylcyclohexane	0.58	0.39	0.47	0.70	0.71	0.47	0.42	0.53	25%
7	n-heptane	0.86	0.55	0.64	1.03	1.01	0.66	0.56	0.76	27%
7	toluene	9.98	11.34	11.00	10.07	10.69	10.37	9.06	10.36	7%
7	trans-2-heptene	0.00	0.03	0.01	0.04	0.02	0.00	0.04	0.02	83%
7	trans-3-heptene	0.09	0.04	0.02	0.06	0.05	0.03	0.30	0.08	119%
8	1,1-methylethylcyclopentane	0.06	0.03	0.02	0.07	0.06	0.04	0.10	0.05	52%

8	1,2,4-trimethylcyclopentene	0.06	0.04	0.07	0.12	0.08	0.08	0.05	0.07	40%
8	1-octene	0.00	0.01	0.01	0.02	0.02	0.02	0.00	0.01	74%
8	1c,2t,3-trimethylcyclopentan	0.00	0.03	0.04	0.07	0.02	0.03	0.00	0.03	91%
8	2,2,4-trimethylpentane	4.32	2.54	3.41	5.38	5.00	3.74	2.72	3.87	28%
8	2,2-dimethylhexane	0.06	0.04	0.04	0.07	0.09	0.04	0.10	0.06	39%
8	2,3,4-trimethylpentane	1.72	1.04	1.52	2.51	2.57	1.38	1.20	1.71	36%
8	2,3-dimethylhexane	0.44	0.29	0.43	0.67	0.74	0.36	0.43	0.48	34%
8	2,4,4-trimethyl-2-pentene	0.00	0.00	0.00	0.03	0.00	0.00	0.06	0.01	182%
8	2,4-dimethylhexane	0.74	0.46	0.66	0.92	0.84	0.62	0.51	0.68	25%
8	2,5-dimethylhexane	0.67	0.40	0.54	0.96	0.96	0.51	0.48	0.65	35%
8	2-methylheptane	0.29	0.21	0.29	0.47	0.47	0.28	0.24	0.32	32%
8	3,3-dimethylhexane	0.00	0.01	0.00	0.02	0.01	0.00	0.00	0.01	127%
8	3,4-dimethylhexane	0.11	0.07	0.12	0.18	0.17	0.10	0.08	0.12	36%
8	3-methylheptane	0.35	0.25	0.40	0.59	0.58	0.37	0.32	0.41	31%
8	4-methylheptane	0.12	0.09	0.12	0.19	0.19	0.11	0.10	0.13	32%
8	c-1,2-dimethylcyclohexane	0.00	0.02	0.02	0.02	0.02	0.00	0.00	0.01	95%
8	cis-1,3-dimethylcyclohexane	0.17	0.13	0.18	0.26	0.28	0.16	0.16	0.19	29%
8	cis-2-octene	0.00	0.02	0.02	0.00	0.02	0.04	0.06	0.02	95%
8	ethylbenzene	1.37	1.94	2.10	1.37	1.88	1.68	1.65	1.71	16%
8	ethylcyclohexane	0.00	0.03	0.03	0.03	0.07	0.04	0.04	0.04	62%
8	m-xylene	4.51	6.98	3.54	4.79	6.05	5.58	5.51	5.28	21%
8	n-octane	0.19	0.15	0.21	0.33	0.35	0.18	0.18	0.23	34%
8	o-xylene	1.57	2.37	2.47	1.83	2.80	1.99	2.09	2.16	19%
8	styrene	0.22	0.12	0.15	0.26	0.10	0.26	0.25	0.19	36%
8	t-1-methyl-3-ethylcyclopenta	0.05	0.05	0.05	0.08	0.09	0.06	0.09	0.07	27%
8	tolualdehyde	0.04	0.00	0.01	0.01	0.00	0.00	0.00	0.01	196%
8	trans-1,3-dimethylcyclohexan	0.08	0.04	0.08	0.16	0.14	0.07	0.19	0.11	48%
8	trans-1,4-dimethylcyclohexan	0.08	0.06	0.07	0.13	0.13	0.07	0.07	0.09	34%
8	trans-2-octene	0.00	0.02	0.01	0.01	0.01	0.00	0.00	0.01	103%
8	trans-4-octene	0.00	0.00	0.00	0.04	0.02	0.00	0.00	0.01	186%
9	1,2,3-trimethylbenzene	0.23	0.35	0.52	0.27	0.51	0.35	0.35	0.37	30%
9	1,2,4-trimethylbenzene	1.31	1.96	2.43	1.36	2.69	1.73	1.85	1.9	27%
9	1,3,5-trimethylbenzene	0.46	0.71	0.87	0.50	0.96	0.62	0.65	0.68	27%
9	1,3,5-trimethylcyclohexane	0.00	0.04	0.03	0.08	0.09	0.00	0.06	0.04	84%
9	1-methyl-3-ethylbenzene	0.98	1.52	1.83	1.00	1.80	0.55	1.38	1.29	36%
9	1-methyl-4-ethylbenzene	0.42	0.63	0.73	0.43	0.79	0.03	0.61	0.52	50%
9	1-methyl-4-ethylcyclohexane	0.00	0.02	0.02	0.02	0.04	0.03	0.00	0.02	82%
9	1-nonene	0.00	0.01	0.00	0.01	0.01	0.00	0.05	0.01	140%
9	2,2,4-trimethylhexane	0.00	0.02	0.06	0.04	0.04	0.03	0.05	0.03	57%
9	2,2,5-trimethylhexane	1.53	1.18	1.74	2.51	2.65	1.46	1.29	1.77	33%
9	2,3,5-trimethylhexane	0.23	0.18	0.31	0.26	0.49	0.24	0.25	0.28	36%
9	2,3-dimethylheptane	0.00	0.00	3.48	0.00	0.01	0.05	0.00	0.5	260%
9	2,4,4-trimethylhexane	0.00	0.01	0.04	0.06	0.06	0.00	0.00	0.02	123%
9	2,4-dimethylheptane	0.11	0.03	0.04	0.12	0.09	0.05	0.13	0.08	50%
9	2,6-dimethylheptane	0.06	0.05	0.07	0.12	0.13	0.07	0.08	0.08	39%
9	2-methyloctane	0.00	0.00	0.00	0.08	0.00	0.00	0.00	0.01	265%
9	3,5-dimethylheptane	0.12	0.11	0.13	0.20	0.25	0.10	0.13	0.15	38%
9	3-methyloctane	0.10	0.10	0.15	0.22	0.26	0.12	0.13	0.15	41%
9	4-methyloctane	0.15	0.15	0.21	0.23	0.38	0.18	0.21	0.22	37%

9	indan	0.12	0.15	0.26	0.10	0.23	0.06	0.17	0.16	44%
9	isopropylbenzene (cumene)	0.04	0.06	0.08	0.07	0.09	0.06	0.07	0.07	24%
9	n-nonane	0.08	0.10	0.09	0.16	0.25	0.05	0.13	0.12	53%
9	n-propylbenzene	0.24	0.29	0.39	0.28	0.47	0.30	0.33	0.33	23%
9	o-ethyltoluene	0.30	0.45	0.62	0.34	0.83	0.49	0.64	0.52	35%
10	1,2,3,4-tetramethylbenzene	0.00	0.04	0.06	0.02	0.04	0.00	0.03	0.03	87%
10	1,2,3,5-tetramethylbenzene	0.11	0.09	0.16	0.08	0.15	0.10	0.08	0.11	32%
10	1,2,4,5-tetramethylbenzene	0.07	0.08	0.08	0.06	0.13	0.09	0.00	0.07	53%
10	1,2-diethylbenzene (ortho)	0.00	0.02	0.07	0.01	0.01	0.00	0.00	0.02	152%
10	1,2-dimethyl-3-ethylbenzene	0.00	0.03	0.04	0.04	0.06	0.06	0.03	0.04	52%
10	1,2-dimethyl-4-ethylbenzene	0.20	0.21	0.27	0.14	0.31	0.04	0.22	0.2	46%
10	1,3-diethylbenzene (meta)	0.07	0.09	0.18	0.08	0.12	0.26	0.11	0.13	52%
10	1,3-dimethyl-2-ethylbenzene	0.05	0.05	0.07	0.07	0.11	0.03	0.10	0.07	43%
10	1,3-dimethyl-4-ethylbenzene	0.09	0.12	0.20	0.10	0.16	0.03	0.12	0.12	46%
10	1,3-dimethyl-5-ethylbenzene	0.20	0.24	0.40	0.17	0.33	0.00	0.25	0.23	56%
10	1,4-diethylbenzene (para)	0.10	0.10	0.16	0.10	0.19	0.26	0.13	0.15	41%
10	1,4-dimethyl-2-ethylbenzene	0.12	0.14	0.24	0.14	0.24	0.13	0.16	0.17	30%
10	1-methyl-2-isopropylbenzene	0.04	0.04	0.09	0.08	0.16	0.04	0.06	0.07	59%
10	1-methyl-2n-propylbenzene	0.06	0.06	0.12	0.08	0.13	0.05	0.08	0.08	39%
10	1-methyl-3-isopropylbenzene	0.00	0.03	0.05	0.01	0.02	0.04	0.03	0.03	61%
10	1-methyl-3n-propylbenzene	0.18	0.22	0.42	0.25	0.43	0.00	0.27	0.25	58%
10	1-methyl-4-isopropylbenzene	0.00	0.02	0.03	0.04	0.02	0.00	0.00	0.02	98%
10	2,2,4-trimethylheptane	0.00	0.03	0.09	0.03	0.00	0.00	0.00	0.02	156%
10	2,2-dimethyloctane	0.00	0.02	0.00	0.02	0.06	0.00	0.05	0.02	112%
10	2,3-dimethyloctane	0.00	0.03	0.04	0.08	0.03	0.06	0.03	0.04	62%
10	2,4-dimethyloctane	0.00	0.03	0.07	0.05	0.06	0.13	0.04	0.06	71%
10	2,5-dimethyloctane	0.00	0.03	0.03	0.05	0.07	0.02	0.04	0.04	63%
10	2,6-dimethyloctane	0.00	0.02	0.04	0.05	0.08	0.03	0.05	0.04	61%
10	2-methylindan	0.07	0.03	0.05	0.04	0.05	0.00	0.04	0.04	55%
10	2-methylnonane	0.20	0.20	0.28	0.38	0.25	0.22	0.06	0.23	43%
10	3,3-dimethyloctane	0.00	0.02	0.03	0.05	0.05	0.02	0.00	0.02	78%
10	4-methylindan	0.00	0.02	0.05	0.01	0.01	0.05	0.00	0.02	104%
10	5-methylindan	0.06	0.03	0.07	0.04	0.09	0.03	0.06	0.05	39%
10	isobutylbenzene	0.00	0.02	0.02	0.05	0.03	0.06	0.06	0.03	64%
10	n-decane	0.09	0.05	0.11	0.12	0.16	0.00	0.15	0.1	58%
10	naphthalene	0.00	0.06	0.10	0.03	0.03	0.02	0.01	0.04	95%
11	1-ethyl-2n-propylbenzene	0.00	0.02	0.00	0.01	0.02	0.00	0.00	0.01	133%
11	1-methyl-2-n-butylbenzene	0.00	0.01	0.03	0.00	0.01	0.00	0.00	0.01	153%
11	1-methyl-2-tert-butylbenzene	0.00	0.00	0.10	0.01	0.02	0.00	0.10	0.03	148%
11	n-pentylbenzene	0.00	0.01	0.05	0.00	0.01	0.00	0.00	0.01	180%
11	n-undecane	0.00	0.02	0.05	0.05	0.05	0.00	0.00	0.03	102%
12	1,3-dipropylbenzene	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.01	102%
12	1-(1,1-dme)-3,5-dmbenzene	0.00	0.01	0.03	0.01	0.01	0.05	0.00	0.02	107%
12	n-dodecane	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0	175%
13	2,2,5-triethylheptane	0.08	0.08	0.08	0.20	0.21	0.12	0.14	0.13	43%
	sum	99.98	99.96	99.97	100.03	100.06	100.04	100.00	100.00	
	Mass (mg/mi)	5662	3042	1487	6720	5774	1574	6432	4384	52%
	MIR	3.22	3.82	3.74	3.05	3.07	3.56	3.66	3.45	9%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).

The COVs were calculated before the mean and standard deviation were rounded.

MIR means Maximum Incremental Reactivity (g ozone/g NMOG).

Start emissions are represented by Bag 1 minus Bag 3 of Unified Cycle.

Table 24 Exhaust Gasoline Organic Gas Species Test Results

(Et2.0%, Start Emissions, Weight Percent)

CNUM	CHEMNAME	VEH1	VEH3	VEH4	VEH5	VEH6	VEH7	MEAN	COV
1	formaldehyde	0.66	1.10	0.48	0.90	1.24	0.64	0.84	35%
1	methyl alcohol	0.45	0.00	0.27	0.37	0.00	0.22	0.22	85%
2	acetaldehyde	0.85	0.96	0.53	0.80	1.16	0.46	0.79	33%
2	acetylene	9.33	3.33	1.79	3.52	6.04	9.18	5.53	58%
2	ethane	0.79	0.84	0.74	0.31	0.88	0.64	0.70	30%
2	ethyl alcohol	2.61	3.00	0.99	3.11	0.00	1.61	1.89	66%
2	ethylene	10.94	8.24	5.81	3.93	10.42	8.43	7.96	34%
3	1,2-propadiene	0.35	0.25	0.00	0.00	0.00	0.37	0.16	112%
3	1-propyne	0.54	0.00	0.13	0.21	0.35	0.00	0.21	103%
3	acetone	0.24	0.28	0.22	0.22	0.31	0.08	0.22	35%
3	acrolein (2-propenal)	0.00	0.00	0.00	0.00	0.03	0.00	0.01	245%
3	propane	0.06	0.07	0.07	0.00	0.08	0.05	0.06	52%
3	propionaldehyde	0.20	0.19	0.09	0.18	0.32	0.14	0.19	41%
3	propylene	4.03	4.37	2.79	1.99	5.36	3.88	3.74	32%
4	1,2-butadiene	0.00	0.00	0.01	0.02	0.02	0.59	0.11	224%
4	1,3-butadiene	0.73	0.09	0.32	0.18	0.75	1.17	0.54	77%
4	1,3-butadiyne	0.03	0.00	0.01	0.00	0.00	0.00	0.01	173%
4	1-butene	0.75	0.91	0.34	0.36	0.87	0.71	0.66	38%
4	2-butyne	0.04	0.06	0.00	0.00	0.02	0.22	0.05	150%
4	2-methyl-2-propenal	0.09	0.07	0.04	0.06	0.09	0.04	0.07	35%
4	butyraldehyde	0.03	0.04	0.00	0.02	0.03	0.02	0.02	58%
4	cis-2-butene	0.22	0.35	0.14	0.11	0.38	0.19	0.23	47%
4	crotonaldehyde	0.09	0.09	0.04	0.07	0.11	0.04	0.07	41%
4	isobutane	0.10	0.04	0.00	0.00	0.00	0.07	0.03	119%
4	isobutene	1.35	0.25	0.71	0.46	1.17	1.30	0.87	53%
4	methyl ethyl ketone (MEK)	0.05	0.04	0.00	0.04	0.07	0.02	0.04	66%
4	n-butane	0.09	0.21	0.33	0.38	0.53	0.18	0.29	55%
4	trans-2-butene	0.31	0.37	0.19	0.14	0.41	0.22	0.27	38%
4	vinylacetylene	0.19	0.08	0.06	0.10	0.13	0.00	0.09	70%
5	1-pentene	0.10	0.13	0.07	0.08	0.16	0.17	0.12	35%
5	2-methyl-1-butene	0.21	0.07	0.02	0.02	0.03	0.19	0.09	98%
5	2-methyl-2-butene	0.17	0.10	0.17	0.15	0.26	0.00	0.14	61%
5	3-methyl-1-butene	0.10	0.11	0.06	0.00	0.00	0.08	0.06	83%
5	cis-2-pentene	0.06	0.07	0.04	0.04	0.09	0.06	0.06	32%
5	cyclopentane	0.35	0.45	0.48	0.43	0.39	0.44	0.42	11%
5	cyclopentene	0.11	0.16	0.06	0.03	0.12	0.10	0.10	48%
5	isopentane	2.85	4.62	4.85	4.98	4.13	4.07	4.25	18%
5	isoprene	0.02	0.03	0.02	0.04	0.06	0.25	0.07	125%
5	isovaleraldehyde	0.05	0.00	0.01	0.01	0.05	0.01	0.02	104%
5	methyl t-butyl ether (MTBE)	0.18	0.05	0.09	0.10	0.06	0.61	0.18	118%
5	n-pentane	0.91	1.22	1.22	1.02	1.05	1.18	1.10	11%
5	trans-1,3-pentadiene	0.01	0.00	0.00	0.00	0.00	0.08	0.01	207%
5	trans-2-pentene	0.11	0.13	0.08	0.06	0.16	0.10	0.11	32%
6	1-hexene	0.06	0.08	0.05	0.00	0.10	0.13	0.07	64%
6	2,2-dimethylbutane	1.55	1.79	1.94	1.46	1.56	1.63	1.65	11%
6	2,3-dimethylbutane	1.32	1.32	1.70	1.37	1.22	1.33	1.38	12%

6	2-methyl-1-pentene	0.00	0.00	0.01	0.06	0.00	0.00	0.01	203%
6	2-methyl-2-pentene	0.05	0.05	0.04	0.01	0.06	0.08	0.05	47%
6	2-methylpentane	4.73	4.66	6.04	4.87	4.20	4.77	4.88	13%
6	3,3-dimethyl-1-butene	0.01	0.00	0.01	0.00	0.00	0.00	0.00	157%
6	3-methyl-1-pentene	0.06	0.05	0.03	0.02	0.05	0.04	0.04	33%
6	3-methylcyclopentene	0.04	0.04	0.03	0.02	0.05	0.06	0.04	36%
6	3-methylpentane	3.02	2.94	3.92	3.17	2.64	2.99	3.11	14%
6	4-methyl-1-pentene	0.00	0.04	0.04	0.03	0.08	0.04	0.04	64%
6	4-methyl-trans-2-pentene	0.01	0.00	0.02	0.01	0.03	0.00	0.01	96%
6	benzene	2.52	2.81	3.37	1.56	3.34	2.10	2.62	27%
6	cis-2-hexene	0.02	0.00	0.01	0.01	0.02	0.00	0.01	88%
6	cyclohexane	0.71	0.72	0.99	0.89	0.65	0.80	0.79	16%
6	cyclohexene	0.05	0.06	0.03	0.07	0.06	0.06	0.05	25%
6	hexaldehyde	0.00	0.00	0.00	0.00	0.02	0.01	0.00	178%
6	methylcyclopentane	2.48	2.35	3.20	2.80	2.12	2.58	2.59	14%
6	n-hexane	0.78	0.74	1.05	0.88	0.69	0.80	0.82	15%
6	trans-2-hexene	0.03	0.03	0.02	0.02	0.03	0.03	0.03	21%
6	trans-3-hexene	0.02	0.00	0.01	0.01	0.02	0.00	0.01	84%
7	1-c-3-dimethylcyclopentane	0.31	0.29	0.47	0.40	0.27	0.34	0.35	22%
7	1-t-2-dimethylcyclopentane	0.10	0.30	0.00	0.00	0.00	0.13	0.09	135%
7	1-t-3-dimethylcyclopentane	0.34	0.32	0.52	0.45	0.29	0.37	0.38	23%
7	2,2,3-trimethylbutane	0.00	0.02	0.05	0.03	0.03	0.04	0.03	56%
7	2,3-dimethylpentane	0.76	0.73	1.06	0.91	0.63	0.84	0.82	18%
7	2,4-dimethyl-1-pentene	0.02	0.00	0.01	0.01	0.00	0.00	0.01	114%
7	2,4-dimethyl-2-pentene	0.09	0.10	0.14	0.11	0.10	0.12	0.11	16%
7	2,4-dimethylpentane	0.47	0.45	0.69	0.55	0.41	0.49	0.51	19%
7	2-methyl-2-hexene	0.02	0.00	0.02	0.00	0.00	0.00	0.01	159%
7	2-methyl-trans-3-hexene	0.01	0.00	0.00	0.00	0.00	0.00	0.00	245%
7	2-methylhexane	1.26	1.13	2.12	1.68	1.09	1.30	1.43	28%
7	3,3-dimethylpentane	0.01	0.00	0.02	0.02	0.03	0.00	0.01	88%
7	3,4-dimethyl-1-pentene	0.03	0.00	0.00	0.00	0.00	0.00	0.00	245%
7	3-ethyl-2-pentene	0.02	0.00	0.00	0.00	0.00	0.00	0.00	245%
7	3-ethylpentane	0.32	0.10	0.70	0.58	0.38	0.35	0.41	52%
7	3-methyl-cis-2-hexene	0.00	0.00	0.01	0.00	0.00	0.00	0.00	245%
7	3-methyl-trans-3-hexene	0.00	0.00	0.00	0.00	0.00	0.16	0.03	245%
7	3-methylhexane	1.36	1.27	2.17	1.78	1.15	1.47	1.53	25%
7	4-methyl-trans-2-hexene	0.00	0.00	0.01	0.00	0.00	0.00	0.00	245%
7	benzaldehyde	0.21	0.27	0.11	0.15	0.27	0.02	0.17	59%
7	cis-2-heptene	0.02	0.00	0.01	0.01	0.02	0.00	0.01	79%
7	ethylcyclopentane	0.00	0.00	0.24	0.21	0.13	0.00	0.10	115%
7	methylcyclohexane	1.00	0.98	1.64	1.42	0.87	1.16	1.18	25%
7	n-heptane	1.00	0.95	1.67	1.38	0.85	1.15	1.17	27%
7	toluene	7.57	8.32	8.51	8.32	8.11	7.30	8.02	6%
7	trans-2-heptene	0.00	0.00	0.01	0.01	0.02	0.00	0.01	111%
7	trans-3-heptene	0.02	0.00	0.01	0.01	0.00	0.00	0.01	113%
8	1,1-methylethylcyclopentane	0.08	0.06	0.16	0.09	0.05	0.10	0.09	42%
8	1,2,4-trimethylcyclopentene	0.19	0.19	0.25	0.21	0.13	0.22	0.20	20%
8	1-octene	0.06	0.00	0.11	0.00	0.00	0.08	0.04	118%
8	1c,2t,3-trimethylcyclopentan	0.08	0.09	0.15	0.12	0.08	0.10	0.10	28%

8	2,2,4-trimethylpentane	1.87	1.85	3.15	2.50	1.69	2.12	2.20	25%
8	2,2-dimethylhexane	0.08	0.08	0.22	0.18	0.13	0.09	0.13	43%
8	2,3,4-trimethylpentane	0.70	0.73	1.43	1.19	0.68	0.90	0.94	33%
8	2,3-dimethylhexane	0.29	0.32	0.69	0.57	0.35	0.37	0.43	37%
8	2,4-dimethylhexane	0.49	0.50	0.80	0.65	0.43	0.57	0.57	23%
8	2,5-dimethylhexane	0.46	0.46	0.65	0.55	0.32	0.53	0.50	22%
8	2-methylheptane	0.49	0.52	0.95	0.80	0.45	0.61	0.64	31%
8	3,3-dimethylhexane	0.00	0.00	0.09	0.07	0.05	0.00	0.03	116%
8	3,4-dimethylhexane	0.10	0.11	0.19	0.16	0.10	0.13	0.13	28%
8	3-methylheptane	0.68	0.65	1.35	1.00	0.56	0.83	0.84	34%
8	4-methylheptane	0.21	0.22	0.41	0.35	0.21	0.25	0.28	31%
8	c-1,2-dimethylcyclohexane	0.05	0.00	0.10	0.00	0.00	0.00	0.02	167%
8	cis-1,3-dimethylcyclohexane	0.23	0.10	0.45	0.39	0.24	0.29	0.28	44%
8	cis-2-octene	0.03	0.00	0.01	0.00	0.00	0.00	0.01	193%
8	ethylbenzene	1.66	2.12	1.61	2.04	1.83	2.37	1.94	15%
8	ethylcyclohexane	0.08	0.00	0.14	0.13	0.08	0.10	0.09	56%
8	m-xylene	0.04	7.43	5.92	8.08	6.83	5.88	5.69	51%
8	n-octane	0.34	0.40	0.70	0.61	0.33	0.43	0.47	32%
8	o-xylene	2.02	2.65	2.11	2.87	2.41	2.02	2.35	15%
8	styrene	0.23	0.19	0.21	0.04	0.36	0.43	0.24	56%
8	t-1-methyl-3-ethylcyclopenta	0.09	0.08	0.17	0.14	0.10	0.14	0.12	27%
8	tolualdehyde	0.00	0.00	0.02	0.02	0.02	0.00	0.01	113%
8	trans-1,3-dimethylcyclohexan	0.13	0.15	0.30	0.23	0.14	0.16	0.18	36%
8	trans-1,4-dimethylcyclohexan	0.09	0.26	0.18	0.15	0.10	0.12	0.15	42%
8	trans-2-octene	0.03	0.04	0.00	0.04	0.02	0.04	0.03	55%
9	1,2,3-trimethylbenzene	0.39	0.64	0.33	0.62	0.56	0.40	0.49	27%
9	1,2,4-trimethylbenzene	1.93	2.94	1.60	3.11	2.64	2.09	2.38	25%
9	1,3,5-trimethylbenzene	0.69	1.04	0.59	1.11	0.96	0.73	0.85	25%
9	1,3,5-trimethylcyclohexane	0.07	0.10	0.15	0.13	0.09	0.00	0.09	58%
9	1-methyl-3-ethylbenzene	1.40	2.01	1.16	1.99	1.72	1.39	1.61	22%
9	1-methyl-4-ethylbenzene	0.62	0.89	0.51	0.99	0.78	0.62	0.74	25%
9	1-methyl-4-ethylcyclohexane	0.03	0.03	0.06	0.06	0.04	0.04	0.04	33%
9	1-nonene	0.00	0.06	0.06	0.00	0.00	0.08	0.03	112%
9	2,2,4-trimethylhexane	0.02	0.03	0.02	0.02	0.02	0.00	0.02	52%
9	2,2,5-trimethylhexane	0.26	0.32	0.47	0.38	0.29	0.31	0.34	22%
9	2,3,5-trimethylhexane	0.05	0.07	0.12	0.09	0.07	0.07	0.08	29%
9	2,3-dimethylheptane	6.34	0.00	0.02	0.02	0.00	0.00	1.06	243%
9	2,4,4-trimethylhexane	0.01	0.04	0.07	0.05	0.04	0.05	0.04	44%
9	2,4-dimethylheptane	0.06	0.07	0.12	0.10	0.07	0.10	0.08	29%
9	2,6-dimethylheptane	0.09	0.09	0.23	0.18	0.11	0.14	0.14	39%
9	2-methyloctane	0.00	0.00	0.37	0.00	0.16	0.00	0.09	173%
9	3,5-dimethylheptane	0.13	0.17	0.37	0.31	0.18	0.18	0.22	42%
9	3-methyloctane	0.21	0.27	0.44	0.43	0.24	0.28	0.31	32%
9	4-methyloctane	0.28	0.35	0.24	0.34	0.18	0.36	0.29	25%
9	indan	0.18	0.27	0.13	0.26	0.23	0.15	0.20	29%
9	isopropylbenzene (cumene)	0.14	0.17	0.12	0.11	0.13	0.02	0.12	44%
9	n-nonane	0.13	0.15	0.26	0.27	0.15	0.16	0.19	34%
9	n-propylbenzene	0.38	0.49	0.39	0.61	0.46	0.39	0.46	19%
9	o-ethyltoluene	0.42	0.67	0.61	0.48	0.57	0.13	0.48	40%

10	1,2,3,4-tetramethylbenzene	0.06	0.06	0.03	0.08	0.08	0.04	0.06	33%
10	1,2,3,5-tetramethylbenzene	0.09	0.24	0.09	0.22	0.21	0.13	0.16	42%
10	1,2,4,5-tetramethylbenzene	0.01	0.19	0.07	0.17	0.16	0.09	0.11	61%
10	1,2-diethylbenzene (ortho)	0.02	0.04	0.03	0.00	0.03	0.02	0.02	59%
10	1,2-dimethyl-3-ethylbenzene	0.06	0.03	0.05	0.09	0.08	0.07	0.06	34%
10	1,2-dimethyl-4-ethylbenzene	0.19	0.35	0.16	0.37	0.34	0.20	0.27	35%
10	1,3-diethylbenzene (meta)	0.09	0.15	0.14	0.11	0.13	0.04	0.11	37%
10	1,3-dimethyl-2-ethylbenzene	0.04	0.03	0.06	0.06	0.07	0.08	0.06	37%
10	1,3-dimethyl-4-ethylbenzene	0.13	0.23	0.10	0.20	0.04	0.14	0.14	49%
10	1,3-dimethyl-5-ethylbenzene	0.29	0.54	0.21	0.43	0.41	0.31	0.37	32%
10	1,4-diethylbenzene (para)	0.13	0.26	0.20	0.13	0.18	0.06	0.16	43%
10	1,4-dimethyl-2-ethylbenzene	0.15	0.27	0.12	0.24	0.20	0.16	0.19	30%
10	1-methyl-2-isopropylbenzene	0.04	0.08	0.06	0.10	0.04	0.11	0.07	42%
10	1-methyl-2n-propylbenzene	0.07	0.15	0.08	0.13	0.11	0.09	0.11	29%
10	1-methyl-3-isopropylbenzene	0.05	0.06	0.06	0.07	0.05	0.06	0.06	15%
10	1-methyl-3n-propylbenzene	0.29	0.46	0.24	0.44	0.39	0.26	0.35	28%
10	1-methyl-4-isopropylbenzene	0.03	0.05	0.04	0.06	0.04	0.03	0.04	28%
10	2,2,4-trimethylheptane	0.04	0.00	0.07	0.06	0.04	0.04	0.04	56%
10	2,2-dimethyloctane	0.04	0.03	0.14	0.13	0.08	0.06	0.08	62%
10	2,3-dimethyloctane	0.02	0.05	0.00	0.00	0.00	0.02	0.01	129%
10	2,4-dimethyloctane	0.18	0.00	0.10	0.13	0.05	0.00	0.08	93%
10	2,5-dimethyloctane	0.04	0.04	0.11	0.10	0.06	0.05	0.07	47%
10	2,6-dimethyloctane	0.05	0.05	0.12	0.14	0.04	0.07	0.08	55%
10	2-methylindan	0.01	0.13	0.04	0.09	0.09	0.06	0.07	60%
10	2-methylnonane	0.13	0.26	0.38	0.50	0.25	0.26	0.30	43%
10	3,3-dimethyloctane	0.05	0.06	0.10	0.09	0.06	0.06	0.07	29%
10	4-methylindan	0.05	0.04	0.02	0.04	0.04	0.00	0.03	63%
10	5-methylindan	0.02	0.11	0.03	0.08	0.07	0.06	0.06	55%
10	isobutylbenzene	0.02	0.03	0.04	0.05	0.00	0.06	0.03	63%
10	n-decane	0.03	0.11	0.11	0.13	0.11	0.06	0.09	43%
10	naphthalene	0.01	0.11	0.03	0.03	0.02	0.05	0.04	86%
10	sec-butylbenzene	0.00	0.00	0.00	0.00	0.00	0.04	0.01	245%
11	1-ethyl-2n-propylbenzene	0.03	0.00	0.02	0.04	0.03	0.00	0.02	89%
11	1-methyl-2-n-butylbenzene	0.03	0.02	0.01	0.01	0.05	0.00	0.02	90%
11	1-methyl-2-tert-butylbenzene	0.11	0.04	0.00	0.00	0.00	0.00	0.03	176%
11	n-pentylbenzene	0.02	0.06	0.01	0.00	0.00	0.00	0.02	146%
11	n-undecane	0.01	0.09	0.02	0.02	0.02	0.00	0.03	121%
12	1,3-dipropylbenzene	0.02	0.04	0.01	0.04	0.03	0.00	0.02	68%
12	1-(1,1-dme)-3,5-dmbenzene	0.04	0.02	0.00	0.00	0.00	0.06	0.02	122%
12	n-dodecane	0.01	0.00	0.00	0.02	0.02	0.00	0.01	112%
13	2,2,5-triethylheptane	0.05	0.08	0.20	0.19	0.12	0.10	0.13	48%
	sum	100.13	99.91	100.23	99.36	100.04	100.01	99.94	
	Mass (mg/mi)	788	19	461	498	22	1415	533.83	98%
	MIR	3.57	3.86	3.97	3.45	3.72	3.72	3.72	5%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).
Start emissions are represented by Bag 1 minus Bag 3 of Unified Cycle.

California Environmental Protection Agency
Air Resources Board

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

Appendix B

Photochemical Modeling

December 1999

Table of Contents

List of Tables

List of Figures

B-1. Introduction

This appendix describes the air quality simulations performed in support of the analysis of the potential impact on air quality caused by the phase-out of gasoline containing methyl *tertiary*-butyl ether (MTBE) and replacement by ethanol-based or non-oxygenated fuels. It is important to bear in mind that the model results for this study are being used in a relative, rather than absolute sense. That is, the model was used to estimate the change from 1997 MTBE gasoline to ethanol-containing and non-oxygenated gasolines in 2003, rather than to predict absolute values in 2003. The estimated changes were then used to adjust the base year (1997) air quality measurements to future (2003) concentrations, as described in Appendix C. The modeling community is in general agreement that models are best used in a relative sense.

In the sections that follow a brief description of the air quality model is presented together with the photochemical mechanism chosen. A description of the input files necessary to run each of the scenarios considered is presented, together with a summary of the results. A discussion of sensitivity simulations and model performance is included. An analysis of the sensitivity of ozone, PAN, and PPN under a wide variety of conditions was conducted with a box model.

B-2. Photochemical Model Description

Photochemical air quality modeling is a primary tool for understanding the complex interrelationships among pollutants emitted and transported in a given area. Photochemical air quality models are computer models that represent the state-of–the-science understanding of how ozone and other secondary pollutants are formed and the relationship to the primary pollutants emitted by different source categories. They have been used to assess the effectiveness of air pollution control strategies to achieve the air quality standards. The Flexible Chemical Mechanism Version of the Urban Airshed Model (UAM-FCM) is an air quality model that has been used by ARB since 1995.

The UAM-FCM is an adaptation of the Urban Airshed Model (UAM) to provide flexibility in incorporating different Carbon Bond IV or SAPRC-type photochemical mechanisms into the UAM (Kumar *et al.*, 1995). The UAM has been the primary air quality regulatory model for ozone control strategy development. However, it has a hard-coded a version of the Carbon Bond IV photochemical mechanism, together with a unique algorithm to solve the set of differential equations representing the chemical transformations that is accurate, robust and fast. The algorithm was designed to take maximum advantage of the Carbon Bond IV features. The treatment of photolytic reactions in the UAM is also unique. All values for the photolytic reaction rates are hard-coded, and depend on the value of the NO_2 photolytic reaction rate. The hard-coded approach in the UAM makes it very difficult to study recent and more updated mechanisms, such as those developed by Dr. W.P.L. Carter at the University of Riverside. Any change or update in the Carbon Bond IV mechanism, photolytic rates, or the implementation of a different chemical mechanism requires changes to the UAM code that need to be done by hand. However, the UAM-FCM can read a text file version of a mechanism and create program subroutines that are readily integrated with the model (Kumar *et al.*, 1995). Below we briefly describe the main aspects of the UAM and the UAM-FCM.

B-2.1. Urban Airshed Model

Morris and Meyers (1990) provide a detailed description of the UAM. Only a brief summary is provided here. The UAM is a gridded 3-dimensional air quality model that can simulate the atmospheric physical and chemical processes that cause air pollution. The basic advection-diffusion equation is:

$$\frac{\partial C_i}{\partial t} + \frac{\partial (uC_i)}{\partial x} + \frac{\partial (vC_i)}{\partial y} + \frac{\partial (wC_i)}{\partial z} = \frac{\partial}{\partial x}(K_H \frac{\partial C_i}{\partial x}) + \frac{\partial}{\partial y}(K_H \frac{\partial C_i}{\partial y}) + \frac{\partial}{\partial z}(K_V \frac{\partial C_i}{\partial z})$$

$$+ R_i + S_i + L_i \qquad \text{(B-1)}$$

The first term on the left-hand side of Equation (1) represents the time-varying concentration of pollutant i, and the last three terms on the left-hand side of Equation (1) represent advection. The first three terms on the right-hand side of Equation (1) represent turbulent diffusion, R_i are chemical reaction processes, S_i are emission source processes, and L_i correspond to losses by deposition. The other terms in Equation (1) are the horizontal and vertical wind speed components -- u, v, and w -- and the horizontal and vertical diffusivity coefficients, K_H and K_V. Equation (1) is solved for each pollutant and grid cell at each time step in the simulation. As designed, the UAM has hard-coded a version of the Carbon Bond IV (CB4) chemical mechanism. The CB4 version implemented in the UAM was last updated in 1993 by adding radical-radical interactions. The hard-coded approach to the atmospheric chemical mechanism used in the UAM prevents the implementation of newer and more up-to-date chemical mechanisms.

B-2.2. Flexible Chemical Mechanism Version of the Urban Airshed Model

The UAM-FCM was developed under contract for ARB (Kumar *et al.*, 1995). The UAM-FCM has a software package (the FCM) that reads a text file describing the photochemical mechanism, and creates a set of mechanism-specific programs that are then integrated into the UAM. The FCM allows the user to incorporate reaction-specific photolytic rates, by providing a file for each photolytic reaction, with data on cross-section and quantum yield for each wavelength of interest. The UAM-FCM has a generalized technique to solve the set of differential equations that is not mechanism specific, but is accurate and robust. The current version of the UAM-FCM can handle up to 220 chemical reactions (including up to 20 photolytic reactions), and up to 140 chemical species.

B-2.3. SAPRC97 Chemical Mechanism

Carter (1993, 1997) developed the atmospheric chemical mechanism designated as SAPRC97 (version D), which is readily processed by the UAM-FCM software. To save computing time in solving the set of differential equations that represent the reaction mechanism, only a small number of hydrocarbon species are treated explicitly in this mechanism. In the SAPRC series of mechanisms, hydrocarbons are grouped together using the lumped-molecule approach. In this approach the reactions of many alkanes, alkenes, and aromatic species that are present in the emission inventory are represented by lumped reaction mechanisms (Carter, 1990). The computer software calculates the kinetic rates and product yield parameters for the lumped species that best represent the unique hydrocarbon mixture in the emission inventory (Carter, 1988; Carter 1990). For this study the one-product mechanism is used to represent the reactions of isoprene (Carter, 1996). In addition, explicit reaction mechanisms (as opposed to a lumped representation) for several compounds of interest (such as benzene, 1,3-butadiene, ethanol, and methyl *tertiary*-butyl ether) were added to the original version of the SAPRC97. It was also desired to distinguish between acetaldehyde and formaldehyde formed as by-products of photochemical reactions (secondary), from those emitted directly from sources (primary). The explicit reactions for the additional species were obtained from Dr. Carter's ftp site (ftp://cert.ucr.edu/pub/carter/mech/saprc97).

A complete listing of this photochemical mechanism is provided in the Attachment B-1. The list of hydrocarbon species that are treated explicitly is given in Table 2.1. Note that in the SAPRC97 chemical mechanism, PPN is used to lump peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates. Thus, modeled PPN cannot be compared directly with measured PPN. In addition to the species listed in Table 2.1, the photochemical mechanism includes a large number of species that are generated by the oxidation of hydrocarbons, as well as a set of chemical reactions that represents the inorganic reactions that take place in air. The mechanism used in our simulations has a total of 99 species and 204 reactions, of which 20 are photolytic. Of the 99 species, 29 are treated as steady state, 4 species are held constant, and hourly average concentrations are generated by the UAM-FCM for the other 66 species.

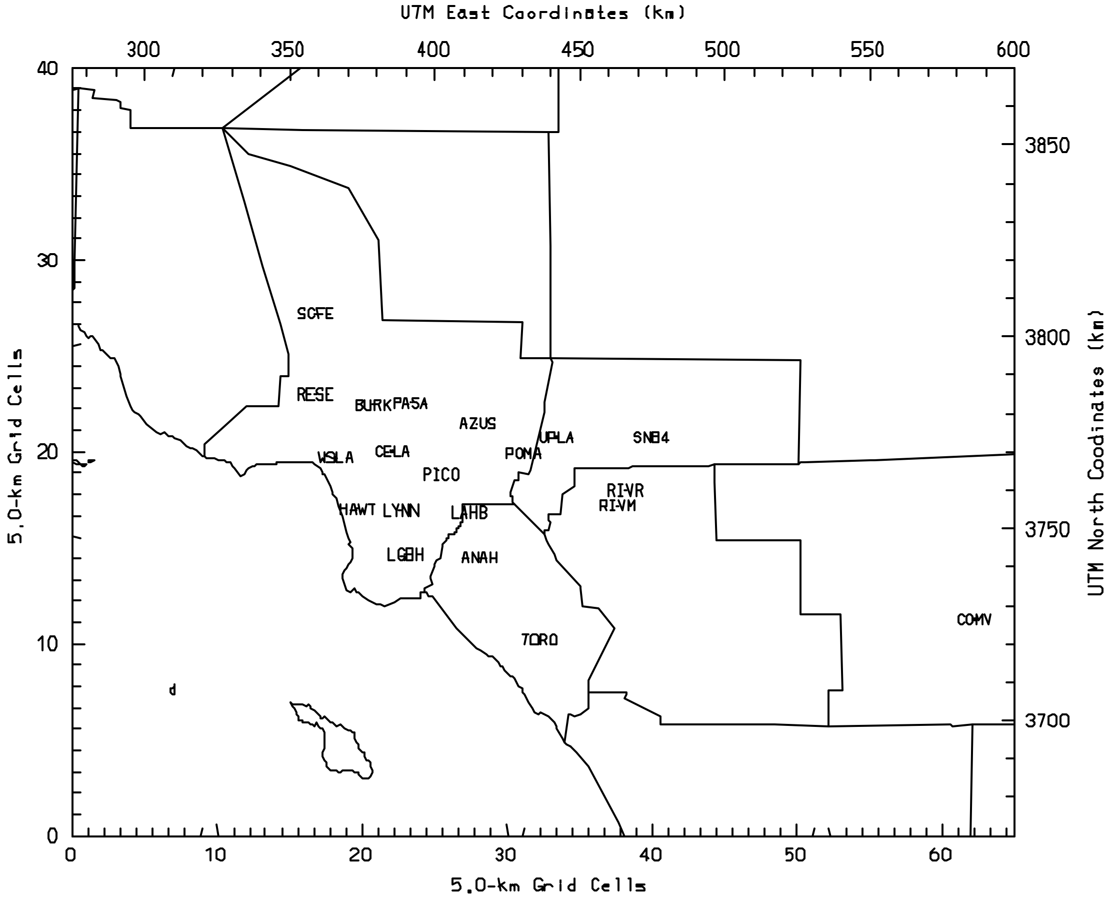
Table 2.1 List of Hydrocarbon Species Treated Explicitly in SAPRC97

Name	Symbol
Formaldehyde (secondary)	**HCHO**
Formaldehyde (primary)	**FORM**
Acetaldehyde (secondary)	**CCHO**
Acetaldehyde (primary)	**ALD**
Acetone	**ACET**
Methyl ethyl ketone	**MEK**
Peroxyacetyl nitrate	**PAN**
Peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates	**PPN**
Methane	**CH4**
Ethene	**ETHE**
Isoprene	**ISOP**
Benzene	**C6H6**
1,3-Butadiene	**BUTD**
***p*-Dichlorobenzene**	**PDCB**
Perchloroethylene	**PERC**
Dichloromethylene	**DICM**
Ethanol	**ETOH**
Methyl *tertiary*-butyl ether	**MTBE**
Glyoxal	**GLY**
Methyl Glyoxal	**MGLY**
Benzaldehyde	**BALD**
Cresols	**CRES**
Phenols	**PHEN**

B-2.4. Computer

The executable UAM-FCM files were prepared and compiled according to the recommended procedure by Kumar *et al.* (1995). The emission inventory corresponding to each year and case under study were used to calculate the reaction rates and product yields of the lumped species. All simulations were run on a Unix workstation. The time to run a 24-hour episode simulation was about 2 hours and twenty minutes.

Figure 2.1 Modeling Domain



B-3. Model Input Description

B-3.1. Episode and Domain

The UAM-FCM was applied to a three-day summer ozone episode in the South Coast, the August 26-28, 1987 Southern California Air Quality Study (SCAQS) episode (Lawson, 1990). The SCAQS domain has been gridded into 65 x 40 x 5 cells. Each horizontal square cell is 5 x 5 km^2, with varying vertical height. The origin of the domain is at (275, 3670) in UTM coordinates (Zone 11). The domain is shown in Figure 2.1. It includes the counties of Los Angeles, Orange, and Kern, and portions of Riverside, San Diego, San Bernardino, and Ventura counties.

The August 26-28, 1987 SCAQS episode corresponds to an episode with very high observed ozone concentrations. We believe that the meteorological conditions of the episode represent close to worst-case conditions conducive to high pollutant concentrations. The SCAQS domain also contains a large fraction of the population in the State. Therefore, this episode and domain also represent worst-case conditions for exposure analysis of photochemically generated pollutants (e.g., ozone, NO_2, acetaldehyde, formaldehyde, PAN and PPN). For these reasons we believe that modeling of this single episode is sufficient for our study. Therefore, the meteorology of the August 26-28, 1987 SCAQS episode will be used in conjunction with the VOC and NO_x emissions appropriate for the year 1997, and 2003 scenarios described in Table 3.2. Worst-case conditions for directly emitted pollutants (e.g., CO, benzene, 1,3-butadiene, ethanol, and MTBE) are more readily inferred from air quality measurement (see Appendix C).

B-3.2. Basic Input Files

The UAM-FCM requires 13 input files that provide information on the initial and boundary conditions of the domain, temperature, wind direction, wind speed, terrain, photolytic rates, reaction rate constants, and product yields, and emissions from area and point sources. Mobile sources and biogenic emissions are included in the area source file. The files used in our simulations, (except for the initial and boundary conditions, and area and point source emissions) were prepared by the South Coast Air Quality Management District for the 1994 State Implementation Plan (SCAQMD, 1994). The same diffusion break, region top, metscalars, terrain, temperature, and meteorological input files were used in all simulations, since these characterize the meteorological conditions for the episode and terrain. Table 3.1 provides a description of these files. Other files, such as initial and boundary conditions, point sources and area emissions were created for each specific simulation.

Table 3.1 List of the Meteorological and Terrain Files for the SCAQS August 26-28, 1987 Episode

Input File Identification	Description
ms238d11.b, ms239d11.b, ms240d11.b	Metscalar file
sim238bl, sim239bl, sim240bl	Control file
df238d11.b	Diffusion break file
tm238d11.b, tm239d11.b, tm240d11.b	Temperature file
rt238d11.b	Region top file
tr238d11.b	Terrain file
wd238d11.b, wd239d11.b, wd240d11.b	Wind file

B-3.3. Region Top and Boundary Conditions

The region top and boundary conditions (together with the point and area sources) are specific to each of the different scenarios considered in this modeling study. The scenarios considered include the years 1997 and 2003 with different types of gasoline. These scenarios are listed in Table 3.2.

Table 3.2 Scenarios Considered for the Photochemical Modeling

Scenario	Description of Motor Vehicle Fuel Used
1997 MTBE	Current MTBE-based California Phase 2 Reformulated Gasoline (CaRFG)
2003 MTBE	Year 2003 MTBE-based CaRFG
2003 Et2.0%	Year 2003 Ethanol-based fully complying fuel (with oxygen content of 2.0 wt%)
2003 Et3.5%	Year 2003 Ethanol-based fully complying fuel (with oxygen content of 3.5 wt%)
2003 NonOxy	Year 2003 Non-oxygenated fully complying fuel

The region top and boundary condition files describe the air quality at the boundaries of the domain under study. These two files specify hourly ambient levels of each of the species in the SAPRC mechanism. For these simulations the region top and boundary conditions were treated as constant for all species throughout the episode. Region top concentrations were essentially the same as those used for the boundary conditions. Table 3.3 and Table 3.4 show the pollutant concentrations used for the boundary and region top, respectively.

Table 3.3 Baseline Boundary Concentration (ppb)

Species	1997 MTBE	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
O3	40.0	40.0	40.0	40.0	40.0
NO	0.9095	0.8285	0.8285	0.8285	0.8285
NO2	1.6832	1.4	1.4	1.4	1.4
N2O5	1.0	1.0	1.0	1.0	1.0
HONO	0.08371	0.06913	0.06913	0.06913	0.06913
CO	200.0	200.0	200.0	200.0	200.0
CO2	1000.0	1000.0	1000.0	1000.0	1000.0
CCHO	0.5	0.53	0.53	0.53	0.53
HCHO	0.5	0.5	0.5	0.5	0.5
RCHO	0.98	0.98	0.98	0.98	0.98
ETHE	0.829	0.7626	0.7626	0.7626	0.7626
CH4	1720.0	1720.0	1720.0	1720.0	1720.0
ALK1	0.49	0.49	0.49	0.49	0.49
ALK2	1.01	1.01	1.01	1.01	1.01
ARO1	0.4273	0.3962	0.3962	0.3962	0.3962
ARO2	0.14507	0.13538	0.13538	0.13538	0.13538
OLE1	0.7048	0.69056	0.69056	0.69056	0.69056
OLE2	0.01	0.01	0.01	0.01	0.01
C6H6	0.08	0.08	0.08	0.08	0.08
NO3	1.0	1.0	1.0	1.0	1.0
HO2	0.1	0.1	0.1	0.1	0.1
MTBE	0.1	0.1	0.01	0.01	0.01
ETOH	0.01	0.01	0.3	0.41	0.01
All other species	0.01	0.01	0.01	0.01	0.01

Table 3.4 Region Top Concentrations (ppb)

Species	1997 MTBE	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
O3	40.0	40.0	40.0	40.0	40.0
NO	0.9095	0.8285	0.8285	0.8285	0.8285
NO2	1.6832	1.4	1.4	1.4	1.4
N2O5	1.0	1.0	1.0	1.0	1.0
HONO	0.08371	0.06913	0.06913	0.06913	0.06913
CO	200.0	200.0	200.0	200.0	200.0
CO2	1000.0	1000.0	1000.0	1000.0	1000.0
CCHO	0.5	0.53	0.53	0.53	0.53
HCHO	0.5	0.5	0.5	0.5	0.5
RCHO	0.98	0.98	0.98	0.98	0.98
ETHE	0.829	0.7626	0.7626	0.7626	0.7626
CH4	1720.0	1720.0	1720.0	1720.0	1720.0
ALK1	0.49	0.49	0.49	0.49	0.49
ALK2	1.0	1.0	1.0	1.0	1.0
ARO1	0.4218	0.3912	0.3912	0.3912	0.3912
ARO2	0.14507	0.13538	0.13538	0.13538	0.13538
OLE1	0.7048	0.69056	0.69056	0.69056	0.69056
OLE2	0.01	0. 01	0.01	0. 01	0. 01
C6H6	0.08	0. 08	0. 08	0. 08	0. 08
NO3	1.0	1.0	1.0	1.0	1.0
HO2	0.1	0.1	0.1	0.1	0.1
MTBE	0.1	0.1	0.01	0.01	0.01
ETOH	0.01	0.01	0.3	0.41	0.01
All other species	0.01	0.01	0.01	0.01	0.01

B-3.4. Initial Conditions

All simulations were started with the same initial conditions given in Table 3.5. Because of this, only the results of the last simulation day, August 28, are used in the analysis. The results of the last simulation day, based on our past experience, are insensitive to the initial conditions.

Table 3.5 Initial Species Concentrations (ppb)

Species	Concentration
O3	70.0
NO	1.0
NO2	2.0
HNO3	0.1
HONO	0.1
CO	200.0
CO2	0.1
H2O2	0.1
CCHO	1.1
HCHO	5.8
RCHO	0.98
ETHE	1.4
CH4	1720.0
ALK1	0.49
ALK2	1.01
ARO1	0.7
ARO2	0.23
OLE1	0.83
OLE2	0.23
OLE3	0.00
C6H6	0.16
All other species	0.01

B-3.5. Point and Area Sources

Point source emission and area source emission files were prepared for each specific scenario studied. The preparation of each file is discussed in Appendix A.

B-3.6. Air Quality Monitoring Sites

Table 3.6 lists the 20 air quality monitoring sites in the South Coast modeling domain used to analyze the results of each different scenario studied. In addition to these sites, the domain maximum was also used. Table 3.6 shows the site locations in the domain.

Table 3.6 Sites in the Modeling Domain Used to Study the Impact of Each of the Scenarios Studied

Site Name	Id
Anaheim	ANAH
Azusa	AZUS
Burbank	BURK
Los Angeles North Main	CELA
Costa Mesa - Mesa Verde Drive	COMV
Hawthorne	HAWT
La Habra	LABH
North Long Beach	LGBH
Lynwood	LYNN
Pasadena - S. Wilson Avenue	PASA
Pico Rivera	PICO
Pomona	POMA
Reseda	RESE
Riverside - Rubidoux	RIVR
Riverside - Magnolia	RIVM
Santa Clarita - County Fire Station	SCFE
San Bernardino - 4th Street	SNB4
El Toro	TORO
Upland	UPLA
West Los Angeles - VA Hospital	WSLA

B-4. Results

As indicated above, only the results of the third day of the episode simulated (August 28) were used in the analysis to avoid dependence on the initial conditions.

B-4.1. Domain Maximum 1-Hour-Average Concentrations

Table 4.1 shows the domain maximum concentration of the pollutants of interest for each scenario simulated. As shown in Table 4.1, the domain maximum ozone decreases (6 - 8%) from 1997 to 2003 because of reductions in overall emissions. CO shows a more significant decrease (25 - 35%). Nitric acid and ethanol both decrease by up to 9%. The maximum 1-hour-average ethanol concentration is dominated by a non-motor vehicle emission source. Although total ethanol emissions increase from 1997 to the

2003 ethanol-containing fuel scenarios, emissions from a single stationary source (which dominates the magnitude of the maximum ethanol concentration) have decreased. In general the predicted concentrations do not show a large change from 1997 to 2003 for most of the pollutants, except for NO, NO_2, CO, benzene, ethanol, and nitric acid.

Maximum ozone concentrations among the year 2003 simulations are very similar, within 1-2%. CO concentration is higher for the NonOxy scenario among the 2003 simulations, and is lowest for the Et3.5% scenario.

Table 4.1 Domain Maximum 1-Hour-Average Concentrations for Each Scenario

	Domain Maximum 1-Hour-Average Concentration (ppb)											
Simulation	**O_3**	**NO**	**NO_2**	**CO**	**Formaldehyde**	**Acetaldehyde**	**C_6H_6**	**BUTD**	**MTBE**	**ETOH**	**PAN**	**PPN**	**HNO_3**
1997 MTBE	**235.9**	**214.3**	**105.3**	**3,023.6**	**22.7**	**9.2**	**3.4**	**3.0**	**6.1**	**45.6**	**4.4**	**1.4**	**57.7**
2003 MTBE	**222.2**	**190.7**	**97.2**	**2,189.1**	**23.0**	**8.7**	**1.9**	**3.0**	**3.9**	**41.4**	**4.2**	**1.4**	**52.3**
2003 Et2.0%	**220.2**	**190.6**	**97.0**	**2,189.1**	**22.7**	**8.8**	**1.9**	**3.0**	**0.0**	**42.3**	**4.1**	**1.4**	**52.3**
2003 Et3.5%	**221.0**	**190.6**	**97.1**	**2,083.3**	**22.9**	**8.9**	**2.0**	**3.0**	**0.0**	**42.8**	**4.2**	**1.4**	**52.2**
2003 NonOxy	**220.4**	**190.6**	**97.0**	**2,262.6**	**22.7**	**8.8**	**1.9**	**3.0**	**0.0**	**41.4**	**4.0**	**1.4**	**52.4**

[a] **Formaldehyde and acetaldehyde refer to total concentrations from primary emissions and secondary formation, C_6H_6 is benzene, BUTD is 1,3-butadiene, MTBE is methyl *tertiary*-butyl ether, ETOH is ethanol, PAN is peroxyacetyl nitrate, PPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates, and HNO_3 is nitric acid.**

The model predicts a domain maximum 1-hour PAN concentration of 4.2 ppb and 4.1 ppb for the 2003 MTBE, and 2003 Et2.0% scenarios, respectively. The differences in predicted PAN concentrations for each scenario are due to differences in the emissions of various VOCs with higher PAN formation potentials than ethanol. From Table 4.9 in Appendix A, it is clear that the 2003 Et2.0% scenario has higher ethanol emissions than the 2003 MTBE. However, the 2003 MTBE has higher emissions of alkanes, aromatics, and olefins compared to the 2003 Et2.0%. Figure 7.3 and Figure 7.4 in later in the appendix suggest that the lumped species ALK2, ARO2, OLE1, OLE2, and OLE3 can have (depending on the environmental conditions) higher PAN formation potentials than ethanol. Another factor is that although ethanol emissions are higher in the 2003 Et2.0% scenario, they only represent 8% of the nonmethane VOC emissions. For comparison, ALK2, ARO2, OLE1, OLE2, and OLE3 comprise about 31% of the nonmethane VOC emissions in 2003 Et2.0%. Hence, PAN formation is primarily governed by the differences in alkane, aromatic, and olefinic emissions between scenarios, rather than the emissions of ethanol.

Figure 4.1 through Figure 4.5 show hourly the 1997 and 2003 scenarios for ozone, NO, and NO_2, at Anaheim (ANAH), Burbank (BURK), downtown Los Angeles (CELA), Riverside-Rubidoux (RIVR), and at the grid cell with the domain maximum (GMX). The time plots clearly show that the 1997 and 2003 scenarios have very similar predicted ozone concentrations during the last day of the simulation. There are significant differences in predicted NO_2 concentrations between 1997 and 2003, as expected. All 2003 scenarios have the essentially the same predicted NO and NO_2 hourly concentrations.

Figure 4.6 through Figure 4.10 show ethanol, MTBE, and CO time series plots for Anaheim, Burbank, downtown Los Angeles, Riverside-Rubidoux, and at the grid with the domain maximum. The plots are only for the 2003 scenarios (Et2.0%, Et3.5%, NonOxy, and MTBE). As expected, the 2003 Et3.5% scenario has highest predicted ethanol concentrations, while the 2003 MTBE is the only scenario with significant MTBE hourly concentrations among all the 2003 scenarios.

Figure 4.11 through Figure 4.15 show time series plots of hourly PAN (and higher molecular weight acyl peroxy nitrates), and nitric acid concentrations for the 1997 and 2003 scenarios, at Anaheim, Burbank, downtown Los Angeles, Riverside-Rubidoux, and at the domain maximum. Predicted PAN, PPN, and nitric acid concentrations are the same for all 2003 scenarios. Both PAN and PPN show a large maximum on the second day of the episode that has significantly decreased by the third day of the episode simulated.

From Figure 4.1 through Figure 4.5, it is clear that although hydrocarbon and NO_X emissions decreased from 1997 to 2003, the reduction did not significantly impact the O_3, NO, and NO_2 levels predicted by the photochemical mechanism. This is confirmed by the small impact on the predicted maximum ozone concentrations. In addition, the NO_X-to-hydrocarbon ratio may not have significantly changed from 1997 to 2003, which may explain the essentially similar PAN, PPN (and higher molecular weight acyl peroxy nitrates), and nitric acid predicted concentrations for these years (see Figure 4.11 through Figure 4.15).

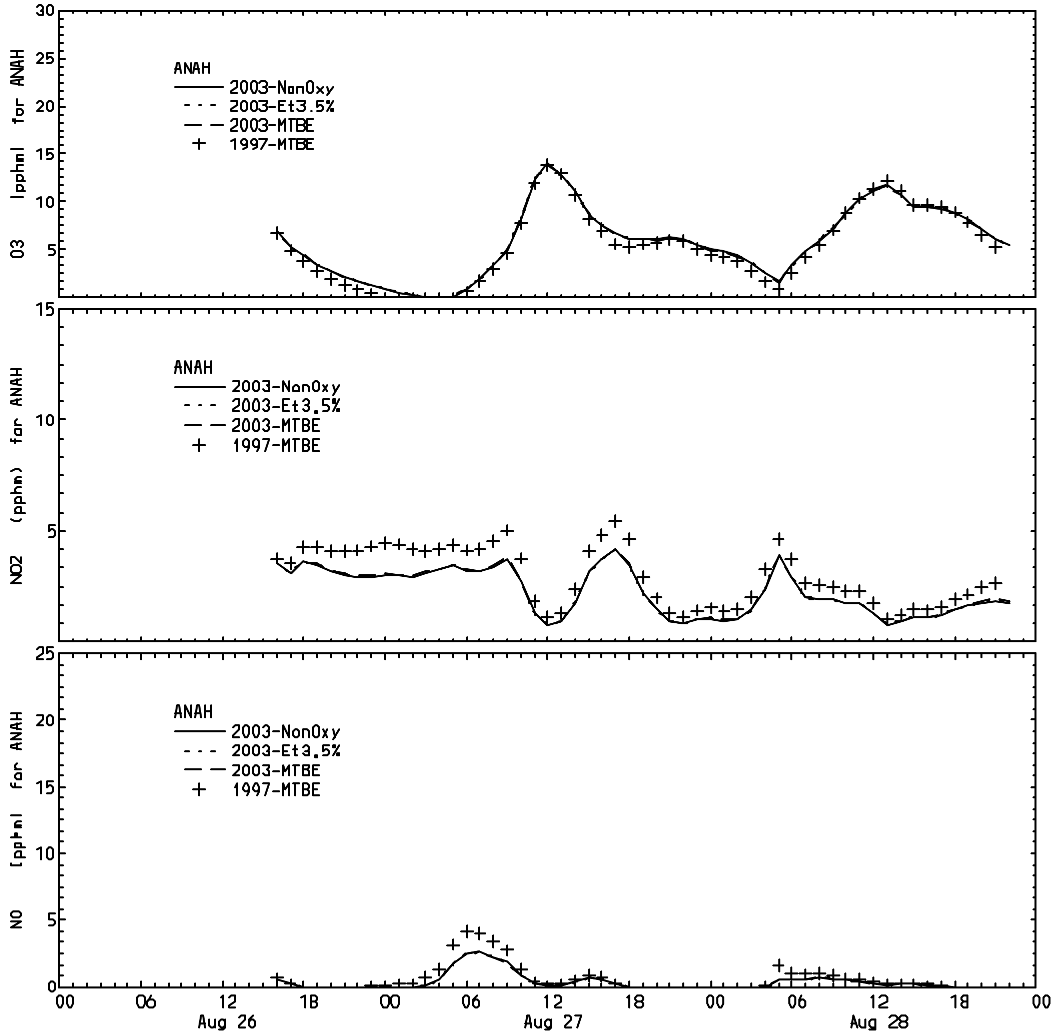


Figure 4.1 Time Series for Ozone, NO_2, and NO at Anaheim for 1997 and 2003 Scenarios

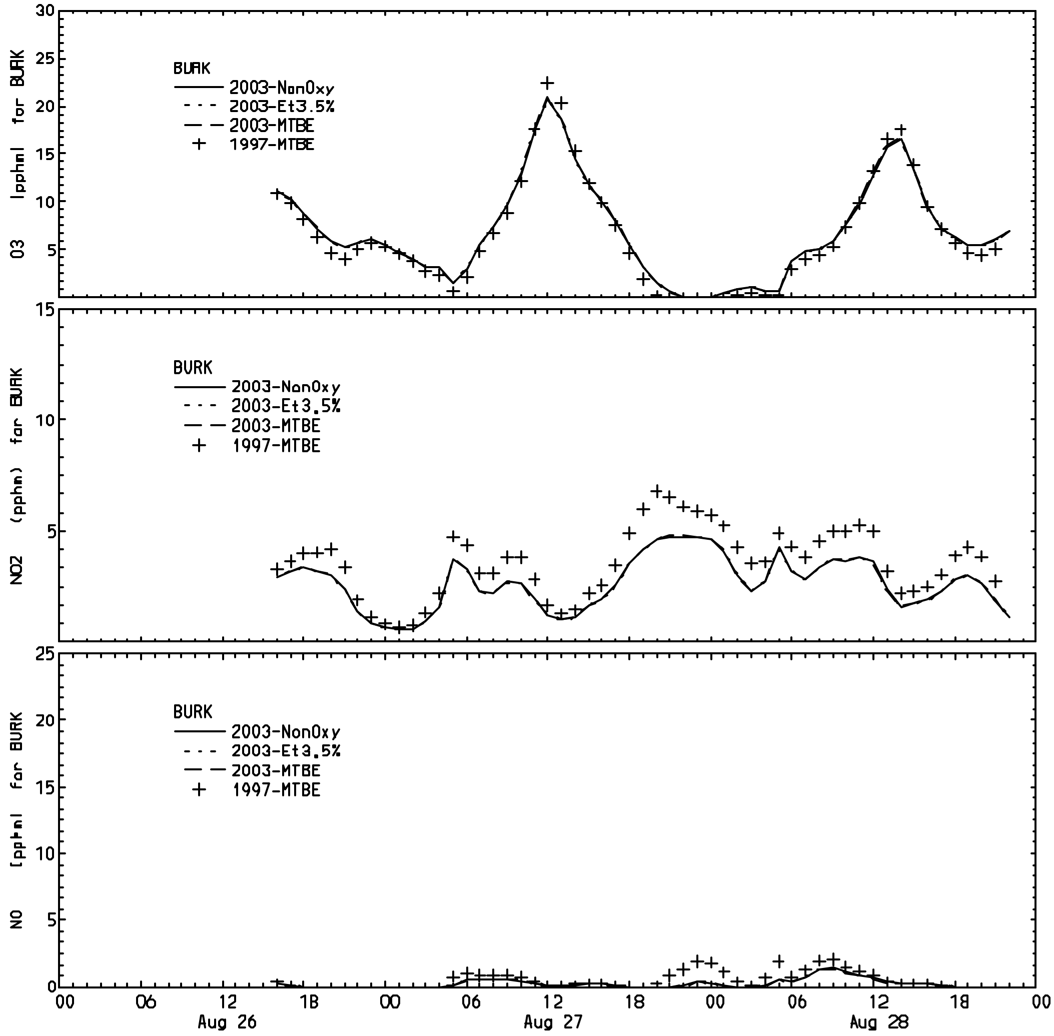


Figure 4.2 Time Series for Ozone, NO_2, and NO at Burbank for 1997 and 2003 Scenarios

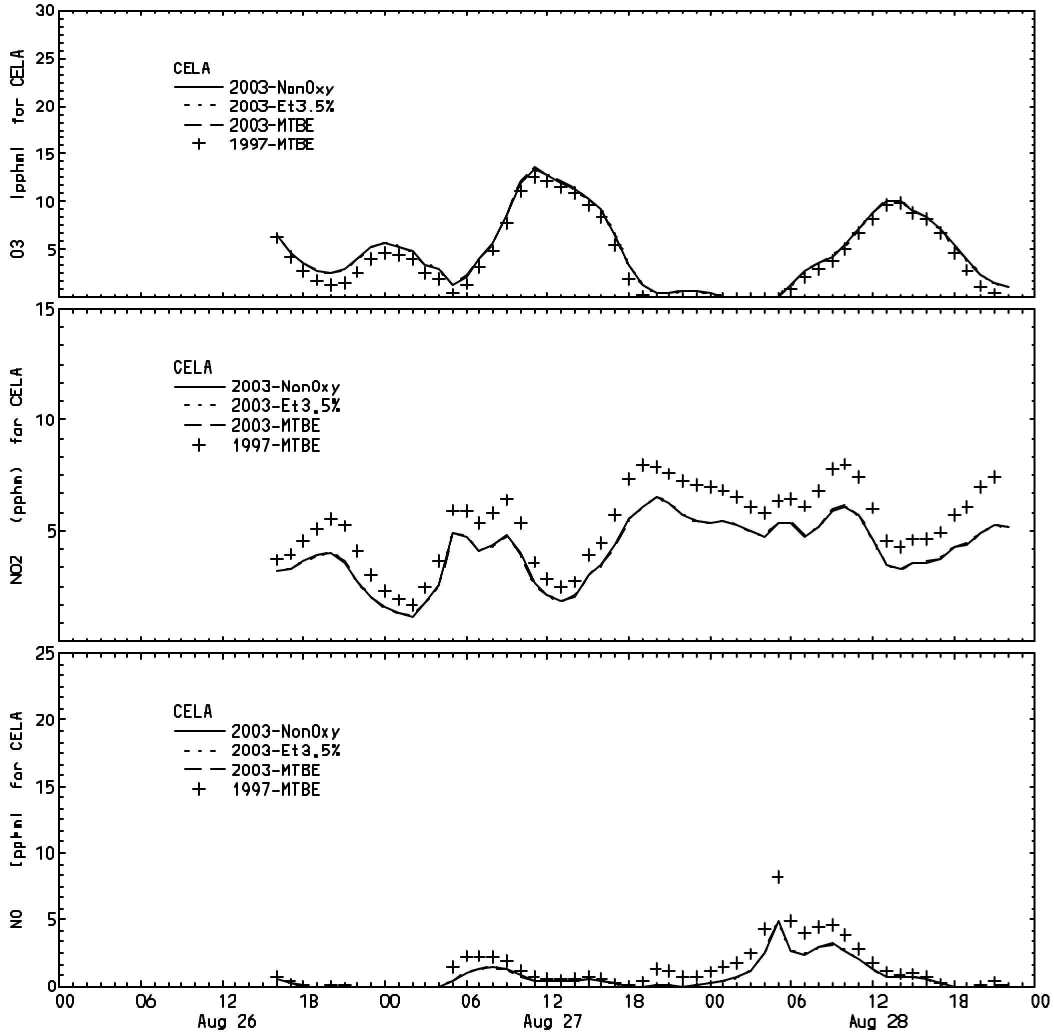


Figure 4.3 Time Series for Ozone, NO_2, and NO at Los Angeles for 1997 and 2003 Scenarios

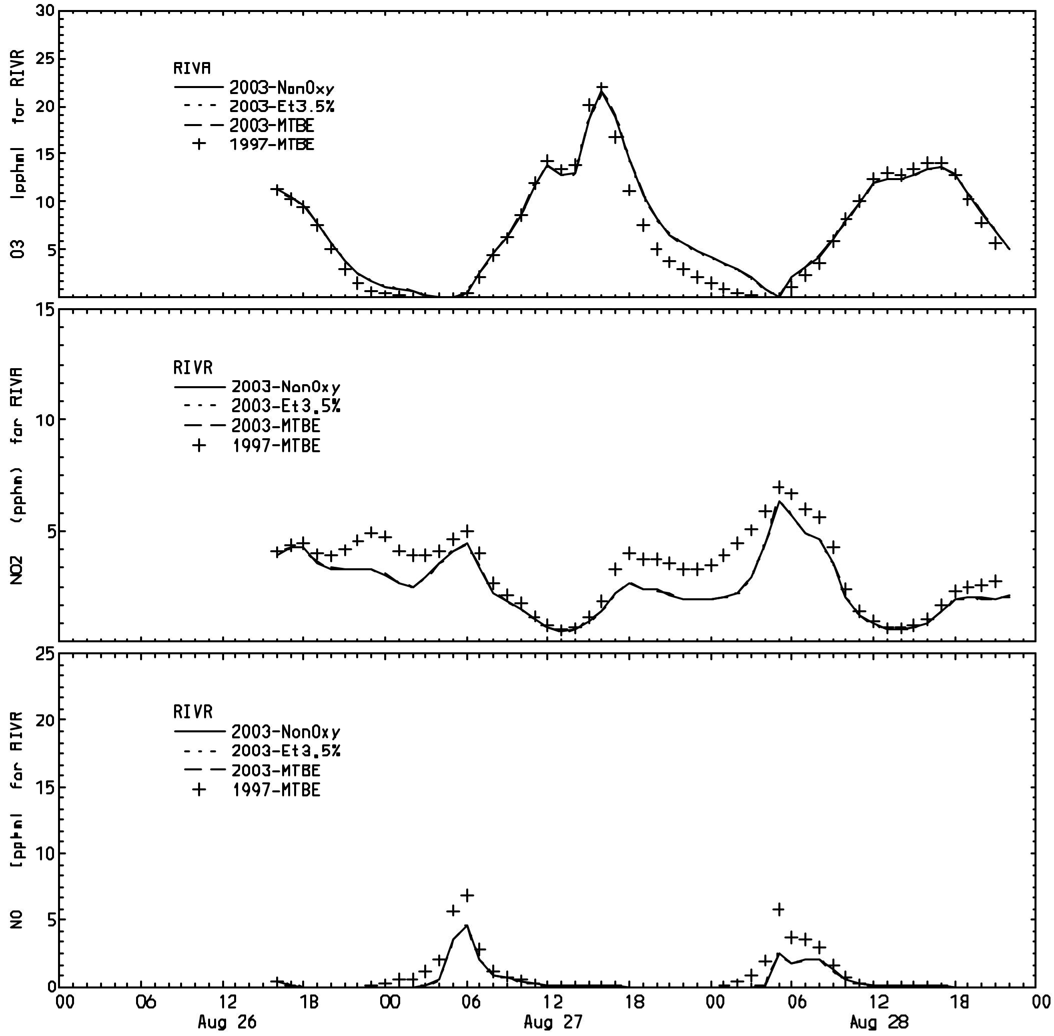


Figure 4.4 Time Series for Ozone, NO_2, and NO at Riverside for 1997 and 2003 Scenarios

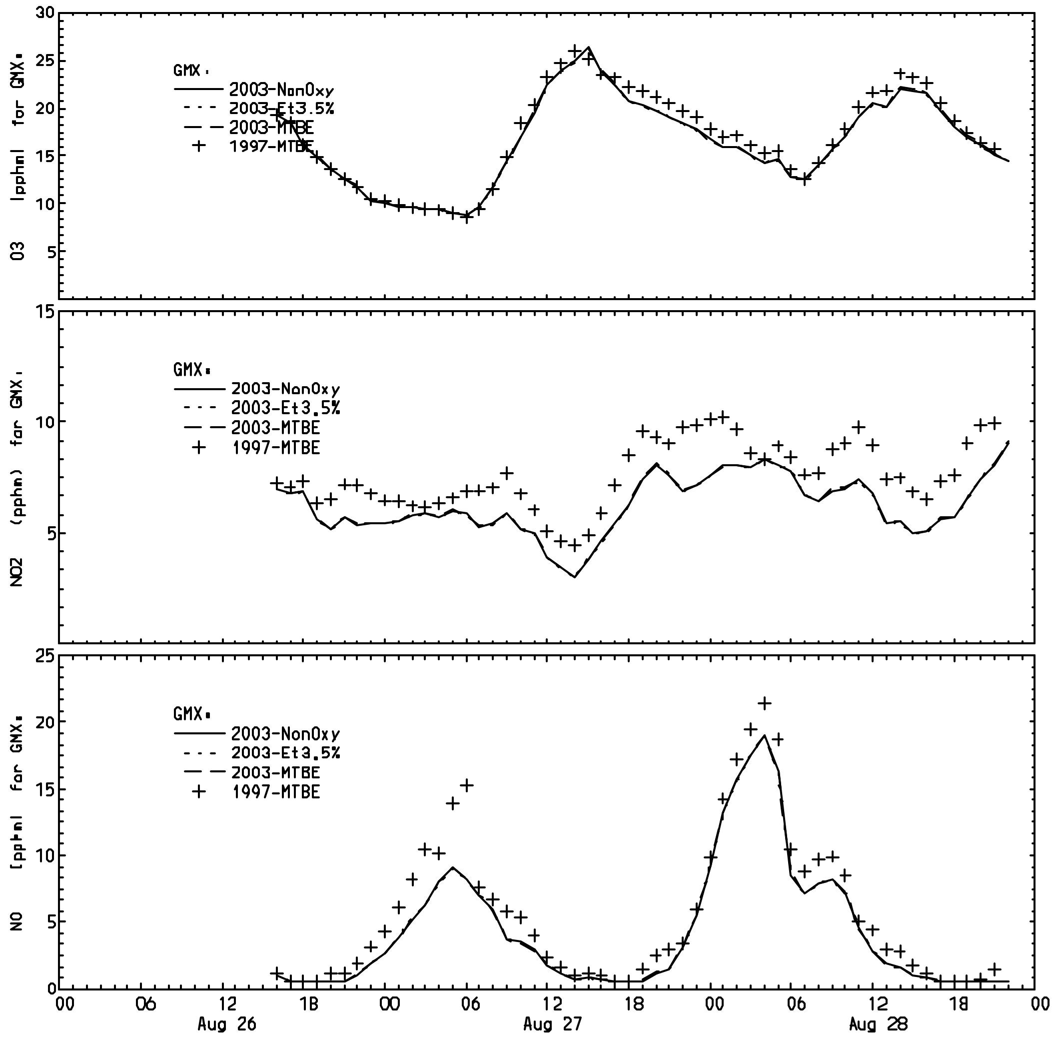


Figure 4.5 Time Series for Ozone, NO_2, and NO at Grid with Domain Maximum for 1997 and 2003 Scenarios

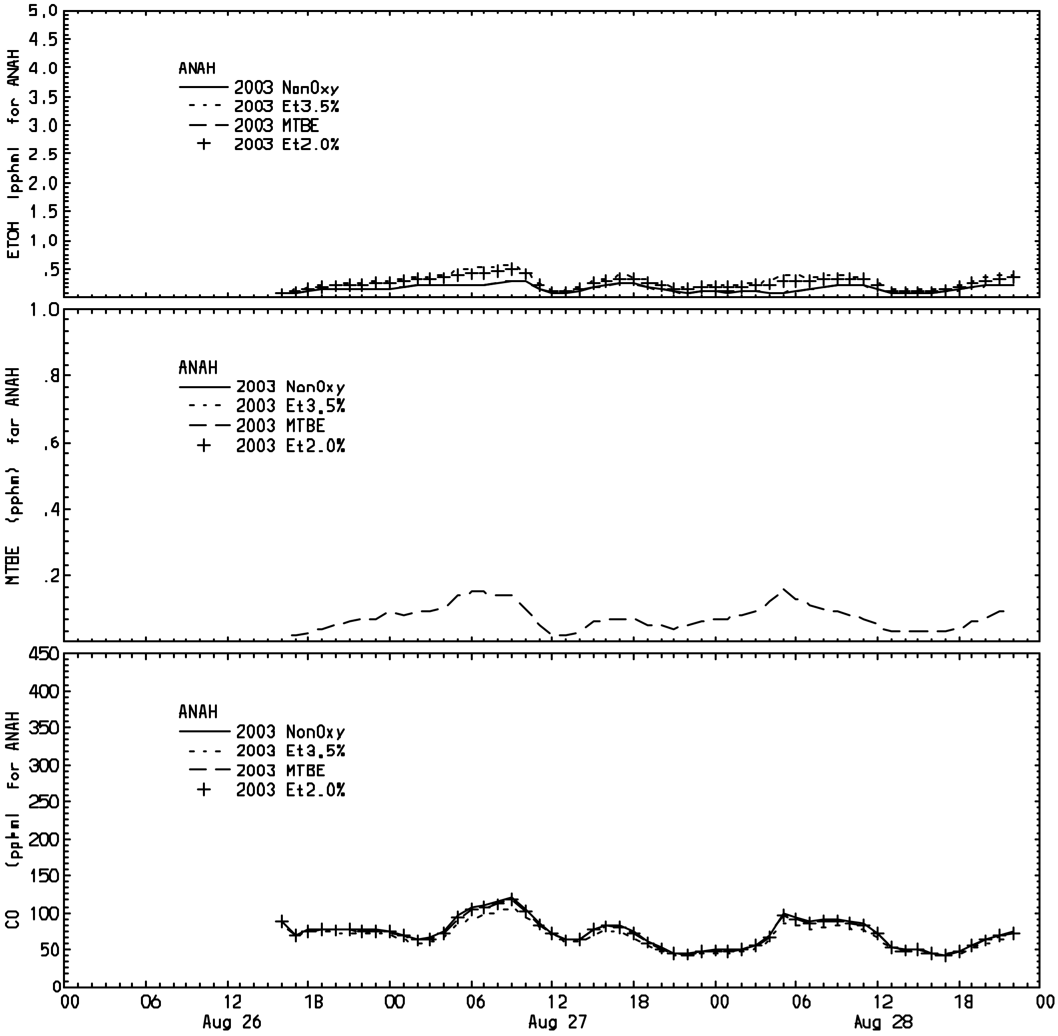


Figure 4.6 Time Series for MTBE, Ethanol, and CO at Anaheim for 2003 Scenarios

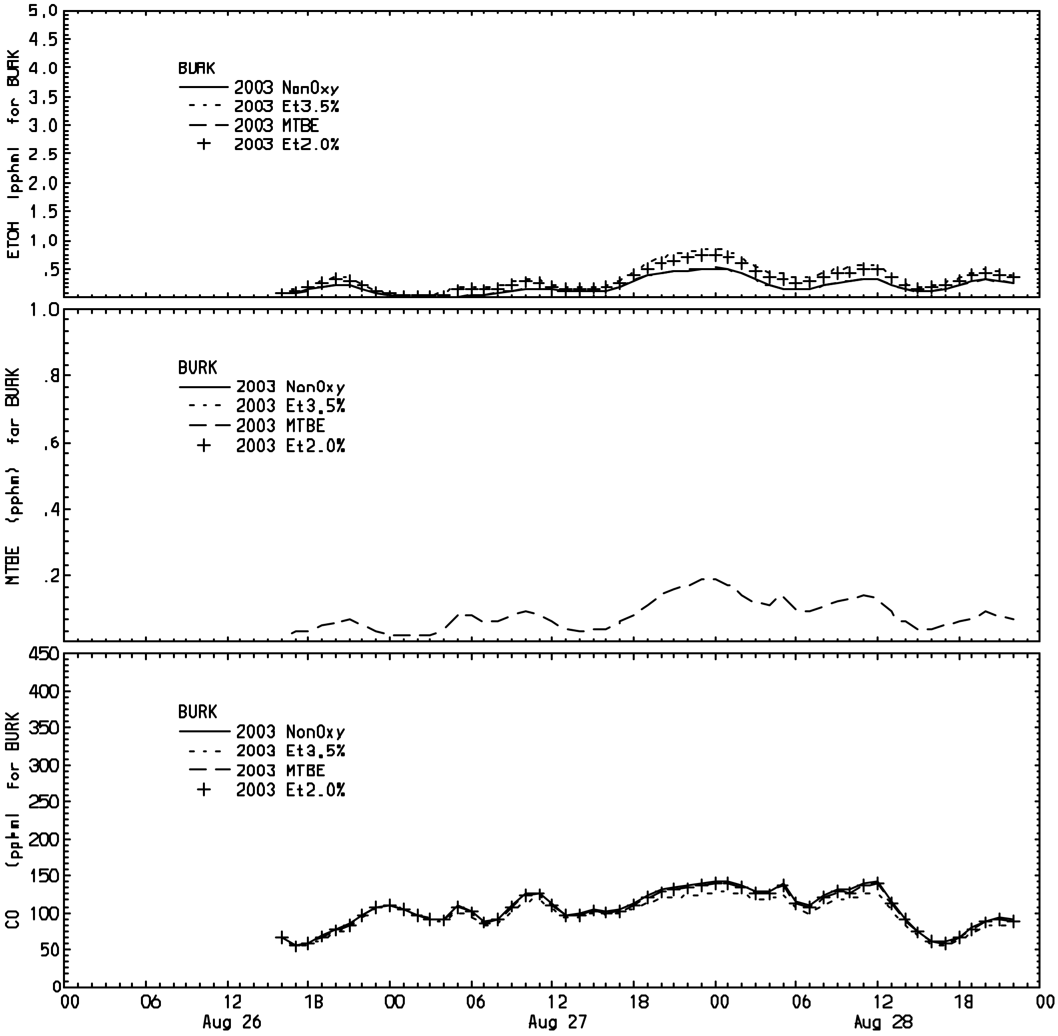


Figure 4.7 Time Series for MTBE, Ethanol, and CO at Burbank for 2003 Scenarios

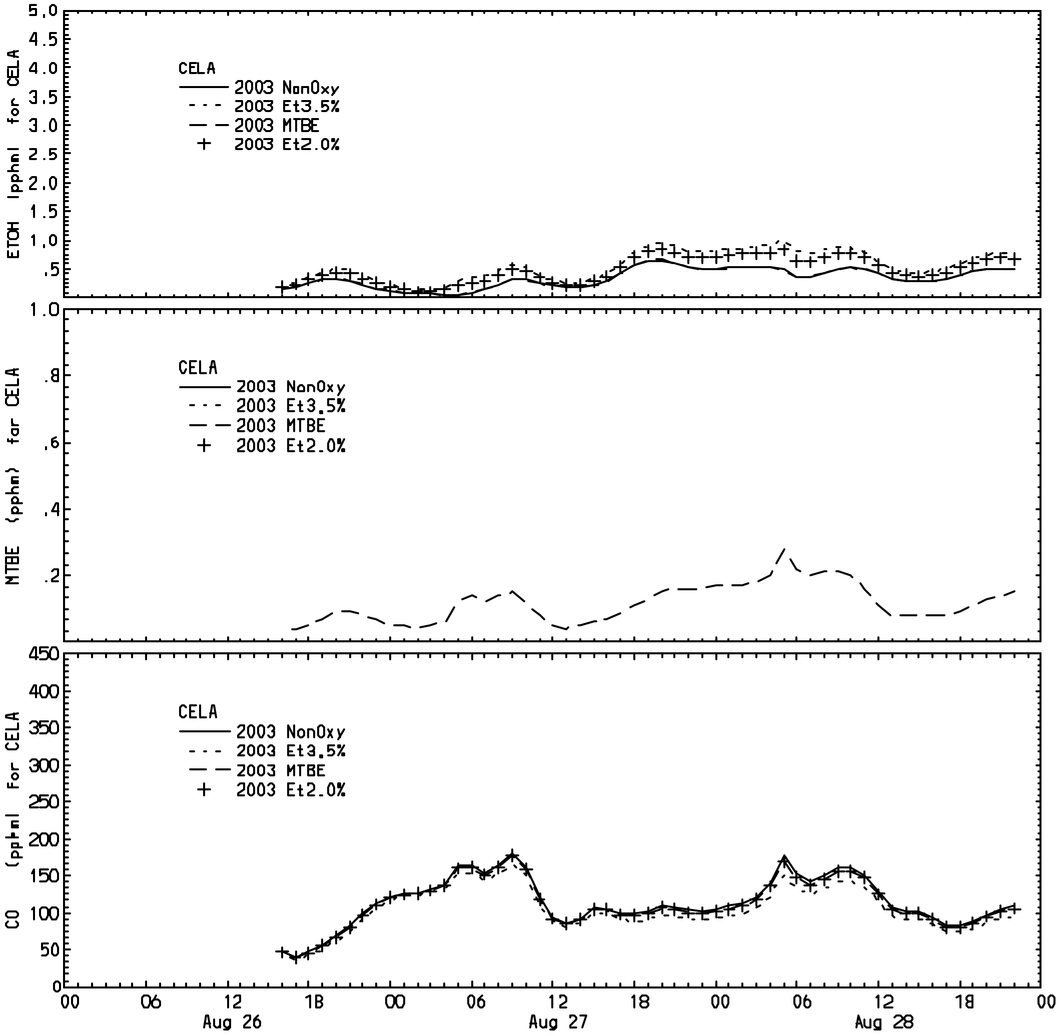


Figure 4.8 Time Series for MTBE, Ethanol, and CO at Los Angeles for 2003 Scenarios

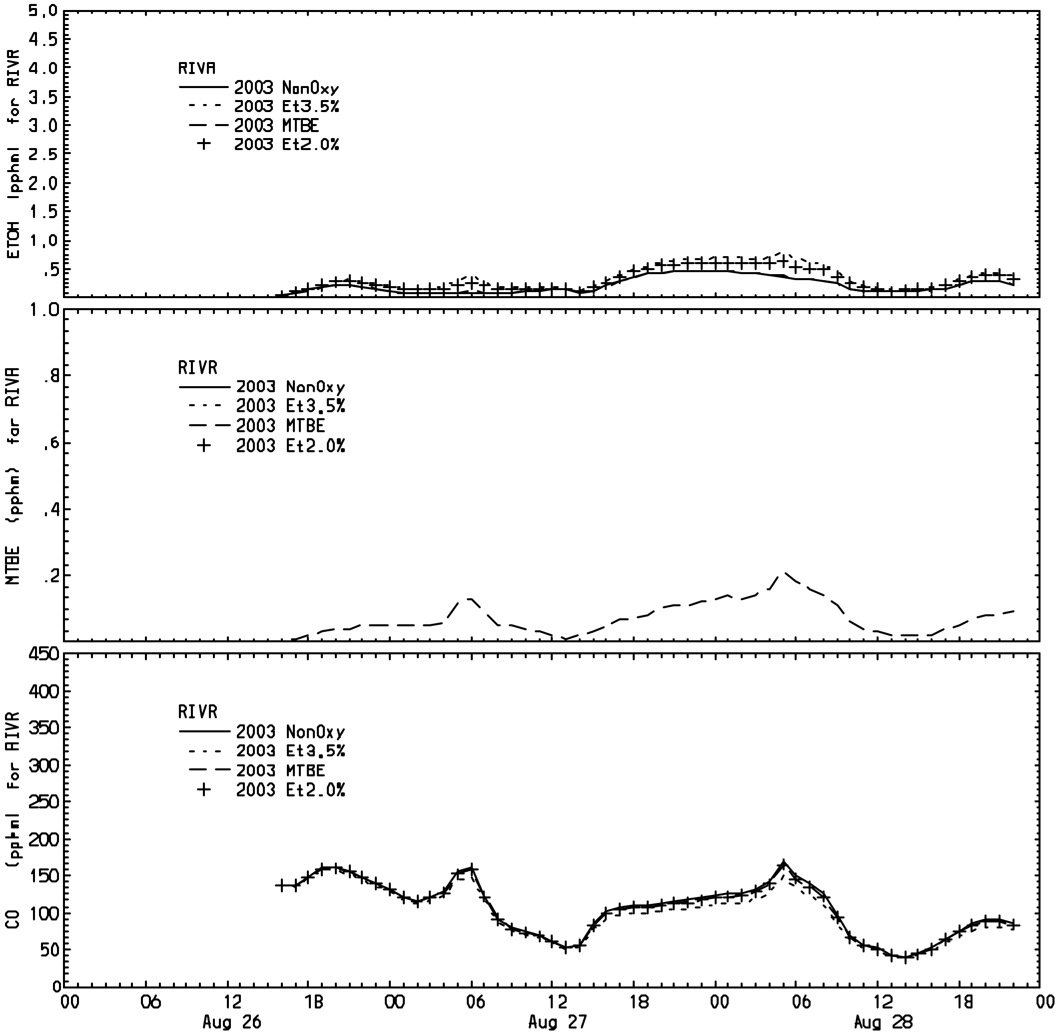


Figure 4.9 Time Series for MTBE, Ethanol, and CO at Riverside for 2003 Scenarios

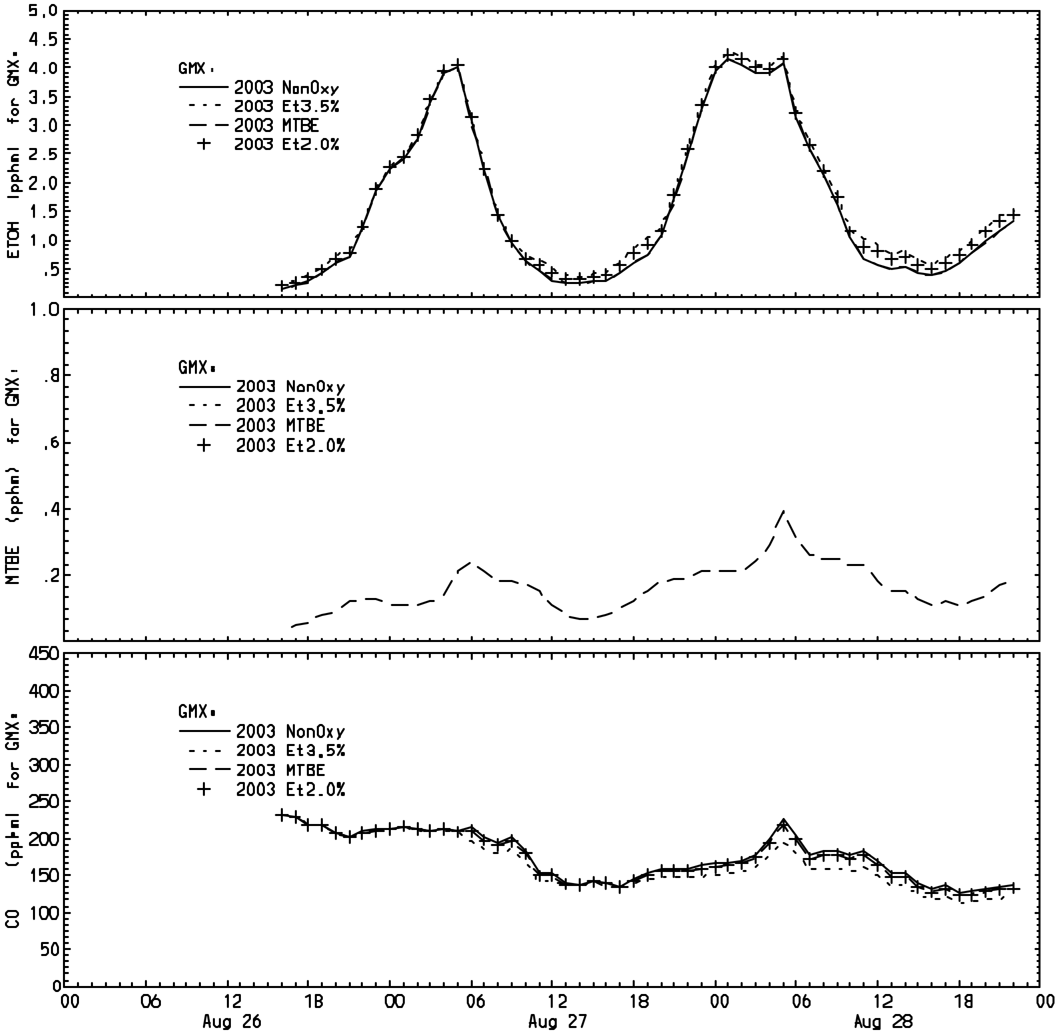


Figure 4.10 Time Series for MTBE, Ethanol, and CO at Grid with Domain Maximum for 2003 Scenarios

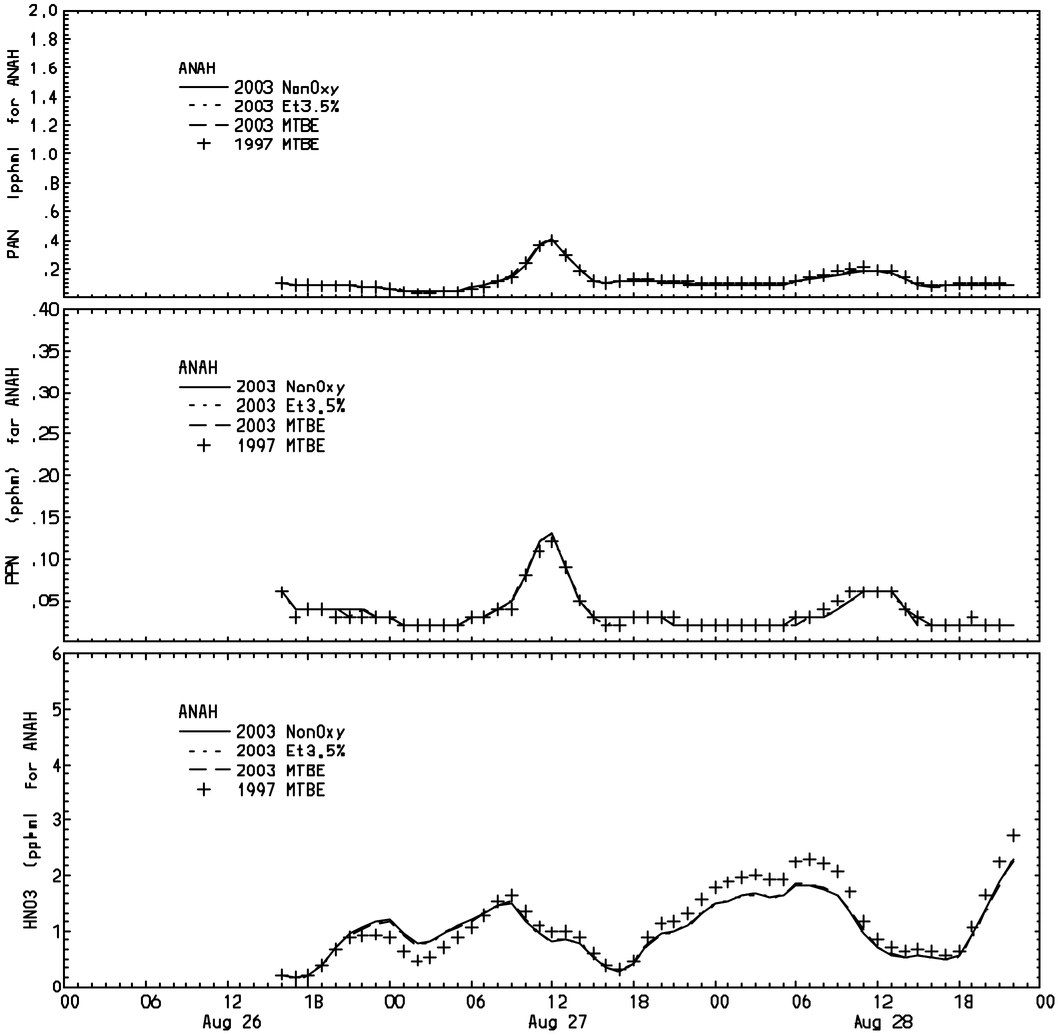


Figure 4.11 Time Series for PAN, PPN, and Nitric Acid at Anaheim for 1997 and 2003 Scenarios

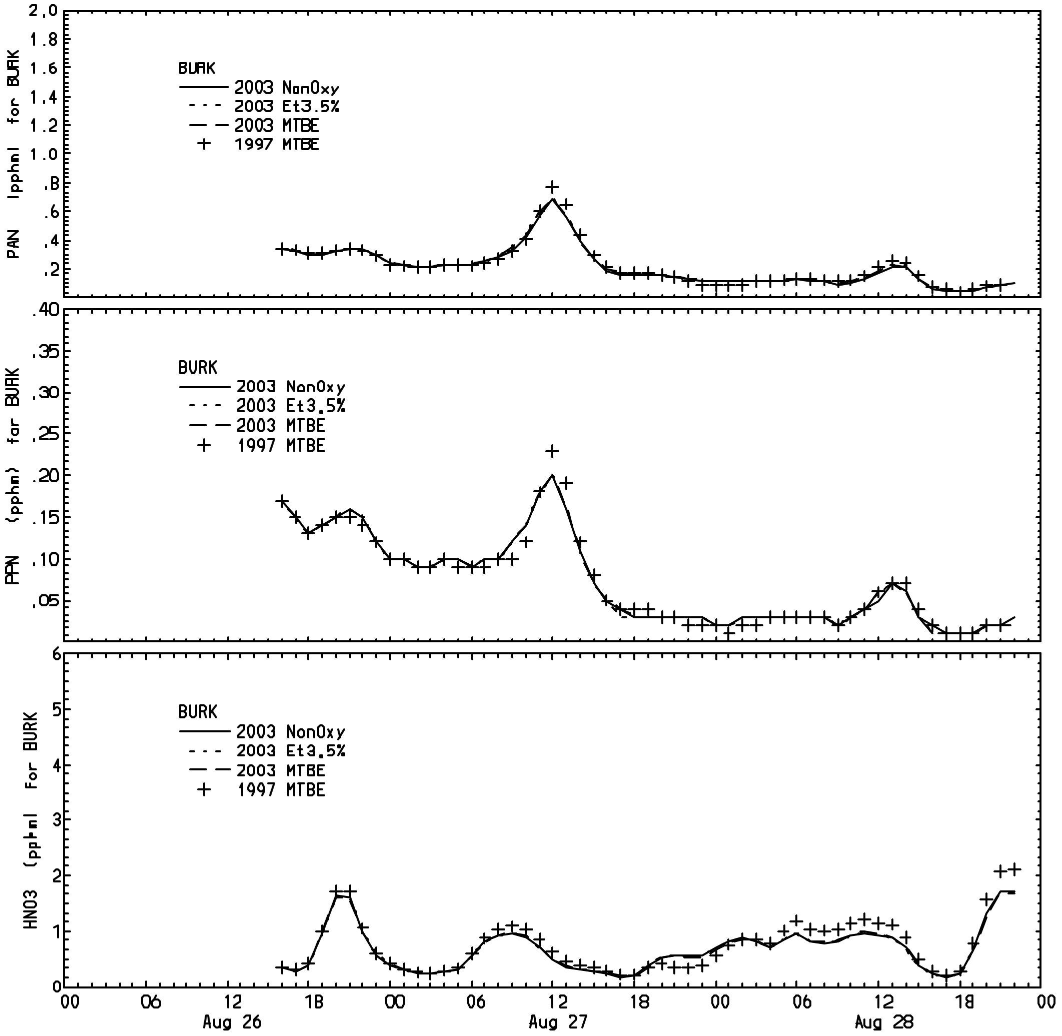


Figure 4.12 Time Series for PAN, PPN, and Nitric Acid at Burbank for 1997 and 2003 Scenarios

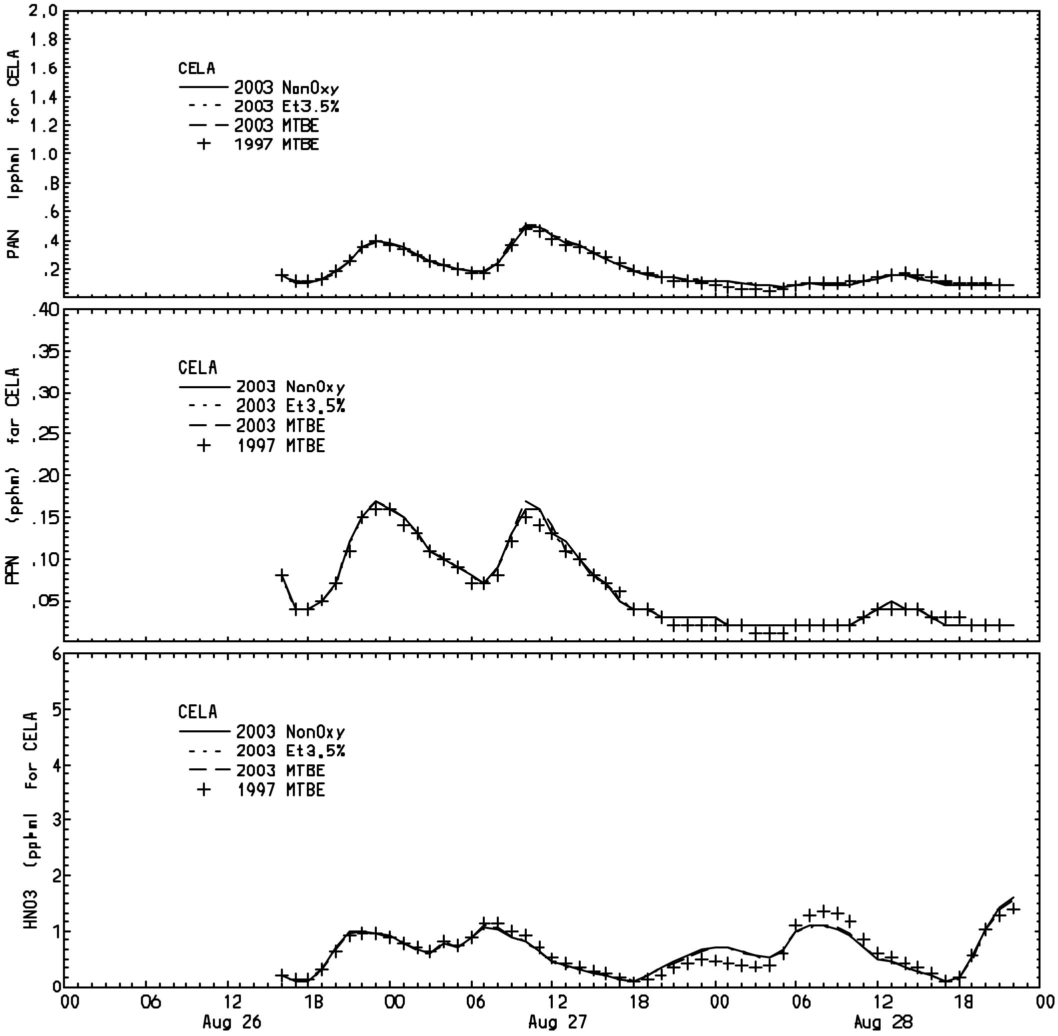


Figure 4.13 Time Series for PAN, PPN, and Nitric Acid at Los Angeles for 1997 and 2003 Scenarios

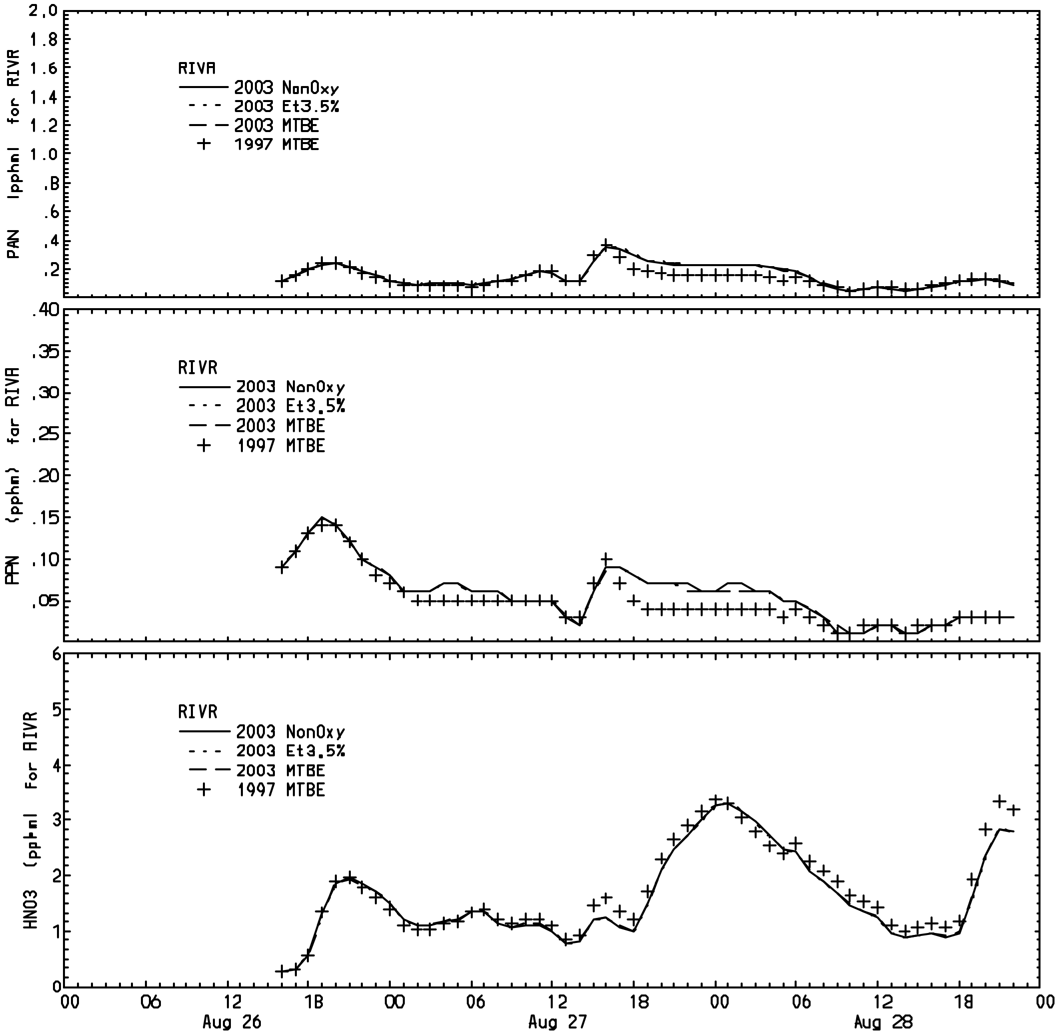


Figure 4.14 Time Series for PAN, PPN, and Nitric Acid at Riverside for 1997 and 2003 Scenarios

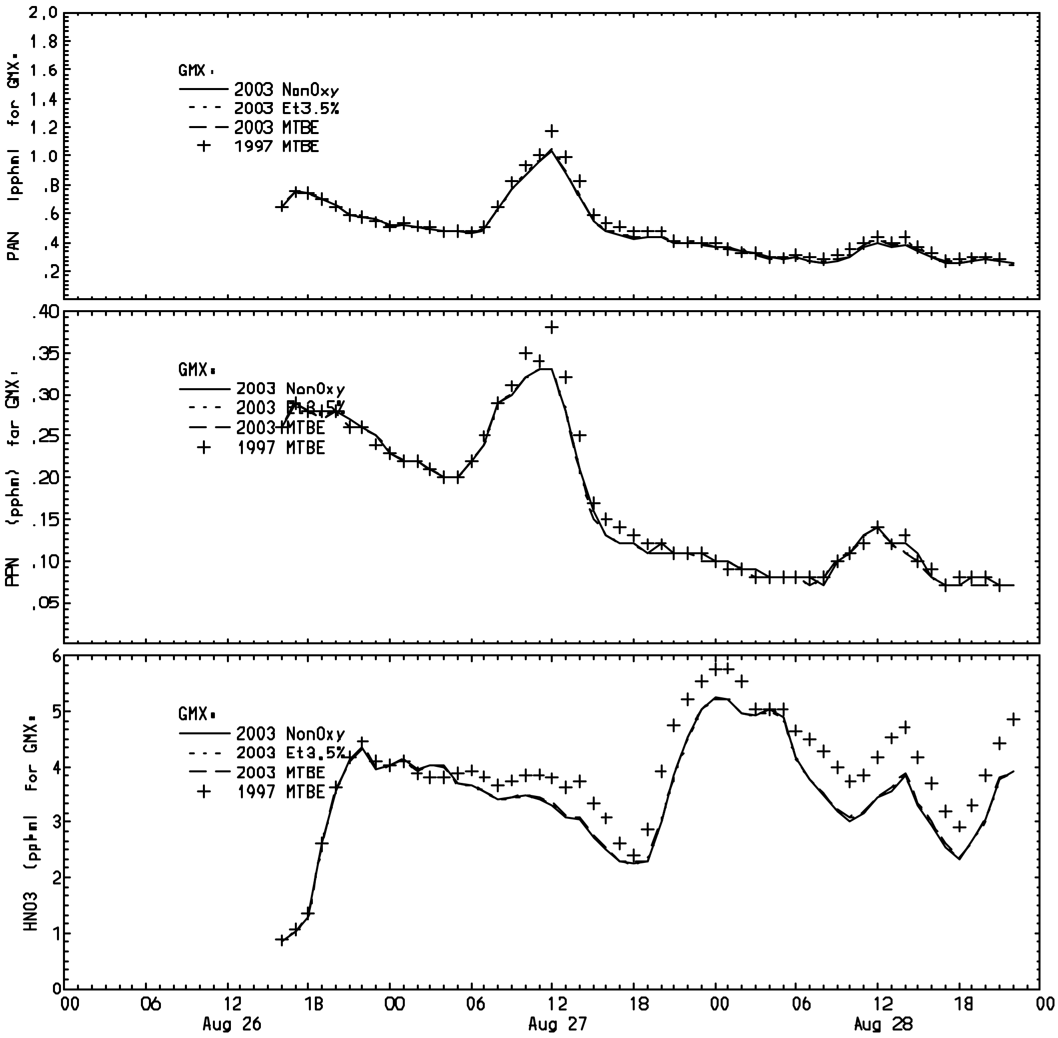


Figure 4.15 Time Series for PAN, PPN, and Nitric Acid at Grid with Domain Maximum for 1997 and 2003 Scenarios

B-4.2. Domain Maximum 8-Hour-Average Concentrations

Table 4.2 shows domain maximum 8-hour-average concentrations for selected pollutants. As shown, the 8-hour-average ozone concentration decreases by up to 5% from 1997 to 2003. CO is reduced by up to 32% for the Et3.5% scenario. Similarly, the 8-hour benzene concentration is reduced by 37% between 1997 and 2003. The 8-hour-average formaldehyde is reduced by 4%, but the 8-hour-average acetaldehyde decreases by up to 13% from 1997. The 8-hour nitric acid predicted concentration is seen to decrease by 5% from 1997 to 2003, while 8-hour PPN and BUTD are essentially unchanged. PAN and ethanol 8-hour-average concentrations decrease by up to 9% from 1997 baseline. As discussed in Section B-4.1, the predicted ethanol concentrations are dominated by non-motor vehicle sources, which may explain the predicted decrease in ethanol 8-hour-average concentrations

Table 4.2 Domain Maximum 8-Hour-Average Concentrations for Each Scenario

	Domain Maximum 8-Hour-Average Concentration[a] (ppb)												
Simulation	**O_3**	**NO**	**NO_2**	**CO**	**Formaldehyde**	**Acetaldehyde**	**C_6H_6**	**BUTD**	**MTBE**	**ETOH**	**PAN**	**PPN**	**HNO_3**
1997 MTBE	**187.3**	**150.3**	**86.4**	**2,432**	**16.8**	**7.7**	**2.46**	**2.08**	**4.1**	**40.9**	**3.25**	**0.99**	**47.9**
2003 MTBE	**177.9**	**133.4**	**75.0**	**1,816**	**16.3**	**6.7**	**1.60**	**2.05**	**2.7**	**37.2**	**2.98**	**0.94**	**45.6**
2003 Et2.0%	**178.0**	**133.2**	**74.9**	**1,816**	**16.1**	**6.8**	**1.59**	**2.05**	**0.0**	**38.0**	**2.98**	**0.94**	**45.5**
2003 Et3.5%	**178.1**	**133.2**	**74.9**	**1,741**	**16.2**	**6.8**	**1.61**	**2.05**	**0.0**	**38.5**	**3.01**	**0.94**	**45.5**
2003 NonOxy	**178.3**	**133.2**	**75.0**	**1,872**	**16.1**	**6.8**	**1.56**	**2.05**	**0.0**	**37.2**	**2.96**	**0.95**	**45.6**

[a] **Formaldehyde and acetaldehyde refer to total concentrations from primary emissions and secondary formation, C_6H_6 is benzene, BUTD is 1,3-butadiene, MTBE is methyl *tertiary*-butyl ether, ETOH is ethanol, PAN is peroxyacetyl nitrate, PPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates, and HNO_3 is nitric acid.**

B-4.3. Domain Maximum 24-Hour-Average Concentrations

Table 4.3 shows maximum 24-hour-average concentrations in the domain for selected pollutants. As shown, the 24-hour-average ozone concentration decreases by up to 4% from 1997 to 2003. CO is reduced by up to 29% for the 2003 Et3.5% scenario. Similarly, the 24-hour benzene concentration is reduced by almost 37% between 1997 and 2003. The 24-hour-average formaldehyde is reduced by up to 16%, but the 24-hour-average acetaldehyde is unchanged. The 24-hour nitric acid concentration is seen to decrease by 12% from 1997 to 2003, while PPN decreases by 2% for the 2003 Et3.5%, increases by 3% for the 2003 NonOxy, and is unchanged for the 2003 MTBE ands 2003 Et2.0%. The impact on 24-hour PAN concentration is also modest, with a decrease of up to 6% for the 2003 NonOxy scenario. The 24-hour-average ethanol concentration is reduced up to 9% for the 2003 NonOxy case. As discussed in Section B-4.1, the predicted ethanol concentrations are dominated by non-motor vehicle sources, which may explain the predicted decrease in ethanol 24-hour-average concentrations.

Table 4.3 Domain Maximum 24-Hour-Average Concentrations For Each Scenario

	Domain Maximum 24-Hour-Average Concentration[a] (ppb)												
Simulation	**O_3**	**NO**	**NO_2**	**CO**	**Formaldehyde**	**Acetaldehyde**	**C_6H_6**	**BUTD**	**MTBE**	**ETOH**	**PAN**	**PPN**	**HNO_3**
1997 MTBE	148.0	66.2	72.8	1,614	11.35	6.2	1.72	0.88	2.63	19.05	2.12	0.58	36.73
2003 MTBE	142.7	57.8	60.7	1,252	9.90	6.2	1.10	0.88	1.67	17.35	2.03	0.58	32.41
2003 Et2.0%	142.7	57.7	60.4	1,252	9.57	6.2	1.09	0.87	0.00	17.89	2.02	0.58	32.28
2003 Et3.5%	142.8	57.7	60.5	1,206	9.78	6.2	1.10	0.88	0.00	18.14	2.06	0.58	32.27
2003 NonOxy	142.9	57.7	60.5	1,286	9.49	6.2	1.06	0.87	0.00	17.36	2.00	0.60	32.28

[a] **Formaldehyde and acetaldehyde refer to total concentrations from primary emissions and secondary formation, C_6H_6 is benzene, BUTD is 1,3-butadiene, MTBE is methyl *tertiary*-butyl ether, ETOH is ethanol, PAN is peroxyacetyl nitrate, PPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates, and HNO_3 is nitric acid.**

B-5. Sensitivity Simulations

Sensitivity analysis is an evaluation of the model response to variations in one or more of the model inputs. The sensitivity simulations performed in our study represent the cumulative effect of 1) use of EMFAC2000 instead of EMFAC7G, 2) consideration of chlorine radical chemistry, 3) use of updated rate constants for the reactions of hydroxyl radical with ethanol and MTBE, and 4) revised boundary conditions. The sensitivity simulations considered for this study are listed in Table 5.1, and a brief description of the each of the effects considered in the sensitivity simulations is provided below.

B-5.1. Increasing Motor Vehicle Hydrocarbon and CO Emissions

The on-road motor vehicle emissions were increased to evaluate the potential impact of using EMFAC2000 (ARB, 1999) instead of EMFAC7G. EMFAC2000 was not available at the time of this study, but emissions from motor vehicles increase substantially with EMFAC2000. A large increase in hydrocarbon emissions will change the NO_X-to-hydrocarbon ratio and potentially impact the radical flux. This may increase the photochemical oxidation of ethanol and lead to increase acetaldehyde and PAN impacts. For this purpose, hydrocarbon emissions were multiplied by a factor of three to place an upper-limit to the impact of using EMFAC2000, which at one time proposed multiplication factors of 2.34 and 1.84 for the 2000 on-road motor vehicle emission inventory in the South Coast Air Basin for hydrocarbons and NO_X, respectively. The factor of three is also consistent with an independent fuel-based inventory for the South Coast Air Basin in 1997 which proposes a multiplication factor of 3.5±0.6 for on-road motor vehicle hydrocarbon emissions of stabilized exhaust (Singer and Harley, 2000). The Singer and Harley (2000) fuel-based inventory is for stabilized exhaust emissions and does not include cold start or evaporative emissions, so it is not necessarily inconsistent with draft versions of EMFAC2000. We also have some concerns with Singer and Harley's methodology (primarily lack of freeway measurements where gm/gallon emission rates are likely to be lower) and view it as an upper-bound estimate. The motor vehicle CO emissions were also increased by a factor of three to represent the impact of using EMFAC2000, which proposes a significant (a factor of about three) increase of motor vehicle CO emissions.

Table 5.1 Sensitivity Scenarios

Scenario	Description
1997 MTBE Sens	**Increased on-road motor vehicle ROG and motor vehicle CO by factor of 3 for the 1997 MTBE fuel, added of chlorine + ethanol reaction, updated OH radical rate constant for OH + ethanol, and OH + MTBE, and used revised boundary conditions**
2003 MTBE Sens	**Increased on-road motor vehicle ROG and motor vehicle CO by factor of 3 for the 2003 MTBE fuel, added of chlorine + ethanol reaction, updated OH radical rate constant for OH + ethanol, and OH + MTBE, and used revised boundary conditions**
2003 Et2.0% Sens	**Increased on-road motor vehicle ROG and motor vehicle CO by factor of 3 for the 2003 Et2.0% fuel, added of chlorine + ethanol reaction, updated OH radical rate constant for OH + ethanol, and OH + MTBE, and used revised boundary conditions**
2003 Et3.5% Sens	**Increased on-road motor vehicle ROG and motor vehicle CO by factor of 3 for the 2003 Et3.5% fuel, added of chlorine + ethanol reaction, updated OH radical rate constant for OH + ethanol, and OH + MTBE, and used revised boundary conditions**
2003 NonOxy Sens	**Increased on-road motor vehicle ROG and motor vehicle CO by factor of 3 for the 2003 NonOxy fuel, added of chlorine + ethanol reaction, updated OH radical rate constant for OH + ethanol, and OH + MTBE, and used revised boundary conditions**

B-5.2. Potential Impact of the Chlorine Radical Reaction With Ethanol

In addition to the increase in on-road motor vehicle emissions described above, the chemical mechanism used was modified in response to concerns on the impact of including chlorine radical reactions in the atmospheric chemical mechanism (Finlayson-Pitts, 1999). Reactions of chlorine radical with hydrocarbons are not part of SAPRC97 mechanism used in our study (see Attachment B1).

The chlorine (Cl) radical behaves similarly to the hydroxyl radical on its reaction with hydrocarbons. Cl radicals can be generated during daylight through photolysis of Cl_2 present in the air (Spicer *et al.*, 1998; Seinfeld and Pandis, 1998). Other sources of Cl radical are sea salt interaction with nitrogen oxides, and the hydroxyl radical reaction with the gaseous HCl produced by the acidification of sea salt with sulfuric acid or nitric acid (Fantechi *et al.*, 1998, and references cited therein). The Cl radical is known to have a key role on the reactions that cause stratospheric ozone depletion (Seinfeld and Pandis, 1998). In addition, it has been recognized that it can also play a role in the tropospheric oxidation of hydrocarbons near coastal areas (Finlayson-Pitts, 1999; de Haan *et al.*, 1999; Hov, 1985). Other reactive halogenated species, such as bromine and iodide, can also play a role in the tropospheric ozone budget in some areas (Platt *et al.*, 1999; Stutz *et al.*, 1999), but are not believed to be of relevance to the South Coast Air Basin.

A proper treatment of the Cl radical reactions in an atmospheric chemical mechanism should include reactions of Cl radical with all hydrocarbons, including methane, 1,3-butadiene, isoprene, MTBE, ethanol, benzene, and their reaction products (for example, see Fantechi *et al.*, 1998), including reactions with other inorganic species. However, there are significant uncertainties in the reliability of models on chlorine chemistry, because there are limited smog chamber data to test mechanisms for chlorine radical reactions (Carter, 1999a). Hence, the addition of Cl radical reactions will require a revision of the atmospheric chemical mechanism, which is outside the scope of this study. A way to address, the potential impact of adding Cl radical reactions is to focus on its effect on ethanol. We added a Cl radical reaction with ethanol, assuming the same lumped products as with the OH reaction with ethanol in the SAPRC97 chemical mechanism (see Attachment B3), and using a constant reaction rate of 9.4×10^{11} $cm^3 molecule^{-1} s^{-1}$ (Finlayson-Pitts, 1999):

ETOH + CL = #.1 RO2-R + #.9 HO2 + #.156 HCHO + #.922 CCHO + #.1 RO2

The above reaction is a coarse approximation, since the reaction products and product yields could be very different from the real reaction (for example, HCl is not included as a byproduct of the Cl radical reaction with ethanol). Two additional assumptions were made to place an upper-limit on the potential effect of including the Cl radical reaction with ethanol. First, the reaction was not restricted to daylight hours only; and, second, we assumed a constant Cl radical concentration of $1\text{x}10^4$ atoms per cm^3 (Finlayson-Pitts, 1999; Fantechi *et al.*, 1998) throughout the domain. The impact of adding the above reaction is to greatly increase the oxidation of ethanol and lead to increased acetaldehyde and PAN impacts. It is expected that the maximum impact will be for the 2003 Et3.5% scenario, because of the higher ethanol emission rates in the inventory, relative to the other scenarios.

B-5.3. Updated Rate Constants

In response to comments received (Atkinson, 1999a), we also revised, for the sensitivity simulations, the rate constants used in our chemical mechanism so that the OH + ETOH reaction will have a rate constant given by $k=5.56\times10^{13}(T/300)^{2}\exp(532/T)\ cm^{3} molecule^{-1}s^{-1}$, and the OH + MTBE reaction the rate constant was updated to be $k=5.89\times10^{-13}(T/300)^{2}\exp(483/T)\ cm^{3} molecule^{-1}s^{-1}$ (Atkinson, 1999b). These changes increased the OH + ethanol rate constant by only 0.03%, and the OH + MTBE rate constant by 3.8%, with respect to the values originally used (see Attachment B.3). The use of the revised kinetic rate constants will increase slightly the photochemical oxidation of ethanol and MTBE.

B-5.4. Revised Boundary Conditions

In response to comments received (Atkinson, 1999a), we also revised the HONO, N_2O_5, and NO_3 concentrations used in the boundaries and top concentration when performing the sensitivity simulations. The revised concentrations are shown in Table 5.2. The HONO boundary and top concentrations used in the sensitivity simulations are larger by a factor of 9 for the 1997 MTBE sens, and by a factor of 8 for the 2003 scenarios than those used in the baseline simulations (see Table 3.3 and Table 3.4). The N_2O_5 and NO_3 concentrations used in the boundaries and top concentration are lower by a factor of three for the 1997 MTBE sens, and by a factor of 50 for the 2003 scenarios than those used in the baseline simulations (see Table 3.3 and Table 3.4). The reason for using higher N_2O_5 and NO_3 in the boundaries and top concentrations for the 1997 MTBE sens was dictated by the model's ability to resolve the set of non-linear simultaneous equations represented by the chemical reactions. Use of lower N_2O_5 and NO_3 concentrations in the 1997 MTBE sens scenario will cause the model to not to converge on a solution due to very stiff conditions. We do not believe that the different N_2O_5 and NO_3 boundary and top concentrations used for the 1997 and 2003 sensitivity scenarios will affect any of the conclusions derived from the results of these simulations.

Table 5.2 Boundary and Top Concentrations Used in the Sensitivity Simulations (ppb)

Sensitivity Simulation	HONO	N_2O_5	NO_3
1997 MTBE Sens	**0.784**	**0.307**	**0.307**
2003 MTBE Sens	**0.660**	**0.020**	**0.020**
2003 Et2.0% Sens	**0.660**	**0.020**	**0.020**
2003 Et3.5% Sens	**0.660**	**0.020**	**0.020**
2003 NonOxy Sens	**0.660**	**0.020**	**0.020**

B-5.5. Sensitivity Results

The predicted domain maximum 1–hour-average concentrations from the sensitivity simulations are given in Table 5.3. The results in Table 5.3 reflect the factor of three increase in on-road motor vehicle hydrocarbon and CO emissions, the use of revised rate constants for the OH + ethanol and OH + MTBE reactions, the effect of the Cl + ethanol reaction, and the revised top concentrations and boundaries, as described above. By comparing Table 4.1 and Table 5.3, it is clear that the predicted domain maximum 1-hour-average concentrations increased significantly for many species when the motor vehicle hydrocarbon emissions were increased by a factor of three. Ethanol, 1,3-butadiene, and nitric acid are notable exceptions. As discussed in Section B-4.1, the maximum 1-hour-average ethanol concentration is dominated by a non-motor vehicle emission source. The 1,3-butadiene domain maximum 1-hour concentration occurs at 0400 over the same location in Ventura County (upwind from the Los Angeles urban area) for all the sensitivity scenarios. At this hour, only nighttime reactions of 1,3-butadiene with NO_3 radical and O_3 are important. Assuming a nighttime O_3 concentration of 100 ppb, and a NO_3 radical concentration of 0.02 ppb, the NO_3 radical reaction is a factor of 3 faster than the O_3 reaction. The lack of sensitivity of 1,3-butadiene domain maximum 1-hour concentration to hydrocarbon emission increases is then presumably due to a local source. Nitric acid is formed by reaction of NO_2 with the hydroxyl radical. Hydroxyl radical concentrations increase as ozone increases, so nitric acid concentrations appear to be limited by NO_X emissions for this summertime episode, especially for the 2003 scenarios.

Table 5.3 Domain Maximum 1-Hour-Average Concentrations for Sensitivity Simulations

	Domain Maximum 1-Hour-Average Concentration (ppb)												
Simulation	**O_3**	**NO**	**NO_2**	**CO**	**Formaldehyde**	**Acetaldehyde**	**C_6H_6**	**BUTD**	**MTBE**	**ETOH**	**PAN**	**PPN**	**HNO_3**
1997 MTBE Sens	425	214	120	7,448	37.4	19.1	9.1	3.1	16.5	45.2	18.1	5.7	69.8
2003 MTBE Sens	331	191	97	4,982	26.2	13.4	4.7	3.1	9.9	41.1	11.4	3.7	54.4
2003 Et2.0% Sens	318	191	97	4,982	24.8	13.7	4.6	3.1	0.0	43.1	10.9	3.7	54.2
2003 Et3.5% Sens	323	191	97	4,670	25.6	14.7	4.7	3.1	0.0	44.2	11.7	3.6	54.1
2003 NonOxy Sens	317	191	97	5,193	24.6	13.3	4.3	3.1	0.0	41.1	10.4	3.8	54.4

[a] **Formaldehyde and acetaldehyde refer to total concentrations from primary emissions and secondary formation, C_6H_6 is benzene, BUTD is 1,3-butadiene, PAN is peroxyacetyl nitrate, PPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates, and HNO_3 is nitric acid**

The 1997 MTBE sensitivity scenario shows a larger increase in maximum concentrations for many species than the 2003 sensitivity scenarios. For example, the predicted maximum 1-hour-average ozone concentration increases by a factor of 1.8 from the 1997 MTBE base case to the 1997 MTBE sensitivity simulation, whereas it only increases by an average factor of 1.46 for the 2003 scenarios. Acetaldehyde increases by a factor of 2.1 in 1997 when motor vehicle hydrocarbon emissions are tripled, but it only increases by a factor of 1.51 for the 2003 NonOxy scenario. Similarly, formaldehyde increases by factor of 1.65 for the 1997 MTBE scenario, but only a factor of 1.08 for the 2003 NonOxy scenario. This difference also occurs for benzene, PAN, and PPN. Presumably, these differences are because the motor vehicle emissions are a larger fraction of the total inventory in 1997 as compared to 2003 (42% of ROG in 1997 versus 30% in 2003).

The major finding is that the predicted maximum 1-hour-average concentrations for acetaldehyde and PAN from the ethanol-containing gasoline (Et3.5%) are now 1.4 ppb and 1.3 ppb, respectively, greater than the maximum predicted for the non-oxygenated gasoline (NonOxy). These acetaldehyde and PAN impacts from the ethanol-containing gasoline represent an upper limit because the factor of three increase in all on-road hydrocarbon emissions is larger than expected from EMFAC2000 when it becomes final and the ozone episode modeled here is an extreme ozone event.

B-6. Model Performance

A performance evaluation is the process of establishing that the air quality model is adequately reproducing the chemical and physical processes that generate ozone and other pollutants. One aspect of model performance includes the sensitivity simulations described in Section B-5. In this section we test the model's ability to reproduce measured air quality data. For this purpose, an area and point emission inventory was prepared for a 1987 baseline simulation. Differences and ratios of observed and simulated maximum concentrations were calculated for each day of the August 26-28, 1987 episode in the SCAQS domain. Historical model performance evaluations have focused on ozone, and to a lesser extent, NO_2. Results are presented for other pollutants under study, including CO, NO, PAN, acetaldehyde, benzene, 1,3-butadiene, and formaldehyde. Although nitric acid data is available from the 1987 SCAQS field program, UAM-FCM does consider the thermodynamic equilibrium of nitric acid with ammonia and ammonium nitrate. We were also unable to conduct a model performance evaluation for ethanol, MTBE, or PPN, as there are no air quality measurements available for these pollutants for the 1987 episode.

B-6.1. Model Performance Statistics

Several statistical measures were used (ARB, 1992), including the Mean Absolute Gross Error (MAGE):

$$MAGE = \sum \frac{|C_s - C_o|}{N} \qquad \text{(B-2)}$$

where N is the number of observations, C_s is the simulated concentration and C_o is the observed concentration.

Mean Absolute Normalized Gross Error (MANGE):

$$MANGE = \frac{1}{N} \sum \frac{|C_s - C_o|}{C_o} \qquad \text{(B-3)}$$

Mean Bias (MBIAS):

$$MBIAS = \sum \frac{C_s - C_o}{N} \qquad \text{(B-4)}$$

Normalized Mean Bias (NBIAS):

$$NBIAS = \frac{1}{N} \sum \frac{C_s - C_o}{C_o} \qquad \text{(B-5)}$$

and the Unpaired Peak Estimation Accuracy (UPEA):

$$UPEA = \frac{C_s^{\max} - C_o^{\max}}{C_o^{\max}} \qquad \text{(B-6)}$$

Where C_s^{max} is the maximum estimated 1-hour concentration at any site in the domain, and C_o^{max} is the maximum observed 1-hour concentration at any site in the domain.

B-6.2. Ozone, CO, NO, and NO_2

The average statistics for all sites in the domain are given in Table 6.1 for August 28, 1987 (the last day of the 3-day simulation). The UAM-FCM SAPRC97 tends to over-predict maximum ozone by only 4%. The predicted maximum NO_2 is within 10% of the observed maximum, but the model significantly under-predicts maximum CO and NO, as is typical for grid-based predictions of directly emitted compounds.

Table 6.1 UAM-FCM with SAPRC97 Model Performance Evaluation

	O_3[a]	CO[b]	NO[c]	NO_2[d]
UPEA (%)	**4**	**-21**	**-56**	**7**
MBIAS (ppb)	**28**	**-142**	**-49**	**-14**
MAGE (ppb)	**38**	**771**	**51**	**31**
NBIAS (%)	**32**	**7**	**-71**	**-14**
MANGE (%)	**38**	**48**	**76**	**60**

[a] **Only ozone concentrations over 61 ppb were used.**

[b] **Only CO concentrations over 201 ppb were used.**

[c] **Only NO concentrations over 21 ppb were used.**

[d] **Only NO_2 concentrations over 11 ppb were used.**

Although the UAM has been widely applied to a number of episodes (see for example, Morris and Meyers, 1990), the UAM-FCM, on the other hand, has had limited application since its development in 1995. Therefore it was considered appropriate to examine the model performance of the UAM-FCM when using a different chemical mechanism, such as the Carbon-Bond IV (CB-IV).

The CB-IV chemical mechanism uses the lumped structure approach to represent the atmospheric oxidation of hydrocarbons in ambient air (Gery *et al.*, 1989). Carbon-bond surrogates are used to represent the chemistry of the three most common type of carbon bonds (single: PAR, double: OLE, and the CHO- group: ALD2), and two molecular surrogates represent the chemistry of aromatic compounds (monoalkylbenzenes: TOL based on toluene; dialkylbenzenes and trialkylbenzenes: XYL based on *m*-xylene). Ethene, isoprene, ethanol, methanol, formaldehyde, methylglyoxal, glyoxal, and PAN are treated explicitly.

Carbon-Bond IV (version 6.21) was implemented into the UAM-FCM. We speciated area and point source emission files, together with initial and boundary conditions for the August 26-28, 1987, for the CB-IV mechanism. Table 6.2 summarizes the performance of the UAM-FCM with CBIV. Compared to the performance of the SAPRC97 mechanism in Table 6.1, CB-IV tends to under-predict maximum ozone concentration by 11% on the last day of the episode. However, both SAPRC97 and CB-IV have similar average performance for CO, NO, and NO_2. Overall, the UAM-FCM has similar model performance with either SAPRC97 or CB-IV. Figure 6.1 through Figure 6.5 show a comparison of ozone, NO and NO_2, as predicted by SAPRC97 and CB-IV (together with the measured concentrations), for Anaheim, Burbank, Downtown Los Angeles, and Riverside. Figure 6.5 shows a comparison of ozone, NO, and NO_2, as predicted by SAPRC97 and CB-IV, for the cell with the maximum pollutant concentration in the domain (no measured data are shown, since there is no monitoring station at this location).

Table 6.2 UAM-FCM with CB4 Model Performance Evaluation

	O_3[a]	CO[b]	NO[c]	NO_2[d]
UPEA (%)	**-11**	**-23**	**-42**	**0**
MBIAS (ppb)	**-1**	**-251**	**-38**	**-13**
MAGE (ppb)	**27**	**771**	**45**	**28**
NBIAS (%)	**5**	**0**	**-50**	**-12**
MANGE (%)	**24**	**46**	**67**	**56**

[a] **Only ozone concentrations over 61 ppb were used.**

[b] **Only CO concentrations over 201 ppb were used.**

[c] **Only NO concentrations over 21 ppb were used.**

[d] **Only NO_2 concentrations over 11 ppb were used.**

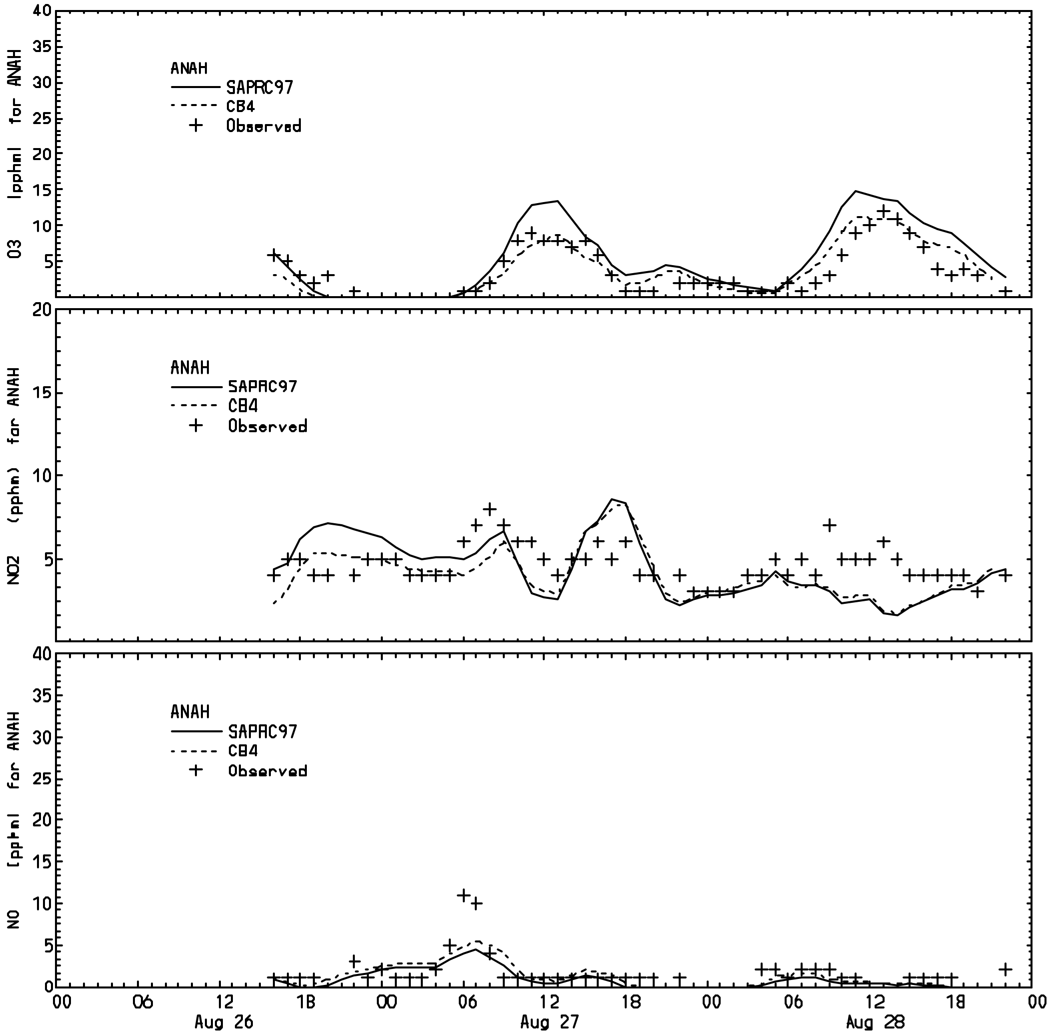


Figure 6.1 Comparison of Predicted Ozone, NO, and NO_2 by SAPRC97 and CB-IV Against Ambient Data at Anaheim (1987 SCAQS)

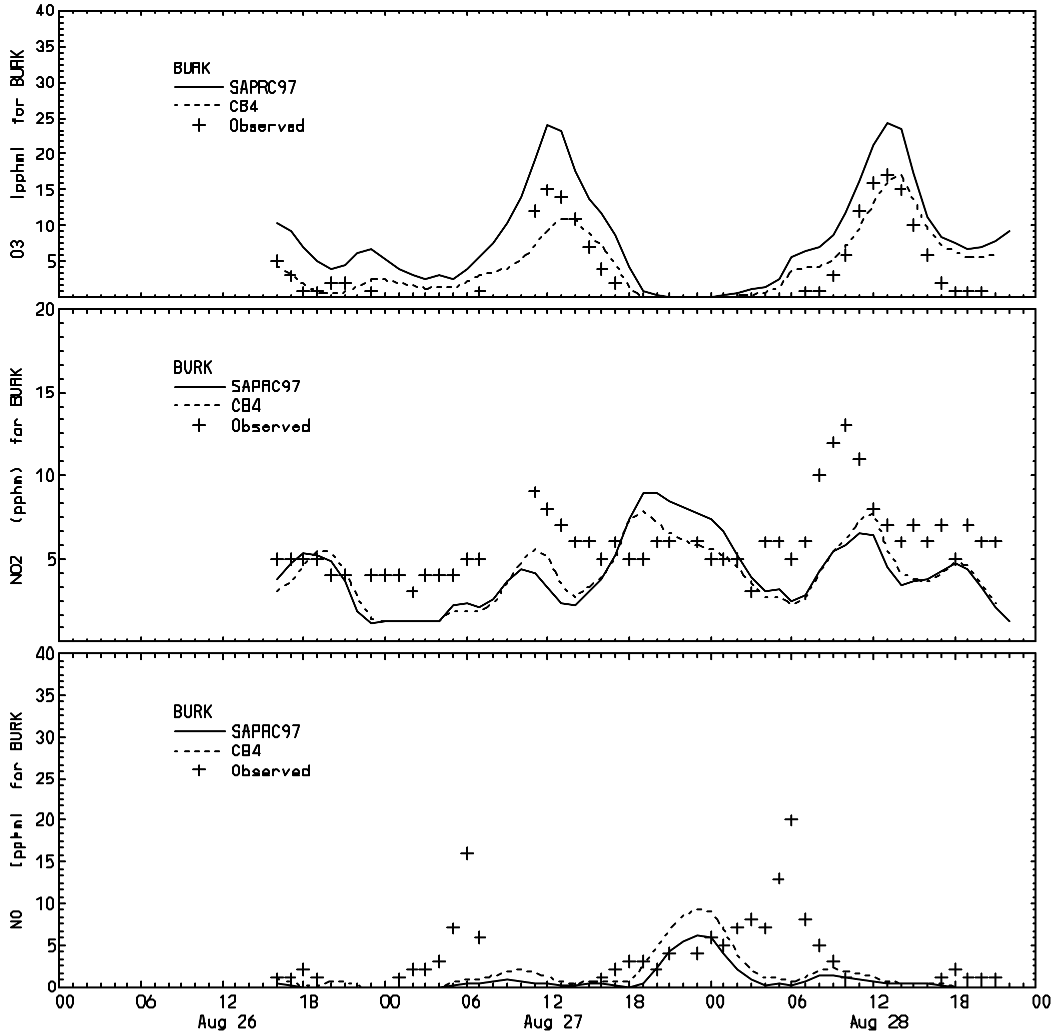


Figure 6.2 Comparison of Predicted Ozone, NO, and NO_2 by SAPRC97 and CB-IV Against Ambient Data at Burbank (1987 SCAQS)

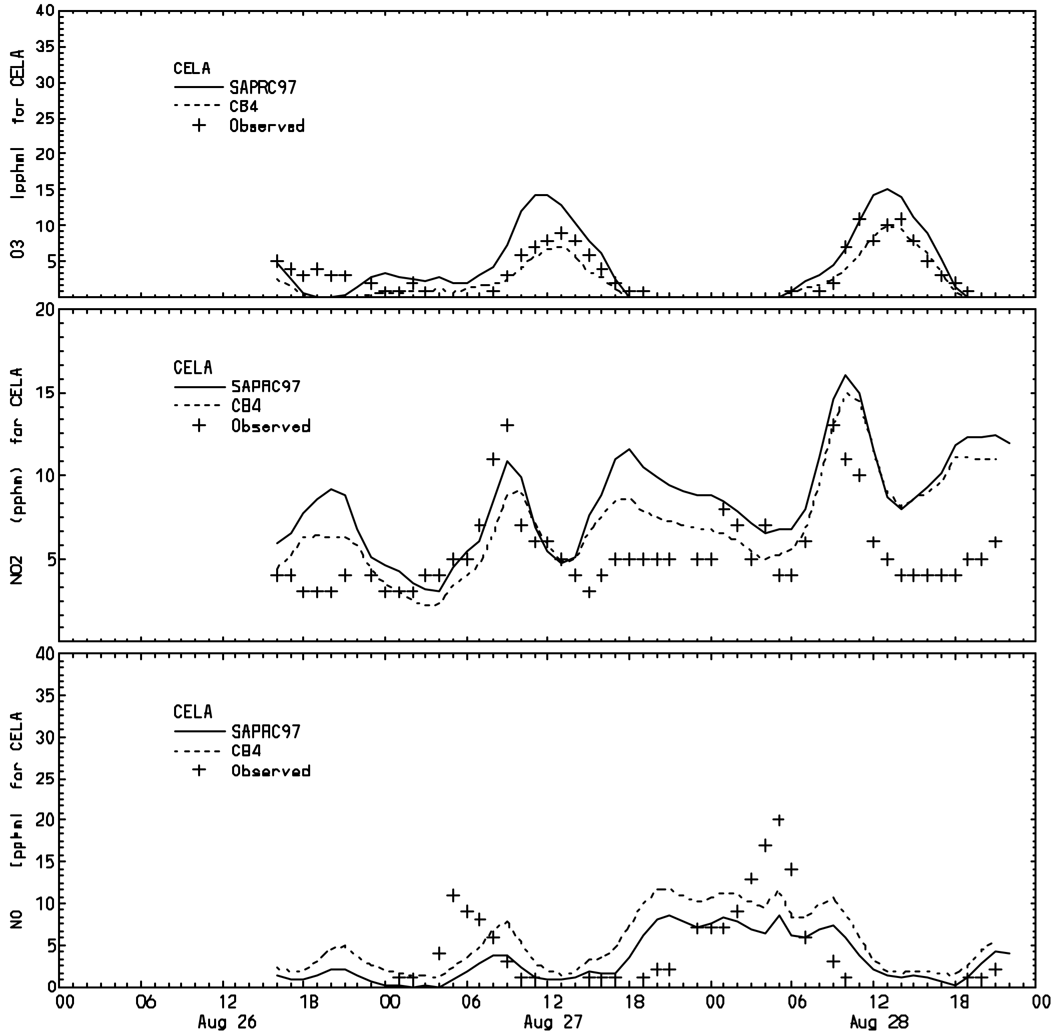


Figure 6.3 Comparison of Predicted Ozone, NO, and NO_2 by SAPRC97 and CB-IV Against Ambient Data at Los Angeles (1987 SCAQS)

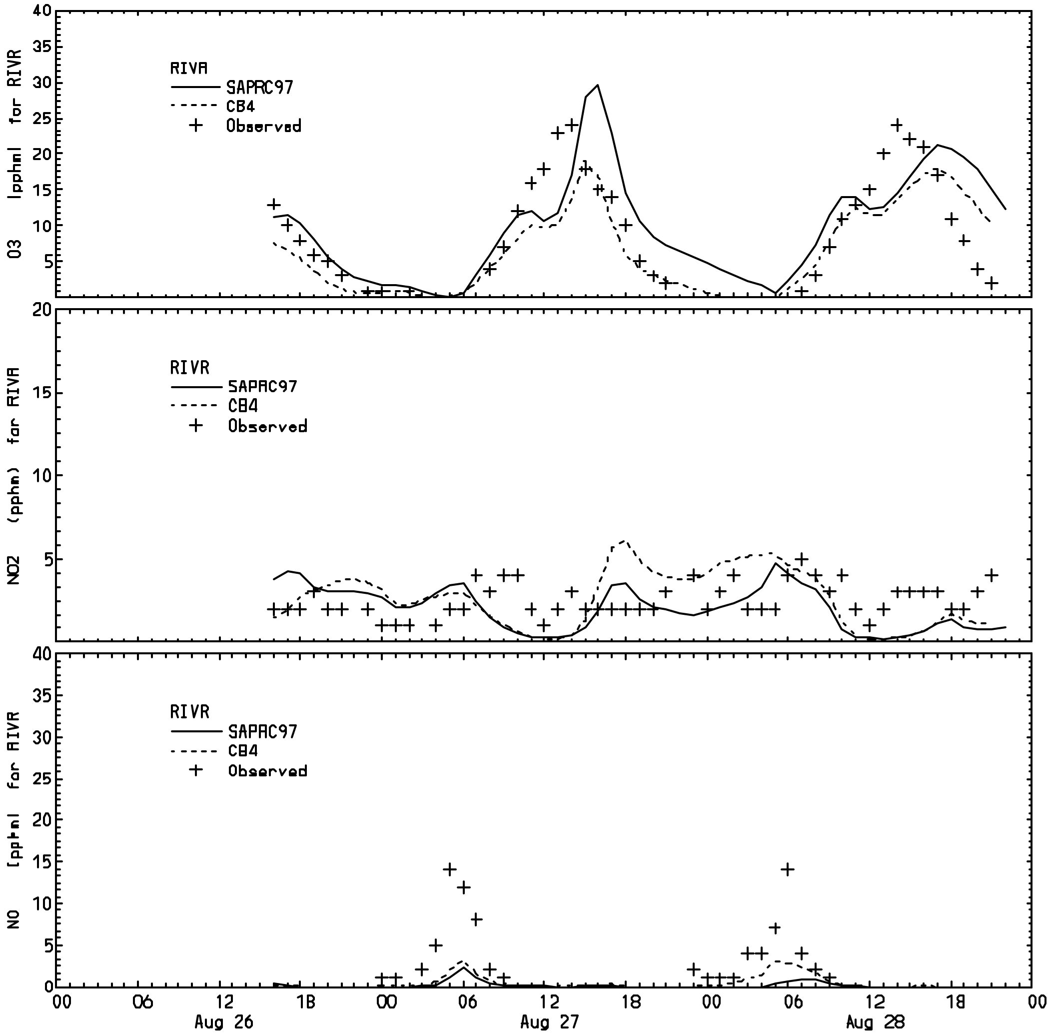


Figure 6.4 Comparison of Predicted Ozone, NO, and NO$_2$ by SAPRC97 and CB-IV Against Ambient Data at Riverside (1987 SCAQS)

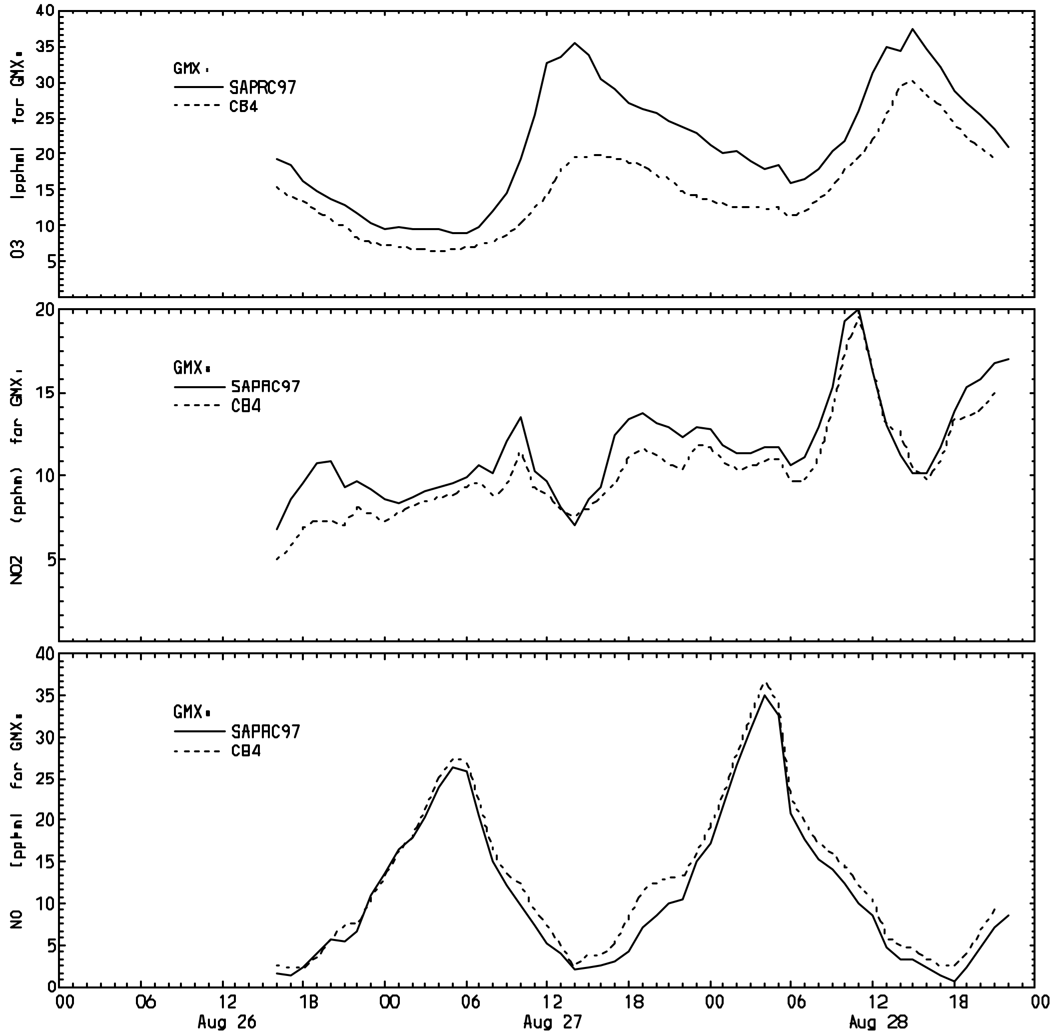


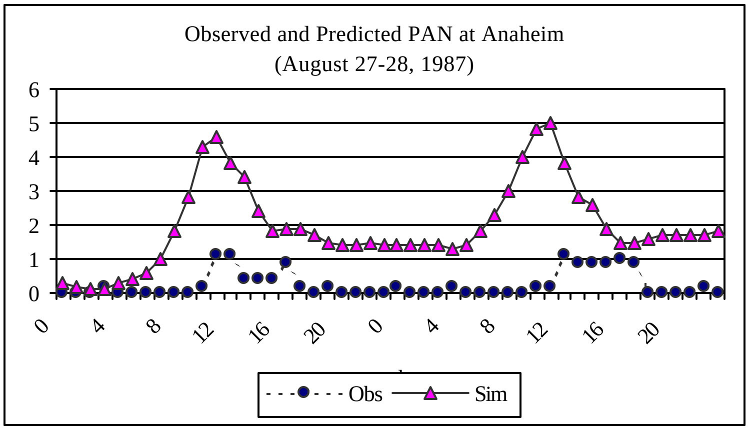
Figure 6.5 Comparison of Predicted Ozone, NO, and NO_2 by SAPRC97 and CB-IV at the Domain Maximum

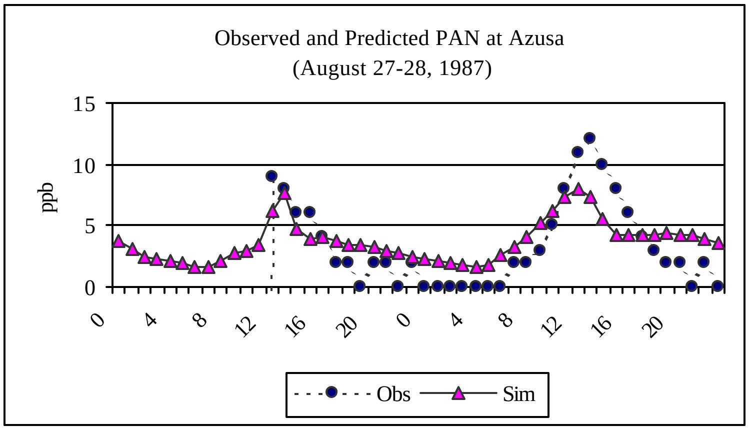
B-6.3. PAN

PAN measurements are available at six sites in the SCAQS domain during August 27-28, 1987. Comparisons of hourly PAN concentrations against observations for each site are shown in Figure 6.6 and Figure 6.7. These figures show that, on the last day of the episode, the model underpredicts PAN concentrations at Burbank, Los Angeles, and, especially, at Claremont and Riverside. However, the model overestimates PAN at Anaheim. Table 6.3 shows the maximum observed and predicted 1-hour-average PAN concentrations. PAN concentrations are sensitive to local variations in the NO to NO_2 ratio and temperature, microscale features that cannot be simulated by gridded models like UAM-FCM.

Table 6.3 Observed and Predicted Maximum 1-Hour-Average PAN Concentrations for August 28, 1987

Site	Observed (ppb)	Predicted (ppb)
Anaheim	**1.1**	**5.0**
Azusa	**12**	**8.0**
Burbank	**12**	**6.6**
Claremont	**30**	**6.1**
Los Angeles	**10**	**6.0**
Riverside	**13**	**5.2**





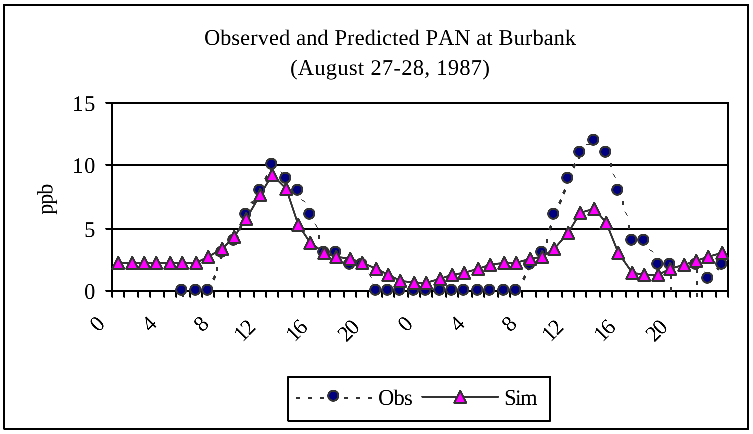
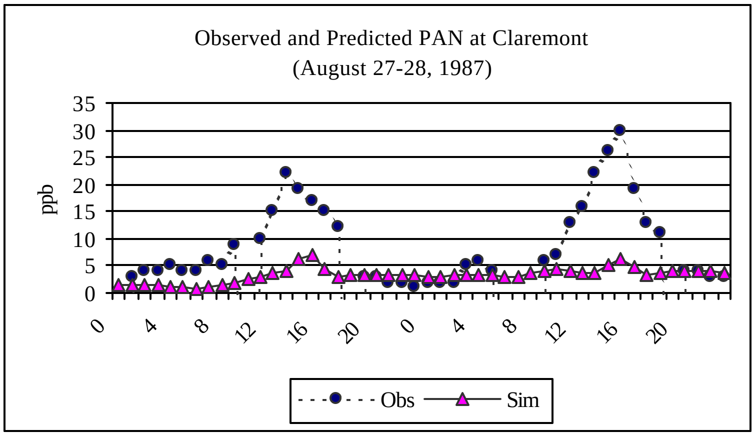
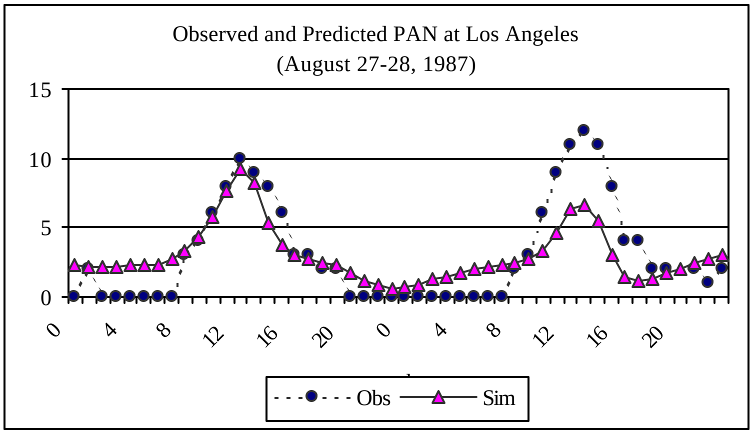


Figure 6.6 Comparison of Observed and Predicted PAN at Anaheim, Azusa, and Burbank





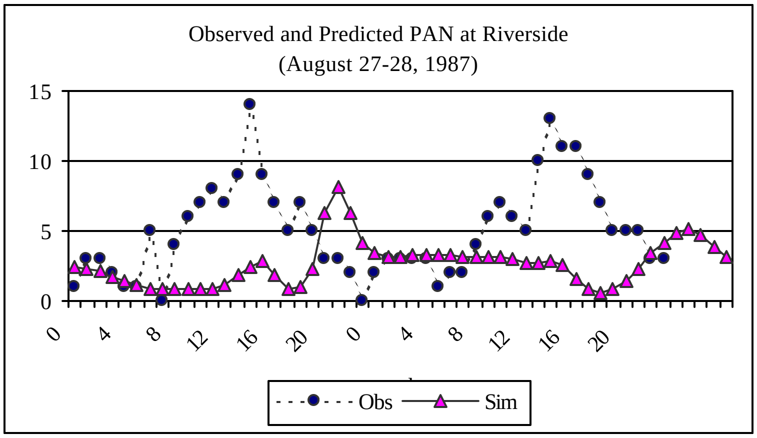


Figure 6.7 Comparison of Observed and Predicted PAN at Claremont, Los Angeles, and Riverside

B-6.4. Acetaldehyde, Benzene, 1,3-Butadiene, and Formaldehyde

As an additional evaluation of the air quality model performance, we compare in Table 6.4 the predicted and measured 3-hour-average concentrations for benzene, 1,3-butadiene, total formaldehyde, and total acetaldehyde. Note that concentrations in Table 6.4 are expressed in ppb, and not in ppbC. There are large discrepancies for all species and times between predicted and observed 3-hour-average concentrations at the Los Angeles and Riverside sites. For the other sites, the air quality model predicts a value comparable to that measured. For example, at start time of 0600, the model predicts good agreement with measured data at Anaheim and Hawthorne (for benzene and acetaldehyde), at Long Beach (all species), and Burbank (acetaldehyde). However, when averaging of all the values for a start time of 0600, the model overpredicts for benzene and 1,3-butadiene, and underpredicts the aldehydes. The comparison between model and measurements does not significantly improve later in the day (start time of 1100). However, on average there is better agreement between model predictions and measured data in the late morning (start time of 1100). Overall, the predicted results for acetaldehyde and formaldehyde are in rough agreement with the measurements, while the model severely under-predicts benzene and 1,3-butadiene concentrations. The instantaneous mixing of emissions into a large grid cell by UAM-FCM is a reasonable approximation for secondary pollutants like ozone, NO_2, acetaldehyde, and formaldehyde, but not for directly emitted pollutants such as benzene and 1,3-butadiene.

Table 6.4 Measured and Predicted 3-Hour-Average Concentrations for Selected VOCs on August 28, 1987 (ppb)

Site	Start Hour	Benzene Measured	Benzene Predicted	1,3-Butadiene Measured	1,3-Butadiene Predicted	Formaldehyde Measured	Formaldehyde Predicted	Acetaldehyde Measured	Acetaldehyde Predicted
Anaheim	**600**	**1.8**	**2.1**	**0.3**	**0.2**	**6.8**	**9.8**	**4.7**	**4.9**
Anaheim	**1100**	**2.6**	**1.7**	**0.3**	**0.0**	**19.0**	**11.0**	**17.0**	**6.1**
Azusa	**600**	**6.0**	**3.0**	**1.1**	**0.3**	**8.7**	**17.0**	**5.8**	**8.4**
Azusa	**1100**	**5.1**	**2.4**	**0.1**	**0.0**	**19.0**	**17.0**	**17.0**	**10.0**
Burbank	**600**	**8.9**	**1.5**	**1.5**	**0.1**	**8.1**	**13.0**	**5.3**	**5.3**
Burbank	**1100**	**6.3**	**2.9**	**0.3**	**0.1**	**17.0**	**20.0**	**16.0**	**12.0**
Los Angeles	**600**	**38.0**	**4.6**	**2.1**	**0.8**	**7.8**	**15.0**	**3.5**	**7.9**
Los Angeles	**1100**	**5.9**	**4.3**	**0.2**	**0.1**	**10.0**	**26.0**	**9.9**	**17.0**
Hawthorne	**600**	**1.2**	**1.6**	**0.1**	**0.2**	**3.0**	**6.4**	**3.1**	**3.6**
Hawthorne	**1100**	**0.6**	**1.6**	**0.1**	**0.1**	**4.9**	**7.7**	**4.1**	**4.7**
Long Beach	**600**	**5.0**	**3.8**	**0.5**	**0.6**	**11.0**	**10.0**	**5.5**	**5.5**
Long Beach	**1100**	**2.8**	**3.4**	**0.1**	**0.1**	**14.0**	**16.0**	**13.0**	**12.0**
Riverside	**600**	**5.9**	**2.6**	**0.7**	**0.1**	**8.5**	**18.0**	**5.7**	**9.1**
Riverside	**1100**	**2.5**	**0.7**	**0.1**	**0.0**	**13.0**	**6.8**	**13.0**	**3.2**
Average (600)		**9.5**	**2.8**	**0.9**	**0.3**	**7.7**	**13.0**	**4.8**	**6.4**
Average (1100)		**3.7**	**2.4**	**0.2**	**0.1**	**14.0**	**15.0**	**13.0**	**9.2**
Average (600 & 1100)		**6.6**	**2.6**	**0.5**	**0.2**	**11.0**	**14.0**	**8.8**	**7.8**

B-7. Ozone, PAN, and PPN Formation Potentials

In addition to the 3-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 SAPRC97 chemical mechanism. This was used to explain the lack of sensitivity of PAN formation to the ethanol content of the gasoline observed in Section B-4.

B-7.1. Description of Formation Potentials

The formation of secondary pollutants in an airshed is a complex process, which involves a series of photochemical reactions driven by the sunlight. It has been recognized that individual organic compounds can contribute differently to the creation of secondary air pollutants in atmosphere. Over decades, a variety of scales of VOC formation potential have been devised to quantify the degree to which different organic compounds affect formation of a given pollutant, such as ozone. More generally, the potential of a given organic compound in atmospheric chemistry refers to the reactivity of that compound to promote formation of products. Among these scales, the incremental reactivity developed by Carter and Atkinson (1989) is the simplest method of calculating the potential of an organic compound to form ozone or any other pollutant.

Given a VOC_i, its ozone incremental reactivity is defined as the ratio of the ozone concentration change to a small perturbation of the VOC_i:

$$\textit{Ozone formation potential} = \lim_{\Delta VOC_i \to 0}\left[\frac{O_3(VOC_i + \Delta VOC_i) - O_3(VOC_i)}{\Delta VOC_i}\right] \qquad \text{(B-7)}$$

where $O_3(VOC_i + \Delta VOC_i)$ and $O_3(VOC_i)$ are the ozone concentrations of the perturbed case and base case of VOC_i, respectively. Yang *et al.* (1995) show that ozone formation potential can be estimated as the local sensitivity of the predicted ozone concentration to the *initial* concentrations of each organic compound in a mixture.

Similarly, the PAN formation potential of a given organic compound, VOC_i, in a mixture or airshed can be calculated by:

$$\textit{PAN formation potential} = \lim_{\Delta VOC_i \to 0}\left[\frac{PAN(VOC_i + \Delta VOC_i) - PAN(VOC_i)}{\Delta VOC_i}\right] \qquad \text{(B-8)}$$

where $PAN(VOC_i + \Delta VOC_i)$ and $PAN(VOC_i)$ are the PAN concentrations of the perturbed case and base case of VOC_i, respectively. The equation, in essence, is a local sensitivity of PAN to the concentration change of an organic compound and can be computed by the partial differentiation of PAN with respect to VOC_i. The PAN sensitivity coefficient, i.e.,

$$\frac{\partial PAN}{\partial VOC_i}$$

is interpreted as the amount of PAN formed per unit amount of VOC_i changed in the mixture and has units of ppm-PAN/ppm-VOC or ppm-PAN/ppm-C. As mentioned above, the PAN formation potential was estimated as the local sensitivity of the predicted ozone concentration to the *initial* concentrations of each organic compound in a mixture (Yang *et al.* (1995).

The total formation potential for ozone, PAN, and PPN (which includes higher molecular weight acyl peroxy nitrates) can be calculated by using a first-order approximation:

$$\textit{Total PAN formation potential} = \sum_i \left(\frac{\partial PAN}{\partial VOC_i} \right) \Delta VOC_i \qquad \text{(B-9)}$$

B-7.2. Model Description and Inputs

The scenario for the ozone, PAN, and PPN (and includes higher molecular weight acyl peroxy nitrates) formation potential calculations is adopted from the average condition of 39 cities across the U.S. designed by Carter (1994) for ozone incremental reactivity. Pollutant formation potential scales are time varying over the 10-hour simulation. The results presented here are the formation potentials of ozone, PAN, and PPN (and includes higher molecular weight acyl peroxy nitrates) estimated at 1800 where the maximum ozone occurs in the simulation period, because the time satisfies the condition of maximum incremental reactivity scale (Yang *et al.*, 1995).

We implemented the SAPRC97 chemical mechanism -- as described in Attachment B1 -- in a box model to evaluate the ozone, PAN, and PPN (and includes higher molecular weight acyl peroxy nitrates) formation potential of selected individual VOCs and lumped VOC categories. Table 7.1 gives the PAN and PPN (and includes higher molecular weight acyl peroxy nitrates) reactions, together with the value of their corresponding kinetic parameters (as used in the box model). Table 7.2 provides the default meteorological inputs for the box-model simulations. Table 7.3 gives the initial conditions for several episodes in the South Coast Air Basin, and Table 7.4 has the initial conditions for episodes representative of two large cities in Brazil.

Table 7.1 PAN and PPN Equilibrium Reaction Rate Constants

Reactions	$CCO\text{-}O_2 + NO_2 = PAN^a$	$PAN^a = CCO\text{-}O_2 + NO_2 + RCO_3$	$C_2CO\text{-}O_2 + NO_2 = PPN^b$	$PPN^b = C_2CO\text{-}O_2 + NO_2 + RCO_3$
Kinetic	$A_o = 2.57\text{x}10^{-28}$	$A_o = 4.9\text{x}10^{-3}$	$A = 8.4\text{x}10^{-12}$	$A = 1.6\text{x}10^{17}$
Parameters	$E_o = 0.0$	$E_o = 23.972$	$E = 0.0$	$E = 27.966$
	$B_o = -7.1$	$B_o = 0.0$	$B = 0.0$	$B = 0.0$
	$A_i = 12.0\text{x}10^{-12}$	$A_i = 4.0\text{x}10^{16}$		
	$E_i = 0.0$	$E_i = 27.079$		
	$B_i = -0.9$	$B_i = 0.0$		
	$F = 0.3$	$F = 0.3$		
	$N = 1.0$	$N = 1.0$		
K(298°K)	$3.3\text{x}10^{4}$ ppm^{-1}min^{-1}	$3.9\text{x}10^{-2}$ min^{-1}	$1.2\text{x}10^{4}$ ppm^{-1}min^{-1}	$4.1\text{x}10^{-2}$ min^{-1}

Note: **All kinetic parameters in cm-molecules-sec units. PPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates (see Attachment B1).**

[a] rate constant expression given by $k = [k0*M/(1+(K0*M/K1))]*F^{Z}$, with $Z = 1/[\ 1+\log_{10}(k0*M/k1)/N^{2}\ ]$. Where, $k0 = A0*[(T/T_{REF})^{B0}]*\exp(-E0/RT)$, and, $k1 = A1*[(T/T_{REF})^{B1}]*\exp(-E1/RT)$

[b] rate constant expression given by $k = A(T/T_{REF})^{B}\exp(-E/RT)$, where k and A are in cm-molecule-s units, T is temperature in °K, R=0.0019872 kcal mol^{-1} °K , and E is in kcal mol^{-1}

Table 7.2 Meteorological Inputs[a]

Time	Temperature (°K)	Mixing Height (m)	Zenith Angle (degrees)[b]
800	295.5	292.9	71.6
900	297.7	595.7	59.5
1000	299.9	998.5	47.5
1100	301.8	1201	35.9
1200	303.3	1503	25.9
1300	304.5	1610	20.1
1400	305.6	1716	22.1
1500	305.8	1823	30.4
1600	306.1	1823.1	41.3
1700	305.9	1823.2	53.1
1800	305.1	1823.3	65.2

[a] **Adopted from the average scenario of 39 cities, Carter (1994).**

[b] **Evaluated at the latitude of 36.22° and the solar declination of 16.5° (Los Angeles)**

Table 7.3 Initial Concentrations for South Coast Air Basin Scenarios (ppm)

Initial Concentrations	South Coast[b] 1968	Los Angeles[c] 1968	LARPP[d] 1973	Los Angeles 8/28/87[a]	SCAQS 8/28/87[a]	Los Angeles 12/3/87[a]	Claremont[f] 9/8/93	Azusa[e] 8/6/97	Azusa[e] 10/4/97	Azusa[e] 8/22/97
O_3	0.01	0.01	0.01	0.0067	0.01	0.01	0.04	0.02	0.0043	0.001
NO	0.24	0.341	0.034	0.1	0.04	0.19	0.18	0.031	0.05	0.141
NO_2	0.049	0.069	0.007	0.05	0.05	0.06	0.12	0.104	0.065	0.072
CO	10.3	10.3	1.91	5.4	2.0	6.64	4.0	2.64	2.53	3.1
Methane	3.3	3.3	2.01	2.62	2.6	3.44	2.6	2.82	2.58	2.6
Ethene	0.065	0.076	-	0.0526	0.027	0.036	0.018	0.028	0.026	0.0301
Formaldehyde	0.005	0.005	0.01	0.008	0.005	0.011	-	0.011	0.0074	0.0003
Acetaldehyde	0.005	0.005	0.005	0.0035	0.005	0.0067	-	0.006	0.0028	0.0009
Acetone	-	-	-	0.057	-	0.0083	-	0.016	0.0075	0.0007
MEK	-	-	-	0.0008	-	0.0032	-	0.005	0.001	0.0003
Benzene	-	-	-	0.038	0.0078	0.011	0.0029	-	0.013	0.0025
Isoprene	-	-	-	0.0008	-	0.0005	-	0.000	0.0008	0.0041
Ethanol	-	-	-	-	-	-	-	-	-	-
MTBE	-	-	-	-	-	-	-	-	-	-
1,3 Butadiene	-	0.0028	-	-	-	-	0.0003	-	-	0.00018
Dichloromethane	-	-	-	0.001	-	0.014	0.0004	0.000	-	-
ALK1 (lumped alkanes, $k_{OH}<1.0x10^4$ $ppm^{-1} min^{-1}$)	0.37	0.455	0.286	0.506	0.18	0.245	0.081	0.373	0.24	0.078
ALK2 (lumped alkanes, $k_{OH} \geq 1.0x10^4$ $ppm^{-1} min^{-1}$)	0.038	0.039	0.021	0.18	0.018	0.014	0.0094	0.13	0.083	0.014
ARO1 (lumped aromatics, $k_{OH}<2.0x10^4$ $ppm^{-1} min^{-1}$)	0.033	0.06	0.024	0.206	0.06	0.034	0.0068	0.083	0.068	0.011
ARO2 (lumped aromatics)	0.044	0.081	0.02	0.11	0.081	0.019	0.0058	0.089	0.051	0.007
OLE1 (lumped terminal alkenes, $k_{OH} \geq 2.0x10^4$ $ppm^{-1} min^{-1}$)	0.016	0.036	0.023	0.094	0.036	0.108	0.004	0.023	0.075	0.0076
OLE2 (lumped internal alkenes)	-	0.02	0.017	0.0098	0.02	0.005	0.0022	0.019	0.01	0.0026
OLE3 (terpenes)	-	-	-	-	-	-	0.00017	-	-	0.0041
ROG/NO_X	8.3	8.3	3.1	44	13.3	6.8	1.6	30.8	25.1	3.05

[a] Lawson, 1990	[d] Calvert, 1976
[b] Lonemann, 1968	[e] McCauley, 1999
[c] Kopczynski, 1968	[f] Pasek, 1999

Note: Other constant concentrations are included in the simulation runs, i.e., CO_2, O_2, Air, and H_2.

Table 7.4 Initial Concentrations for Brazil Scenarios (ppm)

Initial Concentrations	Porto Alegre, Brazil 1998[a]	Avenida Brazil, Rio de Janeiro 1999[b]
O_3	0.01	0.01
NO	0.143	0.22
NO_2	0.029	0.045
CO	3.34	5.1
Methane	1.70	1.90
Ethene	0.036	0.056
Formaldehyde	0.0124	0.0097
Acetaldehyde	0.014	0.0102
Acetone	-	-
MEK	-	-
Benzene	0.038	0.068
Isoprene	0.0042	-
Ethanol	0.012	0.0485
MTBE	0.066	-
1,3 Butadiene	0.062	0.012
Dichloromethane	-	-
ALK1 (lumped alkanes, $k_{OH}<1.0x10^4$ $ppm^{-1} min^{-1}$)	0.315	1.03
ALK2 (lumped alkanes, $k_{OH} \geq 1.0x10^4$ $ppm^{-1} min^{-1}$)	0.2	0.57
ARO1 (lumped aromatics, $k_{OH}<2.0x10^4$ $ppm^{-1} min^{-1}$)	0.12	0.245
ARO2 (lumped aromatic)	0.22	0.515
OLE1 (lumped terminal alkenes, $k_{OH} \geq 2.0x10^4$ ppm^{-1} min^{-1})	0.061	0.075
OLE2 (lumped internal alkenes)	0.10	0.164
OLE3 (terpenes)	-	-
ROG/NO_X	44.5	67.0

[a] Grosjean *et al*. (1998)

[b] Grosjean (1999)

Note: Other constant concentrations are included in the simulation runs, i.e., CO_2, O_2, Air, and H_2.

B-7.3. Results

Figure 7.1 and Figure 7.2 present the individual ozone formation potentials for the twelve cases described in Table 7.3 and Table 7.4. Note that all box model simulations were conducted with all VOC and NO_X inputs as initial conditions, i.e., no emissions over the simulation time period. This is a reasonable approach for a Lagrangian model that simulates an air parcel as it travels over a region, but will likely underestimate the contribution from fast-reacting species in comparison to more slowly reacting compounds (e.g., alkanes, ethanol). The ranking has a general consistency with relatively high ozone formation potentials for ethene, 1,3-butadiene, formaldehyde, acetaldehyde, isoprene, ARO2, and the three lumped olefin classes. However, the ozone formation potential for ARO1 is negative for some of the cases. Previous studies have shown that aromatic compounds could have negative ozone reactivity under some high-VOC loading conditions (Carter, 1994; Khan *et al.*, 1998).

For PAN production, 1,3-butadiene, acetaldehyde, isoprene, ARO2, and the three lumped olefin classes have relatively high formation potential compared to other compounds, as shown in Figure 7.3 and Figure 7.4. As with ozone, the ARO1 class was found to have negative formation potential for some cases. For the ten explicit VOC compounds in the figures, the rank of PAN formation potentials estimated here has general agreement with a recent study by Derwent *et al.* (1998). Figure 7.5 and Figure 7.6 show that 1,3-butadiene, isoprene, and the three lumped olefin classes have higher PPN (including higher molecular weight acyl peroxy nitrates) formation potentials. For most simulated cases, ARO1 and ARO2 have negative potential for PPN (and higher molecular weight acyl peroxy nitrates) production.

The total ozone formation potentials for the ten explicit VOCs are given in Table 7.5 and Table 7.6. The total PAN formation potentials are provided in Table 7.7 and Table 7.8, and the total PPN formation potentials are shown in Table 7.9 and Table 7.10. Note that the missing values in Table 7.5 to Table 7.10 denote compounds that were not included in the initial conditions and, hence, do not have calculated formation potentials. For the Los Angeles cases in the last 1960s and early 1970s, the lumped alkane class ALK1 is the main contributor to ozone, PAN, and PPN (and higher molecular weight acyl peroxy nitrates) concentrations. The lumped aromatic class ARO2 also contributes significantly for these historical cases. For the more recent cases in the 1980s and 1990s, ALK1 remains a large contributor, but the role of ARO2 diminishes and the contribution of the lumped olefin classes increase. This shift most likely reflects the effects of a decreasing aromatic content in gasoline and diesel fuel.

In the two Brazilian cases, ALK1 is the major contributor to ozone, and ARO2, OLE1, and OLE2 dominate PAN concentrations. OLE2 is the major contributor to PPN (and higher molecular weight acyl peroxy nitrates). Even though ethanol and acetaldehyde concentrations are relatively high, they are not the major contributors to PAN. Thus, 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 in increase in PAN concentrations.

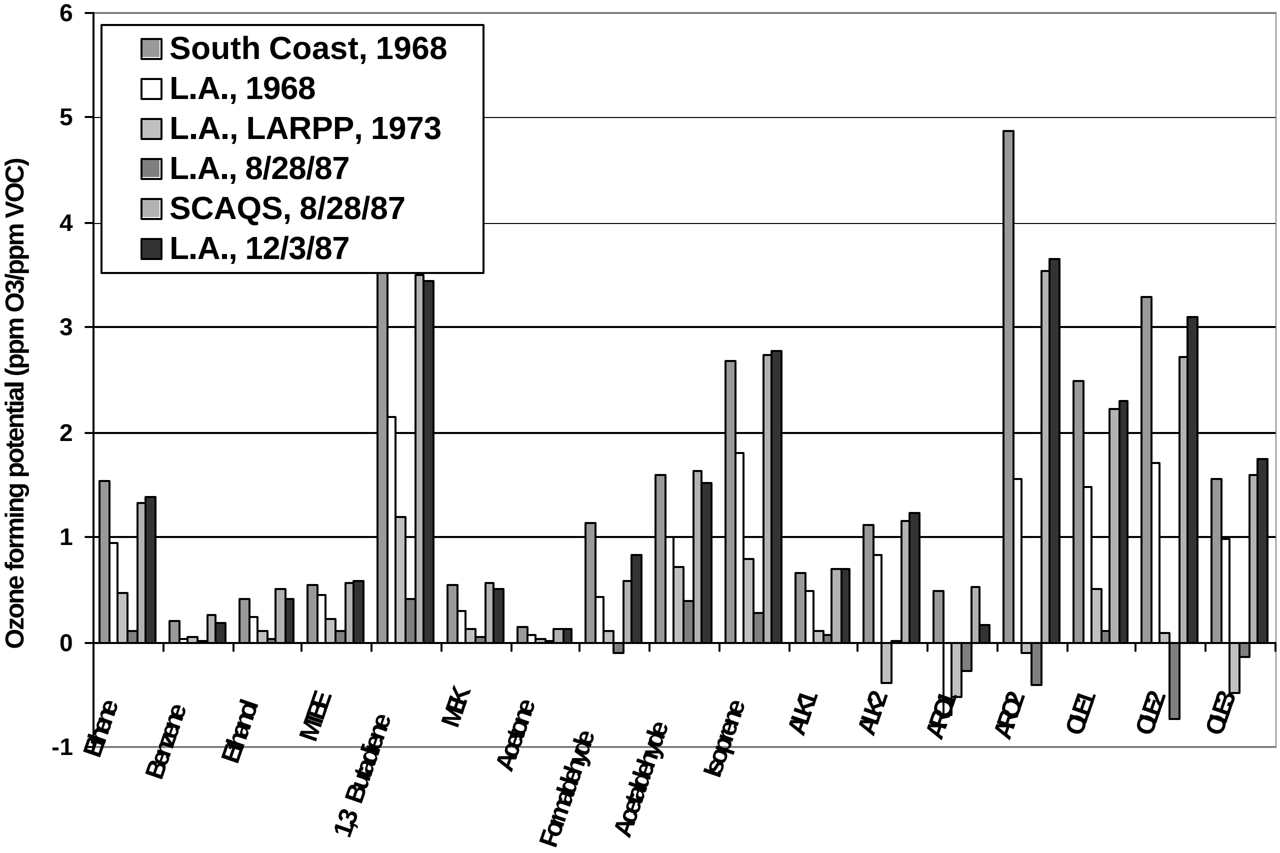


Figure 7.1 Ozone Formation Potentials From Individual VOCs

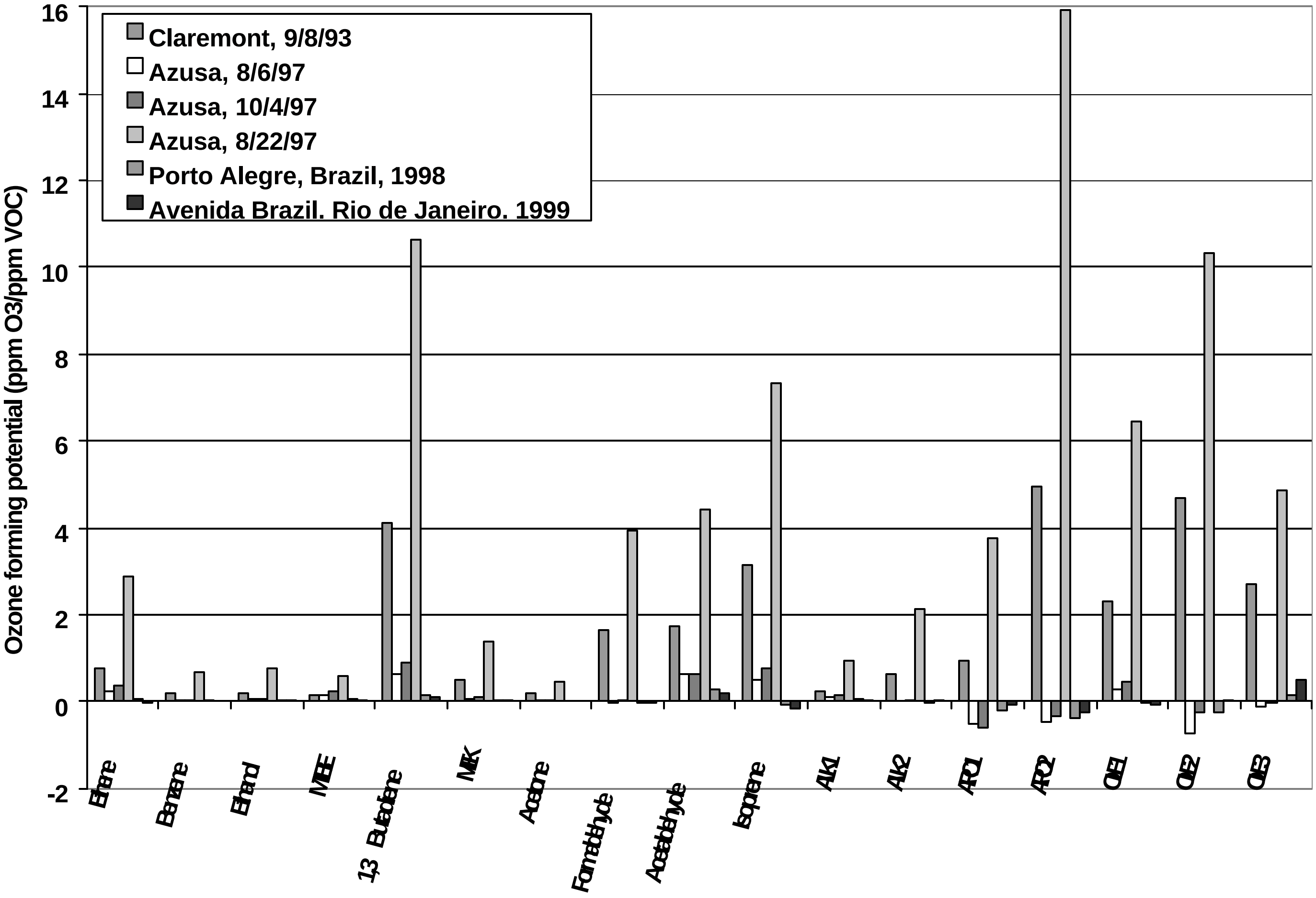


Figure 7.2 Ozone Formation Potentials From Individual VOCs (continued)

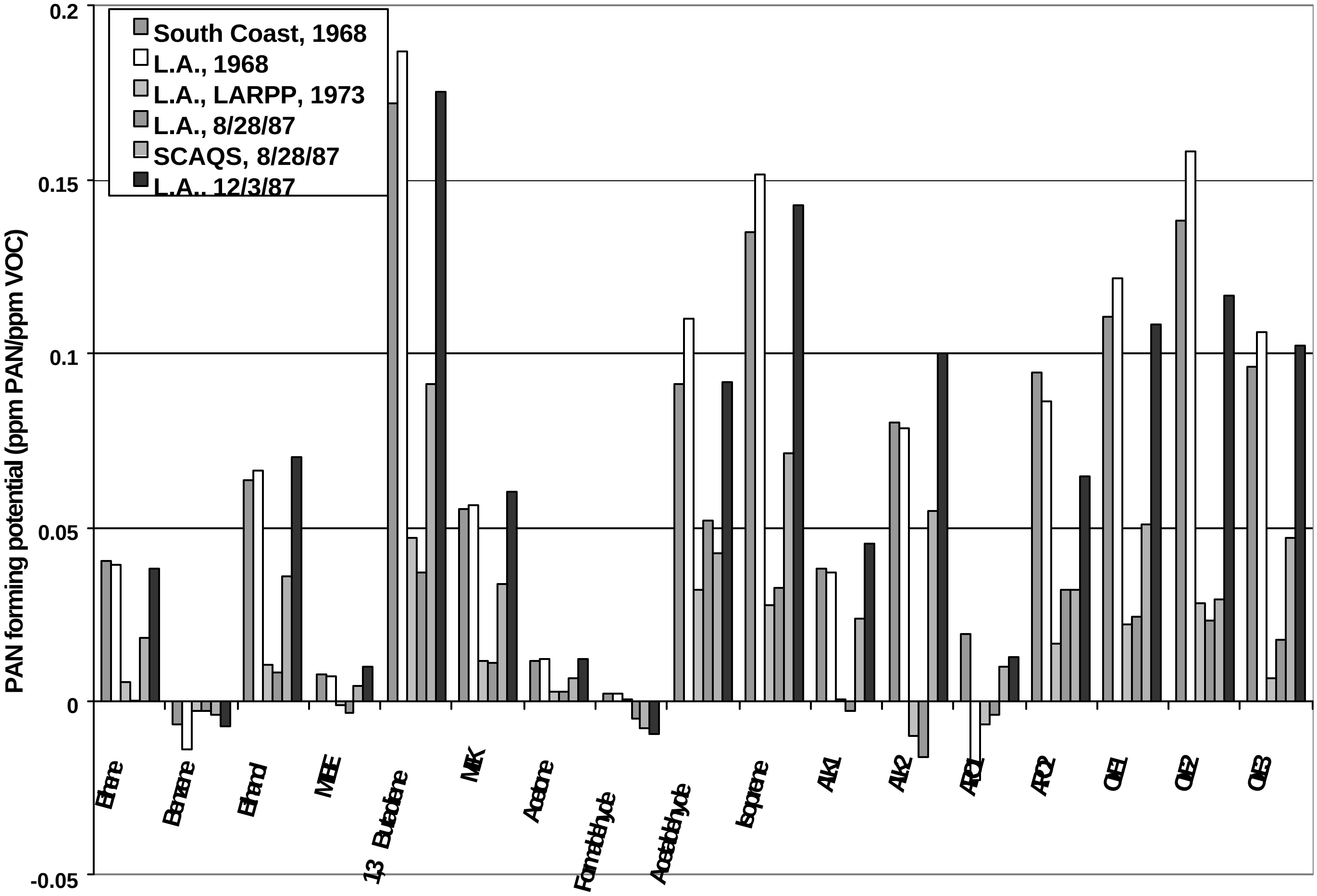


Figure 7.3 PAN Formation Potentials From Individual VOCs

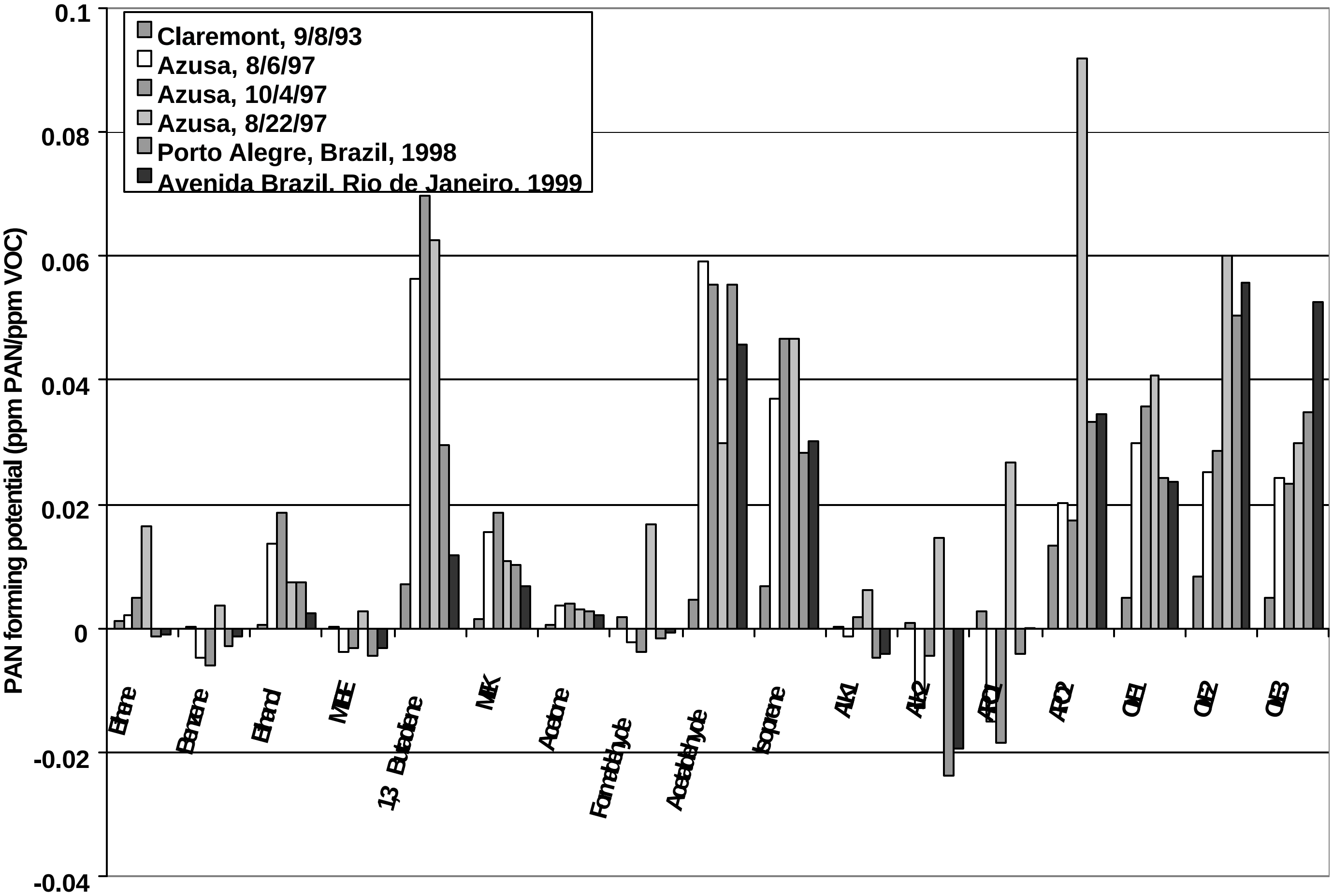


Figure 7.4 PAN Formation Potentials From Individual VOCs (continued)

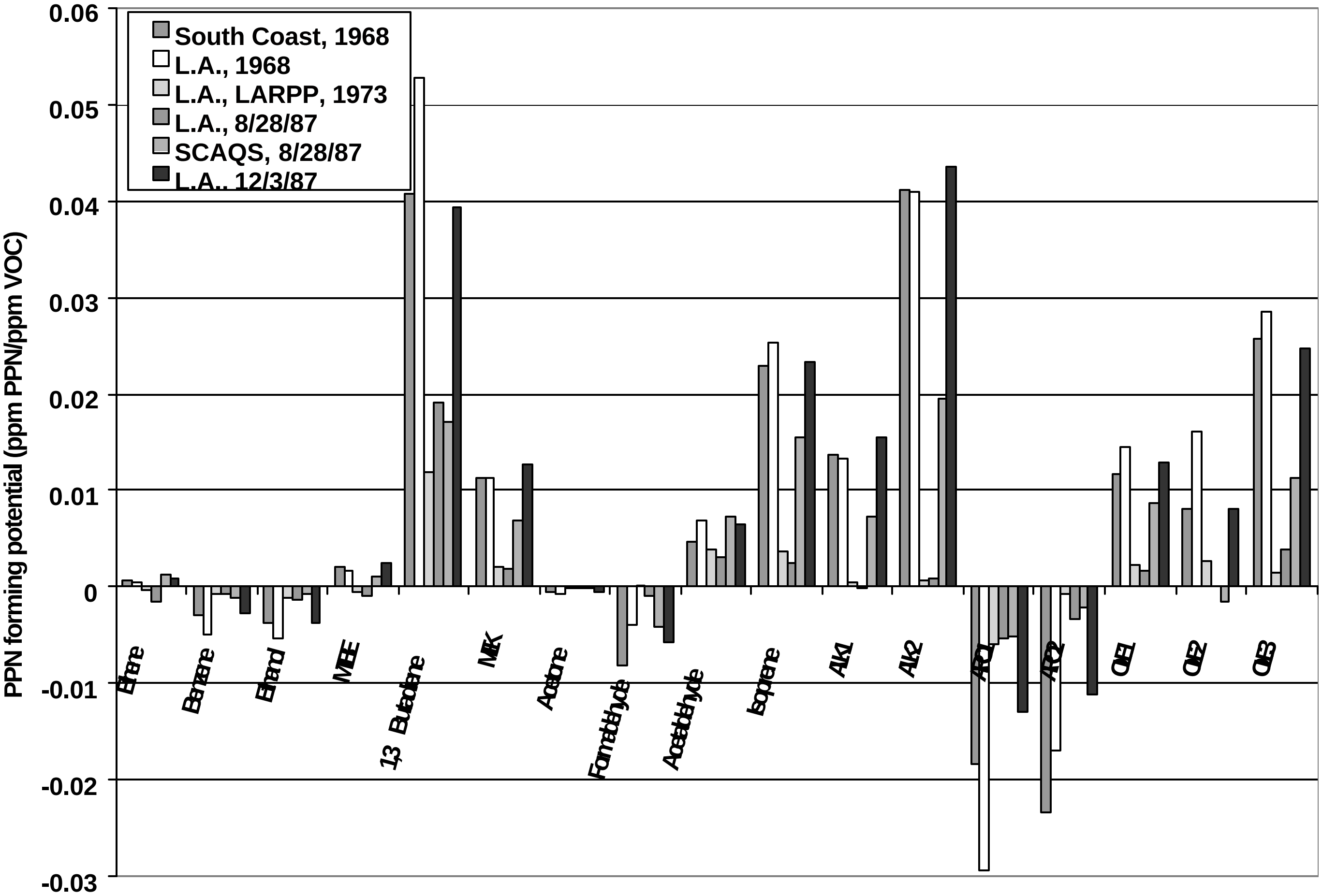


Figure 7.5 PPN Formation Potentials From Individual VOCs

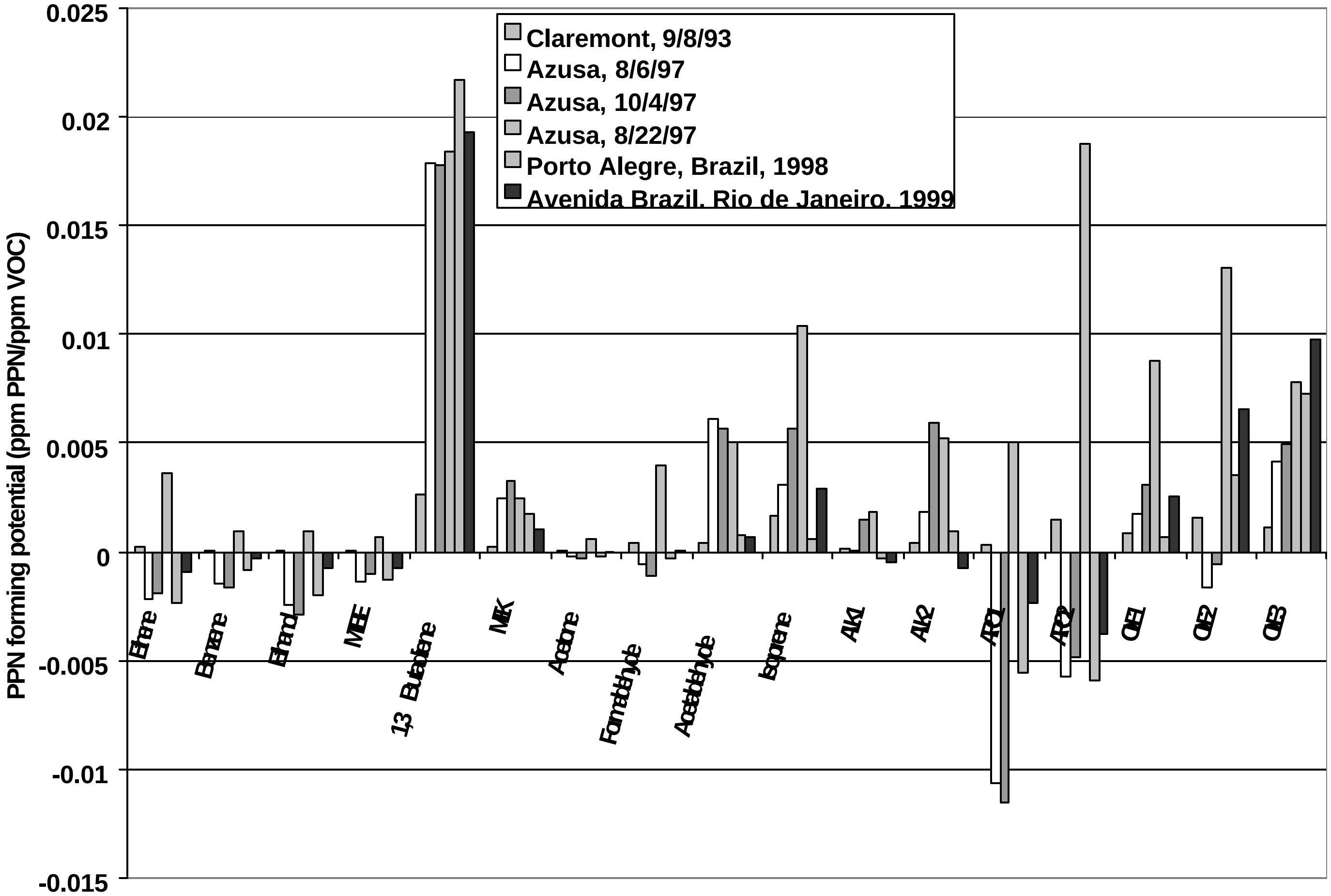


Figure 7.6 PPN Formation Potentials From Individual VOCs (continued)

Table 7.5 Contribution From Individual VOCs to Total Ozone Formation* (ppm)

VOCs	South Coast[b] 1968	Los Angeles[c] 1968	Los Angeles LARPP[d] 1973	Los Angeles 8/28/87[a]	SCAQS 8/28/87[a]	Los Angeles 12/3/87[a]	Claremont[f] 9/8/93	Azusa[e] 8/6/97	Los Angeles[e] 10/4/97	Los Angeles[e] 8/22/97
Ethene	0.09953	0.07193		0.00520	0.03515	0.05048	0.01409	0.00636	0.00939	0.08674
Benzene				0.00043	0.00205	0.00197	0.00049		0.00042	0.00168
Ethanol										
MTBE										
1,3-Butadiene		0.00592					0.00124			0.00186
MEK				0.00004		0.00163		0.00043	0.00010	0.00040
Acetone				0.00004		0.00101		0.00023	0.00014	0.00032
Formaldehyde	0.00569	0.00214	0.00100	-0.00081	0.00290	0.00916		-0.00008	0.00007	0.00113
Acetaldehyde	0.00793	0.00503	0.00362	0.00135	0.00816	0.01019		0.00404	0.00179	0.00414
Isoprene				0.00023		0.00144		0.00044	0.00062	0.03009
ALK1	0.23994	0.22601	0.03184	0.03925	0.12619	0.17033	0.01895	0.04533	0.03887	0.07233
ALK2	0.04231	0.03239	-0.00820	0.00027	0.02027	0.01738	0.00584	0.00011	0.00084	0.02891
ARO1	0.01625	-0.04142	-0.01254	-0.05754	0.00915	0.00557	0.00628	-0.04218	-0.04161	0.04027
ARO2	0.21484	0.12599	-0.00205	-0.04482	0.06570	0.07153	0.02865	-0.04196	-0.01717	0.11135
OLE1	0.04005	0.05394	0.01191	0.01022	0.01559	0.24770	0.00917	0.00613	0.03381	0.04902
OLE2		0.03445	0.00150	-0.00713		0.01561	0.01034	-0.01380	-0.00258	0.02715
OLE3							0.00046			0.01989

*TOFP = $\sum_i (OFP_i)(VOC_i^o)$

[a] Lawson, 1990
[b] Lonemann, 1968
[c] Kopczynski, 1968
[d] Calvert, 1976
[e] McCauley, 1999
[f] Pasek, 1999

Table 7.6 Contribution From Individual VOCs to Ozone Formation[*] (ppm)

VOCs	Porto Alegre, Brazil 1998[a]	Avenida Brazil, Rio de Janeiro 1999[b]
Ethene	0.00178	-0.00276
Benzene	0.00042	0.00016
Ethanol	0.00009	0.00035
MTBE	0.00050	
1,3-Butadiene	0.00080	0.00130
MEK		
Acetone		
Formaldehyde	-0.00057	-0.00049
Acetaldehyde	0.00385	0.00203
Isoprene	-0.00026	
ALK1	0.01700	0.03412
ALK2	-0.00676	0.01356
ARO1	-0.02446	-0.02267
ARO2	-0.08406	-0.12305
OLE1	-0.00190	-0.00541
OLE2	-0.02467	0.00484
OLE3		

[*] **TOFP** = $\sum_i (OFP_i)(VOC_i^o)$

[a] Grosjean *et al.* (1998)

[b] Grosjean (1999)

Table 7.7 Contribution From Individual VOCs to PAN Formation* (ppm)

VOCs	South Coast[b] 1968	Los Angeles[c] 1968	Los Angeles LARPP[d] 1973	Los Angeles 8/28/87[a]	SCAQS 8/28/87[a]	Los Angeles 12/3/87[a]	Claremont[f] 9/8/93	Azusa[e] 8/6/97	Los Angeles[e] 10/4/97	Los Angeles[e] 8/22/97
Ethene	0.00263	0.00295		0.00001	0.00048	0.00139	0.00002	0.00006	0.00013	0.00050
Benzene				-0.00009	-0.00003	-0.00007	< 1E-05		-0.00008	0.00001
Ethanol										
MTBE										
1,3-Butadiene		0.00051					< 1E-05			0.00001
MEK				0.00001		0.00019		0.00008	0.00002	< 1E-05
Acetone				0.00002		0.00010		0.00006	0.00003	< 1E-05
Formaldehyde	0.00001	0.00001		-0.00004	-0.00004	-0.00010		-0.00002	-0.00003	< 1E-05
Acetaldehyde	0.00046	0.00055	0.00016	0.00018	0.00021	0.00061		0.00037	0.00015	0.00003
Isoprene			0.00000	0.00003		0.00007		0.00003	0.00004	0.00019
ALK1	0.01394	0.01687	0.00011	-0.00129	0.00430	0.01113	0.00003	-0.00041	0.00044	0.00050
ALK2	0.00305	0.00308	-0.00021	-0.00291	0.00096	0.00142	0.00001	-0.00168	-0.00036	0.00020
ARO1	0.00065	-0.00136	-0.00016	-0.00081	0.00017	0.00043	0.00002	-0.00125	-0.00124	0.00028
ARO2	0.00415	0.00701	0.00034	0.00359	0.00060	0.00127	0.00008	0.00179	0.00089	0.00064
OLE1	0.00178	0.00444	0.00052	0.00229	0.00036	0.01166	0.00002	0.00068	0.00267	0.00031
OLE2		0.00319	0.00048	0.00023		0.00059	0.00002	0.00048	0.00029	0.00016
OLE3							< 1E-05			0.00012

* TPANFP= $\sum_i (PANFP_i)(VOC_i^o)$

[a]Lawson, 1990, [b]Lonemann, 1968, [c]Kopczynski, 1968, [d]Calvert, 1976, [e]McCauley, 1999, [f]Pasek, 1999

Table 7.8 Contribution From Individual VOCs to PAN Formation* (ppm)

VOCs	Porto Alegre, Brazil 1998[a]	Avenida Brazil, Rio de Janeiro 1999[b]
Ethene	-0.00004	-0.00006
Benzene	-0.00011	-0.00009
Ethanol	0.00009	0.00012
MTBE	-0.00003	
1,3-Butadiene	0.00018	0.00014
MEK		
Acetone		
Formaldehyde	-0.00002	-0.00001
Acetaldehyde	0.00077	0.00047
Isoprene	0.00012	
ALK1	-0.00151	-0.00419
ALK2	-0.00471	-0.01112
ARO1	-0.00048	0.00002
ARO2	0.00726	0.01781
OLE1	0.00149	0.00177
OLE2	0.00505	0.00911
OLE3		

* TPANFP= $\sum_i (PANFP_i)(VOC_i^o)$

[a] Grosjean *et al.*, 1998

[b] Grosjean, 1999

Table 7.9 Contribution From Individual VOCs to PPN Formation[a,b] (ppm)

VOCs	Los Angeles 8/28/87[c]	SCAQS 8/28/87[c]	Los Angeles 12/3/87[c]	Azusa[g] 8/6/97	Los Angeles[g] 10/4/97	Los Angeles[g] 8/22/97	Claremont[h] 9/8/93	South Coast[d] 1968	Los Angeles[e] 1968	Los Angeles LARPP[f] 1973
Ethene	0.00004	0.00003		-0.00008	0.00003	0.00003	< 1E-05	-0.00006	-0.00005	0.00011
Benzene				-0.00003	-0.00001	-0.00003	< 1E-05		-0.00002	< 1E-05
Ethanol										
MTBE										
1,3 Butadiene		0.00015					< 1E-05			< 1E-05
MEK						0.00004		0.00001	< 1E-05	< 1E-05
Acetone						> -1E-05		> -1E-05	> -1E-05	< 1E-05
Formaldehyde	-0.00004	-0.00002		-0.00001	-0.00002	-0.00006		-0.00001	-0.00001	< 1E-05
Acetaldehyde	0.00002	0.00003	0.00002	0.00001	0.00004	0.00004		0.00004	0.00002	< 1E-05
Isoprene				< 1E-05		0.00001		< 1E-05	< 1E-05	0.00004
ALK1	0.00506	0.00608	0.00013	-0.00004	0.00132	0.00380	0.00001	0.00003	0.00035	0.00014
ALK2	0.00156	0.00160	0.00001	0.00015	0.00034	0.00062	< 1E-05	0.00024	0.00049	0.00007
ARO1	-0.00061	-0.00177	-0.00014	-0.00108	-0.00009	-0.00044	< 1E-05	-0.00088	-0.00078	0.00005
ARO2	-0.00103	-0.00138	-0.00002	-0.00038	-0.00004	-0.00022	0.00001	-0.00051	-0.00025	0.00013
OLE1	0.00019	0.00053	0.00005	0.00015	0.00006	0.00139	< 1E-05	0.00004	0.00023	0.00007
OLE2		0.00032	0.00004	< 1E-05		0.00004	< 1E-05	-0.00003	-0.00001	0.00003
OLE3							< 1E-05			0.00003

[a] $\text{TPPNFP} = \sum_i (PPNFP_i)(VOC_i^o)$.

[b]Note that PPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates

[c]Lawson, 1990, [d]Lonemann, 1968 [e]Kopczynski, 1968, [f]Calvert, 1976, [g]McCauley, 1999, [h]Pasek, 1999

Table 7.10 Contribution From Individual VOCs to PPN Formation[a,b] (ppm)

VOCs	Porto Alegre, Brazil 1998[c]	Avenida Brazil, Rio de Janeiro 1999[d]
Ethene	-0.00008	-0.00005
Benzene	-0.00003	-0.00002
Ethanol	-0.00002	-0.00004
MTBE	-0.00001	
1,3-Butadiene	0.00013	0.00023
MEK		
Acetone		
Formaldehyde	> -1E-05	< 1E-05
Acetaldehyde	0.00001	0.00001
Isoprene	< 1E-05	
ALK1	-0.00009	-0.00045
ALK2	0.00019	-0.00044
ARO1	-0.00065	-0.00058
ARO2	-0.00128	-0.00193
OLE1	0.00004	0.00019
OLE2	0.00035	0.00107
OLE3		

[a] TPPNFP = $\sum_i (PPNFP_i)(VOC_i^o)$

[b] Note that PPN represents peroxypropionyl nitrate and higher molecular weight. acyl peroxy nitrates

[c] Grosjean *et al.* (1998)

[d] Grosjean (1999)

Individual reactivities or forming potentials from the results show a variation in estimated values across different scenarios, because a VOC reactivity is dependent upon local ambient conditions, such as VOC/NO$_x$ ratios noted in previous studies (Carter, 1989; Derwent and Jenkin, 1991). A relative scale to each base mixture reactivity may significantly eliminate the variation of individual reactivities over different ambient conditions. However, pursuing a robust regulatory reactivity or forming potential scale is beyond the scope of this study.

B-7.4. Other Study of PAN Formation Potentials

The PAN formation potential results in Table 7.7 and Table 7.8 are in agreement with the results obtained by Bowman and Seinfeld (1994) for the relative contribution of lumped VOC species to PAN formation. From Table 7.11, ALK1, ALK2, ARO2, and OLE1 have large contributions to PAN formation, while acetaldehyde has a low contribution to PAN formation.

Table 7.11 Relative Contribution of Lumped VOC Species to PAN Formation[a]

Species	Description[b]	Initial Concentration[d] (ppbC)	Contribution to PAN[d] (%)
CO	Carbon monoxide	1,500	-
CH4	Methane	1,700	-
HCHO	Formaldehyde	8	-
CCHO	Acetaldehyde	5	2.6
RCHO	Higher molecular weight aldehydes	2	0.5
MEK	Higher molecular weight ketones	16	1.4
ALK1	Low molecular weight alkanes	353	18.6
ALK2	Higher molecular weight alkanes	236	13.5
ARO1	Benzene and toluene	147	9.4
ARO2	Higher molecular weight aromatics (mostly xylenes)	108	15.2
ETHE	Ethylene	75	6.8
OLE1	Low molecular weight, less reactive alkenes	60	14.9
OLE2	Low molecular weight, more reactive alkenes	29	8.9
OLE3	Biogenic compounds (isoprene + terpenes)	62	8.3

[a] Adapted from Bowman and Seinfeld (1994)

[b] SAPRC90 (Carter, 1990)

[c] Using 1987 SCAQS emission inventory as input data

[d] At VOC/NO_X = 8.2 ppbC/ppb

B-8. References

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Attachment B1 – Listing of SAPRC97 Chemical Mechanism

This attachment provides a listing of the SAPRC97 mechanism. Separate listings are provided for the isoprene reaction mechanism and for other species treated explicitly in Attachments B2 and B3, respectively. Interpretation of reactions rates constants can be found in Kumar *et al.* (1996). Note that this chemical mechanism contains explicit gas-phase reactions for some organic compounds, such as formaldehyde, acetaldehyde, ethylene, and PAN. However, the PPN model species represents higher acyl peroxy nitrates (e.g., CH_3-CH_2-CH_2-CH_2-CO-OO-NO_2), but not alkyl peroxy nitrates such as CH_3-CH_2-CH_2-CH_2-OO-NO_2. The latter are not represented in the model because of their rapid back-decomposition to reactants at ambient temperatures. PPN does not represent the aromatic acyl peroxy nitrates that are represented by the PBZN model species (Carter, 1990 and 1999a). In the newest version of update to the mechanism, SAPRC99, Carter (1999b) uses PAN2 instead of PPN.

A summary of the reaction rate constants used in the mechanism is provided for the benefit of the reader. The default rate parameter, k, input in the mechanism is:

Label) A, E, B ; reaction list

Where

$$k = A(T/T_{REF})^{B}\exp(-E/RT) \qquad (B1\text{-}1)$$

Where A is the Arrhenius pre-exponential factor in $cm^3 molecule^{-1} sec^{-1}$, T_{REF} is a reference temperature (300 K), B is a constant, E is activation energy in kcal/mole, and R is the ideal gas constant in kcal $mole^{-1}K^{-1}$ (Kumar *et al.*, 1995). For those reaction rate constants that are temperature and pressure dependent, the Troe falloff expression is used. The default input parameters for the falloff rates constant are:

Label) FALLOFF ; reaction list

A0, E0, B0

A1, E1, B1

F, N

The falloff expression is

$$k = [k0*M/(1+(K0*M/K1))]*F^{Z} \qquad (B1\text{-}2)$$

with

$$Z = 1/[\ 1+\log_{10}(k0*M/k1)/N^{2}\ ] \qquad (B1\text{-}3)$$

Where

$$k0 = A0*[(T/T_{REF})^{B0}]*\exp(-E0/RT) \qquad (B1\text{-}4)$$

$$k1 = A1*[(T/T_{REF})^{B1}]*\exp(-E1/RT) \qquad (B1\text{-}5)$$

Here, k0 is the low-pressure limiting rate constant, and A0 its value at 300 K, k1 is the high-pressure limiting rate constant, with A1 its value at 300 K. For second-order reactions, the units of k0, k1, A0, and A1 are in cm^3 molecule^{-1}sec^{-1}, while for first-order reaction the units are in sec^{-1}. F is the broadening factor of the falloff curve, M is the total pressure fixed at 1.0 x10^6 ppm. The constants E0 and E1 are activation energies in kcal mole^{-1} ^{o}K^{-1}, and B0, B1, and N are constants for each reaction (Finlayson-Pitts, 1986; Kumar *et al.*, 1995; Carter, 1990). Finally, photolytic reactions are indicated by the PF= label.

```
1)        PF=NO2                   ;NO2 + HV = NO + O
2) 6.0E-34, 0.0, -2.3              ;O + O2 + M = O3 + M
3A) 6.5E-12,  -0.238               ;O + NO2 = NO + O2
!
3B)       FALLOFF                  ;O + NO2 = NO3 + M
9.0E-32  0.0  -2.0
2.2E-11  0.0   0.0
0.6      1.0
!
4) 2.00E-12,  2.782                ;O3 + NO = NO2 + O2
5) 1.400E-13,  4.968               ;O3 + NO2 = O2 + NO3
 6) 1.7E-11, -0.298                ;NO + NO3 = #2 NO2
7) 3.300E-39, -1.05                ;NO + NO + O2 = #2 NO2
!
 8)       FALLOFF                  ;NO2 + NO3 = N2O5
2.2E-30  0.0  -4.3
1.5E-12  0.0  -0.5
0.6      1.0
!
9) 9.09E+26, 22.26                 ;N2O5 + #RCON8 = NO2 + NO3
10) 1.0E-21 0.0                    ;N2O5 + H2O = #2 HNO3
11) 2.5E-14, 2.44                  ;NO2 + NO3 = NO + NO2 + O2
12A)      PF=NO3NO                 ;NO3 + HV = NO + O2
12B)      PF=NO3NO2                ;NO3 + HV = NO2 + O
13A)      PF=O3O3P                 ;O3 + HV = O + O2
13B)      PF=O3O1D                 ;O3 + HV = O*1D2 + O2
14) 2.2E-10,        0.0            ;O*1D2 + H2O = #2 HO
15) 1.919E-11,     -0.251          ;O*1D2 + M = O + M
!
16)       FALLOFF                  ;HO  + NO = HONO
7.0E-31  0.0  -2.6
1.5E-11  0.0  -0.5
0.6         1.0
!
 17)      PF=HONO                  ;HONO + HV = HO  + NO
!
 18)      FALLOFF                  ;HO  + NO2 = HNO3
2.6E-30  0.0  -3.2
2.4E-11  0.0  -1.3
0.6         1.0
!
 19) 6.45E-15,      -1.652         ;HO  + HNO3 = H2O + NO3     ! 1 ATM ONLY.
21) 2.4E-13, 0.0                   ;HO  + CO = HO2  + CO2      !1 ATM ONLY
22) 1.600E-12,  1.87               ;HO  + O3 = HO2  + O2
 23) 3.700E-12, -0.48              ;HO2  + NO = HO  + NO2
!
24)       FALLOFF                  ;HO2  + NO2 = HNO4
```

```
1.8E-31  0.0  -3.2
4.7E-12  0.0  -1.4
0.6      1.0
!
25) 4.76E+26, 21.66             ;HNO4 + #RCON24 = HO2  + NO2
 27) 1.3E-12,       -0.755      ;HNO4 + HO  = H2O + NO2 + O2
 28) 1.100E-14,  0.994          ;HO2  + O3 = HO  + #2 O2
 29A) 2.2E-13,   -1.23          ;HO2  + HO2  = H2O2 + O2
 29B) 1.9E-33,      -1.95       ;HO2  + HO2  + M = H2O2 + O2
 29C) 3.1E-34,   -5.60          ;HO2  + HO2  + H2O = H2O2 + O2 + H2O
!29D) 2.7E-54,   -6.32          ;HO2  + HO2  + M + H2O = H2O2 + O2  +H2O
 29D) 6.6E-35,   -6.32          ;HO2  + HO2  + H2O = H2O2 + O2 + H2O  !(1 ATM ONLY)
 30A) 2.2E-13,   -1.23          ;NO3 + HO2  = HNO3 + O2
 30B) 1.9E-33,      -1.95       ;NO3 + HO2  + M = HNO3 + O2
 30C) 3.1E-34,   -5.60          ;NO3 + HO2  + H2O = HNO3 + O2 + H2O
 30D) 6.6E-35,   -6.32          ;NO3 + HO2  + H2O = HNO3 + O2 + H2O
31) PF=H2O2                     ;H2O2 + HV = #2 HO
32) 3.300E-12, 0.397            ;H2O2 + HO  = HO2  + H2O
33) 4.60E-11,  -0.457           ;HO  + HO2  = H2O + O2
B1) 4.200E-12, -0.360           ;RO2  + NO = NO
!
B2)       FALLOFF               ;RCO3  + NO = NO
5.65E-28  0.0  -7.1
2.64E-11  0.0  -0.9
0.27      1.0
!
B4)       FALLOFF               ;RCO3  + NO2 = NO2
2.57E-28  0.0  -7.1
12.0E-12  0.0  -0.9
0.30      1.0
!
B5) 3.40E-13,  -1.590           ;RO2  + HO2  = HO2
B6) 3.40E-13,  -1.590           ;RCO3  + HO2  = HO2
B8)  1.0E-15                    ;RO2  + RO2  =
B9)  1.86E-12, -1.053           ;RO2  + RCO3  =
B10) 2.8E-12, -1.053            ;RCO3  + RCO3  =
B11)      SAMEK B1              ;RO2-R  + NO = NO2 + HO2
B12)      SAMEK B5              ;RO2-R  + HO2  = XOOH
B13)      SAMEK B8              ;RO2-R  + RO2  = RO2  + #.5 HO2
B14)      SAMEK B9              ;RO2-R  + RCO3  = RCO3  + #.5 HO2
B19)      SAMEK B1              ;RO2-N  + NO = RNO3
B20)      SAMEK B5              ;RO2-N  + HO2  = XOOH + MEK  + #1.5 XC
B21)      SAMEK B8              ;RO2-N  + RO2  = RO2  + #.5 HO2  + MEK + #1.5 XC
B22)      SAMEK B9              ;RO2-N  + RCO3  = RCO3  + #.5 HO2  + MEK + #1.5 XC
B15)      SAMEK B1              ;R2O2  + NO = NO2
B16)      SAMEK B5              ;R2O2  + HO2  =
B17)      SAMEK B8              ;R2O2  + RO2  = RO2
B18)      SAMEK B9              ;R2O2  + RCO3  = RCO3
B23)      SAMEK B1              ;RO2-XN  + NO = XN
B24)      SAMEK B5              ;RO2-XN  + HO2  = XOOH
B25)      SAMEK B8              ;RO2-XN  + RO2  = RO2  + #.5 HO2
B26)      SAMEK B9              ;RO2-XN  + RCO3  = RCO3  + HO2
G2)       SAMEK B1              ;RO2-NP  + NO = NPHE
G3)       SAMEK B5              ;RO2-NP  + HO2  = XOOH + #6 XC
G4)       SAMEK B8              ;RO2-NP  + RO2  = RO2  + #.5 HO2  + #6 XC
G5)       SAMEK B9              ;RO2-NP  + RCO3  = RCO3  + HO2  + #6 XC
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B7)       PF=CO2H                ;XOOH + HV = HO2  + HO
B7A) 1.18E-12, -0.254            ;HO  + XOOH = HO
B7B) 1.79E-12, -0.435            ;HO  + XOOH = RO2-R  + RO2
C1)       PF=HCHONEWR            ;HCHO + HV = #2 HO2  + CO
C2)       PF=HCHONEWM            ;HCHO + HV = H2 + CO
C3) 1.125E-12 -1.288 2.0         ;HCHO + HO  = HO2  + CO + H2O
C4)  9.7E-15, -1.242             ;HCHO + HO2  = HOCOO
C4A)  2.4E+12,  13.91            ;HOCOO  = HO2  + HCHO
C4B)      SAMEK B1               ;HOCOO  + NO = XC + NO2 + HO2
C9) 2.8E-12,        5.00         ;HCHO + NO3 = HNO3 + HO2  + CO
C10) 5.55E-12, -0.618            ;CCHO + HO  = CCO-O2  + H2O + RCO3
C11A) PF=CCHOR                   ;CCHO + HV = CO + HO2  + HCHO + RO2-R  + RO2
C12) 1.4E-12,  3.696             ;CCHO + NO3 = HNO3 + CCO-O2  + RCO3
C25) 8.5E-12  -0.50              ;RCHO + HO  = C2CO-O2  + RCO3
C26)      PF=RCHO                ;RCHO + HV = CCHO + RO2-R  + RO2  + CO + HO2
C27)  1.4E-12,  3.696            ;NO3 + RCHO = HNO3 + C2CO-O2  + RCO3
C38) 4.81E-13 0.457 2.0          ;ACET + HO  = R2O2  + HCHO + CCO-O2  + RCO3  + RO2
C39)      PF=ACET-93C            ;ACET + HV = CCO-O2  + HCHO + RO2-R  + RCO3  + RO2
C44) 2.92E-13 -0.823 2.0         ;MEK + HO  = H2O + #.5 "CCHO + HCHO + CCO-O2  + &
                                 C2CO-O2 " + RCO3  + #1.5 "R2O2  + RO2 "
C57)      PF=KETONE              ;MEK + HV + #0.1 = CCO-O2  + CCHO + RO2-R  + RCO3  &
                                 + RO2
C95)  2.191E-11, 1.408           ;RNO3 + HO  = NO2 + #.155 MEK + #1.05 RCHO + &
                                  #.48 CCHO + #.16 HCHO + #.11 XC + #1.39 "R2O2  + RO2 "
C13)      SAMEK B2               ;CCO-O2  + NO = CO2 + NO2 + HCHO + RO2-R  + RO2
C14)      SAMEK B4               ;CCO-O2  + NO2 = PAN
C15)      SAMEK B6               ;CCO-O2  + HO2  = XOOH + CO2 + HCHO
C16)      SAMEK B9               ;CCO-O2  + RO2  = RO2  + #.5 HO2  + CO2 + HCHO
C17)      SAMEK B10              ;CCO-O2  + RCO3  = RCO3  + HO2  + CO2 + HCHO
!
 C18)     FALLOFF                ;PAN = CCO-O2  + NO2 + RCO3
4.90E-03  23.972  0.0
4.00E+16  27.079  0.0
0.30      1.00
!
C28)      SAMEK B2               ;C2CO-O2  + NO = CCHO + RO2-R  + CO2 + NO2 + RO2
C29)  8.4E-12 0.0 0.0            ;C2CO-O2  + NO2 = PPN
C30)      SAMEK B6               ;C2CO-O2  + HO2  = XOOH + CCHO + CO2
C31)      SAMEK B9               ;C2CO-O2  + RO2  = RO2  + #.5 HO2  + CCHO + CO2
C32)      SAMEK B10              ;C2CO-O2  + RCO3  = RCO3  + HO2  + CCHO + CO2
C33) 1.6E+17, 27.966             ;PPN = C2CO-O2  + NO2 + RCO3
TBON)  2.4E-11                   ;C2(C)-O  + NO2 = RNO3 + #-2 XC
TBOD)  7.5E+14, 16.2             ;C2(C)-O  = ACET + HCHO + RO2-R  + RO2
C58A)     PF=GLYOXAL1            ;GLY + HV  = #.8 HO2  + #.45 HCHO + #1.55 CO
C58B)     PF=GLYOXAL2            ;GLY + HV + #0.029 = #.13 HCHO + #1.87 CO
 C59)     1.14E-11               ;GLY + HO  = #.6 HO2  + #1.2 CO + #.4 "HCOCO-O2  + &
                                 RCO3 "
 C60)     SAMEK C12              ;GLY + NO3 = HNO3 + #.6 HO2  + #1.2 CO + &
                                  #.4 "HCOCO-O2  + RCO3 "
 C62)     SAMEK B2               ;HCOCO-O2  + NO = NO2 + CO2 + CO + HO2
 C63)     SAMEK B4               ;HCOCO-O2  + NO2 = GPAN
 C64)     SAMEK C18              ;GPAN = HCOCO-O2  + NO2 + RCO3
 C65)     SAMEK B6               ;HCOCO-O2  + HO2  = XOOH + CO2 + CO
 C66)     SAMEK B9               ;HCOCO-O2  + RO2  = RO2  + #.5 HO2  + CO2 + CO
 C67)     SAMEK B10              ;HCOCO-O2  + RCO3  = RCO3  + HO2  + CO2 + CO
C68A)     PF=MEGLYOX1            ;MGLY + HV = HO2  + CO + CCO-O2  + RCO3
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C68B)   PF=MEGLYOX2           ;MGLY + HV + #.107 = HO2  + CO + CCO-O2  + RCO3
C69)    1.72E-11              ;MGLY + HO  = CO + CCO-O2  + RCO3
C70)    SAMEK C12             ;MGLY + NO3 = HNO3 + CO + CCO-O2  + RCO3
G46)    2.63E-11              ;HO  + PHEN = #.15 RO2-NP  + #.85 RO2-R  + #.2 GLY + &
                              #4.7 XC + RO2
G51)    3.6E-12               ;NO3 + PHEN = HNO3 + BZ-O
G52)    4.2E-11               ;HO  + CRES = #.15 RO2-NP  + #.85 RO2-R  + #.2 MGLY + &
                               #5.5 XC + RO2
G57)    2.1E-11               ;NO3 + CRES = HNO3 + BZ-O  + XC
G30)    1.29E-11              ;BALD + HO  = BZ-CO-O2  + RCO3
G31)    PF=BZCHO              ;BALD + HV + #.05 = #7 XC
G32) 1.4E-12,  3.747          ;BALD + NO3 = HNO3 + BZ-CO-O2
G33)    SAMEK B2              ;BZ-CO-O2  + NO = BZ-O  + CO2 + NO2 + R2O2  + RO2
G34) 8.4E-12 0.0 0.0          ;BZ-CO-O2  + NO2 = PBZN
G36)    SAMEK B6              ;BZ-CO-O2  + HO2  = XOOH + CO2 + PHEN
G37)    SAMEK B9              ;BZ-CO-O2  + RO2  = RO2  + #.5 HO2  + CO2 + PHEN
G38)    SAMEK B10             ;BZ-CO-O2  + RCO3  = RCO3  + HO2  + CO2 + PHEN
G35)  1.6E+15,  25.90         ;PBZN = BZ-CO-O2  + NO2 + RCO3
G43) 1.3E-11, -0.596          ;BZ-O  + NO2 = NPHE
G44)    SAMEK B5              ;BZ-O  + HO2  = PHEN
G45)    1.0E-3                ;BZ-O  = PHEN
G58)    3.6E-12               ;NPHE + NO3 = HNO3 + BZ(NO2)-O
G59)    SAMEK G43             ;BZ(NO2)-O  + NO2 = #2 XN + #6 XC       ! DINITROPHENOL
G60)    SAMEK B5              ;BZ(NO2)-O  + HO2  = NPHE
G61)    SAMEK G45             ;BZ(NO2)-O  = NPHE
G7)     1.14E-11              ;HO  + AFG1 = HCOCO-O2  + RCO3
G8)     PF=ACROLEIN           ;AFG1 + HV + #0.077 = HO2  + HCOCO-O2  + RCO3
U2OH)   1.72E-11              ;HO  + AFG2 = C2CO-O2  + RCO3
U2HV)   PF=ACROLEIN           ;AFG2 + HV = HO2  + CO + CCO-O2  + RCO3
RCH4) 6.255E-13 2.548 2.0     ;CH4 + HO  = HCHO + RO2-R  + RO2
RZ1)    1.0                   ;(HCHO2) = #.7 HCOOH + #.12 "HO  + HO2  + CO" + &
                               #.18 "H2 + CO2"
RZ2)    1.0                   ;(CCHO2) = #.25 CCOOH + #.15 "CH4 + CO2" + #.6 HO  + &
                               #.3 "CCO-O2  + RCO3 " + #.3 "RO2-R  + HCHO + CO + &
                               RO2 "
RZ3)    1.0                   ;(RCHO2) = #.25 CCOOH + #.15 CO2 + #.6 HO  + &
                              #.3 "C2CO-O2  + RCO3 " + #.3 "RO2-R  + CCHO + CO + &
                               RO2 " + #.55 XC
RZ4)    1.0                   ;(C(C)CO2) = HO  + R2O2  + HCHO + CCO-O2  + RCO3  + RO2
RZ5)    1.0                   ;(C(R)CO2) = HO  + CCO-O2  + CCHO + R2O2  + RCO3  + RO2
RZ6)    1.0                   ;(CYCCO2) = #.3 "HO  + C2CO-O2  + R2O2  + RCO3  + &
                               RO2 " + #.3 RCHO + #4.2 XC
RZ7)    1.0                   ;(BZCHO2) = #.5 "BZ-O  + R2O2  + CO + HO "
ETOH)  1.960E-12 -0.870       ;ETHE + HO  = RO2-R  + RO2  + #1.56 HCHO + #.22 CCHO
ETO3)  9.140E-15  5.127       ;ETHE + O3 = HCHO + (HCHO2)
ETN3)  5.430E-12  6.043       ;ETHE + NO3 = R2O2  + RO2  + #2 HCHO + NO2
ETOA)  1.040E-11  1.574       ;ETHE + O = RO2-R  + HO2  + RO2  + HCHO + CO

A1OH)                  ;HO  + ALK1 = #A1OHRR RO2-R  + #A1OHNR RO2-N  + &
                        #A1OHXN RO2-XN  + #A1OHNP RO2-NP  + #A1OHRH HO2  + &
                        #A1OHR2 R2O2  + #A1OHRS RO2  + #A1OHA1 HCHO + &
                        #A1OHA2 CCHO + #A1OHA3 RCHO + #A1OHK3 ACET + &
                        #A1OHK4 MEK + #A1OHCO CO + #A1OHC2 CO2 + &
                        #A1OHPH PHEN + #A1OHCR CRES + #A1OHBZ BALD + &
                        #A1OHGL GLY + #A1OHMG MGLY + #A1OHU1 AFG1 + &
                        #A1OHU2 AFG2 + #A1OHTB C2(C)-O  + #A1OHQ1 CCO-O2  + &
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```
                     #A1OHQ2 C2CO-O2  + #A1OHQS RCO3  + #A1OHXC XC
!
A2OH)               ;HO  + ALK2 = #A2OHRR RO2-R  + #A2OHNR RO2-N  + &
                     #A2OHXN RO2-XN  + #A2OHNP RO2-NP  + #A2OHRH HO2  + &
                     #A2OHR2 R2O2  + #A2OHRS RO2  + #A2OHA1 HCHO + &
                     #A2OHA2 CCHO + #A2OHA3 RCHO + #A2OHK3 ACET + &
                     #A2OHK4 MEK + #A2OHCO CO + #A2OHC2 CO2 + &
                     #A2OHPH PHEN + #A2OHCR CRES + #A2OHBZ BALD + &
                     #A2OHGL GLY + #A2OHMG MGLY + #A2OHU1 AFG1 + &
                     #A2OHU2 AFG2 + #A2OHTB C2(C)-O  + #A2OHQ1 CCO-O2  + &
                     #A2OHQ2 C2CO-O2  + #A2OHQS RCO3  + #A2OHXC XC
!
B1OH)               ;HO  + ARO1 = #B1OHRR RO2-R  + #B1OHNR RO2-N  + &
                     #B1OHXN RO2-XN  + #B1OHNP RO2-NP  + #B1OHRH HO2  + &
                     #B1OHR2 R2O2  + #B1OHRS RO2  + #B1OHA1 HCHO + &
                     #B1OHA2 CCHO + #B1OHA3 RCHO + #B1OHK3 ACET + &
                     #B1OHK4 MEK + #B1OHCO CO + #B1OHC2 CO2 + &
                     #B1OHPH PHEN + #B1OHCR CRES + #B1OHBZ BALD + &
                     #B1OHGL GLY + #B1OHMG MGLY + #B1OHU1 AFG1 + &
                     #B1OHU2 AFG2 + #B1OHTB C2(C)-O  + #B1OHQ1 CCO-O2  + &
                     #B1OHQ2 C2CO-O2  + #B1OHQS RCO3  + #B1OHXC XC
!
B2OH)               ;HO  + ARO2 = #B2OHRR RO2-R  + #B2OHNR RO2-N  + &
                     #B2OHXN RO2-XN  + #B2OHNP RO2-NP  + #B2OHRH HO2  + &
                     #B2OHR2 R2O2  + #B2OHRS RO2  + #B2OHA1 HCHO + &
                     #B2OHA2 CCHO + #B2OHA3 RCHO + #B2OHK3 ACET + &
                     #B2OHK4 MEK + #B2OHCO CO + #B2OHC2 CO2 + &
                     #B2OHPH PHEN + #B2OHCR CRES + #B2OHBZ BALD + &
                     #B2OHGL GLY + #B2OHMG MGLY + #B2OHU1 AFG1 + &
                     #B2OHU2 AFG2 + #B2OHTB C2(C)-O  + #B2OHQ1 CCO-O2  + &
                     #B2OHQ2 C2CO-O2  + #B2OHQS RCO3  + #B2OHXC XC
!
O1OH)               ;OLE1 + HO  = #O1OHRR RO2-R  + #O1OHRN RO2-N  + &
                     #O1OHRS RO2  + #O1OHA1 HCHO + #O1OHA2 CCHO + &
                     #O1OHA3 RCHO + #O1OHK3 ACET + #O1OHK4 MEK + &
                     #O1OHBZ BALD + #O1OHXC XC
!
O1O3)               ;OLE1 + O3 = #O1O3A1 HCHO + #O1O3A2 CCHO + &
                     #O1O3A3 RCHO + #O1O3K3 ACET + #O1O3K4 MEK + &
                     #O1O3BZ BALD + #O1O3Z1 (HCHO2) + #O1O3Z2 (CCHO2) + &
                     #O1O3Z3 (RCHO2) + #O1O3Z4 (C(C)CO2) + &
                     #O1O3Z5 (C(R)CO2) + #O1O3Z6 (CYCCO2) + &
                     #O1O3Z8 (BZCHO2) + #O1O3OH HO  + #O1O3RR RO2-R  + &
                     #O1O3RN RO2-N  + #O1O3XN RO2-XN  + #O1O3NP RO2-NP  + &
                     #O1O3RH HO2  + #O1O3R2 R2O2  + #O1O3RS RO2  + &
                     #O1O3Q1 CCO-O2  + #O1O3Q2 C2CO-O2  + #O1O3QS RCO3  + &
                     #O1O3XC XC
!
O1OA)               ;OLE1 + O = #O1OARR RO2-R  + #O1OARH HO2  + &
                     #O1OARS RO2  + #O1OAA1 HCHO + #O1OAA3 RCHO + &
                     #O1OAK4 MEK + #O1OACO CO + #O1OAXC XC
!
O1N3)               ;OLE1 + NO3 = #O1N3N2 NO2 + #O1N3N3 HNO3 + &
                     #O1N3RH HO2  + #O1N3RR RO2-R  + #O1N3RN RO2-N  + &
                     #O1N3R2 R2O2  + #O1N3RS RO2  + #O1N3A1 HCHO + &
                     #O1N3A2 CCHO + #O1N3A3 RCHO + #O1N3K3 ACET + &
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```
                              #O1N3K4 MEK + #O1N3BZ BALD + #O1N3XC XC
!
O2OH)                        ;OLE2 + HO  = #O2OHRR RO2-R  + #O2OHRN RO2-N  + &
                              #O2OHRS RO2  + #O2OHA1 HCHO + #O2OHA2 CCHO + &
                              #O2OHA3 RCHO + #O2OHK3 ACET + #O2OHK4 MEK + &
                              #O2OHBZ BALD + #O2OHXC XC
!
O2O3)                        ;OLE2 + O3 = #O2O3A1 HCHO + #O2O3A2 CCHO + &
                              #O2O3A3 RCHO + #O2O3K3 ACET + #O2O3K4 MEK + &
                              #O2O3BZ BALD + #O2O3Z1 (HCHO2) + #O2O3Z2 (CCHO2) + &
                              #O2O3Z3 (RCHO2) + #O2O3Z4 (C(C)CO2) + &
                              #O2O3Z5 (C(R)CO2) + #O2O3Z6 (CYCCO2) + &
                              #O2O3Z8 (BZCHO2) + #O2O3OH HO  + #O2O3RR RO2-R  + &
                              #O2O3RN RO2-N  + #O2O3XN RO2-XN  + #O2O3NP RO2-NP  + &
                              #O2O3RH HO2  + #O2O3R2 R2O2  + #O2O3RS RO2  + &
                              #O2O3Q1 CCO-O2  + #O2O3Q2 C2CO-O2  + #O2O3QS RCO3  +  &
                              #O2O3XC XC
!
O2OA)                        ;OLE2 + O = #O2OARR RO2-R  + #O2OARH HO2  + &
                              #O2OARS RO2  + #O2OAA1 HCHO + #O2OAA3 RCHO + &
                              #O2OAK4 MEK + #O2OACO CO + #O2OAXC XC
!
O2N3)                        ;OLE2 + NO3 = #O2N3N2 NO2 + #O2N3N3 HNO3 + &
                              #O2N3RH HO2  + #O2N3RR RO2-R  + #O2N3RN RO2-N  + &
                              #O2N3R2 R2O2  + #O2N3RS RO2  + #O2N3A1 HCHO + &
                              #O2N3A2 CCHO + #O2N3A3 RCHO + #O2N3K3 ACET + &
                              #O2N3K4 MEK + #O2N3BZ BALD + #O2N3XC XC
!
O3OH)                        ;OLE3 + HO  = #O3OHRR RO2-R  + #O3OHRN RO2-N  + &
                              #O3OHRS RO2  + #O3OHA1 HCHO + #O3OHA2 CCHO + &
                              #O3OHA3 RCHO + #O3OHK3 ACET + #O3OHK4 MEK + &
                              #O3OHBZ BALD + #O3OHXC XC
!
O3O3)                        ;OLE3 + O3 = #O3O3A1 HCHO + #O3O3A2 CCHO + &
                              #O3O3A3 RCHO + #O3O3K3 ACET + #O3O3K4 MEK + &
                              #O3O3BZ BALD + #O3O3Z1 (HCHO2) + #O3O3Z2(CCHO2) + &
                              #O3O3Z3 (RCHO2) + #O3O3Z4 (C(C)CO2) + &
                              #O3O3Z5 (C(R)CO2) + #O3O3Z6 (CYCCO2) + &
                              #O3O3Z8 (BZCHO2) + #O3O3OH HO  + #O3O3RR RO2-R  + &
                              #O3O3RN RO2-N  + #O3O3XN RO2-XN  + #O3O3NP RO2-NP  + &
                              #O3O3RH HO2  + #O3O3R2 R2O2  + #O3O3RS RO2  + &
                              #O3O3Q1 CCO-O2  + #O3O3Q2 C2CO-O2  + #O3O3QS RCO3  + &
                              #O3O3XC XC
!
O3OA)                        ;OLE3 + O = #O3OARR RO2-R  + #O3OARH HO2  + &
                              #O3OARS RO2  + #O3OAA1 HCHO + #O3OAA3 RCHO + &
                              #O3OAK4 MEK + #O3OACO CO + #O3OAXC XC
!
O3N3)                        ;OLE3 + NO3 = #O3N3N2 NO2 + #O3N3N3 HNO3 + &
                              #O3N3RH HO2  + #O3N3RR RO2-R  + #O3N3RN RO2-N  + &
                              #O3N3R2 R2O2  + #O3N3RS RO2  + #O3N3A1 HCHO + &
                              #O3N3A2 CCHO + #O3N3A3 RCHO + #O3N3K3 ACET + &
                              #O3N3K4 MEK + #O3N3BZ BALD + #O3N3XC XC
!
!       END OF FILE
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Attachment B2 – Listing of Reactions of Isoprene (Condensed 1-Product)

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ISOH) 2.54E-11 -0.81     ;ISOP + HO = #.088 RO2N  + #.912 RO2R  + &
                          #.629 HCHO + #.912 ISPD + #.079 R2O2  + &
                          #1.079 RO2
!                         #1.079 RO2 + #.283 XC
ISO3) 7.86E-15  3.80     ;ISOP + O3 = #.4 HCHO + #.6 ISPD + #.55 BHCHO2 + &
                          #.2 CC3O2 + #.2 CC3HO2
!                         #.2 CC3O2 + #.2 CC3HO2 + #.05 XC
ISOA) 3.60E-11           ;ISOP + O = #.75 ISPD + #.25 "C3O3 + &
                          RCO3 + #2 HCHO + RO2R  + RO2"
!ISOA) 3.60E-11          ;ISOP + O = #.75 "ISPD + XC "+ #.25 "C3O3 + &
!                         RCO3 + #2 HCHO + RO2R  + RO2"
ISN3) 3.03E-12  0.89     ;ISOP + NO3 = #.8 "RCHO + RNO3 + RO2R " + &
                          #.2 "ISPD + R2O2  + NO2" + RO2
!                         #.2 "ISPD + R2O2  + NO2" + RO2 + #-2.2 XC
ISN2) 1.50E-19           ;ISOP + NO2 = #.8 "RCHO + RNO3 + RO2R " + &
                          #.2 "ISPD + R2O2  + NO" + RO2
!                         #.2 "ISPD + R2O2  + NO" + RO2 + #-2.2 XC
!
IPOH) 3.36E-11           ;ISPD + HO = #.293 CO + #.252 CCHO + #.126 HCHO + &
                          #.041 GLY + #.021 RCHO + #.168 MGLY + #.314 MEK + &
                          #.503 RO2R  + #.21 CCO3 + #.288 C3O3 + &
                          #.21 R2O2  + #.713 RO2 + #.498 RCO3
!                         #.21 R2O2  + #.713 RO2 + #.498 RCO3 + #-.112 XC
IPO3) 7.11E-18           ;ISPD + O3 = #.02 CCHO + #.04 HCHO + #.01 GLY + &
                          #.84 MGLY + #.09 MEK + #.66 BHCHO2 + &
                          #.09 HCOCHO2 + #.18 HOCCHO2 + #.06 C2O2CHO + &
                          #.01 COHC2O2
!                         #.01 COHC2O2 + #-.39 XC
IPHV) PF=ACROLEIN        ;ISPD + HV + #.0036 = #.333 CO + #.067 CCHO + &
                          #.9 HCHO + #.033 MEK + #.333 HO2 + #.7 RO2R  + &
                          #.267 CCO3 + #.7 C3O3 + #.7 RO2 + &
                          #.967 RCO3
!                         #.967 RCO3 + #-.133 XC
IPN3) 1.0E-15            ;ISPD + NO3 = #.643 CO + #.282 HCHO + #.85 RNO3 + &
                          #.357 RCHO + #.925 HO2 + #.075 C3O3 + &
                          #.075 R2O2  + #.925 RO2 + #.075 RCO3 + #.075 HNO3
!                         #.075 R2O2  + #.925 RO2 + #.075 RCO3 + #.075 HNO3 + &
!                         #-2.471 XC
ISZ1) 1.0                ;CC3O2 = HO + R2O2  + HCHO + C3O3 + RO2 + &
                          RCO3
ISZ2) 1.0                ;CC3HO2 = #.75 RCHO + #.25 ISPD
!ISZ2) 1.0               ;CC3HO2 = #.75 RCHO + #.25 ISPD + #.5 XC
MAZ1) 1.0                ;C2O2CHO = HO + R2O2  + HCHO + HC2O4 + RO2 + &
                          RCO3
M1Z1) 1.0                ;HOCCHO2 = #.6 HO + #.3 "CCO3 + RCO3" + &
                          #.3 "RO2R  + HCHO + CO + RO2"
!                         #.3 "RO2R  + HCHO + CO + RO2" + #.8 XC
```

```
M2Z1) 1.0                    ;HCOCHO2 = #.12 "HO2 + #2 CO + HO" + &
                              #.51 HCHO
!M2Z1) 1.0                   ;HCOCHO2 = #.12 "HO2 + #2 CO + HO" + #.74 XC + &
!                             #.51 "CO2 + HCHO"
M2Z2) 1.0                    ;COHC2O2 = HO + MGLY + HO2 + R2O2  + RO2
 !         END OF FILE
```

Attachment B3 – Listing of Explicit Reaction Mechanisms for Other VOCs

```
OH001) 2.500E-12  0.397  0.000    ;C6H6 + HO = #.236 PHEN + #.207 GLY &
                                   + #1.44 AFG1 + #.764 RO2-R + #.236 HO2 &
                                  + #1.29 XC + #.764 RO2
!
OH033) 1.480E-11 -0.890  0.000    ;BUTD + HO = RO2-R + RO2 + HCHO + RCHO
!
O3033) 1.340E-14  4.537  0.000    ;BUTD + O3 = #.6 HCHO + RCHO + #-1.2 XC &
                                  + #.4 (HCHO2) + #.6 (CCHO2)
!
N3033) 1.000E-13  0.000  0.000    ;BUTD + NO3 = R2O2 + RO2 + HCHO + RCHO &
                  + NO2
!
OA033) 2.100E-11  0.000  0.000    ;BUTD + O = #.4 HO2 + #.5 RCHO + #.5 MEK &
                  + #.5 XC
!
OH018) 3.840E-13  0.000  0.000    ;PDCB + HO = #.236 PHEN + #.207 GLY &
                                  + #1.44 AFG1 + #.764 RO2-R + #.236 HO2 &
                                  + #1.29 XC + #.764 RO2

OH152) 9.640E-12  2.403  0.000    ;PERC + HO = RO2-R + CCHO + RO2
!
OH086) 6.14E-18  1.987  2.000     ;DICM + HO = RO2-R + HCHO + RO2
!
AS1) 6.14E-25                     ; AS = AS
CR1) 6.14E-25                     ; CRVI = CRVI
!
 C1)       PF=HCHONEWR            ;FORM + HV = #2 HO2  + CO
 C2)       PF=HCHONEWM            ;FORM + HV = H2 + CO
 C3) 1.125E-12 -1.288 2.0         ;FORM + HO  = HO2  + CO + H2O
 C4)  9.7E-15, -1.242             ;FORM + HO2  = HOCOO
 C9) 2.8E-12,      5.00           ;FORM + NO3 = HNO3 + HO2  + CO
!
 C10) 5.55E-12, -0.618            ;ALD + HO  = CCO-O2  + H2O + RCO3
 C11A) PF=CCHOR                   ;ALD + HV = CO + HO2  + HCHO + RO2-R  + RO2
 C12) 1.4E-12,  3.696             ;ALD + NO3 = HNO3 + CCO-O2  + RCO3
!
OH091) 5.560E-13 -1.057  2.000    ;ETOH + HO = #.1 RO2-R + #.9 HO2 &
                                  + #.156 HCHO + #.922 CCHO + #.1 RO2
!
OH108) 6.129E-13 -0.914  2.000    ;MTBE + HO = #.02 RO2-N + #.98 RO2-R &
```

```
                    + #.37 R2O2 + #.39 HCHO + #.41 MEK + #2.87 XC &
                    + #1.37 RO2
!       END OF FILE
```

California Environmental Protection Agency

Air Resources Board

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

Appendix C

Baseline and Future Air Quality Concentrations

December 1999

Table of Contents

List of Tables

List of Figures

C-1. Introduction

This appendix discusses the methods used to estimate baseline and future air quality concentrations of important pollutants associated with the phase-out of methyl *tertiary*-butyl ether (MTBE) from gasoline. Analyses were only done for the South Coast Air Basin (SoCAB), the most populated and most polluted air basin in California and the area with the greatest wealth of air quality data. Separate sections are included on data sources, methods for establishing baseline concentrations, methods for estimating future air quality, and results.

C-2. Data Sources Used

The criteria pollutants studied included carbon monoxide (CO), nitrogen dioxide (NO_2), ozone (O_3), and particulate matter (PM_{10}). The key toxic air contaminants studied were benzene, 1,3-butadiene, MTBE, acetaldehyde, and formaldehyde. Ethanol, peroxyacetyl nitrate (PAN), and peroxypropionyl nitrate (PPN) were also studied. Some additional compounds (e.g., toluene, xylenes, isobutene, *n*-hexane, *n*-heptane, alkylates) were evaluated for baseline concentrations but were dropped from further analysis because the potential differences in concentrations due to the use of different fuels relative to risk levels would not pose a significant health concern. Ambient data for criteria pollutants in 1996-1998 were used to represent the 1997 baseline to account for natural year-to-year meteorological fluctuations while only 1996-1997 toxics data were used to represent the 1997 baseline since 1998 data were not readily available at the time of data analysis. Data from before 1996 were not used because the fuels used then did not satisfy the requirements of California Phase 2 Reformulated Gasoline (CaRFG).

Data from the following sources were used in our analysis:

- 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.

These data sets are described briefly below. Because 1997 Southern California Ozone Study-NARSTO (SCOS97-NARSTO) and Multiple Air Toxics Exposure Study (MATES) II data were not readily available at the time of data analysis, data from these studies were not included in our analysis. Although data from a 1999 UC Berkeley Tunnel Study were proposed to be used in the initial work plan, these data were not available at the time of our data analysis, and therefore also were not used.

C-2.1. Criteria Pollutant Monitoring Network

Criteria pollutants are those that have national or state ambient air quality standards. The Air Resources Board (ARB), in conjunction with local districts, operates a criteria pollutant monitoring network throughout California. Currently, there are thirty-one monitoring sites in the SoCAB, monitoring one or more of the pollutants included in our analysis. Further details regarding each monitoring site can be found in the ARB State and Local Air Monitoring Network Plan (ARB, 1998a). Data from the statewide network are stored in the ARB ambient air quality database, Aerometric Data Analysis and Management (ADAM). The 1996-1998 data used in our analysis were extracted from the ADAM database in July 1999 and were used to represent our baseline year of 1997. Hence, changes to data that may have occurred since that time would not be reflected in our analysis, but these are expected to be small.

C-2.2. Toxic Air Contaminant (TAC) Monitoring Network

The California Air Resources Board operates a toxics sampling network, which consists of twenty-one monitoring sites throughout California. This network measures sixty-four pollutants including some of the compounds used in our analysis. Twenty-four-hour toxics samples are collected on a 1-in-12-day basis. The sampling sites in the SoCAB are Burbank-West Palm Avenue, Los Angeles-North Main Street, North Long Beach, Riverside-Rubidoux, and Upland. Both 1996 and 1997 TAC data used in this study were extracted in December 1998 from ADAM and stored on a CD-ROM available to the public (ARB, 1998b). 1998 data were not available in time to use in our analysis. The exception is data for MTBE, which were not on the CD-ROM and were extracted from ADAM in July 1999.

C-2.3. Desert Research Institute Study

Zielinska *et al.* **(**1999) at Desert Research Institute (DRI) undertook a study entitled "Air Monitoring Program for Determination of the Impacts of the Introduction of California Phase 2 Reformulated Gasoline on Ambient Air Quality in the SoCAB" in 1995-1996. The objective of this study was to conduct ambient measurements of speciated hydrocarbons, oxygenated organic gases, methane, carbon monoxide, and carbon dioxide during the summers of 1995 and 1996 in the SoCAB for providing data required to determine air quality impacts of CaRFG. In the study, samples were collected from two source-dominated sites (Burbank-West Palm Avenue and Los Angeles-North Main Street), a downwind receptor site (Azusa), and a background site (Santa Monica Beach) for forty-two days (six weeks) throughout the summers (i.e., from July to the end of September) of 1995 and 1996. Two three-hour samples were taken per sampling day, one in the morning (600 to 900) during rush hour traffic and one in the afternoon (1300 to 1600). Results for 1996 were used in our analysis.

C-2.4. Los Angeles Sepulveda Tunnel Study

Gertler *et al.* (1997) at DRI conducted an impact study of California Phase 2 Reformulated Gasoline at the Los Angeles Sepulveda Tunnel in 1995-1996. The objectives of this study were to quantify automotive emission rates of CO, NMHC, speciated hydrocarbons, NO_X, and CO_2 following the introduction of CaRFG. The Sepulveda Tunnel runs under part of the Los Angeles International Airport (LAX). Eighteen sampling experiments were performed in 1996 over the period of July 23 to July 25 during the hours of 0600 to 2000. One-Hour samples were collected at both ends of the tunnel and analyzed for CO, NMHC, various hydrocarbon species, and NO_X. Results from 17 of the 18 sampling experiments were reported by DRI and used in our analysis.

C-2.5. Bay Area Caldecott Tunnel Study

Kirchstetter *et al.* (1999a; 1999b; 1999c) at the University of California at Berkeley performed a similar CaRFG air quality impact study at the Caldecott tunnel, east of San Francisco Bay on State Highway 24, during the summers of 1994 through 1997. The tunnel was heavily used during commute hours. In the study, two-hour samples were collected for analyzing speciated hydrocarbon and carbonyls during the afternoon commute period (1600 to 1800). On selected days, additional measurements were also performed earlier in the afternoon. Concentrations of CO_2, CO, and NO_X were measured continuously and each was recorded as a five-minute average concentration. The data collected from 1996 and 1997 were used in our analysis.

C-2.6. Data Quality

The air monitoring data used in this evaluation and described above underwent various degrees of quality assurance procedures at the time the data were collected. The quality assurance procedures that apply to the data obtained from the ARB database (criteria and TAC pollutants) is described in the Quality Assurance Manual of the ARB Monitoring and Laboratory Division (ARB, 1999a). The procedures used in the special studies described above are documented in the various reports also referenced above.

C-2.7. Emission Inventory Data

Emission inventories representing summer emissions in 1997 and 2003 for the SoCAB were extracted from the California Emission Forecasting System (CEFS) (ARB, 1999b) in late May 1999. We speciated the hydrocarbon data and produced summer inventories as described in Appendix A. Additionally, 1997 annual and winter emission inventories were extracted from CEFS in late July 1999.

C-3. Establishing Baseline Air Quality Concentrations

C-3.1. Criteria Pollutants

The criteria pollutants evaluated in this study were carbon monoxide, nitrogen dioxide, ozone and particulate matter (PM_{10} and $PM_{2.5}$). Baseline concentrations to represent 1997 were based on 1996-1998 data drawn from the ARB ADAM database.

C-3.1.1. Carbon Monoxide

The maximum measured one-hour and eight-hour concentrations over the 1996-1998 period were 22.5 ppm and 17.5 ppm, respectively. Both were measured at the Lynwood monitoring station.

C-3.1.2. Nitrogen Dioxide

The maximum measured one-hour and daily-average concentrations over the 1996-1998 period were 0.255 ppm and 0.117 ppm, respectively. The one-hour maximum was measured at the Banning monitoring station and the maximum daily-average concentration was measured at the Los Angeles-North Main monitoring station. A maximum annual-average concentration of 0.043 ppm was measured at the Pomona monitoring station.

C-3.1.3. Ozone

The maximum measured one-hour and eight-hour concentrations over the 1996-1998 period were 0.244 ppm and 0.206 ppm, respectively. Both were measured at the Lake Gregory monitoring station.

C-3.1.4. Particulate Matter (PM_{10} and $PM_{2.5}$)

The maximum measured PM_{10} daily-average concentration over the 1996-1998 period was 227 $\mu g/m^3$, measured at the Banning monitoring station. The maximum PM_{10} annual geometric mean concentration of 56 $\mu g/m^3$ was measured at the Riverside-Rubidoux monitoring station. The maximum measured $PM_{2.5}$ daily-average concentration over the 1996-1998 period was 81 $\mu g/m^3$, measured at the North Long Beach monitoring station. The maximum $PM_{2.5}$ annual average concentration of 25.9 $\mu g/m^3$ was measured at the Riverside-Rubidoux monitoring station.

C-3.2. Toxic Pollutants

The toxic pollutants evaluated in our analysis included benzene, 1,3-butadiene, MTBE, acetaldehyde, formaldehyde, toluene, and xylenes. Isobutene, *n*-hexane, and *n*-heptane are also discussed in this section because estimates for these three compounds involve the same analytical procedures. Baseline pollutant concentrations to represent 1997 were based on 1996-1997 data drawn from the ARB toxics database, from DRI data, and from correlation analyses using these same data, tunnel study results and criteria pollutant data. Different approaches were used for different groups of toxic compounds.

C-3.2.1. Benzene, 1,3-Butadiene, and MTBE

Two different approaches were used to estimate benzene, 1,3-butadiene, and MTBE concentrations representative of 1997. First, we used measured concentrations directly from the toxics sampling network. In addition, we developed ratios between these toxic compounds and carbon monoxide and used them to estimate concentrations at locations where there were no direct toxics measurements, but there were CO measurements. This latter approach allowed us to estimate pollutant concentrations at nineteen locations, rather than the five locations for which toxics sampling data are available. The two approaches provide a range in estimates. The next section discusses the rationale for correlating CO with other compounds. The section after that describes the method and results.

C-3.2.1.1. Rationale for Using Ratios of CO to Other Compounds

The concept of establishing a relationship between CO and other pollutants is based on the premise that these pollutants are principally emitted from mobile sources and that for the most part they are primary pollutants. Thus, if CO concentrations are high at a particular site, the related pollutants can be expected to be high as well. This premise is reasonably straightforward for compounds that are primary pollutants and for compounds with low reactivity. However, the relationship holds as well for 1,3-butadiene, which has much higher reactivity. In part, this is because the peak concentrations for both CO and 1,3-butadiene occur during the winter months when photochemistry is minimal. Additionally, the continual infusion of fresh emissions, the ubiquitous presence of mobile sources, and their relatively close proximity to monitoring sites means that there is little time for atmospheric reaction prior to being measured.

Ultimately, we found good correlation between CO and benzene, 1,3-butadiene, MTBE, toluene, *n*-heptane, *n*-hexane, isobutene, the three xylenes, and the alkylates. The specific application of the resulting relationships is discussed in the following sections covering the respective pollutants. Table 3.1 presents the lifetime and the maximum incremental reactivity MIR of selected compounds.

C-3.2.1.2. Development of Ratios Between Toxic Compounds and CO

To estimate toxics concentrations at locations other than those where toxic compounds are sampled, we developed ratios between toxic compounds and CO. The general procedure for determining the ratio between a TAC and CO is described below. The same procedure was applied to all TACs except the aldehydes.

The first step was to extract the TAC and CO data from the aforementioned data sets and select sites where both TACs and CO were measured. CO was not measured at the Upland site (one of five sites in the TAC monitoring network in the SoCAB) in 1996 or 1997, so data collected at Upland were not used in the subsequent calculations. As for the DRI data set, both the AM data and the combined AM plus PM data were analyzed

Table 3.1 Calculated Atmospheric Lifetimes and MIRs for Selected Compounds

Compound	Atmospheric Lifetime[a]	MIR[b]
	(daylight hours)	(g ozone/g NMOG)
Acetaldehyde	5.9	7.25
Alkylates	9.3-92.6	1.0-2.3
Benzene	75.3	0.91
1,3-Butadiene	1.4	12.88
Carbon Monoxide	440.9	0.066
Ethanol	28.3	1.88
Formaldehyde[c]	9.9	9.27
n-Hexane	17.0	1.71
n-Heptane	13.2	1.48
Isobutene	1.8	6.59
MTBE	31.5	0.88
Toluene	15.5	4.24
m-Xylene	3.9	11.04
o-Xylene	6.8	7.87
p-Xylene	6.5	4.56

a. The atmospheric lifetime for each compound was calculated based on the recommended OH rate constants (Atkinson, 1994) and a 12-hr average OH radical concentration of $3.0\text{x}10^6$ molecule/cm^3.

b. Maximum Incremental Reactivity (Carter W.P.L, 1999.)

c. The atmospheric lifetime for formaldehyde is estimated based on the photolysis rate of formaldehyde, which dominates over gas-phase reaction with OH radicals.

separately in this study to consider possible differences between the morning period of direct source contribution and overall behavior during the day.

Then we estimated representative background concentrations and subtracted them from the extracted data. The background subtraction was to facilitate development of a single basin-wide ratio between a TAC and CO. Because there was no significant natural sources for the toxic compounds studied (except aldehydes), atmospheric background for each TAC was determined to be negligible (zero). However, for CO the background was estimated to be 100 ppb, based on measurements at Santa Catalina Island, Point Conception, and San Nicholas Island during SCOS97-NARSTO.

The next step was to exclude concentrations below the level of detection (LOD) and some outliers because such values could distort the ratios being calculated. For the TAC monitoring network data set, for example, 19 benzene data values and two CO data values (out of 109 pairs of matched data values collected in the SoCAB in 1996) were below their LOD values (ARB, 1998b). As for outliers, two exceptionally high benzene concentrations, observed on July 7, 1996 (AM) and July 8, 1996 (PM) in the DRI data, were also excluded in subsequent calculations.

Finally, a least-square linear regression technique was applied to the TAC and CO data and the regression line forced through the origin. Then, the TAC to CO ratios and correlation coefficients were calculated.

The specific application of these procedures to develop ratios to CO for benzene, 1,3-butadiene, and MTBE are discussed further below.

C-3.2.1.2.1. Benzene

Table 3.2 summarizes the ratios and correlation coefficients between benzene and CO derived from the five data sets. Ratios calculated from the emission data were based on ratios of benzene emissions to CO emissions estimated for all sources and for just on-road sources, respectively. In general, good correlation between benzene and CO data was observed, except for the 1997 Caldecott data set. No significant difference in ratios was observed between the DRI AM and AM plus PM data sets. Except for those derived from the Caldecott data sets, the benzene to CO ratios range from 0.81 to 1.21 (ppb/ppm). Statewide ratios between benzene and CO derived from TAC data collected throughout the state in 1996 and 1997 are 1.03 and 0.88 (ppb/ppm), respectively. A ratio of 1.0 (ppb/ppm) was selected as a reasonable ratio of benzene to CO.

Figure 3.1 shows a scatterplot of benzene versus CO for the SoCAB TAC samples collected in 1996. Data collected in different sites are represented by different symbols. Scatterplots of benzene versus CO for the DRI data and the Sepulveda tunnel data are shown in Figure 3.2 and Figure 3.3, respectively.

C-3.2.1.2.2. 1,3-Butadiene

Table 3.3 summarizes the ratios and correlation coefficients for 1,3-butadiene to CO derived from the aforementioned data sets. Good correlation between 1,3-butadiene and CO was observed for all data sets except the two tunnel studies and Riverside data. The ratios range from 0.22 to 0.34 (ppb/ppm), except those obtained from Caldecott tunnel data. Statewide ratios calculated from TAC data collected throughout California in 1996 and 1997 are 0.29 and 0.28 (ppb/ppm), respectively. A ratio of 0.30 (ppb/ppm) was selected as a reasonable ratio of 1,3-butadiene to CO. Scatterplots of 1,3-butadiene versus CO are presented in Figure 3.4, Figure 3.5, and Figure 3.6 for 1996 TAC data, DRI data, and Sepulveda tunnel data, respectively.

C-3.2.1.2.3. MTBE

Table 3.4 summarizes the ratios and correlation coefficients for MTBE to CO derived from the same data sets described above. Good correlation was observed for the DRI data set and the 1997 TAC data. However, correlation was poor for the Caldecott tunnel data and the 1996 Long Beach data. The ratios obtained from the TAC network data and the DRI data range from 2.6 to 4.6 (ppb/ppm), while the ratios derived from emission inventory and tunnel data are substantially lower. Based on these results, a ratio of 3.0 (ppb/ppm) was selected as a reasonable ratio of MTBE to CO. Scatterplots of MTBE versus CO are shown in Figure 3.7, Figure 3.8, and Figure 3.9 for 1996 TAC data, DRI data, and Sepulveda data, respectively.

Table 3.2 Linear Regression Parameters for Correlations Between Ambient Concentrations of Benzene and CO[a]

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	R^2	Ratio	R^2	Ratio	R^2	Ratio	R^2	All Sources	On-road Sources
1996										
California Statewide[c]	1.03	0.61								
South Coast Air Basin[c]	0.90	0.76	1.10	0.93	1.11	0.91			1.21	1.18
Burbank	0.86	0.66	1.14	0.98	1.14	0.98				
Los Angeles	0.84	0.92	1.03	0.89	1.05	0.90				
Long Beach	1.13	0.81								
Riverside	0.98	0.69								
Azusa			1.17	0.95	1.19	0.86				
Sepulveda Tunnel							1.10	0.96		
Caldecott Tunnel							0.59	0.76		
1997										
California Statewide[c]	0.88	0.82								
South Coast Air Basin[c]	0.80	0.89								
Burbank	0.78	0.84								
Los Angeles	0.82	0.95								
Long Beach	0.81	0.88								
Caldecott Tunnel							0.53	0.46		

a. Concentration units are ppmv for CO and ppbv for benzene. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

c. Statewide and basin-wide ratios and correlation coefficients were calculated using the data collected statewide and in the SoCAB, respectively.

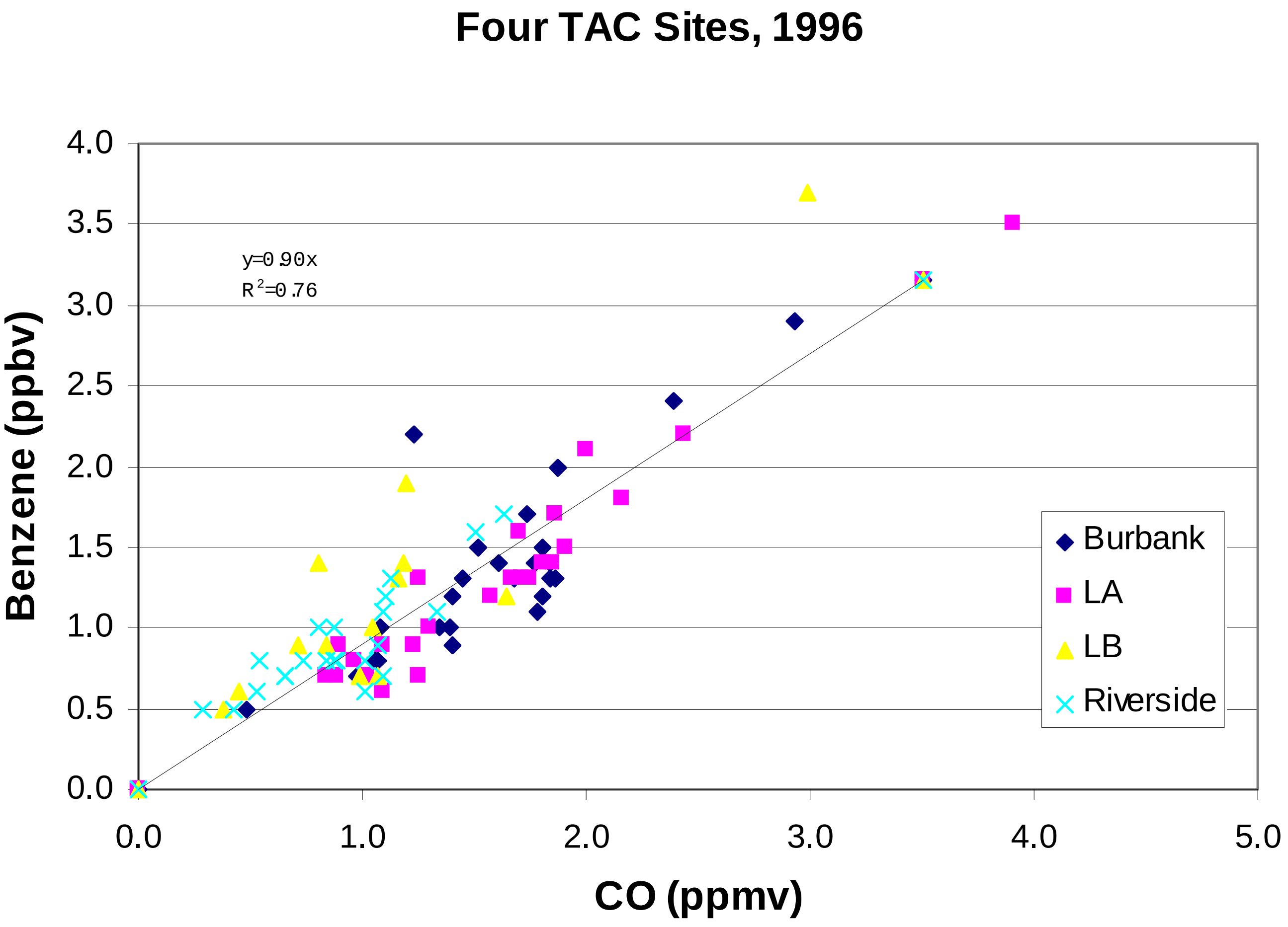

Figure 3.1 Benzene versus CO for SoCAB (Four TAC Sites, 1996)

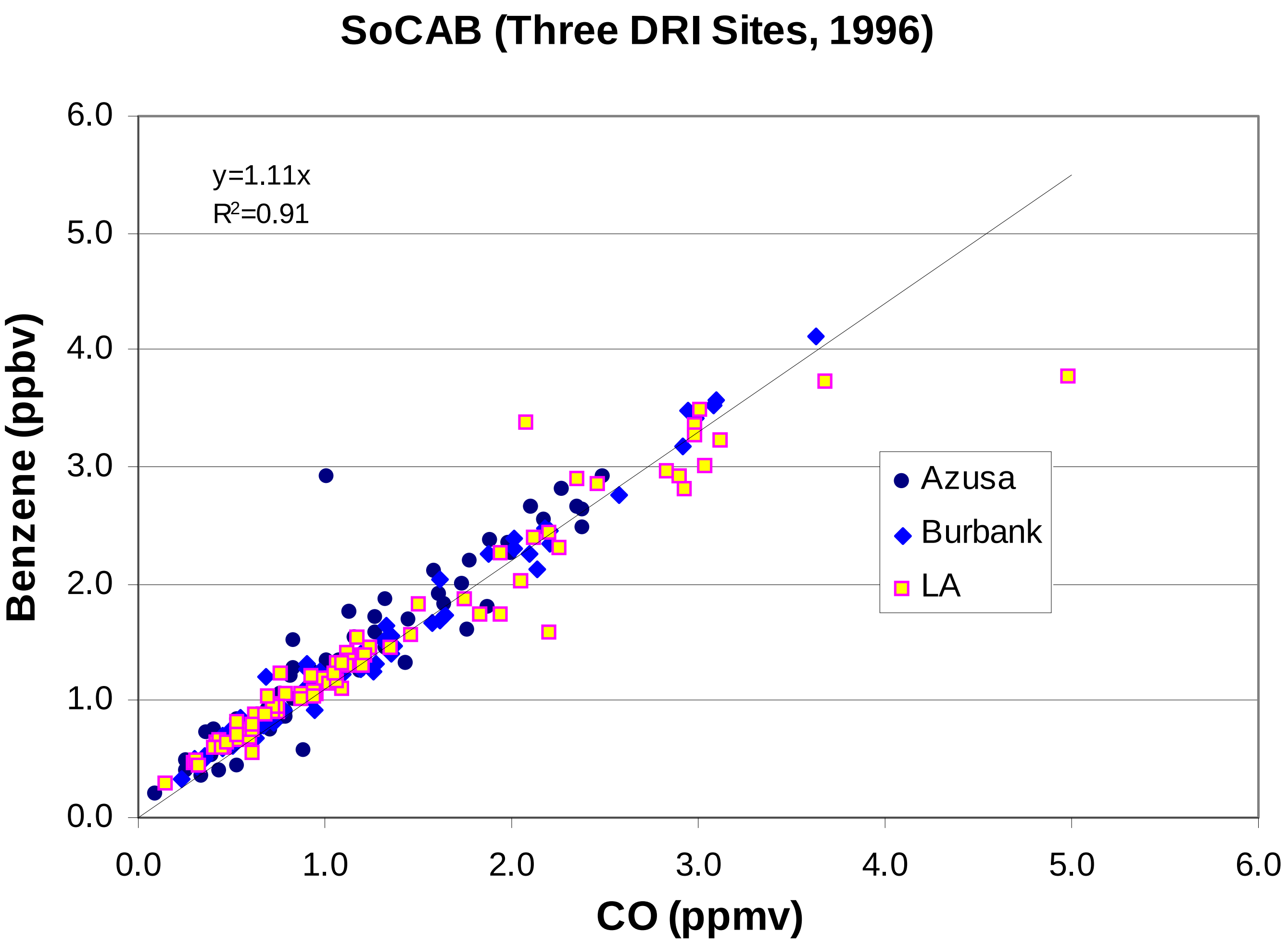

Figure 3.2 Benzene versus CO for SoCAB (Three DRI Sites, 1996)

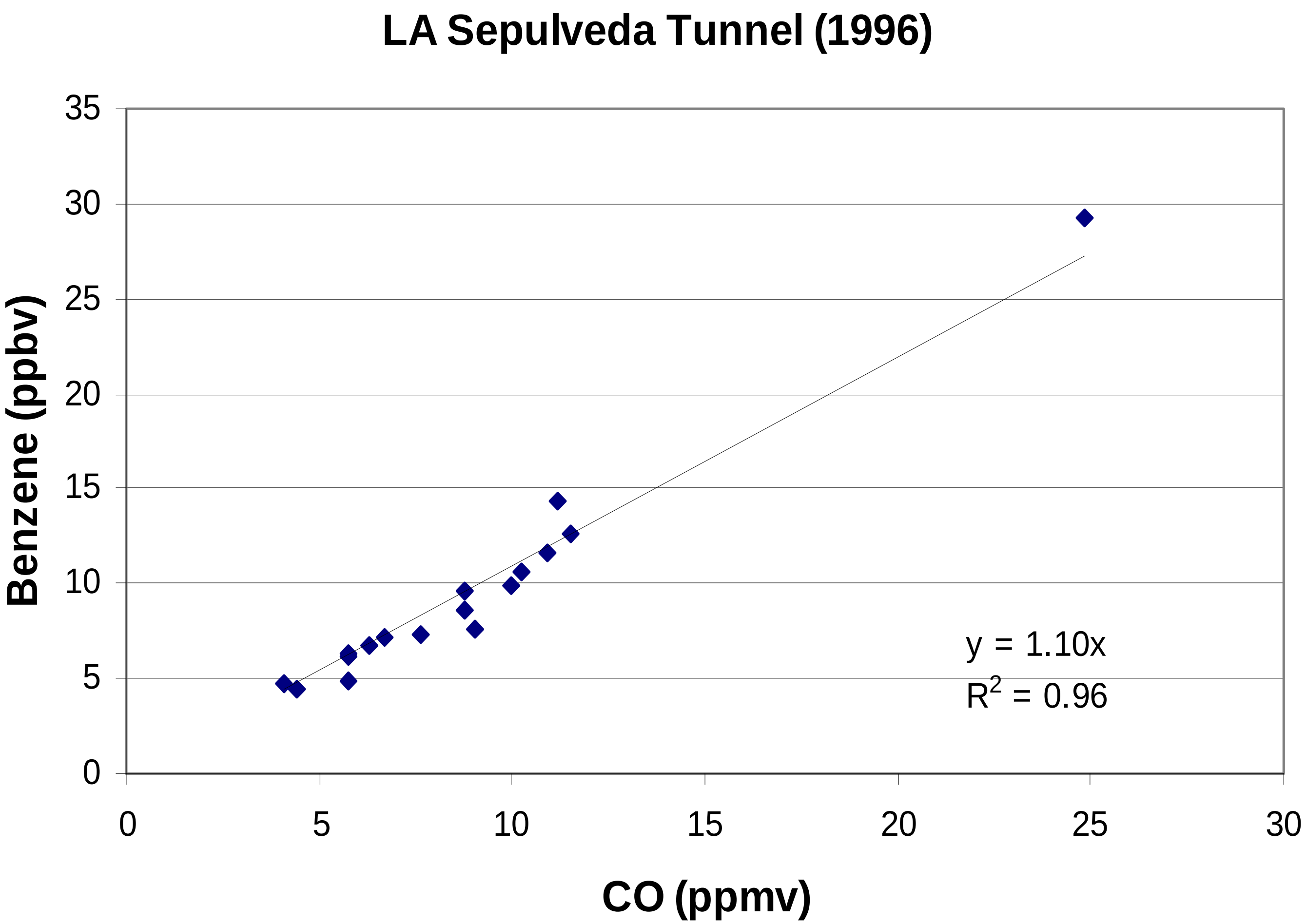

Figure 3.3 Benzene versus CO for LA Sepulveda Tunnel (1996)

Table 3.3 Linear Regression Parameters for Correlations Between Ambient Concentrations of 1,3-Butadiene and CO[a]

	TAC Network		**DRI Data (AM)**		**DRI Data (AM&PM)**		**Tunnel Data**		**Emission Inventory[b]**	
	Ratio	**R^2**	**Ratio**	**R^2**	**Ratio**	**R^2**	**Ratio**	**R^2**	**All Sources**	**On-road Sources**
1996										
California Statewide[c]	0.29	0.79								
South Coast Air Basin[c]	0.27	0.84	0.26	0.76	0.24	0.71			0.33	0.32
Burbank	0.26	0.85	0.26	0.78	0.23	0.72				
Los Angeles	0.27	0.90	0.25	0.68	0.24	0.72				
Long Beach	0.34	0.68								
Riverside	0.26	0.46								
Azusa			0.27	0.83	0.22	0.64				
Sepulveda Tunnel							0.24	0.57		
Caldecott Tunnel							0.13	0.02		
1997										
California Statewide[c]	0.28	0.81								
South Coast Air Basin[c]	0.28	0.82								
Burbank	0.25	0.84								
Los Angeles	0.30	0.90								
Long Beach	0.30	0.74								
Caldecott Tunnel							0.15	0.28		

a. Concentration units are ppmv for CO and ppbv for 1,3-butadiene. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

c. Statewide and basin-wide ratios and correlation coefficients were calculated using the data collected statewide and in the SoCAB, respectively.

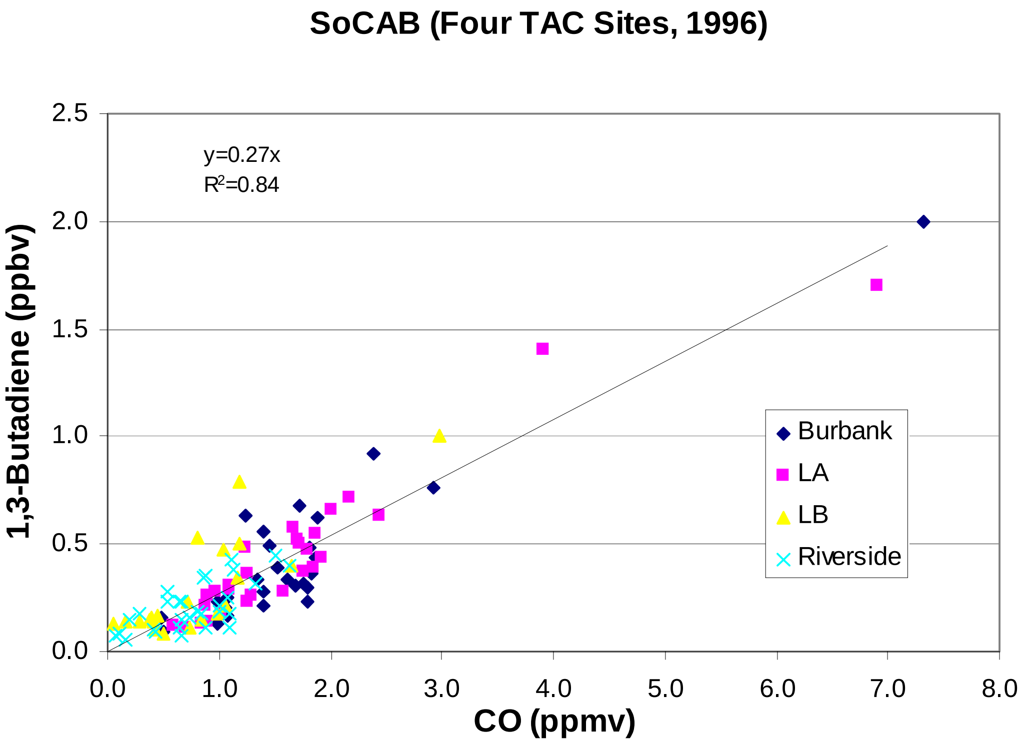

Figure 3.4 1,3-Butadiene versus CO for SoCAB (Four TAC Sites, 1996)

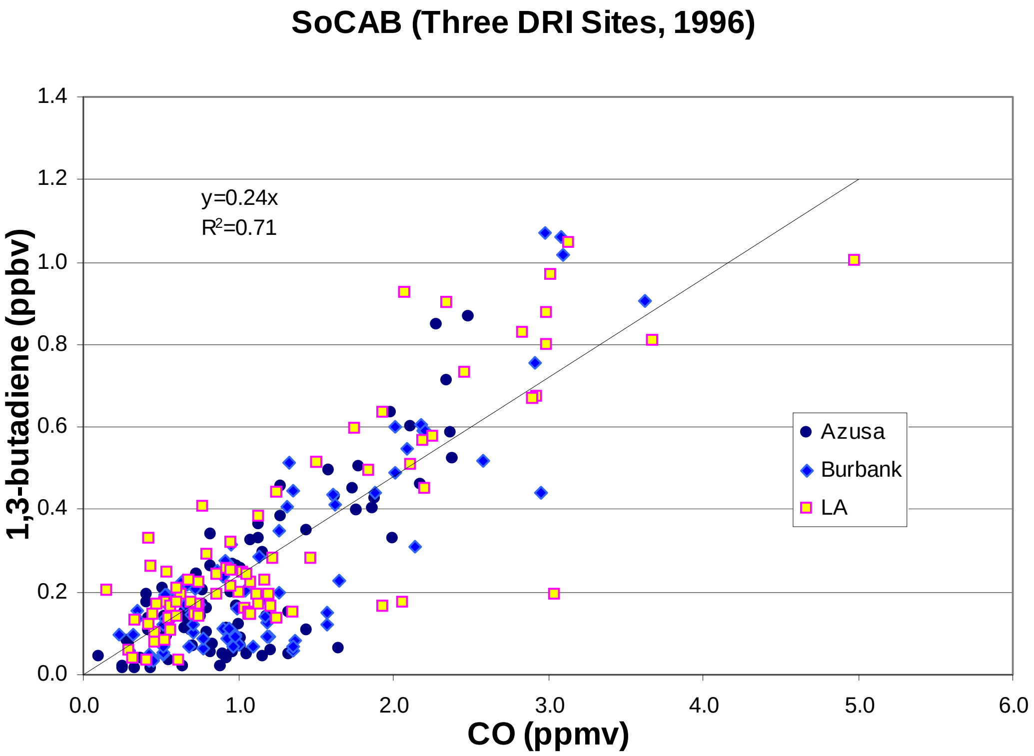

Figure 3.5 1,3-Butadiene versus CO for SoCAB (Three DRI Sites, 1996)

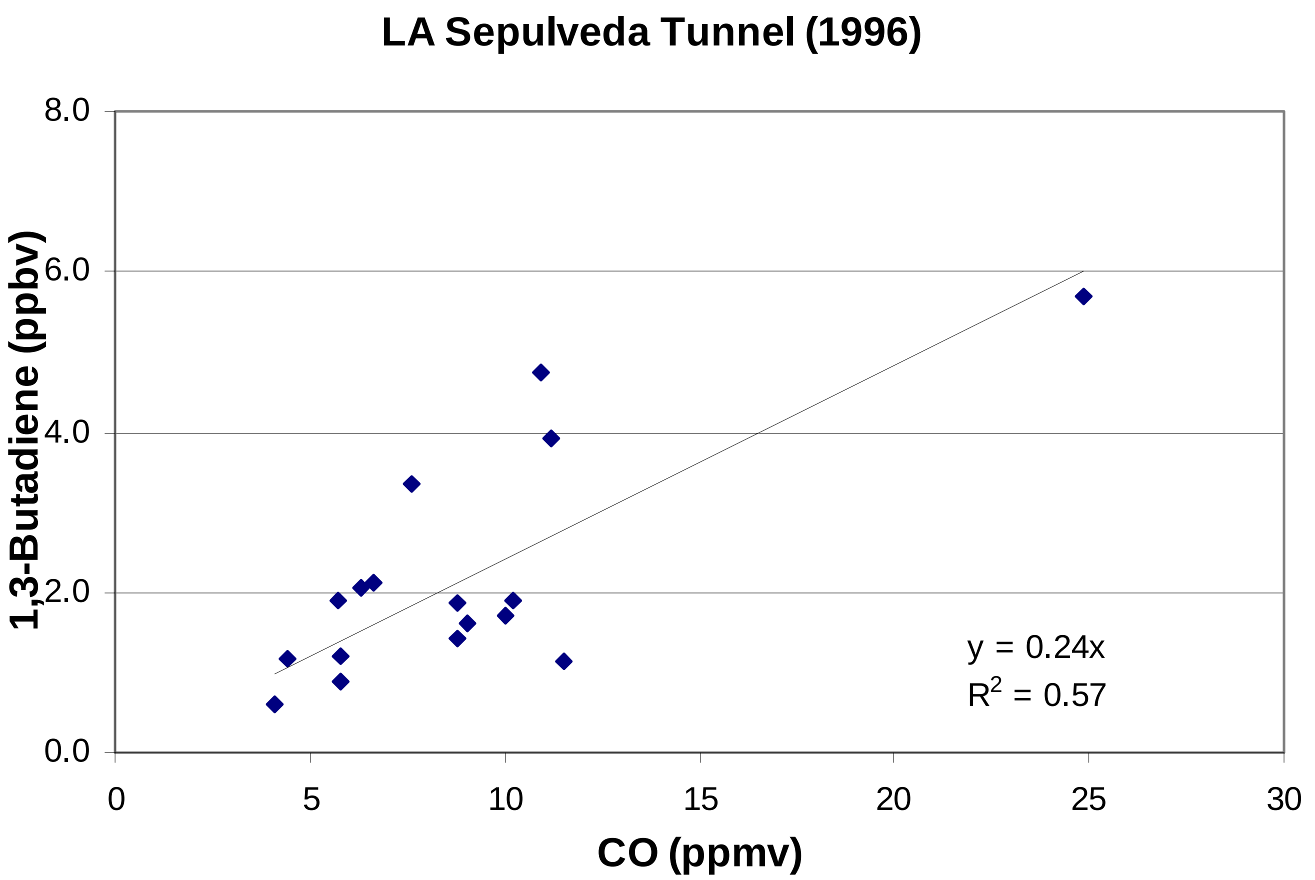

Figure 3.6 1,3-Butadiene versus CO for LA Sepulveda Tunnel (1996)

Table 3.4 Linear Regression Parameters for Correlations Between Ambient Concentrations of MTBE and CO[a]

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	R^2	Ratio	R^2	Ratio	R^2	Ratio	R^2	All Sources	On-road Sources
1996										
South Coast Air Basin[c]	2.90	0.59	4.06	0.84	4.13	0.83			1.82	2.31
Burbank	3.07	0.71	4.56	0.96	4.61	0.95				
Los Angeles	2.66	0.72	3.43	0.81	3.51	0.84				
Long Beach	3.37	0.10								
Riverside										
Azusa			4.45	0.90	4.59	0.79				
Sepulveda Tunnel							2.28	0.93		
Caldecott Tunnel							0.88	0.35		
1997										
South Coast Air Basin[c]	3.00	0.88								
Burbank	3.25	0.90								
Los Angeles	2.59	0.93								
Long Beach	3.12	0.91								
Caldecott Tunnel							0.62	0.33		

a. Concentration units are ppmv for CO and ppbv for MTBE. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

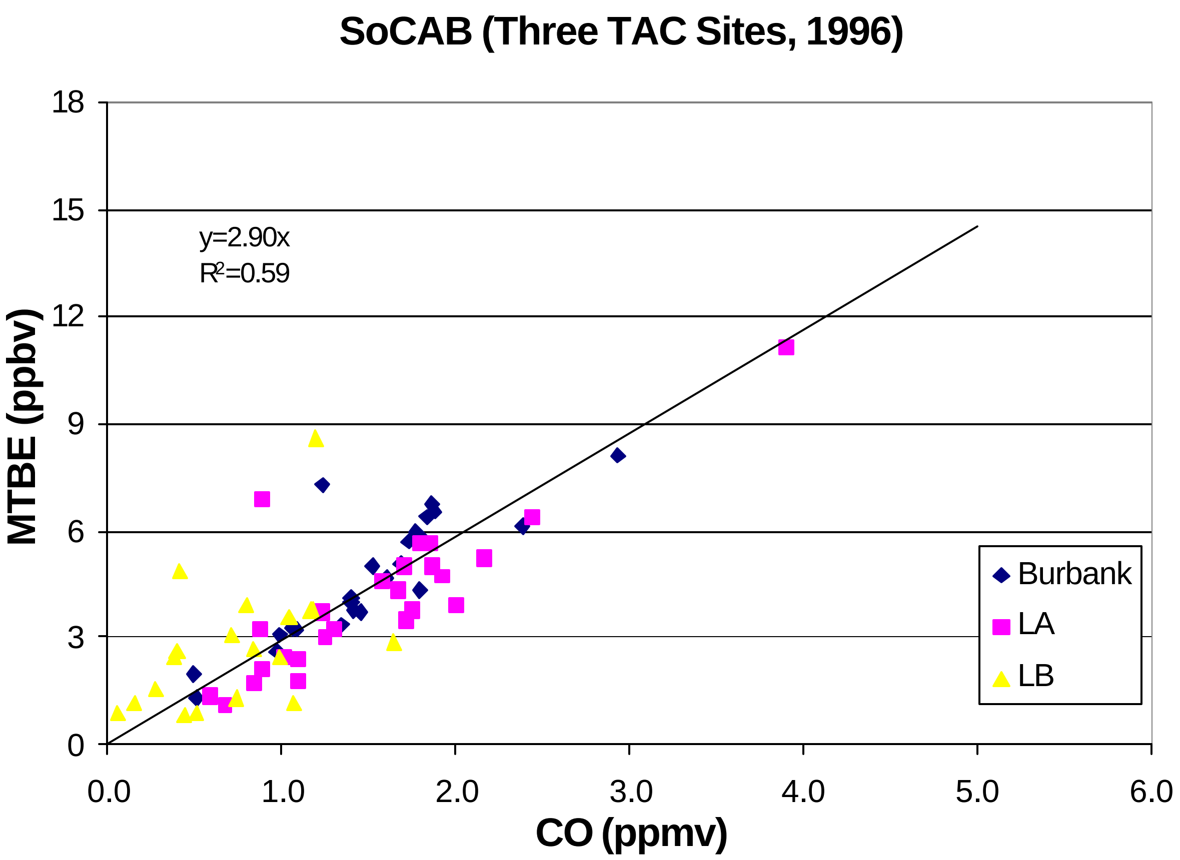

Figure 3.7 MTBE versus CO for SoCAB (Three TAC Sites, 1996)

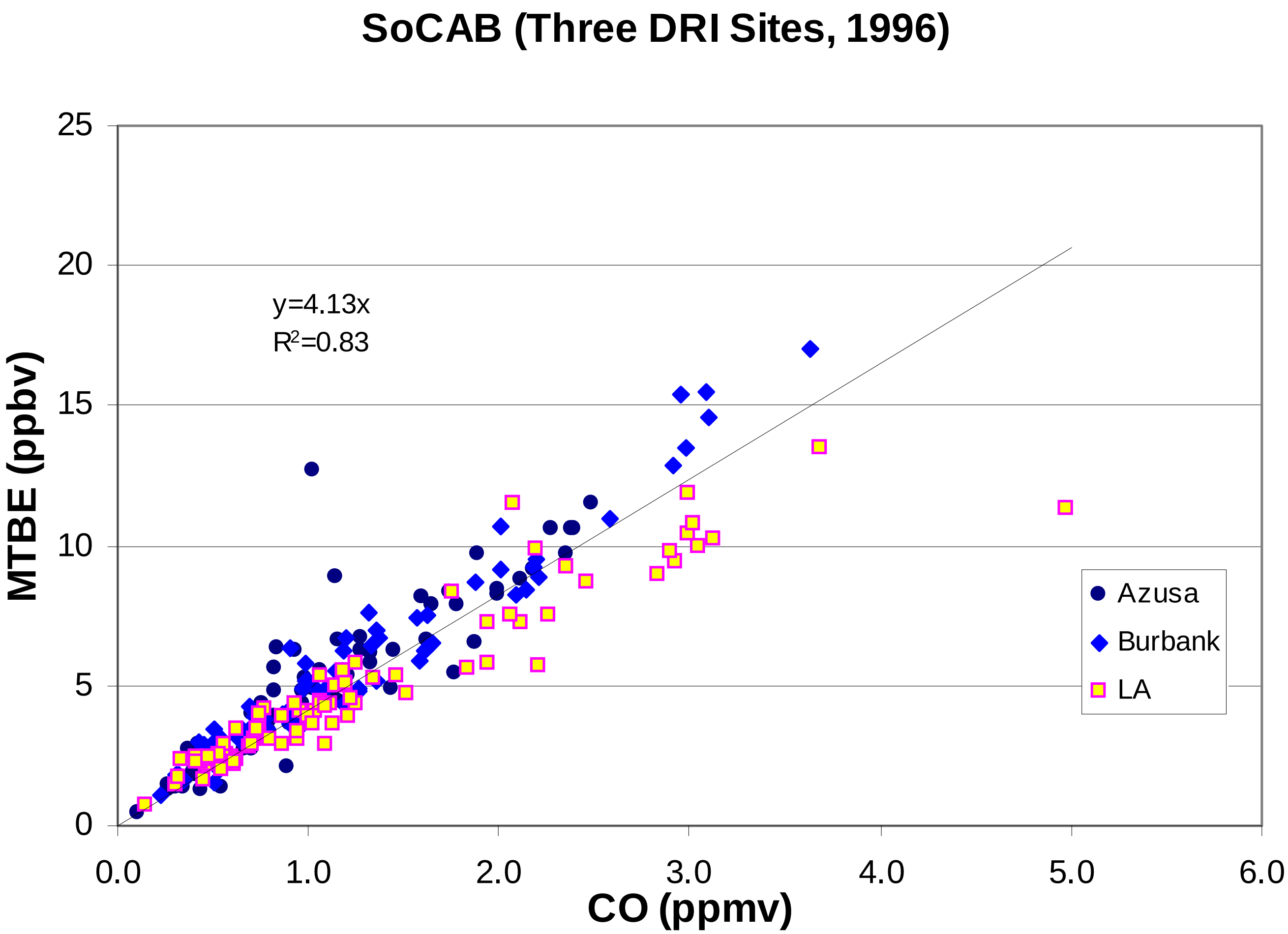

Figure 3.8 MTBE versus CO for SoCAB (Three DRI Sites, 1996)

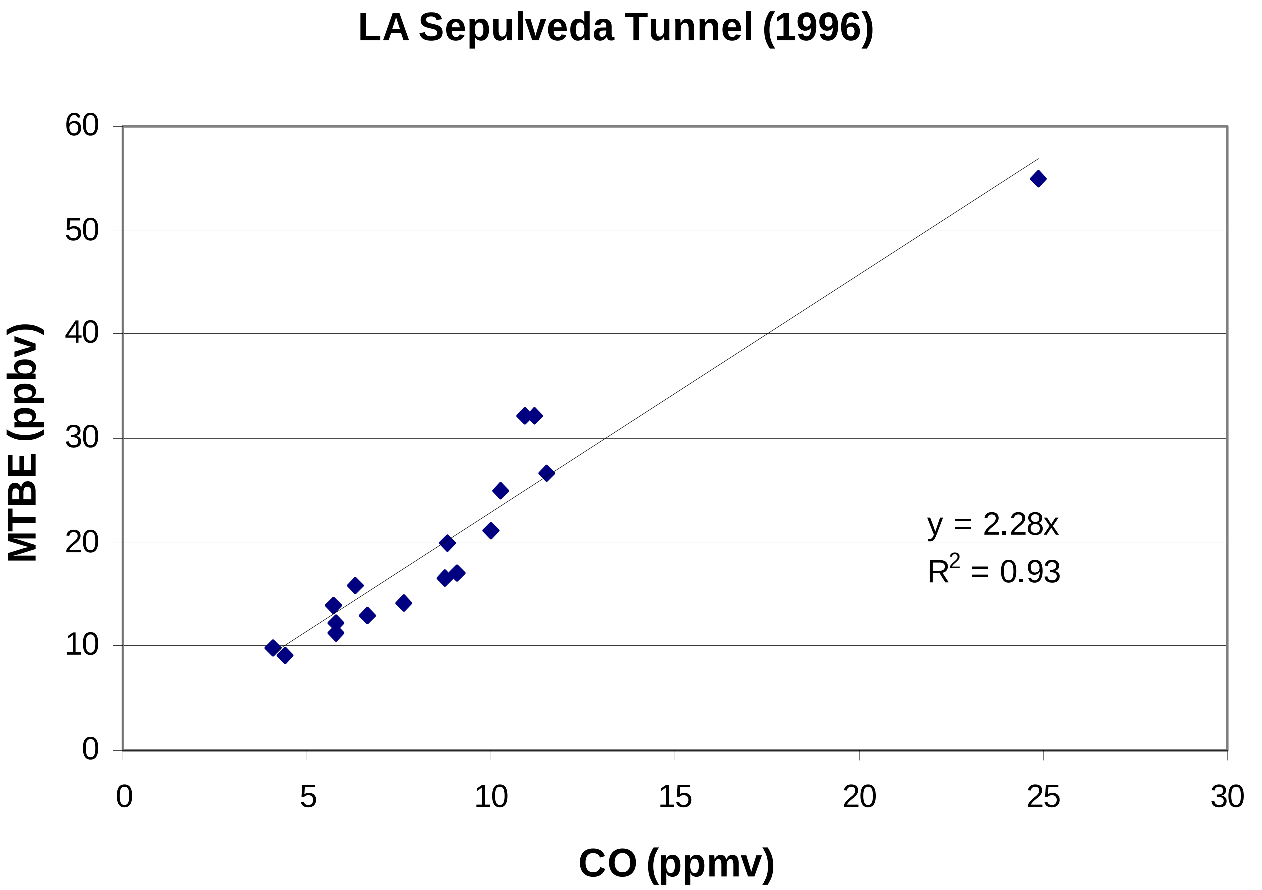

Figure 3.9 MTBE versus CO for LA Sepulveda Tunnel (1996)

C-3.2.1.3. Estimated 1997 Concentrations

In our analyses, we estimated 1997 benzene, 1,3-butadiene, and MTBE concentrations for the maximum daily average, the maximum one-hour average, and the population-weighted annual exposure.

C-3.2.1.3.1. Maximum Daily Average

The maximum measured daily-average benzene concentration in the SoCAB from 1996 to 1997 was 7.4 ppb, measured at Burbank on January 10, 1996. The maximum measured daily-average CO concentration in the SoCAB between 1996 and 1998 was 9.6 ppm, measured at Lynwood on November 1, 1997. Subtracting 0.1 ppm background from this and multiplying it by the benzene to CO ratio of 1.0 (ppb/ppm), the estimated maximum daily-average benzene concentration at Lynwood is 9.5 ppb.

The maximum measured daily-average 1,3-butadiene concentration in the SoCAB from 1996 to 1997 was 2.0 ppb, measured at Burbank on January 10, 1996. Multiplying the background-adjusted maximum daily-average CO concentration (9.5 ppm) by the 1,3-butadiene to CO ratio of 0.3 (ppb/ppm), the estimated maximum daily-average 1,3-butadiene concentration at Lynwood is 2.9 ppb.

The maximum measured daily-average MTBE concentration in the SoCAB from 1996 to 1997 was 13 ppb, measured at Burbank on November 24, 1997. Multiplying the background-adjusted maximum daily-average CO concentration (9.5 ppm) by the MTBE to CO ratio of 3.0 (ppb/ppm), the estimated maximum daily-average MTBE concentration at Lynwood is 29 ppb.

C-3.2.1.3.2. Maximum One-Hour Average

The maximum measured daily-average benzene concentration in the SoCAB from 1996 to 1997 was 7.4 ppb, measured at Burbank on January 10, 1996. The corresponding maximum one-hour and daily-average CO concentrations at Burbank on this day were 11.6 ppm and 7.43 ppm, respectively. Assuming that benzene concentrations vary during the day in proportion to CO concentrations (since they are both primarily emitted by motor vehicles and affected by the same meteorology), the estimated maximum one-hour benzene concentration at Burbank is 11.6 ppb. The maximum measured one-hour-average CO concentration in the SoCAB between 1996 and 1998 was 22.5 ppm, measured at Lynwood on January 6, 1996. Subtracting 0.1 ppm background from this and multiplying it by the benzene to CO ratio of 1.0 (ppb/ppm), the estimated maximum benzene concentration at Lynwood is 22.4 ppb.

The maximum measured daily-average 1,3-butadiene concentration in the SoCAB from 1996 to 1997 was 2.0 ppb, measured at Burbank on January 10, 1996. The corresponding maximum one-hour and daily-average CO concentrations at Burbank on this day were 11.6 ppm and 7.43 ppm, respectively. Assuming that 1,3-butadiene concentrations vary during the day in proportion to CO concentrations (since they are both primarily emitted by motor vehicles and affected by the same meteorology), the estimated maximum one-hour 1,3-butadiene concentration at Burbank is 3.1 ppb.

Multiplying the background-adjusted maximum one-hour-average CO concentration (22.4 ppm) by the 1,3-butadiene to CO ratio of 0.3 (ppb/ppm), the estimated maximum 1,3-butadiene concentration at Lynwood is 6.7 ppb.

The maximum measured daily-average MTBE concentration in the SoCAB from 1996 to 1997 was 13 ppb, measured at Burbank on November 24, 1997. The corresponding maximum one-hour and daily-average CO concentrations at Burbank on this day were 5.9 ppm and 4.03 ppm, respectively. Assuming that MTBE concentrations vary during the day in proportion to CO concentrations (since they are both primarily emitted by motor vehicles and affected by the same meteorology), the estimated maximum one-hour MTBE concentration at Burbank is 19 ppb. Multiplying the background-adjusted maximum one-hour-average CO concentration (22.4 ppm) by the MTBE to CO ratio of 3.0 (ppb/ppm), the estimated maximum MTBE concentration at Lynwood is 67 ppb.

C-3.2.1.3.3. Population-Weighted Annual Exposure

In calculating health risks, the Office of Environmental Health Hazard Assessment (OEHHA) uses population-weighted annual pollutant exposure as an indicator of the concentration to which a typical person is exposed to toxic substances. For benzene, 1,3-butadiene, and MTBE, population-weighted annual-average exposure was calculated two ways.

The first way used available data from the five toxics monitoring sites in the SoCAB. Annual averages for 1996 and 1997 were averaged for the individual monitoring sites. Then the population-weighted annual-average concentration was estimated by interpolating between the five monitoring sites using a previously developed technique (ARB, 1993). This interpolation process starts with population data by census tract and an associated centroid. Then data for any monitoring site within 50 kilometers of the centroid is used in determining a representative concentration to which people in the census tract are exposed. In determining this representative concentration, the contribution from each monitoring site is weighted in proportion to the inverse of the square of the distance from the population centroid to the monitoring site. To determine the population-weighted exposure, the population of individual census tracts is multiplied by their representative concentration, summed over all census tracts and then divided by the total population across all census tracts. The resulting population-weighted annual-average concentrations calculated to represent the SoCAB in 1997 were 1.1 ppb for benzene, 0.34 ppb for 1,3-butadiene, and 3.9 ppb for MTBE, respectively.

The second way used an average of annual-average CO concentrations for 1996-1998 to calculate benzene, 1,3 butadiene and MTBE concentrations at nineteen monitoring locations in the SoCAB using the ratios to CO described in Section C-3.2.1.2 applied to the background-adjusted CO concentrations. Population-weighted annual-average concentrations of 1.2 ppb benzene, 0.36 ppb 1, 3-butadiene, and 3.6 ppb MTBE were calculated using the interpolation and averaging procedure described in the paragraph above.

C-3.2.2. Acetaldehyde and Formaldehyde

Three different approaches were considered in estimating acetaldehyde and formaldehyde concentrations representative of 1997. First was the use of measured concentrations directly from the toxics sampling network. Second was the use of results from the air quality model simulations. Third was developing relationships between aldehydes and CO and oxidant so aldehyde concentrations could be estimated at many more locations than are sampled with the toxics monitoring network. Our attempt to correlate aldehydes with CO and oxidant was not considered sufficiently reliable and was abandoned. A brief discussion of that effort is presented in Section C-3.2.2.2.

C-3.2.2.1. Estimated 1997 Concentrations

In our analyses, we estimated 1997 acetaldehyde and formaldehyde concentrations for the maximum daily average, the maximum one-hour average, and the population-weighted annual exposure.

C-3.2.2.1.1. Maximum Daily Average

The maximum measured daily-average acetaldehyde concentration in the SoCAB from 1996 to 1997 was 5.1 ppb, measured at Upland on August 13, 1996. The maximum measured daily-average formaldehyde concentration in the SoCAB from 1996 to 1997 was 14.0 ppb, measured at Upland on August 13, 1996. In addition, the regional air quality model simulation for 1997 predicted the basin-wide maximum acetaldehyde and formaldehyde concentrations to be 6.2 ppb and 11.35 ppb, respectively. Since the maximum formaldehyde concentration predicted is lower than the maximum measured value, we considered the measured value to be more representative of the maximum concentration.

C-3.2.2.1.2. Maximum One-Hour Average

The maximum one-hour aldehyde concentrations were estimated three ways using three data sources.

First, three-hour DRI data were used as a basis. The maximum three-hour acetaldehyde concentration measured was 13.88 ppb at Azusa on August 28, 1996 between 1300 and 1600 PDT. Corresponding three-hour and maximum one-hour ozone concentrations for this period are 0.11 ppm and 0.14 ppm, respectively. Assuming that acetaldehyde concentrations vary in the afternoon in proportion to ozone concentrations (since both are strongly influenced by atmospheric chemical reactions at this time of day), the estimated maximum one-hour acetaldehyde concentration at Azusa is 17.7 ppb. Similarly for formaldehyde, the maximum 3-hour measurement of 18.17 ppb was in the afternoon on August 29, 1996 in Burbank. The corresponding estimated one-hour maximum is 20.3 ppb.

Second, TAC daily-average data were used. The maximum daily-average acetaldehyde concentration at Upland, measured on August 13, 1996, was 5.1 ppb. The average ratio of maximum one-hour average to daily-average ozone for monitors operating in the SoCAB on August 13, 1996 was 2.7. Assuming that acetaldehyde concentrations at Upland in August vary in proportion to ozone concentrations (photochemical model simulations indicate that over 90% of the acetaldehyde and 85% of the formaldehyde at Upland is from atmospheric chemical reactions on high ozone days), the maximum one-hour acetaldehyde concentration estimated for Upland is 13.8 ppb. Similarly, the maximum daily-average formaldehyde concentration at Upland, measured on August 13, 1996, was 14 ppb and the corresponding estimated maximum one-hour concentration is 37.8 ppb.

Third, the regional air quality model simulation for 1997 predicted the basin-wide maximum acetaldehyde and formaldehyde concentrations to be 9.2 ppb and 22.7 ppb, respectively. Since the model maximum one-hour acetaldehyde concentration of 9.2 ppb was less than the maximum three-hour measured value, we considered the estimates made using the measured values to be more representative of maximum concentrations.

C-3.2.2.1.3. Population-Weighted Annual Exposure

There are five monitoring sites in the SoCAB at which acetaldehyde and formaldehyde measurements were made between 1996 and 1997. The population-weighted annual-average concentrations were calculated using the interpolation and averaging procedure described in Section C-3.2.1.3.3 above. The resulting population-weighted annual-average concentrations calculated to represent the SoCAB in 1997 are 1.75 ppb for acetaldehyde and 4.65 ppb for formaldehyde.

C-3.2.2.2. Attempt to Correlate Aldehydes with CO and Oxidant

To provide a broader base of data for estimating aldehyde concentrations, an attempt was made to correlate acetaldehyde and formaldehyde concentrations with carbon monoxide and oxidant (O_3+NO_2) concentrations. CO was used as an index of primary aldehyde emissions and oxidant as an index of the secondary aldehyde produced through chemical reactions in the atmosphere. To develop a relationship with CO, we plotted aldehydes versus CO using both the TAC data and 0600 to 0900 data for 1996 from the DRI study. Because some of the measured acetaldehyde and formaldehyde may be secondary in origin, we opted to estimate a ratio between primary aldehydes and CO by plotting the aldehyde to CO ratio versus CO and identifying the minimum ratio that generally had most if not all of the points above it. For formaldehyde from the toxics monitoring network, the minimum ratio was 1.4 ppb/ppm CO (see Figure 3.10). For DRI formaldehyde data, the minimum ratio was 2.1 (see Figure 3.11). For acetaldehyde, the minimum ratio was 0.50 (see Figure 3.12) for TAC data and 0.95 (see Figure 3.13) for the DRI data. In developing these minimum ratios we first subtracted background concentrations of 0.1 ppm CO and 0.5 ppb acetaldehyde or formaldehyde from the measured values. These background concentrations were determined from measurements at Santa Catalina Island, Point Conception, and San Nicholas Island during SCOS97-NARSTO.

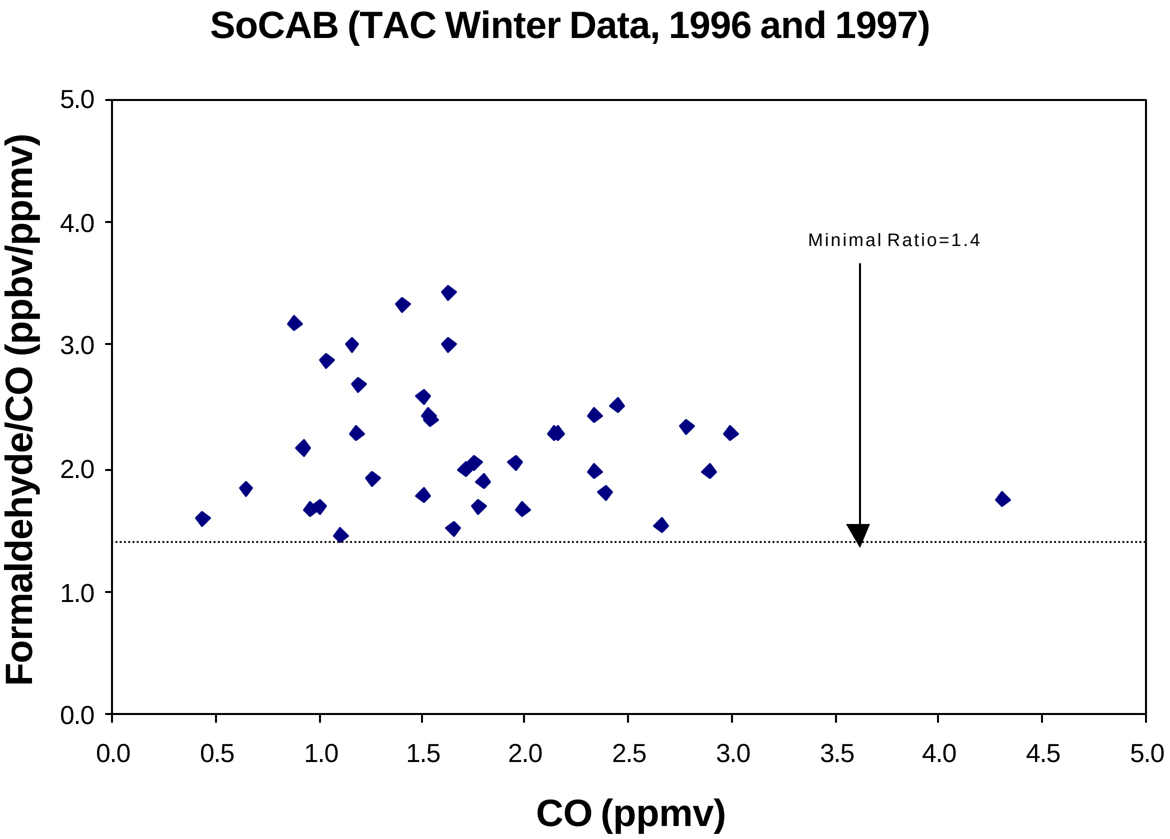

Figure 3.10 Formaldehyde to CO Ratio versus CO for SoCAB (TAC Winter Data, 1996 and 1997)

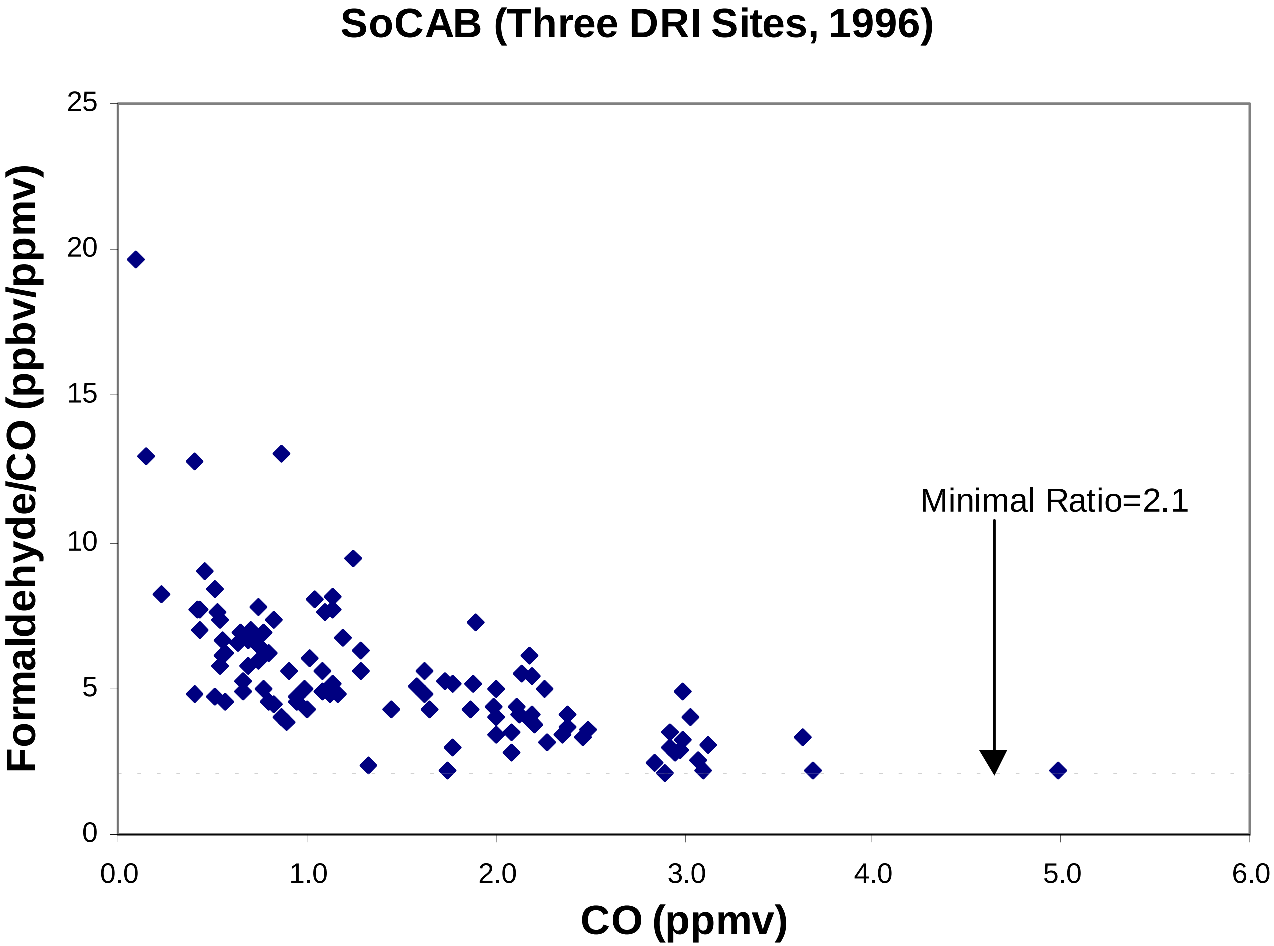

Figure 3.11 Formaldehyde to CO Ratio versus CO for SoCAB (Three DRI Sites, 1996)

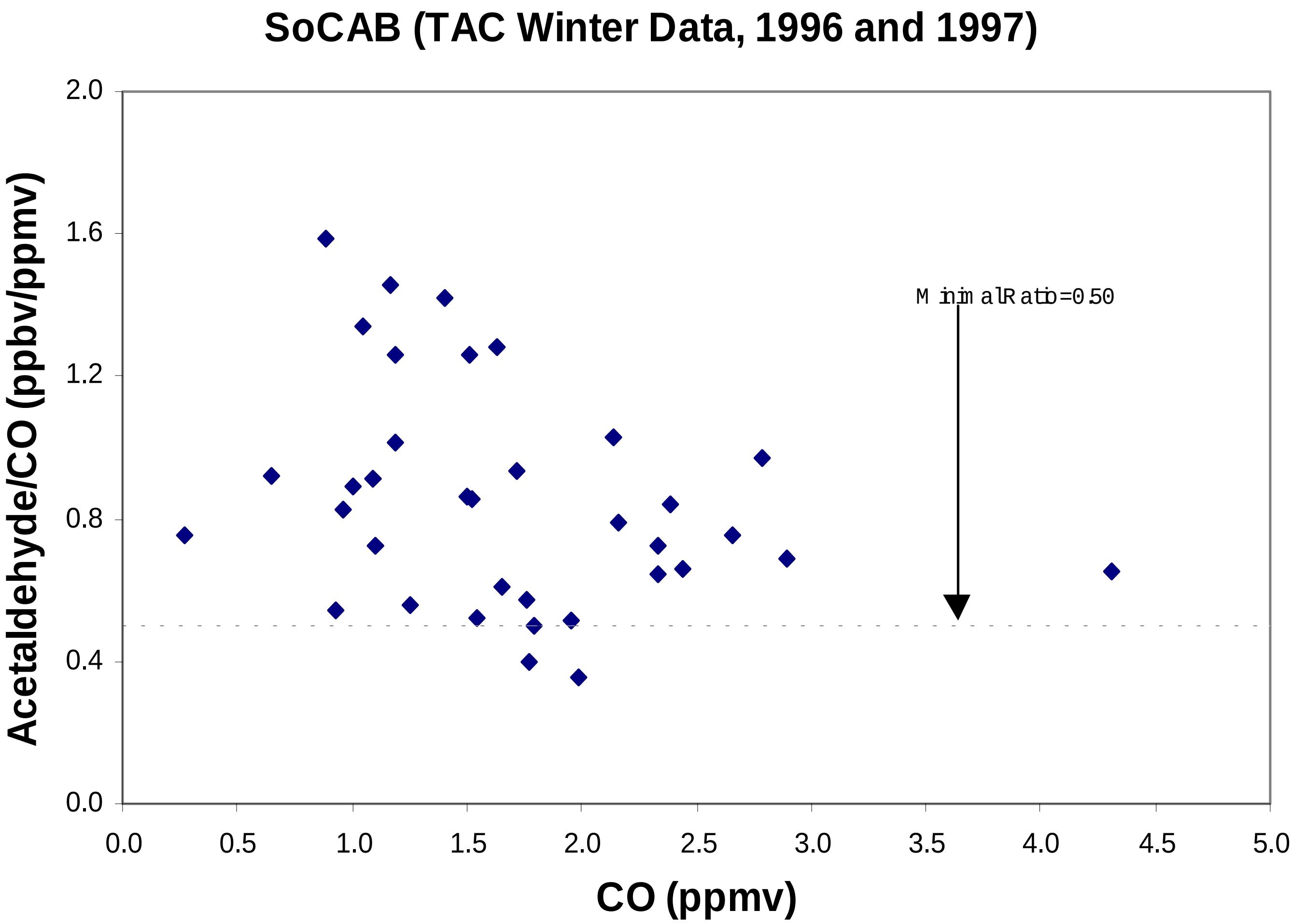

Figure 3.12 Acetaldehyde to CO Ratio versus CO for SoCAB (TAC Winter Data, 1996 and 1997)

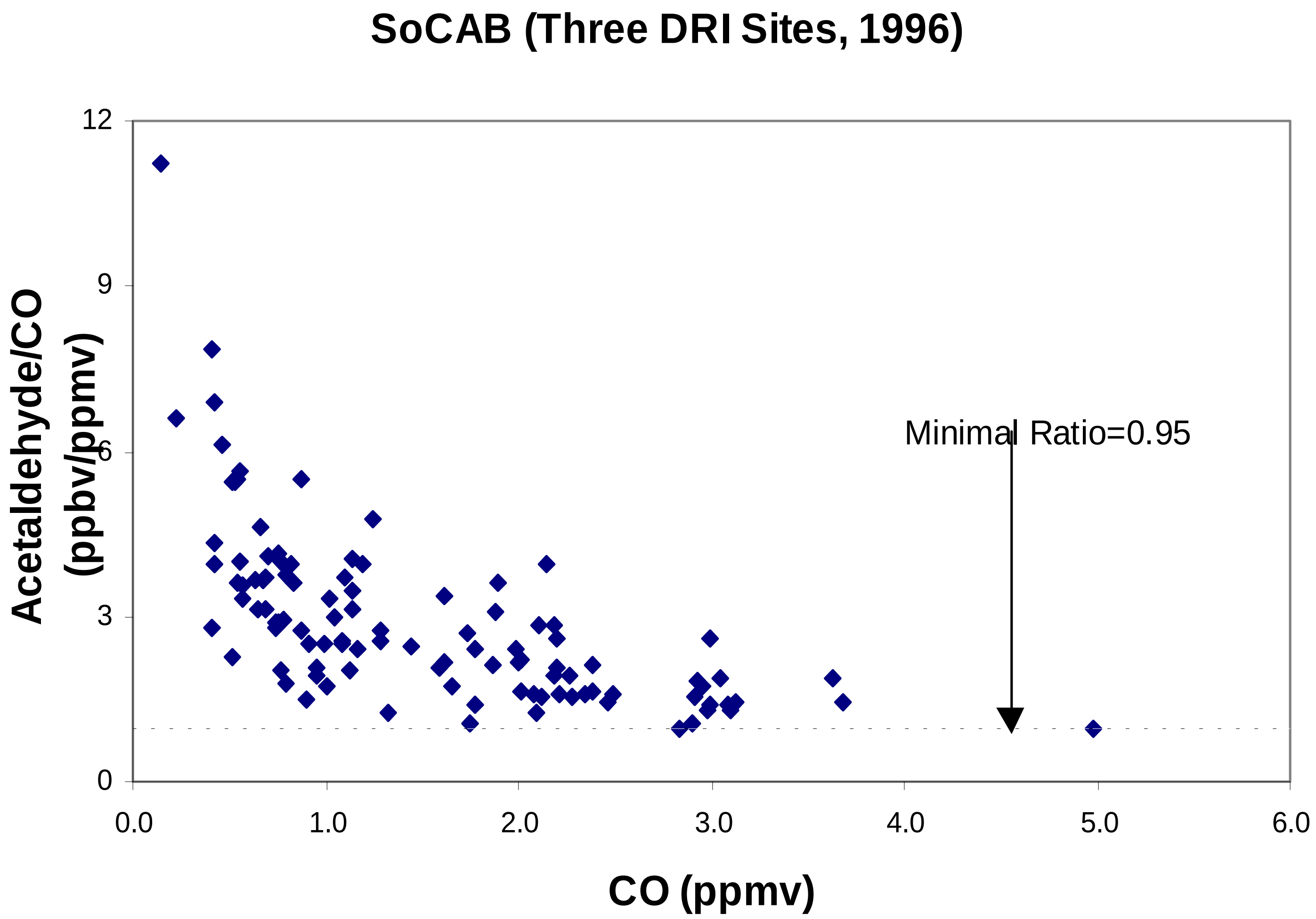

Figure 3.13 Acetaldehyde to CO Ratio versus CO for SoCAB (Three DRI Sites, 1996)

To determine a factor relating aldehydes to oxidant, we assembled carbon monoxide and oxidant (O_3+NO_2) data to match aldehyde measurements from the toxics monitoring network in the SoCAB. First, we used the aldehyde to CO ratios determined above to estimate primary acetaldehyde. Then we subtracted this from the measured aldehyde concentration to obtain a residual aldehyde amount (presumably secondary in origin). Then we plotted the residual aldehyde versus oxidant, after subtracting a background concentration of 0.03 ppm oxidant. This background concentration was determined by looking at the distribution of oxidant concentrations measured in the SoCAB between 1996 and 1998. More than 98.6 % of the measured daily-average concentrations were 0.03 ppm or higher. Using the acetaldehyde to CO ratio of 0.50, a best fit oxidant slope was determined to be 40 for the TAC data. Using the ratio of 0.95 from the DRI data, the best fit oxidant slope for TAC data was determined to be 31. Using the formaldehyde to CO ratio of 1.4, a best fit oxidant slope was determined to be 73 for the TAC data. Using the ratio of 2.1 from the DRI data, the best fit oxidant slope for TAC data was determined to be 80. For residual acetaldehyde our R^2 regression coefficients were .50 to .54, depending on which slope factors were used. For residual formaldehyde our R^2 regression coefficients were .12 to .37, depending on which slope factors were used. When we tried applying the CO and oxidant ratios to predict daily aldehyde concentrations, the maximum predicted concentrations at the toxics monitoring sites in the SoCAB on actual sampling days were 75% or more higher than measured maximum values. Therefore, we decided that this approach did not provide sufficiently reliable estimates to use in our analysis.

C-3.2.3. Toluene, Xylenes, Isobutene, *n*-Hexane, and *n*-Heptane

OEHHA requested information on annual exposure and maximum one-hour concentrations for toluene, xylenes, isobutene, *n*-hexane, and *n*-heptane. In response to this, we did a sensitivity evaluation of 1997 concentrations for these compounds. A key part of the sensitivity evaluation involved developing ratios between the compounds of interest and CO. This is discussed below, followed by estimates of 1997 pollutant concentrations.

After reviewing the estimated 1997 concentrations relative to chronic Reference Exposure Levels (RELs), OEHHA concluded that even a few-fold difference in concentration from the use of one fuel over the other is not going to be a significant health concern. This was because current concentrations of these compounds are one to two orders of magnitude below their chronic RELs. Thus, airshed modeling analysis was not performed to predict future air quality concentrations of these compounds.

C-3.2.3.1. Ratio Between Compounds and CO

Following a procedure similar to that described in Section C-3.2.1.2, we developed ratios between the compounds of interest and CO. The results for each of the compounds evaluated follow:

C-3.2.3.1.1. Toluene

Table 3.5 summarizes the ratios and correlation coefficients between toluene and CO derived from TAC data, DRI data, Sepulveda data, and the emission inventory. This includes ratios derived from each monitoring site as well as sites combined (basin-wide) in the same data set. In general, good correlation was observed in all cases except the Riverside site. The ratios derived from air quality data range from 2.3 to 4.6.

C-3.2.3.1.2. Combined *meta*- and *para*-Xylenes

Table 3.6 summarizes the ratios and correlation coefficients between combined *meta*- and *para*-xylene (*m&p*-xylene) and CO derived from the same data sets. In general, good correlation was observed for all data sets. The ratios obtained range from 1.1 to 1.9.

C-3.2.3.1.3. *o*-Xylene

Table 3.7 summarizes the ratios and correlation coefficients between *o*-xylene and CO derived from the same data sets. In general, good correlation was observed for all data sets. The ratios obtained range from 0.4 to 1.8.

C-3.2.3.1.4. Isobutene

Table 3.8 summarizes the ratios and correlation between isobutene and CO derived from DRI data, the Sepulveda tunnel study, and the emission inventory. This compound is not measured in our TAC network. In general, good correlation was observed for all data sets except Los Angeles. The ratios derived range from 0.9 to 1.6.

C-3.2.3.1.5. *n*-Hexane

Table 3.9 summarizes the ratios and correlation coefficients between *n*-hexane and CO derived from DRI data, the Sepulveda tunnel study, and the emission inventory. Like isobutene, *n*-hexane is not measured in our TAC network. In general, good correlation was observed for all data sets. The ratios derived range from 0.5 to 1.0.

C-3.2.3.1.6. *n*-Heptane

Table 3.10 summarizes the ratios and correlation coefficients between *n*-heptane and CO derived from DRI data, the Sepulveda tunnel study, and the emission inventory. Like isobutene and *n*-hexane, *n*-heptane is not measured in our TAC network. Good correlation was observed for most of the data sets. The ratios derived range from 0.1 to 0.3.

C-3.2.3.2. Estimated 1997 Concentrations

We made estimates of expected maximum annual-average and maximum one-hour-average concentrations for toluene, *m&p*-xylene, *o*-xylene, isobutene, *n*-hexane, and *n*-Heptane. These were done using available measurements from the toxics monitoring network and by establishing a ratio to carbon monoxide and multiplying that ratio by maximum CO concentrations.

Table 3.5 Linear Regression Parameters for Correlations Between Ambient Concentrations of Toluene and CO[a]

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	**R^2**	**Ratio**	**R^2**	**Ratio**	**R^2**	**Ratio**	**R^2**	**All Sources**	**On-road Sources**
1996										
South Coast Air Basin[c]	2.73	0.84	3.91	0.82	3.96	0.78			3.74	
Burbank	2.84	0.85	4.26	0.94	4.35	0.89				
Los Angeles	2.55	0.82	3.24	0.89	3.29	0.86				
Long Beach	2.77	0.86								
Riverside	3.11	0.31								
Azusa			4.56	0.88	4.57	0.77				
Sepulveda Tunnel							2.27	0.95		
Caldecott Tunnel										
1997										
South Coast Air Basin[c]	2.49	0.76								
Burbank	2.66	0.65								
Los Angeles	2.36	0.80								
Long Beach	2.55	0.75								
Caldecott Tunnel										

a. Concentration units are ppmv for CO and ppbv for toluene. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

Table 3.6 Linear Regression Parameters for Correlations Between Ambient Concentrations of *m&p*-Xylene and CO[a]

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	**R^2**	**Ratio**	**R^2**	**Ratio**	**R^2**	**Ratio**	**R^2**	**All Sources**	**On-road Sources**
1996										
South Coast Air Basin[c]	1.29	0.93	1.83	0.87	1.76	0.85			1.33	
Burbank	1.27	0.91	1.90	0.91	1.85	0.94				
Los Angeles	1.31	0.96	1.68	0.82	1.63	0.84				
Long Beach	1.38	0.82								
Riverside	1.32	0.67								
Azusa			2.00	0.91	1.88	0.79				
Sepulveda Tunnel							1.33	0.97		
Caldecott Tunnel										
1997										
South Coast Air Basin[c]	1.15	0.84								
Burbank	1.16	0.62								
Los Angeles	1.15	0.92								
Long Beach	1.13	0.88								
Caldecott Tunnel										

a. Concentration units are ppmv for CO and ppbv for m&p-xylene. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

Table 3.7 Linear Regression Parameters for Correlations Between Ambient Concentrations of *o*-Xylene and CO[a]

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	R^2	Ratio	R^2	Ratio	R^2	Ratio	R^2	All Sources	On-road Sources
1996										
South Coast Air Basin[c]	0.46	0.96	0.66	0.89	0.64	0.87			0.54	
Burbank	0.46	0.98	0.69	0.92	0.67	0.95				
Los Angeles	0.45	0.97	0.60	0.85	0.59	0.87				
Long Beach	0.48	0.87								
Riverside	0.49	0.72								
Azusa			0.73	0.92	0.70	0.83				
Sepulveda Tunnel							1.79	0.97		
Caldecott Tunnel										
1997										
South Coast Air Basin[c]	0.41	0.84								
Burbank	0.41	0.67								
Los Angeles	0.42	0.93								
Long Beach	0.39	0.70								
Caldecott Tunnel										

a. Concentration units are ppmv for CO and ppbv for o-xylene. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

Table 3.8 Linear Regression Parameters for Correlations Between Ambient Concentrations of Isobutene and CO[a]

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	R^2	Ratio	R^2	Ratio	R^2	Ratio	R^2	All Sources	On-road Sources
1996										
South Coast Air Basin[c]			1.05	0.54	0.95	0.62			1.24	
Burbank			1.11	0.68	0.99	0.68				
Los Angeles			0.97	0.40	0.96	0.54				
Long Beach										
Riverside										
Azusa			1.10	0.58	0.89	0.61				
Sepulveda Tunnel							1.55	0.92		
Caldecott Tunnel										
1997										
South Coast Basin-wide										
Burbank										
Los Angeles										
Long Beach										
Caldecott Tunnel										

a. Concentration units are ppmv for CO and ppbv for isobutene. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

Table 3.9 Linear Regression Parameters for Correlations Between Ambient Concentrations of *n*-Hexane and CO[a]

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	**R^2**	**Ratio**	**R^2**	**Ratio**	**R^2**	**Ratio**	**R^2**	**All Sources**	**On-road Sources**
1996										
South Coast Air Basin[c]			0.87	0.58	0.91	0.62			0.71	
Burbank			0.96	0.73	1.02	0.65				
Los Angeles			0.70	0.60	0.74	0.71				
Long Beach										
Riverside										
Azusa			1.03	0.73	1.03	0.74				
Sepulveda Tunnel							0.49	0.92		
Caldecott Tunnel										
1997										
South Coast Air Basin[c]										
Burbank										
Los Angeles										
Long Beach										
Caldecott Tunnel										

a. Concentration units are ppmv for CO and ppbv for n-hexane. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

Table 3.10 Linear Regression Parameters for Correlations Between Ambient Concentrations of *n*-Heptane and CO[a]

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	**R^2**	**Ratio**	**R^2**	**Ratio**	**R^2**	**Ratio**	**R^2**	**All Sources**	**On-road Sources**
1996										
South Coast Air Basin[c]			0.10	0.64	0.10	0.44			0.20	
Burbank			0.10	0.72	0.12	0.36				
Los Angeles			0.08	0.76	0.08	0.80				
Long Beach										
Riverside										
Azusa			0.12	0.73	0.12	0.54				
Sepulveda Tunnel							0.27	0.95		
Caldecott Tunnel										
1997										
South Coast Air Basin[c]										
Burbank										
Los Angeles										
Long Beach										
Caldecott Tunnel										

a. Concentration units are ppmv for CO and ppbv for *n*-heptane. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

C-3.2.3.2.1. Estimated Maximum Using Ratio to CO

We calculated ranges of maximum annual-average and one-hour toxic compound concentrations using maximum measured CO concentrations in the SoCAB for 1996-1998 and the range of ratios to CO established in Section C-3.2.3.1. The background-adjusted maximum annual-average and one-hour CO concentrations were both measured at Lynwood in 1996 and are 2.4 ppm and 22.4 ppm, respectively. The calculated maximums for the various compounds are shown in Table 3.11.

Table 3.11 Estimated Maximum Annual and One-Hour Toxics Concentrations using CO as a Surrogate

Compound	Annual Average (ppbv)	One-Hour Average (ppbv)
Toluene	**6-11**	**52-103**
***m*&*p*-Xylene**	**2.6-4.6**	**25-43**
***o*-Xylene**	**1.0-4.3**	**9-40**
Isobutene	**2.2-3.8**	**20-36**
***n*-Hexane**	**1.2-2.4**	**11-22**
***n*-Heptane**	**0.2-0.7**	**2-7**

C-3.2.3.2.2. Maximum One-Hour Averages Extrapolated from Maximum Daily Averages

We estimated the maximum one-hour concentrations by extrapolating from measured maximum daily concentrations. For toluene and *o*-xylene the measured maximum daily concentrations for 1996-1997 in the SoCAB were 19 ppb and 3.5 ppb, respectively, and were measured at Burbank on January 10, 1996. For *m*&*p*-xylene the maximum daily concentration was 9.7 ppb, measured on January 10, 1996 at Los Angeles-North Main. We used measured CO daily and maximum one-hour CO concentrations at Burbank and Los Angeles on January 10, 1996 to extrapolate to maximum one-hour toxics concentration assuming proportionality between CO and toxics concentrations at each location. At Burbank the daily and maximum one-hour CO concentrations were 7.43 ppm and 11.6 ppm, respectively. The calculated maximum one-hour-average toluene and *o*-xylene concentrations are 29.7 ppb and 5.5 ppb, respectively. At Los Angeles the daily and maximum one-hour CO concentrations were 7.0 ppm and 10.3 ppm, respectively. The calculated maximum one-hour *m*&*p*-xylene concentration is 14.3 ppb. Isobutene, *n*-hexane, and *n*-heptane are not measured as part of the TAC monitoring program, and no estimates were made for these three compounds.

C-3.2.3.2.3. Maximum Measured Annual Average

Based on TAC data for 1996-1997, the maximum measured annual-averages for the SoCAB were measured at Burbank in 1996 and were 5.12 ppb for toluene, 2.2 ppb for *m*&*p*-xylene, and 0.77 ppb for *o*-xylene.

C-3.3. Ethanol

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 population-weighted annual and maximum daily average and maximum one-hour average for 1997. The 1995 data were not used because cleaner burning gasoline was not widely available until 1996. 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.

Similar to other pollutants, we attempted to correlate ethanol with CO. The results summarized in Table 3.12 showed poor correlation. This was not surprising, given that on-road vehicles currently emit less than one percent of the estimated ethanol emissions in the SoCAB (see Appendix A). Correlations with various organic compounds (not shown) were equally unsuccessful.

C-3.3.1. Maximum Daily Average

The maximum daily-average ethanol concentration is expected to occur in winter, and was calculated using one procedure with two different assumptions. The general equation for calculating the maximum daily-average concentration is as follows:

$$\text{Ethanol (Max 24hr)} = \text{Ethanol(Hi 6hr Ave.)} \times \frac{\dfrac{\text{Annual Maximum 24hr Avg. CO}}{\text{Winter CO Emissions}}}{\dfrac{\text{Summer Matching 6hr CO Air Quality}}{\text{Summer CO Emission}}}$$

In the equation above, the CO air quality concentrations are divided by the relevant seasonal (winter or summer) emission estimates to adjust for the effects of higher CO emissions in winter. This is because CO is being used as an index of dispersion and mixing under the assumption that CO emissions are kept constant.

This procedure was applied two ways -- once using only data for Los Angeles (the monitoring site with the highest ethanol measurements), and once using the CO data for Lynwood (the site with the highest CO concentrations) and ethanol data for Los Angeles. The latter application was made attempting to represent conditions of very limited mixing and dispersion that occur at Lynwood. A maximum daily-average ethanol concentration of 47 ppb was calculated using the Los Angeles maximum as follows:

$$\text{Ethanol (Max 24hr)} = 25.7\ \text{ppb} \times \frac{\dfrac{7.0\ \text{ppm}}{6520\ \text{tons/day}}}{\dfrac{3.10\ \text{ppm}}{5283\ \text{tons/day}}} = 47\ \text{ppb}$$

A similar calculation yielded 51 ppb using Lynwood CO data.

Table 3.12 Linear Regression Parameters for Correlations Between Ambient Concentrations of Ethanol and CO[a]

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	R^2	Ratio	R^2	Ratio	R^2	Ratio	R^2	All Sources	On-road Sources
1996										
South Coast Air Basin[c]			4.55	0.22	4.43	0.27			3.75	0.04
Burbank			4.25	0.12	4.32	0.23				
Los Angeles			4.37	0.17	4.34	0.23				
Long Beach										
Riverside										
Azusa			5.27	0.35	4.71	0.34				
Sepulveda Tunnel										
Caldecott Tunnel										
1997										
South Coast Air Basin[c]										
Burbank										
Los Angeles										
Long Beach										
Caldecott Tunnel										

a. Concentration units are ppmv for CO and ppbv for ethanol. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

C-3.3.2. Maximum One-Hour Average

The maximum one-hour-average ethanol concentration is expected to occur in winter and was calculated using one procedure with two different assumptions. The general equation for calculating the maximum one-hour average is as follows:

$$\text{Ethanol (Max 1hr)} = \text{Ethanol (Hi 3hr Ave.)} \times \frac{\dfrac{\text{Annual Maximum 1hr Avg. CO}}{\text{Winter CO Emissions}}}{\dfrac{\text{Summer Matching 3hr CO Air Quality}}{\text{Summer CO Emissions}}}$$

This procedure was applied two ways -- once using only data for Los Angeles (the monitoring site with the highest ethanol measurements), and once using the maximum one-hour-average CO from Lynwood (the site with the highest CO concentrations) and the rest of the data from Los Angeles. The latter application was made attempting to represent conditions of very limited mixing and dispersion that occur at Lynwood. A maximum one-hour-average ethanol concentration of 78 ppb was calculated using the Los Angeles maximum as follows:

$$\text{Ethanol (Max 1hr)} = 37.0 \text{ ppb} \times \frac{\dfrac{10.3 \text{ ppm}}{6520 \text{ tons/day}}}{\dfrac{3.97 \text{ ppm}}{5283 \text{ tons/day}}} = 78 \text{ ppb}$$

A similar calculation yielded 108 ppb using Lynwood CO data.

C-3.3.3. Population-Weighted Annual Exposure

There were three sites for which data were collected in the DRI study -- Azusa, Burbank and Los Angeles -North Main. For each site, an estimated annual-average ethanol concentration was calculated using carbon monoxide concentrations as an index of ventilation and dispersion. The following equation was used:

$$\text{Ethanol (Annual)} = \text{Ethanol (Summer 1996 Avg.)} \times \frac{\dfrac{\text{Annual CO Air Quality}}{\text{Annual CO Emissions}}}{\dfrac{\text{Summer 1996 CO Air Quality}}{\text{Summer CO Emissions}}}$$

The time period for averaging the summer 1996 CO data was 600-900 and 1300-1600 PDT for July 7, 1996 through September 29, 1996. This corresponds to the time period over which the DRI ethanol data were collected. Applying the above equation to Burbank data, we obtain:

$$\text{Ethanol (Annual)} = 5.35\ \text{ppb} \times \frac{\dfrac{1.705\ \text{ppm}}{5782\ \text{tons/day}}}{\dfrac{1.651\ \text{ppm}}{5283\ \text{tons/day}}} = 5.04\ \text{ppb}$$

The population-weighted annual-average concentration was calculated using annual-average data for the three monitoring sites and the procedure described in Section C-3.2.1.3.3 above. The population-weighted annual-average concentration calculated to represent the SoCAB in 1997 is 5.4 ppb ethanol.

C-3.4. Alkylates

Similar to the analysis performed for toluene, we also did a sensitivity evaluation of 1997 concentrations for the class of organic compounds known as alkylates. Alkylates is a class of C_6+ branched alkanes and cycloalkanes present in motor vehicle fuels. Based on the ambient measurements by DRI in the SoCAB in 1996, there were thirty-two alkylates observed in the atmosphere, which are listed in Table 3.13, together with the weight percentage of each alkylate of the total alkylates observed at each monitoring site. We used the DRI data and measured CO concentrations in 1996-1998 to estimate annual-average and maximum one-hour total alkylate concentrations, using a procedure similar to that used in Section C-3.2.3 for isobutene, *n*-hexane, and *n*-heptane. Below we discuss the development of a ratio between the total alkylates and CO followed by an estimate of the 1997 pollutant concentration.

We provided the 1997 estimated pollutant data for alkylates to OEHHA. Since OEHHA concluded that there are no data that would indicate a toxicological problem with any of the alkylates, primarily due to lack of data, there was no need to model air quality concentrations for the 2003 scenarios.

C-3.4.1. Ratio Between Total Alkylates and CO

Following a procedure similar to that described in Section C-3.2.1.2, we developed ratios between the total alkylates and CO. Both DRI data and Sepulveda Tunnel data were used in our analysis. Alkylates are not measured in the TAC monitoring network.

Table 3.14 summarizes the ratios and correlation coefficients between total alkylates and CO derived from DRI data and Sepulveda data. Excellent correlation was observed for all data sets. The ratios obtained range from 6.5 to 9.6

Table 3.13 Weight Percentage of Each Alkylate of the Total Alkylates Observed at Each Monitoring Site

Chemical Name	Azusa	Burbank	LA-North Main
2,2-Dimethylbutane	3.31%	3.20%	3.34%
2,3-Dimethylbutane	0.08%	0.11%	0.05%
2-Methylpentane	15.93%	15.35%	15.88%
3-Methylpentane	9.36%	9.13%	9.29%
Methylcyclopentane	0.00%	0.00%	0.00%
Methylcyclopentane	9.46%	9.52%	10.06%
2,4-Dimethylpentane	4.26%	4.53%	4.25%
2,2,3-Trimethylbutane	0.20%	0.19%	0.17%
3,3-Dimethylpentane	0.66%	0.62%	0.65%
2,3-Dimethylpentane	6.48%	7.31%	6.73%
1,3-Dimethylcyclopentane	2.06%	2.09%	2.18%
3-Ethylpentane	2.90%	2.78%	3.96%
2,2,4-Trimethylpentane	14.16%	12.65%	12.03%
Methylcyclohexane	6.15%	7.92%	5.78%
2,5-Dimethylhexane	1.68%	1.64%	1.51%
2,4-Dimethylhexane	3.65%	3.61%	3.36%
2,3,4-Trimethylpentane	4.78%	4.14%	3.95%
2-Methylheptane	2.42%	2.70%	2.56%
4-Methylheptane	0.99%	1.04%	1.03%
3-Methylheptane	2.00%	2.18%	2.20%
2,2,5-Trimethylhexane	0.52%	0.52%	0.56%
1,1-Dimethylcyclohexane	0.01%	0.01%	0.02%
2,3,5-Trimethylhexane	1.51%	2.15%	3.36%
2,4-Dimethylheptane	0.13%	0.11%	0.13%
4,4-Dimethylheptane	0.48%	0.48%	0.52%
2,6-Dimethylheptane	0.63%	0.56%	0.61%
2,5-Dimethylheptane	1.75%	1.57%	1.67%
3,3-Dimethylheptane	0.95%	0.72%	0.82%
2-Methyloctane	1.39%	1.36%	1.41%
3-Methyloctane	1.20%	1.12%	1.18%
2,6-Dimethyloctane	0.17%	0.18%	0.16%
3,6-Dimethyloctane	0.73%	0.53%	0.60%
Total	100.00%	100.00%	100.00%

Table 3.14 Linear Regression Parameters for Correlations Between Ambient Concentrations of Total Alkylates and CO[a]

	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory[b]	
	Ratio	**R^2**	**Ratio**	**R^2**	**Ratio**	**R^2**	**Ratio**	**R^2**	**All Sources**	**On-road Sources**
1996										
South Coast Air Basin[c]			8.79	0.86	8.88	0.83				
Burbank			9.49	0.96	9.64	0.91				
Los Angeles			7.77	0.82	7.90	0.85				
Long Beach										
Riverside										
Azusa			9.55	0.92	9.53	0.80				
Sepulveda Tunnel							6.53	0.95		
Caldecott Tunnel										
1997										
South Coast Air Basin[c]										
Burbank										
Los Angeles										
Long Beach										
Caldecott Tunnel										

a. Concentration units are ppmv for CO and ppbv for total alkylates. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

c. Basin-wide ratio and correlation coefficient were calculated using the data collected in the SoCAB.

C-3.4.2. Estimated 1997 Concentrations

We made estimates of expected maximum annual-average and maximum one-hour-average concentrations for the total alkylates. These were done by using maximum measured CO concentrations in the SoCAB from 1996-1998 and the range of ratios to CO established above. The background-adjusted maximum annual-average and one-hour CO concentrations, both measured at Lynwood in 1996, are 2.4 ppm and 22.4 ppm, respectively. The calculated maximum for the total alkylates is shown in Table 3.15.

Table 3.15 Estimated Maximum Annual-Average and One-Hour-average Alkylate Concentrations Using CO as a Surrogate

Compound	Annual Average (ppbv)	One-Hour Average(ppbv)
Total Alkylates	**15.6-23.0**	**146-216**

C-3.5. PAN and PPN

Information used to establish 1997 baseline concentrations for peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) is contained in a separate document (Grosjean, 1999). Table 3.16 compares PAN and PPN measurements made at Azusa during a special study in 1993 and SCOS97-NARSTO with model predictions for the 1997 baseline scenario. The PPN model species represents higher acyl peroxy nitrates in addition to peroxypropionyl nitrate. The measured PPN concentrations should be doubled to roughly approximate the PPN modeled species (Grosjean, personal communication). Based on these data, we established the range of estimated 1997 PAN and PPN concentrations, shown in Table 3.17.

Table 3.16 PAN and PPN Concentrations Measured and Modeled at Azusa

Compound	Year	Max. 1-hr Ave. (ppbv)	Max. Daily Ave. (ppbv)	Average (ppbv)
PAN	**1993**	**9.9**	**5.0**	**3.0**
	1997	**4.8**	**2.1**	**0.9**
	Model	**1.9**	**1.4**	**-**
PPN	**1993**	**1.5**	**0.9**	**0.5**
	1997	**0.7**	**-**	**0.3**
	Model[a]	**0.3**	**0.5**	**-**

[a] **The PPN model species represents higher acyl peroxy nitrates in addition to peroxypropionyl nitrate.**

Table 3.17 Estimated Maximum 1-Hour-Average and Daily-Average 1997 PAN and PPN Concentrations

Compounds	Max. 1-hr Ave. (ppbv)	Max. Daily Ave. (ppbv)
PAN	5-10	2.5-5.0
PPN[a]	1.5-3.0	1.0-2.0

[a]The PPN model species represents higher acyl peroxy nitrates in addition to peroxypropionyl nitrate.

C-4. Methods to Estimate Future Air Quality Concentrations

C-4.1. Basic Procedure for all Pollutants

Future air quality concentrations were estimated using estimated 1997 concentrations (Section C-3) and results from the photochemical simulation model for the specific pollutant of concern in 2003. Unlike the 1997 estimates, we did not use correlations between CO and toxic compounds to estimate 2003 concentrations. Separate model simulations were made using 1997 and 2003 baseline (MTBE-based CaRFG), 2003 ethanol at 2.0 wt% oxygen, 2003 ethanol at 3.5 wt% oxygen, and 2003 non-oxygenate. Although the model simulation covered three days, the only day deemed suitable for comparison was the third day. This was because results on the first and second day are strongly affected by the choice of initial conditions. The general procedure for calculating 2003 air quality was:

$$\text{2003 Air Quality for Fuel X} = \text{1997 Air Quality} \times \frac{\text{Modeled 2003 Air Quality for Fuel X}}{\text{Modeled 1997 Air Quality}}$$

Departures from this basic procedure are discussed in Sections C-4.2 and C-4.3.

C-4.1.1. Maximum Daily and One-Hour Averages

For estimating 2003 maximum daily and one-hour-average concentrations, we normally used the maximum concentrations for the highest grid cell in the modeling region for the third day of the model simulation as the model air quality parameter in the equation above. In applying this general procedure, the grid cell with the modeled peak concentration and the time at which the peak occurred are not required to be the same in the numerator and denominator of the equation.

Notable exceptions to his general procedure are estimates for benzene, 1,3-butadiene, carbon monoxide, ethanol, and MTBE. For these, we used the modeled daily average and one-hour average for the grid cell containing Lynwood, the monitoring site with the highest measured CO concentrations. The use of the Lynwood grid cell concentrations was because these pollutants are primary pollutants and Lynwood was the site of the highest estimated concentrations for these pollutants in 1997.

C-4.1.2. Population-Weighted Annual Exposure

For the population-weighted annual-average exposure, we normally used the region-wide population-weighted average of the daily-average model results for the third day of the model simulation as the model air quality parameter in the equation above. This was believed reasonable for any compound that is a primary pollutant. Acetaldehyde and formaldehyde have substantial contributions from secondary reactions in the atmosphere and were treated differently as discussed below.

C-4.2. Special Procedures for Criteria Pollutants

Generally we followed the basic procedures for estimating 2003 air quality concentrations except as follows:

For 2003 maximum daily and maximum one-hour-average concentrations for CO, we used the model values for the grid cell containing Lynwood, as discussed above. For estimating 2003 maximum eight-hour-average ozone concentrations, we used the maximum grid cell eight-hour-average model results. For maximum eight-hour CO concentrations, we used model values for the grid cell containing Lynwood.

C-4.3. Special Procedures for Toxic Pollutants

Generally we followed the basic procedures for estimating 2003 air quality concentrations except as follows:

For maximum daily and maximum one-hour-average concentrations for benzene, 1,3-butadiene, ethanol and MTBE, we used the model values for the grid cell containing Lynwood, as discussed above.

For ethanol, the maximum daily and maximum one-hour-average concentrations for Los Angeles-North Main were calculated using model values from the grid cell containing the Los Angeles-North Main monitoring site.

For acetaldehyde and formaldehyde, we used the basic procedure for the maximum daily and maximum one-hour averages. This was deemed reasonable because in 1997 the maximum daily and maximum one-hour concentrations occurred in August, the month of the model simulation. For calculating the maximum daily and maximum one-hour-average concentrations, we used total aldehyde concentrations from the model. For the population-weighted annual-average, a different procedure was needed because the contribution from primary emission sources versus secondary formation in the atmosphere was expected to be different in different seasons of the year. The basic equation for estimating 2003 aldehydes was as follows:

$$
\begin{aligned}
\text{2003 Air Quality} &= \text{0.5 ppb background} \\
&\quad + \text{1997 Primary Air Quality} \times \frac{\text{Modeled 2003 Primary Air Quality}}{\text{Modeled 1997 Primary Air Quality}} \\
&\quad + \text{1997 Secondary Air Quality} \times \frac{\text{Modeled 2003 Secondary Air Quality}}{\text{Modeled 1997 Secondary Air Quality}}
\end{aligned}
$$

This requires that the amount of primary and secondary aldehyde be known for 1997 and for the model results. The model was set up so secondary aldehydes were tracked separately from primary aldehydes. The 1997 Primary Air Quality and 1997 Secondary Air Quality were determined from 1996-1997 aldehyde and CO data using the following procedure:

1. Determine primary aldehyde to CO ratio representative of 1997 -- this was done in Section C-3.2.2.2.
2. Determine average CO for month using all CO measurements at each monitoring site, adjusted to remove 0.1 ppm background.
3. Determine average CO for each site-month combination using just aldehyde sampling days, adjusted to remove 0.1 ppm background.
4. Determine average aldehyde (acetaldehyde or formaldehyde) for site-month combination, adjusted to remove 0.5 ppb background.
5. Estimate average primary aldehyde by month = #1 x #2 unless this exceeds (#4 / #3) x #2, in which case substitute (#4 / #3) x #2.
6. Estimate average secondary aldehyde by month =((#4 - (#1 x #3)) / #3) x #2; unless #1 x #2 exceeds (#4 / #3) x #2, in which case substitute zero.
7. Estimate annual-average primary aldehyde = #5 averaged over 12 months of the year.
8. Estimate annual-average secondary aldehyde = #6 averaged over 12 months of the year.

This procedure was applied separately to the DRI based and TAC Network based aldehyde-to-CO ratios developed in Section C-3.2.2.2. The resulting estimated 1997 annual-average primary and secondary aldehyde concentrations are listed in Table 5.1 for acetaldehyde and Table 5.2 for formaldehyde. To obtain population-weighted results, 2003 aldehyde concentrations were estimated for the four monitoring locations shown in the tables, and then these values were weighted by population.

C-5. Results

The resulting air quality estimates for 1997 and the different fuel scenarios in 2003 are shown in Table 5.3. In general, the table shows the estimated population-weighted annual exposure, maximum daily average, and maximum one-hour average for benzene, 1,3-butadiene, acetaldehyde, formaldehyde, carbon monoxide, nitrogen dioxide, ozone, PM_{10}, $PM_{2.5}$, ethanol, MTBE, PAN, PPN, and nitric acid. In some cases the pollutant averaging times are adjusted to show different averaging times. For example, maximum eight-hour averages instead of maximum daily averages are included for carbon monoxide and ozone since there are eight-hour standards for these two pollutants. In addition, the maximum predicted one-hour-average and daily-average concentrations for nitric acid are also included for 1997 and the various 2003 fuel scenarios. A column on the table indicates whether each row of the table was used (Y) or was not used (N) in producing summaries of the estimated maximum pollutant concentrations. Two reasons that a particular row may not have been used in a summary are that it reflected summer concentrations and winter concentrations were higher, or that it reflected 1997 model results that were lower than estimated 1997 maximum concentrations.

Table 5.1 Estimated 1997 Annual-Average Primary and Secondary Acetaldehyde Based on Different Ratio Assumptions (Concentrations in ppb)

Location / Ratio Source	Acetaldehyde to CO Ratio	Estimated Background	Estimated Primary	Estimated Secondary	Total Acetaldehyde
Burbank					
TAC Data	0.50	0.50	0.82	0.98	2.30
DRI Data	0.95	0.50	1.36	0.44	2.30
Los Angeles - North Main					
TAC Data	0.50	0.50	0.65	0.92	2.07
DRI Data	0.95	0.50	1.10	0.47	2.07
North Long Beach					
TAC Data	0.50	0.50	0.44	0.38	1.32
DRI Data	0.95	0.50	0.71	0.11	1.32
Riverside - Rubidoux					
TAC Data	0.50	0.50	0.33	0.90	1.73
DRI Data	0.95	0.50	0.57	0.65	1.73

Table 5.2 Estimated 1997 Annual-average Primary and Secondary Formaldehyde Based on Different Ratio Assumptions (Concentrations in ppb)

Location / Ratio Source	Formaldehyde to CO Ratio	Estimated Background	Estimated Primary	Estimated Secondary	Total Formaldehyde
Burbank					
TAC Data	1.40	0.50	2.31	4.01	5.33
DRI Data	2.10	0.50	3.34	2.91	5.33
Los Angeles - North Main					
TAC Data	1.40	0.50	1.95	3.95	5.14
DRI Data	2.10	0.50	2.85	2.99	5.14
North Long Beach					
TAC Data	1.40	0.50	1.25	2.56	3.51
DRI Data	2.10	0.50	1.88	2.02	3.51
Riverside - Rubidoux					
TAC Data	1.40	0.50	1.03	3.15	4.02
DRI Data	2.10	0.50	1.53	2.57	4.02

Table 5.3 Estimated Pollutant Concentrations for 1997 and 2003 in the SoCAB

	Used for Range?	1997 MTBE	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy	Comments
Benzene, ppbV							
Population Weighted Annual Exposure							
Based on Measured Values	Y	1.07	0.72	0.70	0.73	0.69	
Projected Level based on CO levels	Y	1.19	0.80	0.78	0.81	0.76	
Model Output Pop Wt Summer Daily	N	0.82	0.55	0.54	0.56	0.53	Summer
Maximum Daily Average							
Measured Daily Max.	Y	7.4	5.3	5.1	5.3	4.9	
Projected Maximum based on CO levels	Y	9.5	6.8	6.5	6.8	6.4	
Model Output - Lynwood	N	0.69	0.49	0.47	0.49	0.46	Summer
Maximum from Model Output	N	1.72	1.10	1.09	1.10	1.06	Summer
Maximum One-hour Average							
Extrapolated from Measured Daily Max.	Y	11.6	7.4	7.4	7.4	7.4	
Projected Maximum based on CO levels	Y	22.4	14.3	14.3	14.3	14.3	
Model Output - Lynwood	N	1.1	0.7	0.7	0.7	0.7	Summer
Maximum from Model Output	N	3.4	1.9	1.9	2.0	1.9	Summer
1,3-Butadiene, ppbV							
Population Weighted Annual Exposure							
Based on Measured Values	Y	0.34	0.19	0.19	0.19	0.19	
Projected Level based on CO levels	Y	0.36	0.20	0.20	0.20	0.20	
Model Output Pop Wt Summer Daily	N	0.074	0.042	0.041	0.041	0.041	Summer
Maximum Daily Average							
Measured Daily Max.	Y	2.0	0.8	0.8	0.8	0.8	
Projected Maximum based on CO levels	Y	2.9	1.2	1.2	1.2	1.2	
Model Output - Lynwood	N	0.05	0.02	0.02	0.02	0.02	Summer
Maximum from Model Output	N	0.88	0.87	0.87	0.87	0.87	Summer
Maximum One-hour Average							
Extrapolated from Measured Daily Max.	Y	3.1	1.6	1.6	1.6	1.6	
Projected Maximum based on CO levels	Y	6.7	3.4	3.4	3.4	3.4	
Model Output - Lynwood	N	0.2	0.1	0.1	0.1	0.1	Summer
Maximum from Model Output	N	3.0	3.0	3.0	3.0	3.0	Summer
Acetaldehyde, ppbV							
Population Weighted Annual Exposure							
Based on Measured Values							
TAC Based Value and Projection	Y	1.75	1.59	1.60	1.74	1.58	
DRI/TAC Based Projection	Y		1.55	1.58	1.79	1.54	
Model Output Pop Wt Summer Daily	N	3.23	2.81	2.81	2.93	2.78	Summer
Maximum Daily Average							
Measured Daily Max.	Y	5.1	5.1	5.1	5.1	5.1	
Maximum from Model Output	Y	6.2	6.2	6.2	6.2	6.2	
Model Output - Upland	N	4.43	3.83	3.86	3.99	3.83	
Maximum One-hour Average							
Extrapolated from DRI Measured Three-hour Max.using O3	Y	17.7	16.7	16.9	17.1	16.9	
Extrapolated from Measured Daily Max.using O3	Y	13.8	13.1	13.2	13.4	13.2	
Maximum from Model Output	N	9.2	8.7	8.8	8.9	8.8	
Model Output - Upland	N	6.4	5.6	5.5	5.7	5.5	

	Used for Range?	1997 MTBE	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy	Comments
Formaldehyde, ppbV							
Population Weighted Annual Exposure							
Based on Measured Values							
TAC Based Value and Projection	Y	4.65	4.22	4.06	4.14	4.04	
DRI/TAC Based Projection	Y		4.12	3.97	4.04	3.95	
Model Output Pop Wt Summer Daily	N	6.85	5.95	5.74	5.86	5.70	Summer
Maximum Daily Average							
Measured Daily Max.	Y	14.0	12.2	11.8	12.1	11.7	
Maximum from Model Output	N	11.35	9.90	9.57	9.79	9.49	
Model Output - Upland	N	9.13	7.96	7.73	7.90	7.66	
Maximum One-hour Average							
Extrapolated from DRI Measured Three-hour Max.using O3	Y	20.3	20.6	20.3	20.5	20.3	
Extrapolated from Measured Daily Max.using O3	Y	37.8	38.3	37.8	38.1	37.8	
Maximum from Model Output	Y	22.7	23.0	22.7	22.9	22.7	
Model Output - Upland	N	13.9	11.8	11.5	11.6	11.4	
Carbon Monoxide, ppmV							
Maximum Eight-hour Average							
Measured Eight-hour Max.	Y	17.5	14.3	14.3	13.4	14.7	
Model Output - Lynwood	N	1.010	0.828	0.828	0.773	0.846	Summer
Maximum from Model Output	N	2.43	1.82	1.82	1.66	1.87	Summer
Maximum One-hour Average							
Measured One-hour Max.	Y	22.5	19.2	19.2	18.0	19.7	
Model Output - Lynwood	N	1.11	0.95	0.95	0.89	0.97	Summer
Maximum from Model Output	N	3.02	2.19	2.19	1.97	2.26	Summer
Nitrogen Dioxide, ppmV							
Maximum Annual Average Exposure							
Based on Measured Values	Y	0.043	No significant difference expected among 2003 scenarios				
Maximum Daily Average							
Measured Daily Max.	Y	0.117	0.098	0.097	0.097	0.097	
Maximum from Model Output	N	0.073	0.061	0.060	0.060	0.060	Summer
Maximum One-hour Average							
Measured One-hour Max.	Y	0.255	0.235	0.235	0.235	0.235	
Maximum from Model Output	N	0.105	0.097	0.097	0.097	0.097	Summer
Ozone, ppbV							
Maximum Eight-hour Average							
Measured Eight-hour Max.	Y	0.206	0.196	0.196	0.196	0.196	
Maximum from Model Output	N	0.187	0.178	0.178	0.178	0.178	
Maximum One-hour Average							
Measured One-hour Max.	Y	0.244	0.230	0.228	0.228	0.228	
Maximum from Model Output	N	0.236	0.222	0.220	0.220	0.220	

	Used for Range?	1997 MTBE	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy	Comments
Particulate Matter (10 μm or less), μg/m^3							
Maximum Annual Geometric Mean							
Based on Measured Values	Y	56	No significant difference expected among 2003 scenarios				
Maximum Daily Average							
Measured Daily Max.	Y	227	No significant difference expected among 2003 scenarios				
Particulate Matter (2.5 μm or less), μg/m^3							
Maximum Annual Geometric Mean							
Based on Measured Values	Y	25.9	No significant difference expected among 2003 scenarios				
Maximum Daily Average							
Measured Daily Max.	Y	81	No significant difference expected among 2003 scenarios				
Ethanol, ppbV							
Population Weighted Annual Exposure							
Estimated from Summer Measurements	Y	5.4	5.1	7.6	8.8	5.1	Whole Year
Model Output Pop Wt Summer Daily	N	2.05	1.95	2.87	3.35	1.94	Summer
Maximum Daily Average							
Extrapolated Daily Summer Max.	N	21	20	29	33	20	Summer
Estimated Daily Winter Max.							
Lynwood	Y	51	49	71	81	49	Winter
LA-N Main	Y	47	45	64	75	45	Winter
Model Output							
Lynwood	N	1.86	1.77	2.58	2.96	1.77	Summer
LA-N Main	N	4.60	4.40	6.29	7.30	4.38	Summer
Maximum from Model Output	N	19.1	17.3	17.9	18.1	17.4	Summer
Maximum One-hour Average							
Extrapolated One-hour Summer Max.	N	42	39	56	64	39	Summer
Estimated One-hour Winter Max.							
Lynwood	Y	108	101	145	165	101	Winter
LA-N Main	Y	78	74	114	140	74	Winter
Model Output							
Lynwood	N	3.2	3.0	4.3	4.9	3.0	Summer
LA-N Main	N	5.7	5.4	8.3	10.2	5.4	Summer
Maximum from Model Output	N	45.6	41.4	42.3	42.8	41.4	Summer
MTBE, ppbV							
Population Weighted Annual Exposure							
Based on Measured Values	Y	3.9	2.6	0	0	0	
Projected Level based on CO levels	Y	3.6	2.4	0	0	0	
Model Output Pop Wt Summer Daily	N	1.09	0.72	0	0	0	Summer
Maximum Daily Average							
Measured Daily Max.	Y	13	9	0	0	0	
Projected Maximum based on CO levels	Y	29	20	0	0	0	
Model Output - Lynwood	N	0.97	0.67	0	0	0	Summer
Maximum from Model Output	N	2.63	1.67	0	0	0	Summer
Maximum One-hour Average							
Extrapolated from Measured Daily Max.	Y	19	13	0	0	0	
Projected Maximum based on CO levels	Y	67	46	0	0	0	
Model Output - Lynwood	N	1.6	1.1	0	0	0	Summer
Maximum from Model Output	N	6.1	3.9	0	0	0	Summer

	Used for Range?	1997 MTBE	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy	Comments
PAN, ppbV							
Maximum Daily Average							
Upper Baseline	Y	5.0	4.8	4.8	4.9	4.7	
Lower Baseline	Y	2.5	2.4	2.4	2.4	2.4	
Maximum from Model Output	N	2.12	2.03	2.02	2.06	2.00	
Maximum One-hour Average							
Upper Baseline	Y	10.0	9.5	9.3	9.5	9.1	
Lower Baseline	Y	5.0	4.8	4.7	4.8	4.5	
Maximum from Model Output	N	4.4	4.2	4.1	4.2	4.0	
"Model PPN", ppbV							
Maximum Daily Average							
Upper Baseline	Y	2.0	2.0	2.0	2.0	2.1	
Lower Baseline	Y	1.0	1.0	1.0	1.0	1.0	
Maximum from Model Output	N	0.579	0.575	0.588	0.571	0.600	
Maximum One-hour Average							
Upper Baseline	Y	3.0	3.0	3.0	3.0	3.0	
Lower Baseline	Y	1.5	1.5	1.5	1.5	1.5	
Maximum from Model Output	N	1.4	1.4	1.4	1.4	1.4	
Nitric Acid, ppb (Model Output Only)							
Population Weighted Summer Daily Exposure							
From Model	Y	12.4	11.0	11.0	11.0	11.0	
Maximum Daily Average							
Maximum from Model Output	Y	36.7	32.4	32.3	32.2	32.3	

C-6. References

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California Environmental Protection Agency

Air Resources Board

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

Appendix D

Scientific Peer Review
and Public Comments

December 1999

Table of Contents

List of Tables

D-1. University of California Scientific Peer Review

This section contains comments received from a scientific peer review conducted by four reviewers approved by the University of California Office of the President under a process defined by Health and Safety Code section 57004. The reviewers commented on the November 18, 1999 version of the main report and versions of Appendix A through Appendix D dated November 10, 1999. This is the version of the report presented at the December 9, 1999 hearing of the Air Resources Board (ARB). Each reviewer was asked to comment on the Executive Summary and sections of the report related to their particular area of expertise. The reviewers were selected by the University of California Office of the President to complement one another, so each section of the report was reviewed by at least one individual. Each comment is presented as received in normal font and is followed by the ARB staff response inserted in italics.

D-1.1. Professor Roger Atkinson of the University of California at Riverside

Attached are my comments on selected portions of the above report and its appendices

Summary

The findings of this report are supported by the evidence presented, and indicate that vehicle exhaust emissions and their impact on ozone formation will not be significantly affected by replacing one oxygenate for another, or by eliminating the oxygenate, in reformulated gasoline. In addition, the findings are consistent with previous, more restricted, investigations and/or reviews of the impacts of oxygenated (containing methyl tert-butyl ether (MTBE) or ethanol) and non-oxygenated reformulated gasolines on air quality. The report presents the results of a rather complete assessment in a logical manner, and does point out areas of uncertainty (especially in the mobile source emissions inventory).

Detailed comments are as follows:

Appendix B: Photochemical Modeling

1. Page B-6, Section B-3.1. Based on the text, I conclude that the meteorology of the August 26-28, 1987 episode was used in conjunction with the VOC and NO_x emissions appropriate for 1997 with present MTBE-containing gasoline and for 2003 with three gasolines (2.0 wt% O_2 ethanol-containing, 3.5 wt% O_2 ethanol-containing, and a non-oxygenated gasoline). This needs to be stated more explicitly than presently done. The use of "August 26-28, 1987" further on in this Appendix makes for potential confusion on the part of the reader. One specific example of this confusion is on page B-12, 13-18 lines from bottom, where the sentences state that "Figure 4.1 through 4.5 show hourly O_3, NO, and NO_2 for August 26-28, 1987, . .. The time plots clearly show that the 1997 and 2003 scenarios . ." I suggest that it is made clear on page B-6 that all of the scenarios are for the August 26-28, 1987, meteorology and that "August 26-28, 1987" not be referred to again except on page B-32 (which deals with sensitivity studies).

   Response: We have added a paragraph in Section B-3.1 explaining that the meteorology of August 26-28, 1987 will be used in all simulations, in conjunction with the appropriate

VOC and NO_X emissions for the 1997 and 2003 scenarios. We have deleted reference to August 26-28, 1987 in other parts of the report, except in the section of the report that discusses model performance (instead of sensitivity studies as stated in the comment).

2. Pages B-8 (Table 3.3) and B-9 (Table 3.4). The "baseline boundary" and "region top" concentrations assumed for N_2O_5 (1.0 ppb) and NO_3 radicals (1.0 ppb) are unrealistically high. While the assumed NO_2, N_2O_5 and NO_3 radical concentrations are close to equilibrium (from the $NO_2 + NO_3 \Leftrightarrow N_2O_5$ reactions), the NO_3 radical concentration is a factor of 2 higher than ever observed and a factor of 10 higher than previously observed "high" concentrations. These boundary layer and upper level concentrations need to be more realistic.

   Response: A subsequent conversation with Professor Atkinson determined that 20 ppt is a more appropriate boundary and region top concentration for both N_2O_5 and NO_3 radicals. We do not expect any impact on the simulation results and overall conclusions as MTBE and ethanol do not have significant atmospheric reaction pathways with NO_3 radicals (see Section 2.1 of the main report) and the effect of lowering the NO_3 radical concentration by a factor of 50 will decrease the ozone formation potential of the alkylates, further supporting the overall conclusions of the report. However, we made the suggested changes for upper-bound model simulations now described in the main report and Appendix B.

3. Page B-13, line 6. The concentrations of radical species such as OH, HO_2, organic peroxy radicals, *etc*., are neither tabulated nor graphically shown in this report. I therefore suggest that "radical flux" be replaced by "O_3, NO and NO_2".

   Response: The suggested change has been incorporated into the report.

4. Page B-29, line 10 of text, and page B-30, line 1. Surely the emissions inventory used allows a definitive assessment of whether or not the non-motor vehicle source(s) of ethanol dominate over vehicle sources. The use of "also appears" gives the impression that no one bothered to look into it.

   Response: Please note that the word “appears” was also used on page B-11, line 2 from the bottom, and on page B-12, line 2 of the text, in the same context. The emission inventory clearly shows that ethanol emissions are dominated by non-motor vehicle sources for each of the scenarios (see Appendix A, Table 4.1 through Table 4.5). To avoid any potential confusion on this matter by our choice of words, we have omitted the use of the word “appears” in the text, where appropriate.

5. Page B-29, lines 4 and 5 from bottom. I believe that "2003 3.5%" should be replaced by "2003 Et3.5%".

   Response: The label has been corrected.

6. Page B-30 on. The fact that VOC emissions from vehicles using EMFAC2000 are a factor of 2-3 higher than predicted using EMPAC7G casts some doubt on the analysis carried out in the previous 30 pages of this Appendix. The use of EMFAC7G appears to be necessitated because of time-constraints, and the sensitivity analysis supports the analysis using the EMFAC7G emissions inventory in that replacing MTBE in gasoline by ethanol (or removing the oxygenates altogether) will have no significant impact on air quality. However, the uncertainties in the mobile source emissions inventory (or the use of an

outdated emissions inventory) is troubling and leads to uncertainties in the 2003 (and 1997!) predicted air quality contained in this report. A number of questions arise:

> Is the 1987 inventory (and hence the comparison of predicted *vs* observed 1987 ambient concentrations) subject to changes in the mobile source VOC and NO_x emissions ?
>
> Is the 1997 inventory, multiplied by the factor of 3, realistic - and if so then the LA Basin maximum O_3 levels could have been (if the meteorology had been conducive to it) almost as high as 1970's values (400 ppb). Since 1997 has come and gone (with a large-scale field study for ozone having been conducted), what does modeling the 1997-SCOS data tell us about the mobile source inventory ?
>
> If the 2003 inventories used in Tables 5.1 and 5.2 are close to reality then O_3 levels in the basin may well increase significantly over the next few years.
>
> Why were'nt the NO_x emissions increased as indicated by EMFAC2000, and what is the impact of increasing vehicle NO_x emissions by a factor of 1.8 ?

This rather casual mention of (in essence) "and by the way the real VOC and NO_x emissions from vehicles are believed to be higher than used by factors of around 2.3 and 1.8, respectively" subtracts from the credibility of this report. Significantly more discussion needs to be given concerning the "real" 1987, 1997 and 2003 inventories (or at least CARB's best opinion of them) and the implications for maximum (and 8-hr) O_3 levels. As mentioned above, surely the 2003 inventories should use VOCs increased by a factor of 2.3 and NO_x by a factor of 1.8 in addition to, or instead of, those used in Table 5.1.

Response: The new California on-road motor vehicle emission factor model, EMFAC2000, is still under development and we are reluctant to use it until it receives public scrutiny and possible Board approval in March 2000. We are conducting a detailed in-house comparison of EMFAC2000 against "top-down" studies (i.e., tunnel, ambient ratio, fuel-based). The Singer and Harley (2000) fuel-based inventory discussed in the report is for stabilized exhaust emissions and does not include cold start or evaporative emissions, so it is not necessarily inconsistent with draft versions of EMFAC2000. We also have some concerns with Singer and Harley's methodology (primarily lack of freeway measurements where gm/gallon emission rates are likely to be lower) and view it as an upper-bound estimate. We share your concern that EMFAC2000 will increase the 1987 inventory and significantly erode model performance, and may predict 1997 ozone levels well above those observed in July 1998 (0.244 ppm maximum) when meteorology was more conducive to high ozone than in August 1987. Unfortunately, SCOS97-NARSTO modeling results will not be available until sometime late in 2000. Because of these concerns, we tripled the gasoline-related VOC emissions to bracket the effect of EMFAC2000. Increasing the VOC emissions without a concurrent increase in NO_X *maximizes the effect on photochemically generated pollutants and is consistent with producing upper-bound model simulations. More complete results and discussion are now included in the main report and Appendix B.*

7. Page B-31, first paragraph of text. Reaction with O_3 will not be the dominant loss process for 1,3-butadiene during daylight hours. Even assuming 200 ppb of O_3 and

1.0×10^6 molecule cm^{-3} of OH (a low daytime value), the OH radical reaction is a factor of 2 faster than the O_3 reaction.

Response: We agree with the comment that during daylight hours the OH radical reaction is the dominant loss process, with the OH radical reaction a factor of 2 faster than the O_3 *reaction (when using the* O_3 *and OH radical concentrations in the comment). However, we neglected to mention in the report that the model predicted that the peak 1,3-butadiene was at 0400 hours, when nighttime reactions with* O_3 *and* NO_3 *radicals are the important loss processes. Assuming a nighttime* O_3 *concentration of 100 ppb, and a* NO_3 *radical concentration of 0.02 ppb, the* NO_3 *radical reaction is a factor of 3 faster than the* O_3 *reaction. The lack of sensitivity of the 1,3-butadiene domain peak to emission changes in the sensitivity scenarios was incorrectly attributed to an increase in its reaction with ozone. The domain peak 1,3-butadiene also happens at the same location in Ventura County for all sensitivity scenarios because a local source is influencing the domain peak. We modified the text to reflect this finding.*

8. Page B-40, line 4. Replace "under predict PAN" by "underpredicts PAN".

   Response: The text has been corrected.

9. Page B-43, line 1. Replace "compared" by "compare".

   Response: The text has been corrected.

10. Page B-46, Table 7-1. The rate parameters given in this table for PAN formation and decomposition use the Troe fall-off expression. Somewhere (here or in Attachment B.1) the Troe fall-off expression needs to be given and the parameters used therein defined. Otherwise Table 7.1 is useless.

    Response: We have included expressions for the rate constant parameters used in the SAPRC97 mechanism at the bottom of Table 7-1, and also at the beginning of Attachment B1.

11. Page B-49. For essentially all of the individual compounds shown in Figures, the O_3 formation potentials vary significantly. Some discussion of why this variation occurs (different VOC/NO_x ratio, *etc.* ?) needs to be given. The O_3 formation potentials should be compared on a relative basis to see if the variations of the absolute numbers diminish. In my opinion, this complete section (B-7) dealing with O_3, PAN and PPN formation potentials could be deleted with no adverse impact on the report.

    Response: Ozone formation potentials are dependent on local ambient conditions, such as the VOC/NO_X *ratio and the chemical composition (Carter and Atkinson, 1989; Derwent and Jenkin, 1991). Additional variability is introduced from the lack of complete VOC speciation for some of the historical episodes and differences in lumped reaction rates. This explanation is now contained in the text. We believe the box modeling complements the airshed model's finding that ethanol and directly emitted acetaldehyde are not major contributors to ozone and PAN formation and is a necessary part of the analysis.*

12. Page B-49, PPN formation potentials. A minor point: because PPN is a "lumped" higher peroxyacyl nitrate, the data cannot indicate which specific higher PAN is involved.

Response: Elsewhere in the report we have noted that PPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates. We have modified the text for the PPN formation potentials to reflect the lumped nature of PPN.

13. Page B-56, Table 7.5. The heading for this table caused me some confusion (because of the words "total" and "individual"), and may be better given as "Contribution from individual VOCs to ozone formation", since $(OFP)_i(VOC)_i$ is the amount of ozone predicted to be formed because of the presence of VOC_i.

    Response: Similar headings are used in Table 7.6 through Table 7.10 and can also be a potential source of confusion for the reader. We have used the suggested text in the headings for Table 7.5 through Table 7.10.

14. Page B-61, last sentence. I am surprised that acetaldehyde does not have a significant contribution to PAN formation, because PAN formation arises from the OH radical-initiated reaction of acetaldehyde and from the production of acetyl radicals arising from alkoxy radical decomposition reactions. I suspect that this "acetaldehyde" is that directly-emitted (or initially present) and does not include acetaldehyde formed *in situ* in the atmosphere from VOCs (including from ethanol) [this would then be consistent with the data in Table 7.11]. If so, this needs to be stated.

    Response: You correctly inferred that the ozone, PAN, and PPN (including higher molecular weights acyl peroxy nitrates) formation potentials of a given VOC were estimated from the initial VOC concentration. This is the same methodology used by Bowman and Seinfeld (1994b). This was made clear only for the ozone formation potential on page B-44, where it says "the ozone forming potential can be estimated as the local sensitivity of the predicted ozone concentration to the initial concentrations of each organic compound in the mixture". We have added this clarification in Section B-7 where appropriate.

15. Attachment B1, page B-66. See Comment #10. Also a legend for the kinetic parameters should be given at the beginning of this section. After looking at the OH + ethanol and OH + MTBE rate constants, I figured out that the parameters are A (cm^3 $molecule^{-1}$ s^{-1}), E (kcal mol^{-1}) and n in $k = A(T/300)^n\ e^{-E/RT}$.

    Response: We have added a description of the kinetic parameters used in the SAPRC97 chemical mechanism at the beginning of Appendix B1.

16. Attachment B3, page B-74, and also Executive Summary, section 2.1.2. The most recent (1997 and 1999) IUPAC evaluations and that of Atkinson (*J. Phys. Chem. Ref. Data*, **Monograph 2**, 1-216, 1994) recommend that the OH + ethanol reaction proceeds by (reaction channels numbered as in the Executive Summary):

$$\begin{array}{lcll} & & \rightarrow H_2O + H_2CH_2OH & (3) \\ OH + CH_3CH_2OH & \rightarrow & \rightarrow H_2O + CH_3\ HOH & (4) \\ & & \rightarrow H_2O + CH_3CH_2 & (5) \end{array}$$

with channels (3) and (5) each accounting for 5^{+10}_{-5} % of the overall reaction at 298 K. The relative importance of reaction (5) in the IUPAC evaluations and in Atkinson (1994) is based on the assumption that H-atom abstraction from the O-H group in ethanol occurs with a rate constant equal to that for the corresponding reaction in methanol. The rate constant for reaction (3) is based on an estimation and on the elevated temperature data of Hess and Tully (see the above references). In the atmosphere, reactions (4) and (5) give rise to the same products (acetaldehyde plus HO_2) and are hence indistinguishable.

Response: The suggestion will have a slight impact on the product yield parameters currently used in the SAPRC97 chemical mechanism currently implemented in the UAM-FCM. We defer to Dr. Carter to provide us with a representation of the OH + ethanol reaction appropriate for the airshed model simulation and will use the updated reaction in any future simulations. In addition, based on a follow-up discussion with Professor Atkinson, we will also use an updated OH + ethanol reaction rate constant according to the most recent IUPAC recommendation of $k=5.56´10^{-13}(T/300)^2 exp(532/T)$ *) cm*^{3} *molecule*$^{-1}$ *s*$^{-1}$ *(Atkinson et al., 1999) which results in a 0.03% increase at 298 K. We included this correction in upper-bound model simulations.*

17. Attachment B3, page B-74, and also Executive Summary. The OH + MTBE mechanism is "lumped" in that the specific products are not represented as such. However, this is not going to make any difference for ozone predictions. The rate parameters used for OH + MTBE are from Atkinson (*J. Phys. Chem. Ref. Data*, **Monograph 1**, 1-246, 1989) and have been superseded by a very slightly different rate constant in Atkinson (1994).

*Response: The OH + MTBE reaction in the SAPRC97 chemical mechanism uses a lumped representation of the reaction products, which is deemed appropriate for airshed model simulations. A detailed mechanism with inclusion of all the potential reaction channels is not possible, since it will be very computer resource intensive. Hence, to save time, and at the same time have a good representation of the overall effect of a reaction (including the reactions of the products), a lumped representation is appropriate. Please note that the same approach is used for the other "explicit" mechanisms used in the model. These representations of explicit mechanisms are available by Dr. W.P.L. Carter at his web page (*ftp://cert.ucr.edu/pub/carter/mech/saprc97*). The OH + MTBE reaction rate constant was updated to* $5.89´10^{-13}(T/300)^2 exp(483/T)$ *cm*^{3} *molecule*$^{-1}$ *s*$^{-1}$*, which results in a 3.8% increase at 298 K. We included this correction in upper-bound model simulations.*

Staff Report

18. Page 2, Executive Summary. Two typographical errors.

On line 20, sentence starting "Prior studies". "greater" should be "greater than".

10 lines from bottom, "decreases" should be "decrease".

Response: The text has been corrected.

19. Page 3, Executive Summary. The discussion concerning the increased VOC emissions predicted using EMFAC2000 glosses over the fact that (at least with the emissions scenarios used in the sensitivity studies and using the August 26-28, 1987 meteorology) the predicted maximum ozone levels are 300 ppb for 2003 and the peak 1-hr PAN concentrations are increased by a factor of 3. As noted above in Comment #6, the use of the "correct" emissions (or the most up-to-date estimates) for both VOCs and NO_x would have been optimum. For the scenarios given in Table 1, the basin may be NO_x-limited and relatively

small changes in VOC emissions and/or profiles would then have little or no effect on ozone.

Response: See response to Comment #6 above.

20. Page 6, Section 2.1.1. The rate constant cited is from Atkinson (1994) [IUPAC (Atkinson *et al*. 1999a) did not evaluate OH + MTBE]; see also Comment #17 above. The product data cited are correct; however, it should be noted that these data are for NO being present and are therefore applicable to urban areas but possibly not to downwind areas with low NO_x concentrations. Based on the same studies used by Koshland *et al*. (1998), the reaction mechanism in the presence of NO has been discussed in more detail by Atkinson (1994) and a product profile of *tert*-butyl formate (76%), formaldehyde (48%), methyl acetate (18%) and acetone (6%) recommended [formation of *tert*-butyl nitrite was observed in one of the laboratory studies due to the $(CH_3)_3CO + NO \rightarrow (CH_3)_3CONO$ reaction competing with the $(CH_3)_3CO \rightarrow CH_3C(O)CH_3 + CH_3$ decomposition reaction; under atmospheric conditions the decomposition reaction will totally dominate]. No comment is made concerning the products expected to be formed at low NO_x concentrations from the reactions of $(CH_3)_3COCH_2OO$ and $CH_3OC(CH_3)_2CH_2OO$ radicals with HO_2 and RO_2 radicals, namely $(CH_3)_3COCH_2OOH$, $(CH_3)_3COCHO$ (also formed in the presence of NO as noted above and in the Executive Summary), $(CH_3)_3COCH_2OH$, $CH_3OC(CH_3)_2CH_2OOH$, $CH_3OC(CH_3)_2CH_2OH$ and $CH_3OC(CH_3)_2CHO$ (plus HCHO, methyl acetate and acetone formed from the $CH_3OC(CH_3)_2CH_2O$ and $(CH_3)_3COCH_2O$ radicals). Some mention should be made that *tert*-butyl formate is less reactive in the atmosphere than is MTBE (by about a factor of 4).

Response: The suggested changes have been incorporated into the report.

21. Page 6, Section 2.1.2. See Comment #16 above. Reaction pathway (5) has not been shown experimentally to be negligible under atmospheric conditions, and the only experimental data concerning the importance of the three possible reaction channels are a branching ratio of $k_4/(k_3 + k_4 + k_5) = 0.75 \pm 0.15$ at room temperature (Meier *et al*., *Chem. Phys. Lett*., **115**, 221-225, 1985; *Ber. Bunsenges. Phys. Chem*., **89**, 325-327, 1985) and an acetaldehyde yield under atmospheric conditions of 80 ± 15% (Carter *et al*., *J. Phys. Chem*., **83**, 2305-2311, 1979). The formation of CH_3CHOH and CH_3CH_2O radicals from reactions (4) and (5) lead to the formation of acetaldehyde plus HO_2, independent of the presence or absence of NO, and hence the data of Carter *et al*. (1979) indicate that $(k_4 + k_5)/(k_3 + k_4 + k_5) = 0.80 \pm 0.15$. Formation of $HOCH_2CH_2$ radicals leads to the formation of glycolaldehyde [$HOCH_2CHO$] (22%) and HCHO + HCHO (78%) in the presence of NO (yields are for 298 K and atmospheric pressure of air), and to $HOCH_2CH_2OOH$, $HOCH_2CH_2OH$, $HOCH_2CHO$ and HCHO in the absence of NO. The atmospheric reactions of the $HOCH_2CH_2$ radical have been reviewed by Atkinson (*J. Phys. Chem. Ref. Data*, **26**, 215-290, 1997). Formation of methyl nitrate is not expected to be of any significance; rather the formation of ethyl nitrate in very small overall yield (<0.1%) could occur from the reaction of the ethyl peroxy radical with NO.

Response: The suggested changes have been incorporated into the report.

22. Page 7, Section 2.1.3. The atmospheric chemistry of the "alkylates" was most recently reviewed and evaluated by Atkinson (1997). The rate constants for NO_3 + C_4 alkanes at

298 K range from 5 x 10^{-17} cm^3 $molecule^{-1}$ s^{-1} to 4 x 10^{-16} cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 1997); the rate constants ascribed to Aschmann and Atkinson (1995) are incorrect by 4 orders of magnitude. The products observed and expected in the presence of NO include carbonyls, alkyl nitrates, hydroxycarbonyls and hydroxynitrates, and at low NO_x concentrations will include hydroperoxides, alcohols, hydroxycarbonyls, diols, and hydroxyhydroperoxides (Atkinson, 1997).

Response: The suggested changes have been incorporated into the report.

23. Page 8, Table 2.1. The use of a 12-hr daytime OH radical concentration of 1.6 x 10^6 molecule cm^{-3} seems low, because the global tropospheric 24-hr (annual) average OH radical concentration is 1.0 x 10^6 molecule cm^{-3} (Prinn *et al*., *Science*, **269**, 197-192, 1995).

    Response: Table 2.1 has been updated with a 12-hour daytime OH radical concentration of 3 ´ 10^6 molecule cm^{-3}, as suggested by Professor Atkinson in a subsequent conversation.

24. Page 8, Section 2.1.5. Should include the formation of hydroxycarbonyls and hydroxynitrates from alkylates.

    Response: The suggested change has been incorporated into the report.

25. Page 16, footnote 5. I suspect that on line 7 of this footnote, the "RVP of about 8.5" should be "RVP of about 7.5" [further on it is stated that there will be a 1.0 psi increase (from the 6.5 psi of the gasoline mixture)].

    Response: The text has been corrected.

Appendix B: Emissions

26. Page A-17, 9 lines from bottom. Why was the SAPRC97 mechanism not used for these reactivity calculations ? The NRC (1999) report shows that the absolute MIRs change significantly from SAPRC90 to SAPRC97, although on a relative basis the changes are much less. On line 12 from bottom, the units of specific reactivity (gO_3/g organic) should be given.

    Response: The suggested changes have been incorporated into the report.

27. Page A-19. Units need to be given for the data in Tables 3.7 and 3.8.

    Response: Table 3.7 now clarifies that the units are gram ozone/gram NMOG. Table 3.8 is a listing of profile codes used for the alternate scenarios so there are no units.

28. Page A-24 states that vegetative emissions were incorporated into the source inventory, yet Table 4.1, under "natural sources", has only "wildfires". Some comment is needed.

    Response: The text on this page now states that the total vegetative emissions from the SCAQS August episode are 103.5, 128.8, and 139.8 tons/day for August 26, 27, and 28, respectively. Since these vegetative emissions are constant for all scenarios they do not affect the anthropogenic emission comparisons.

29. Page A-47. The units at the head of this table (kilogram moles/day) appear incorrect; either kilograms/day or moles/day.

    Response: The correct units of kilomoles/day are now noted on Table 4.9.

D-1.2. Professor Barbara J. Finlayson-Pitts of the University of California at Irvine

As per your request, I have reviewed the Staff Report, “Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline”, and my comments are attached. Overall, the ARB staff have done a good job in this initial examination of the potential effects of the use of ethanol in fuels, especially given the time constraints.

As you can see from the first part of my comments, my major concern is that historically, emissions from vehicles have been underestimated both in California and nationally. As a result, what might have been thought in the past to be unrealistic “worst case” scenarios have turned out to be closer to reality. Because of this, I think that it would be important for the ARB to treat some “worst case” scenarios for ethanol use (e.g. in which the RVP is assumed to be higher than 7, the canisters are assumed to malfunction etc.).

I think this is particularly important in that despite all the caveats in the report, this initial assessment will likely end up being used extensively both inside and outside California. I fear that the preliminary assessment may give a misleadingly positive impression which may not ultimately be representative of the “real world” effects.

Response: We now more fully discuss the results of the ARB (1998) analysis of a non-complying ethanol-blended fuel (which shows significant air quality impacts) in the main report and Executive Summary. This serves both as a caution that it is important to meet the RVP requirements (including addressing the commingling and permeation issues) and to not extend our findings to the parts of the country (non-Federal RFG areas) that the U.S. EPA allows an RVP exemption for ethanol.

COMMENTS ON DRAFT REPORT:

AIR QUALITY IMPACTS OF THE USE OF ETHANOL IN CALIFORNIA REFORMULATED GASOLINE

This report is a good initial approach to addressing air quality impacts from the potential future use of ethanol in reformulated gasoline. Appropriately, it includes a number of caveats and areas of uncertainty which will be the subject of ongoing work by the ARB on this problem.

My major concern is that this report will be taken by many, both inside and outside California, as a final assessment. As such, the initial conclusions regarding potential impacts on air quality being minimal are likely to be cited in a widespread manner. However, as detailed in the following comments, I believe that this may change significantly as new data become available, and hence the intial impression left by this assessment may be overly optimistic. In this regard, I have two major concerns, one regarding the emissions estimates and one regarding the use of population-weighted exposures.

<u>Major Overall Concerns</u>:

Emissions: The history of air pollution both in California and the U.S. shows that emissions, particularly from motor vehicles, have been significantly underestimated. This was pointed out, for example, in the 1991 National Research Council Report *Rethinking the Ozone Problem in Urban* *and Regional Air Pollution.* Adjustments were subsequently made to motor vehicle emission models, but as this current draft report on ethanol points out, the EMFAC2000 model is expected to include additional new multiplication factors of 2.3 for VOC and 1.8 for NO_x. These very large adjustments were not forseen by the scientific community, and it is not clear to me that the reasons for the underestimations are thoroughly understood even today.

Response: We agree and that is why our study included a review of ambient air quality studies for areas that have already introduced large amounts of ethanol into their fuel supply and why we have already implemented an ambient air quality measurement program to provide a "real-world" check on our analysis. This is now discussed more thoroughly in the main report and Executive Summary.

This history suggests to me that what are often taken as "worst cases" end up being more typical cases. In the particular case of ethanol, there are some areas of uncertainty discussed in the report which are already known to possibly contribute to underestimates of emissions:

1. The Executive Summary states that "Our analysis did not include the possibility of increased evaporative emissions due to reduced canister function or commingling". The issue of impacts on canister function is discussed in detail on page 15, where it is pointed out that "Oxygenates such as ethanol and MTBE bind more tightly to the activated carbon than hydrocarbons such as butane...... 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...".

   Response: There issues are prominent in the California Phase 3 Reformulated Gasoline Regulations and the report know includes additional discussion on steps being taken to address these issues.

2. Throughout the report, it appears to be assumed that the RVP will not increase with the use of ethanol because of the California RVP requirements. In the Executive Summary, it is stated that 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 results of an ethanol-for-MTBE substitution".

   The summary of recent assessments in Section 2.2 cites many studies where ethanol has been stated to significantly increase species such as acetaldehyde and PAN, but these are dismissed as not being germane. For example, in Section 2.2.1 in the discussion of the University of California MTBE report, it is stated: "However, these findings are not applicable to fully complying CaRFG2 fuels that have the same Reid vapor pressure (RVP) requirement and are constrained by the ARB Predictive Model .. to meet the same limits on exhaust emissions of VOC, NO_x and cancer risk-weighted toxic air contaminants." On page 19, with regard to the predicted emissions, it is stated that "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".

   These assumptions may indeed be the case but it seems to me that given the history of underpredicting emissions, the possibility of increased emissions in the "real-world" should not be discounted. This may be particularly important since as pointed out on page 15, "Hot soak emissions from a test program conducted by the 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%..".

Response: We now more fully discuss the results of the ARB (1998) analysis of a non-complying ethanol-blended fuel (which shows significant air quality impacts) in the main report. This serves both as a caution that it is important to meet the RVP requirements (including addressing the commingling and permeation issues) and to not extend our findings to the parts of the country (non-Federal RFG areas) that the U.S. EPA allows an RVP exemption for ethanol.

3. On page 5, it states that "We also did not consider the possible mileage penalty from increasing the oxygen content of the ethanol-containing gasoline to 3.5 wt %". I do not know what sort of penalty this would be or the effects on emissions, but again, this is an example of a potential source of underestimation.

   Response: Relative to typical current CaRFG2 made with MTBE, CaRFG2 containing 2 wt% oxygen as ethanol would only provide a slightly different fuel economy (change of 0.6% or less). CaRFG2 with 3.5 wt% oxygen would likely provide less fuel economy (by ~2%) than current gasoline, while a non-oxygenated CARFG2 would improve fuel economy by ~2%. However, mass emissions rate should not change in proportion to the change in fuel economy. The Predictive Model tends to force emissions to meet constant standards regardless of the oxygen content. The model is built from data on emissions versus oxygen content of gasoline. with emissions measured in mass per <u>mile</u>, not in mass per volume of fuel. This discussion is now included in the main report.

4. It is not clear to me whether evaporative emissions during refueling were considered in the air quality analysis?

   Response: All sources with either gasoline evaporative or gasoline exhaust emissions reflect gasoline reformulation. Evaporative losses from refueling or storage evaporation were assigned the headspace vapor organic gas species profile.

The report does point out that many of these issues are being examined, but again, my fear is that this ***initial*** assessment, which indicates there will be little impact on air quality due to the use of ethanol, will tend to be the one which will be generally used.

I would recommend that some "worst case" scenario's be treated in which it is assumed that the mandated requirements are not met, e.g. the RVP is higher than 7.0, the evaporative emissions are greater and have relatively more ethanol etc. These could provide some idea of what could happen in an less-than-ideal control scenario.

Response: See response to Comment #2 above.

Use of Population-Weighted Exposures: The results of the photochemical modeling are summarized in Tables 4.4 – 4.6 for four scenarios. While Table 4.6 shows population-weighted exposure, maximum daily average and maximum 1-hour average for a variety of pollutants, Tables 4.4 and 3.5 show only the population-weighted averages for the organics of major concern, acetaldehyde, ethanol and formaldehyde. Air quality standards both in California and the U.S. are expressed in terms of maxima for a given time span, not as population-weighted values. There are clearly many potential problems with the use of population-weighted values. While it appears that the ARB was asked by OEHAA to express the modeling results in part in this form (page 26), I am particularly concerned to see only the population weighted data cited in Tables 4.4 and 4.5. The same is true of the air quality numbers in Tables 4.8 and 4.9. I recommend that the 1-hour, and where appropriate the 8-hour, maxima be cited first and the emphasis put on these values since they represent estimates of the effects expected on the ambient concentrations due to the introduction of ethanol.

Response: We agree that the averaging times presented in Table 4.4 and Table 4.5 were not as comprehensive as the information presented in Table 4.6 and this has now been corrected. The purpose of Table 4.8 and Table 4.9 is to present a reality check between the changes in estimated emissions and modeled air quality. Since the emissions estimates are a daily total for the entire modeling domain, it is more appropriate to compare these results with the 24-hour population-weighted modeled air quality results.

Comments and Questions on Modeling:

1. There is an increasing recognition [e.g. De Haan *et al. Int. Rev. Phys. Chem.* **18**, 343 (1999)] that chlorine atoms may play a role in the oxidation of organics in coastal areas, which includes such major California cities as Los Angeles, San Francisco and San Diego. Specific measurements of Cl_2 [Spicer *et al., Nature* **394**, 353 (1998)] and non-specific measurements of photolyzable chlorine compounds in coastal areas in the eastern U.S. [e.g. Keene *et al., Environ. Sci. Technol.,* **27**, 866 (1993)] find nighttime concentrations of Cl_2 (and perhaps other species) of ~ 150 ppt. At dawn, photolysis generates highly reactive chlorine atoms at concentrations up to ~ 1×10^5 atoms cm^{-3}. There is also evidence for a continuous daytime source of Cl atoms, giving a steady-state Cl atom concentration of as much as mid- 10^4 Cl atoms cm^{-3} at noon over the somewhat polluted North Atlantic Ocean [Wingenter *et al.*, **101**, 4331 (1996)]. The rate constants for oxidation of ethanol and MTBE by OH are similar (~3×10^{-12} cm^3 $molecules^{-1}$ s^{-1}), giving estimated atmospheric lifetimes of 53-59 hours for OH at 1.6×10^6 cm^{-3}, or 530-590 hours at 1.6×10^5 cm^{-3} which might be typical of early morning hours. The Cl + ethanol rate constant is 9.4×10^{-11} cm^3 $molecules^{-1}$ s^{-1} and that for Cl + MTBE is 1.66×10^{-10} cm^3 $molecules^{-1}$ s^{-1}, corresponding to lifetimes of about 30 and 17 hours respectively at a Cl atom concentration of 1×10^5 cm^{-3} which appears to be reasonable for the early morning hours. That is, if indeed chlorine atom chemistry is important in coastal regions, the oxidations of these oxygenates may be speeded up significantly. It might therefore be worthwhile considering doing some modeling runs with a concentration of Cl_2 of about 10^5 cm^{-3} at dawn (each day, not just the first day which is not used in the modeling results) and a steady-state daytime concentration at the coast of ~10^4 cm^{-3} to see the effect, if any, on the formation of formaldehyde, acetaldehyde and PAN.

   Response: There is a limited chlorine chemistry module available in the SAPRC97 mechanism and, hence, it could be added to our atmospheric chemical mechanism (W.P.L. Carter, personal communication, 1999). However, chlorine chemistry was not included in our simulations since we were unaware of the potential significance of the chlorine radical reaction with hydrocarbons, such as ethanol and MTBE. Note that chlorine chemistry is not included in the more recent SAPRC99 (Carter, 1999). There are significant uncertainties in the reliability *of models on chlorine chemistry because there are limited smog chamber data to test mechanisms for chlorine radical reactions (Carter, personal communication, 1999). We conducted a simulation to bound the effect of chlorine chemistry by adding the Cl + ethanol rate constant suggested above and an upper-bound chlorine atom concentration of 10^4 Cl atoms cm^{-3} throughout the entire modeling domain for all hours, not just coastal areas during daylight hours. We will add the relevant chlorine radical reactions to any future air quality modeling.*

2. Some of the model predictions do not seem to make sense intuitively. For example, Table 4.4 shows that the 1-hour PAN maximum will be lower for the 2003 Et2.0% scenario compared to the 2003 MTBE scenario. Similarly, Table 4.6 shows that although the maximum 1-hour average and maximum daily average ethanol concentrations are expected to be about 50% greater for the 2003 Et2.0% scenario compared to the 2003 MTBE scenario, acetaldehyde and PAN concentrations are predicted either not to be affected at all, or in the case of the 1-hour maximum PAN levels, even decrease. There should be some discussion of the reasons for these suprising results.

   Response: The differences in predicted PAN concentrations for each scenario are due to differences in the emissions of various VOCs with higher PAN formation potentials than ethanol. From Table 4.9 in Appendix A, it is clear that the 2003 Et2.0% scenario has higher ethanol emissions than the 2003 MTBE. However, the 2003 MTBE has higher emissions of alkanes, aromatics, and olefins compared to the 2003 Et2.0%. Figure 7.3 and Figure 7.4 in Appendix B suggest that the lumped species ALK2, ARO2, OLE1, OLE2, and OLE3 can have (depending on the environmental conditions) higher PAN formation potentials than ethanol. Another factor is that although ethanol emissions are higher in the 2003 Et2.0% scenario, they only represent 8% of the nonmethane VOC emissions. For comparison, ALK2, ARO2, OLE1, OLE2, and OLE3 comprise about 31% of the nonmethane VOC emissions in 2003 Et2.0%. Hence, PAN formation is primarily governed by the differences in alkane, aromatic, and olefinic emissions between scenarios, rather than the emissions of ethanol. This discussion is now highlighted in the report.

3. The concentration of CO_2 in Tables 3.3, 3.4 and 3.5 should be 358 ppm, not 1 ppm (no difference to chemistry, I assume, since condensed phase chemistry where CO_2 would act as a buffer is not included). The boundary, top and initial species HONO concentrations also seem low for the Los Angeles region, where something of the order of 1 ppb might be more applicable [e.g. Winer and Biermann, *Res. Chem. Inter.* **20**, 423 (1994)]. In Table 7.4, the methane concentration must be about 1.7 ppm, since this is a global average; smaller values as shown in the table don't seem reasonable.

   Response: CO_2 concentrations do not have an effect on the photochemistry and the major source of HONO is direct emissions (assumed to be 2% of the NO_X) and in situ formation. We revised the boundary, top, and initial conditions that we use for CO_2 and HONO to the suggested values for the upper-bound modeling simulations. The methane concentration used in the Brazilian box model simulations was a mistake that has now been corrected.

4. In Appendix B on pages B-11 and B-12, it is stated that "Although domain ethanol emissions have increased from 1997 to 2003, reflecting changes to the motor vehicle cleaner burning gasoline used, the emissions from non-motor vehicle sources (which appear to dominate the magnitude of the maximum ethanol concentrations) have decreased". The data in Table 4.1

accompanying this statement show a decrease of about 10% in predicted ethanol concentrations. I have two questions:

a. What are the non-motor vehicle sources? It seems surprising that there are sufficient stationery sources of ethanol that they would dominate those associated with motor vehicles.

   Response: Ethanol is a commonly used as a solvent, especially in consumer products. Everyday products from mouthwash to air fresheners, and many household-cleaning products contain ethanol. The 2003 baseline inventory for a non-ethanol fuel contains about 32 tons/day of ethanol, of which 24 tons/day comes from consumer products.

b. What is the difference between the data cited in Table 4.1 of Appendix B and Table 4.6 of the report? The former cites concentrations of ethanol, for example, of 41-45 ppb while the latter cite 78-165 ppb for the maximum 1-hour average.

   Response: The data in Table 4.1 of Appendix B represent model results for an August (summertime) ozone episode day. The data in Table 4.6 are estimated annual maximum or populated-weighted concentration values. The latter tables (which is reported to OEHHA) may have higher values, particularly for primary pollutants where the maximum value typically occurs under stagnant wintertime conditions.

On page B-43, it is stated that there are large discrepancies between predicted and observed 3-hour average concentrations for the Los Angeles site but that others are of the same order of magnitude. This might be strictly correct but the differences are still factors of two or more at some non-Los Angeles sites. Rewording of these sentences might be appropriate.

Response: There is insufficient discussion of the results presented in Table 6.4. Model results and measured data also differ significantly at other sites. For example, at Anaheim, the 1,3-butadiene 3-hour average concentration was measured at 0.3 ppb, while the model predicted an extremely lower concentration, measured formaldehyde is almost twice the predicted values, and measured acetaldehyde is about three times higher than what the model predicts. At Riverside, measured benzene is almost twice the predicted value at 0600, but at 1100 the measured benzene 3-hour-average concentration is three times the predicted value. This section now included the revised discussion.

<u>Minor Comments</u>:

1. In the fifth paragraph of the Executive Summary (starting “It is possible that ethanol’s propensity..”), it should be made clear that this discussion refers to the charcoal canister used for vapor control on automobiles.

   Response: The suggested change has been incorporated into the report.

2. The ethanol concentration in fuel is sometimes given in % by weight and sometimes in % by volume. It would be very helpful to the reader to give it in both units throughout.

   Response: The suggested change has been incorporated into the main report.

3. On page 32, line 6 of Section 4.2.3.3, the end of the sentence "The results are reported in...." is missing.

   Response: The text has been corrected.

4. It is not clear to me what "Upper Baseline" and "Lower Baseline" mean in Table 4.6.

   Response: Upper baseline and lower baseline refer to baseline 1997 concentrations estimated under a variety of methods are discussed in Section C-3 of Appendix C. The highest estimated 1997 concentration became the "Upper Baseline" and the lowest estimated 1997 concentration became the "Lower Baseline." The estimated future year concentrations were generally made starting with the upper and lower baselines and then applying model results to account for changes from the 1997 "baseline". The procedure for estimating future year concentrations is described in Section C-4 of Appendix C.

5. In Table 6.4, the predicted acetaldehyde concentrations are given to 4 significant figures in some cases; 2 significant figures is probably more appropriate.

   Response: The model results in Table 6.4 have been be revised to duplicate the number of significant figures of the measurements.

D-1.3. Dr. Donald Lucas of Lawrence Berkeley National Laboratory and the University of California at Berkeley

This letter contains my review of the California Air Resources Board document titled "Air Quality Impact of the Use of Ethanol in California Reformulated Gasoline." This reviews covers the following parts of this document and several other documents, including the following:

1. Air Quality Impact of the Use of Ethanol in California Reformulated Gasoline – Staff Report (Nov. 18, 1999).
2. Appendix A - Emissions (Nov. 10, 1998).
3. Appendix D – Responses to Scientific Peer Review and Public Comments (Nov. 10, 1999).
4. Attachment A1 – Peer Review of Organic Gas Emission Profiles.
5. Other documents mentioned and/or cited in the above reports.

My review focused on the Executive Summary and Section 3 of the main document, Appendix A, and Sections D-1, D-2 and D-4 of Appendix D.

The purpose of the study was to analyze the environmental fate and transport of ethanol in air, surface water, and groundwater (Executive Order D – 5 – 99). The analysis estimates the changes in ambient air concentrations of potentially detrimental contaminants of the exhaust and evaporative emissions components and subsequent reaction products that would result from substituting ethanol-blended gasolines for gasoline blended with MTBE.

There were few conclusions drawn directly from the part of the work reviewed here. The emissions predicted were used in modeling to calculate how the atmosphere would change as a result of increased use of ethanol in gasoline. The atmospheric results themselves are only part of environmental impact.

The predicted changes in emissions expected from using ethanol in gasoline appear reasonable, both in the direction and magnitude of the changes. With no MTBE in the gasoline, MTBE emissions should decrease to approximately zero (there may be a trace amount of MTBE in future fuels, but its concentration will be capped at 0.05% by the proposed CaRFG3 regulations). Compared with emissions expected for a 2003 fuel with MTBE, ethanol emissions will increase, with the value depending on the level of ethanol in the fuel. Ethanol containing fuels will have higher acetaldehyde emissions and could have lower levels of CO, depending on the amount of oxygenate used. Fuels without oxygen will produce more CO, but no ethanol or MTBE emissions. The predicted levels of NOx and reactive organic gases (ROG) are unchanged.

The calculations presented in this study appear to be consistent and reasonable, and are well documented. The calculations are complicated, and there are many assumptions made regarding emissions. These include the need to predict what fuel will be used in 2003, what the vehicle fleet will be, and what other emissions are significant. In this regard, it is difficult to determine exactly what the best set of assumptions should be, and how significant the results are from a statistical viewpoint. This is not to say that the results are incorrect, but that the uncertainties are large, and additional work needs to be done. The ARB recognized that the results rely on engineering judgement, and that the results need to be confirmed by the planned field measurements.

In developing the emission estimates for 1997 and 2003, the ARB made many adjustments to the profiles developed for MTBE-based CaRFG2. Changes were made for several compounds to be consistent with the fuel. Prof. Robert Harley of UC Berkeley reviewed the emission factors previously, and suggested several changes that were adopted by the ARB. I have no further suggestions. It is important to continue the early review process, as it allowed corrections to be made earlier in the process, probably saving considerable time and resources.

Response: The ARB staff agree.

Future gasoline compositions used in this study are predicted. Even though they may not be the exact formulations that will be sold in California in 2003, they are not unreasonable. The calculations in this study were performed as the new proposed Phase 3 Reformulated Gasoline (CaRFG3) regulations were being written, and both studies have similar deadlines. Since the CaRFG3 regulations may be adopted soon, the follow-up study suggested here should incorporate these changes. The timing of these two related studies made if difficult to use the information generated in the CaRFG3 regulation process, which was ongoing during the same period as this study. While better results could have been obtained by better coordinating the studies, time constraints placed on the ARB prevented this. While I do not think that the results from this study would change significantly if more time were allowed, care must be taken in balancing the need for a timely decision with the effort and time needed to produce sound scientific results.

Response: The ARB staff agree.

The effect of changing CO emissions when oxygenated fuels are used is accounted for in this study. Since CO acts as an organic compound in terms of ozone formation, it must be combined with other emissions. CO is treated here as other compounds, using the well-established and reviewed reactivity. The ARB is consistent in their approach. Whitten (1999) suggested a higher value for the reactivity of CO, and the ARB responded in detail. While the calculations presented by Whitten appear correct, it is difficult to justify using different models and scenarios for a single species. The value of examining issues such as these should not be underestimated, and the continued input from outside experts such as Whitten should be encouraged.

Response: The ARB staff agree.

The effect of consumer commingling, where ethanol-containing and ethanol-free gasolines are mixed, produces a fuel with a higher Reid Vapor Pressure (RVP). The mixed fuel would increase non-exhaust emissions. Under current federal law, where most of the gasoline in California is required to have an oxygenate, it is likely that commingling would not be a significant problem, since all gasolines would probably contain ethanol. However, Governor Davis has requested a waiver (April 12, 1999) from the EPA, and the ARB has supported this request. If granted, commingling could be more common. The effect of a waiver on commingling should be researched in a timely fashion, and potential solutions should be examined.

Response: The ARB staff agree.

The mileage penalty that occurs when using oxygenated fuels was not considered in this study. The mileage penalty is well known from previous research, and could be added as a simple factor. The small change will probably not effect these results, but they should be included in future work.

Response: Relative to typical current CaRFG2 made with MTBE, CaRFG2 containing 2wt% oxygen as ethanol would only provide a slightly different fuel economy (change of 0.6% or less). CaRFG2 with 3.5 wt% oxygen would likely provide less fuel economy (by ~2%) than current gasoline, while a non-oxygenated CARFG2 would improve fuel economy by ~2%. However, mass emissions rate should not change in proportion to the change in fuel economy. The Predictive Model tends to force emissions to meet constant standards regardless of the oxygen content. The model is built from data on emissions versus oxygen content of gasoline with emissions measured in mass per mile, not in mass per volume of fuel. This discussion is now included in the main report.

A small number of vehicles were tested at the ARB laboratory in El Monte. Three different commercially available fuels were used, including an ethanol-blend. However, the fuels are not representative of the fuels expected to be sold in 2003, and the ethanol-blended fuel had a very low sulfur level of approximately 1ppm (the sulfur level in the fuel is known to have a significant effect on exhaust emissions). The vehicles are not representative of the fleet either in terms of vehicle number, miles driven, or fraction of emissions. Given the high cost and difficulty of this type of vehicle testing, this is a disappointing part of the study. It is not clear how the criteria for vehicle selection were made. Half of the vehicles were required to have mid-range emissions of hydrocarbons. The average model year was 1981, and only one car was Japanese. While it is important to learn how the mid- and high-emitters will perform on any new fuels, the ARB has previously reported that it is nearly impossible to test these types of cars under current testing protocols because of their non-reproducible behavior.

Response: We planned to test vehicles that contribute the most to emissions. This is not the same group of vehicles that have the highest vehicle miles traveled (VMT). While the average emission rates and test variability were higher than desired, the results are not a crucial part of our conclusions.

Running and evaporative losses were not measured directly. The composition of emissions expected was estimated in part by measuring vapor in equilibrium with the liquid fuel. Since these emissions are becoming a larger fraction of the total vehicle emissions, it is important to know these emissions, especially since material permeability and cannister performance is not well understood for fuels with varying ethanol levels. The ARB has noted the limitations of their testing in this study. Their conclusions are qualitative, and they claim that they do not contradict the model profiles. Given the uncertainties the claim is probably true, but of little value.

Response: The lack of evaporative emission measurements taken on commercial fuels did not directly bear on evaluating the profiles used to represent evaporative emissions in the photochemical modeling. The modeling input profiles are gasoline composition profiles and their corresponding headspace compositions, rather then actual hot-soak and diurnal/running compositions. This was the type of data taken in the commercial fuel study. While the substitution of gasoline and headspace compositions for actual evaporative emissions introduces uncertainty, that uncertainty could not have been reduced by comparison to speciated evaporative emissions from the commercial fuels. As noted by the reviewer, those fuels cannot be viewed as typical of future MTBE-free CaRFGs.

In summary, the ARB has produced a set of emissions expected in the 2003 if ethanol replaced MTBE in California gasolines. The results are a good starting point for evaluating the environmental impact of ethanol in fuels, and provide the necessary data for further analysis. This type of modeling effort should continue, especially as the composition of the new fuels becomes more certain.

Response: The ARB staff agree.

D-1.4. Professor John Seinfeld of the California Institute of Technology

I am reporting to you on Appendix B Photochemical Modeling. (I looked at the other reports but did not read them closely.) I have reviewed the model application protocol reported in Appendix B and find it to be not inconsistent with standard practice in South Coast Air Basin photochemical modeling. Replacement of the CBM with SAPRC-97 was an important feature. The use of the model simulations in a relative sense enhances their value in looking for differences between scenarios. I have not reviewed the emissions profiles for the MTBE and ETOH cases; I assume they accurately reflect those profiles. The predicted direction of differences in O3 and other pollutants between the scenarios can be considered to be accurate. It is noteworthy that the predicted differences in O3 between the MTBE and ETOH cases are small. (Interestingly, this was also the case a number of years ago when comparisons between gasoline and reformulated gasoline were being made.) Assuming that the MTBE and ETOH emissions profiles and amounts are accurate, this says that other factors are governing the overall concentration of O3, not these ingredients. One can gauge if this makes sense from the change in magnitude of emissions of gaseous products associated with MTBE and ETOH. Presumably this is the case.

Response: The ARB staff agree.

In summary, the photochemical modeling is consistant with current practice. There are no evident danger signals associated with the results. Model performance in an absolute sense could be better, but the use of simulations in a relative sense should bypass these difficulties.

As you have requested, I have read Section D-3 of the report. Gary Whitten's analysis of the effect of CO on ozone formation, as simulated in a three-dimensional model, is correct. The question, though, is not whether Whitten is correct, but what scale is being used to judge reactivity. The ARB has utilized Carter's MIR scale, which is not based on three-dimensional, multiday simulations. Most would agree that three-dimensional, multiday simulations are preferable to trajectory box simulations in assessing reactivity. This point was made by the ARB's Reactivity Advisory Committee at its last meeting. Moreover, the fact that peak ozone reactivities differ between the MIR scale and those predicted on the basis of a 3D model points not to a weakness of 3D models, but to a weakness of the trajectory model MIR simulation. That having been said, however, it is recognized that the ARB has invested in the Carter MIR scale for judging reactivity and changing lock stock and barrel over to a 3D airshed model scale is a nontrivial undertaking. The question is whether the reactivity of CO should be increased by 1.65 in the current application. The ARB response argues that in the interests of consistency they do not wish to alter the scale that has been used and that population exposure correlates better with that predicted by the MIR scale than peak ozone anyway. Short of basing all reactivities on 3D model simulations, I cannot recommend that the ARB make this one single adjustment.

Response: The ARB staff agree.

D-2. Response to Scientific Peer Review of Emission Profiles

This section contains ARB responses to the scientific peer review of Professor Robert Harley of the University of California at Berkeley (see Attachment A1). The focus of Professor Harley review was on organic gas speciation profiles of exhaust and evaporative emissions from alternate gasoline formulations. Each comment by Professor Harley is presented in normal font and is followed by the ARB response inserted in italics.

Comment 1: CAT STABILIZED EXHAUST PROFILE FOR RFG w/MTBE. The stabilized exhaust profile for catalyst-equipped engines (profile 876) is compared in the attached Figure 1 with the on-road running emissions profile measured in the Caldecott tunnel in summer 1996 for 20 individual species that together account for >70% of non-methane organic compound emissions in profile 876 and in the tunnel. The tunnel profile is similar to profile 876 for all species except MTBE, which accounted for 5.0% of tunnel VOC (5.5% of tunnel NMOC), whereas profile 876 includes only 2.0% by weight MTBE. Methane is not shown in Figure 1; it accounted for 15.8% of VOC in profile 876 versus 9.1% of VOC in the Caldecott tunnel. A 1996 emissions-weighted average of the profiles for cat and non-cat stabilized exhaust should give around 10% methane to agree with on-road data.

Comment 2: CAT STABILIZED EXHAUST PROFILES FOR ALL 4 FUELS. The stabilized exhaust profiles for all 4 fuels for catalyst-equipped engines (profiles 876, 663, 673, and 653) are compared for selected species in Figure 2. Abundance of species shown in Figure 2 is similar across all profiles, except for five species shown at the right: isobutene, formaldehyde (HCHO), acetaldehyde (CCHO), MTBE, and ethanol. Changes for these species are expected if changes are made in gasoline oxygenate content.

While addition of MTBE to gasoline is expected to lead to increased emissions of isobutene in vehicle exhaust (Hoekman, 1992; Kirchstetter et al., 1999), further consideration should be given as to whether isobutene would increase as much as shown in Figure 2 when switching from RFG containing ethanol to RFG without any oxygenate.

Response to 2nd paragraph:

We have changed the isobutene content in the exhaust profiles in light of this comment.

The original isobutene content of the profiles was different for the two types of MTBE-free CaRFGs because they were derived from different experiments. The ARB's MTBE/EtOH study showed a 60% decline in isobutene in bag 2 between the EtOH- and MTBE-blended test fuels, while the A/O 17 study showed only a 32% decline between its oxygen-free and MTBE-blended test fuels. (In contrast, the two studies showed more similar declines in isobutene in the bag 1-bag 3 results, 53% and 43%.)

Isobutene is a known product of burning MTBE. It is not known to be produced by burning ethanol. From this information alone, one would not expect the presence or absence of ethanol in MTBE-free gasoline to affect the decline in isobutene from the removal of MTBE.

Since there is isobutene in the exhaust of oxygen-free gasoline, there obviously is some precursor in gasoline other than MTBE. Butenes are intuitive candidates, and they were more plentiful in the oxygen-free A/O fuel than in the MTBE-blended fuel. However, their combined fuel concentrations were too low (~0.1%) to explain the different declines in isobutene between the two studies.

Since MTBE is the only identified determinant of isobutene in the exhaust, it is reasonable to regard the ARB and A/O studies as providing equally valid data on the effect of removing MTBE from the fuel, regardless of whether or not ethanol is added. Then, the estimated decline in isobutene in bag 2 is (0.60 + 0.32)/2 = 46%. This is within the range between the two studies in the decline in the starts emissions (41% to 53%, mean 47%). Therefore, it is reasonable to use a common adjustment factor, 1 - 0.46 = 0.54, for creating the isobutene contents of both exhaust profiles for each CaRFG that does not contain MTBE.

Despite the use of a common adjustment factor, the final profiles will have somewhat different isobutene contents because the adjusted profiles must be separately normalized to 100% after different net changes in their oxygenate contents and in other species.

[Comment 2 resumed]

Given that ethanol accounts for 5.75 and 10.1% of gasoline mass (these values correspond to 2 and 3.5% by weight oxygen, respectively), it is surprising in profiles 663 and 673 that ethanol accounts for only 0.25 and 0.5% of exhaust VOC mass. I would predict that roughly half of the exhaust would be unburned fuel, and so would expect as much as an order of magnitude higher ethanol (3-5%) in exhaust emissions depending on fuel ethanol content. Further consideration of this issue is recommended.

Response to 3rd paragraph:

We changed the ethanol content in the exhaust profiles in light of this comment.

The ethanol content we had assigned to bag 2 exhaust was probably too low. Our algorithm is to directly insert the observed EtOH fraction from the chosen study (ARB's MTBE/EtOH study, in *this case) into the emission profile being built. (For all other species, we multiply the content in ARB's existing MTBE-blended profile by the content ratio between fuels in an external study.) The ethanol content of bag 2 from the EtOH test fuel is very low, as is the MTBE content of bag 2 for the MTBE test fuel. In contrast, the MTBE content in ARB's in-use survey results is much higher, as are exhaust MTBE and EtOH contents in data from other sources. Probably, then, the bag 2 ethanol content we had directly inserted (from the MTBE/EtOH study) is unrealistic.*

In this case, it is better to create the EtOH content of exhaust from ethanol-blended CaRFG as we do for other species, by applying an adjustment factor to the MTBE content in the existing profile. That adjustment factor (taken from the ARB study results) is 1.96 for gasoline with 3.9 wt% oxygen as ethanol. Linearly adjusted according to the oxygen content, it becomes 1.00 or 1.75 for oxygen at 2.0 or 3.5 wt%, respectively.

Comment 3: EXHAUST PROFILES FOR RFG w/MTBE. For gasoline containing 2% oxygen as MTBE, a comparison of exhaust profiles for catalyst/non-catalyst engines and stabilized/start emissions is presented in Figure 3. Isopentane is higher in the stabilized profiles than in the start profiles. Aromatics (toluene, ethylbenzene, xylenes, and 1,2,4-trimethylbenzene) are less abundant in the catalyst stabilized exhaust profile (876) when compared to the other profiles shown in Figure 3. Acetylene in the non-catalyst stabilized exhaust profile (401) is the lowest of all profiles shown in Figure 3, which is unexpected because vehicles with catalytic converters are expected to have the lower acetylene levels. ARB staff should consider specifying a higher acetylene fraction in profile 401. I am concerned that using the highest-emitting vehicles from ARB in-use surveillance testing may not accurately represent non-catalyst engine emissions.

Response:

We did not modify the acetylene fraction. Acetylene is a negligible contributor to ozone and PAN formation.

Comment 4: LIQUID FUEL. In Figures 4 and 5, liquid fuel composition in profile 419 is compared against measured fuel composition in the SF Bay Area from summer 1996 (Kirchstetter et al., 1999). The profiles are similiar in terms of distribution of species across organic compound categories (Figure 4) and for the top 16 identified species listed in profile 419 (Figure 5). These 16 species account for >60% of the mass in profile 419. Profile 419 seems reasonable in comparison to the liquid fuel data from the Bay Area, although differences exist in the specific isomers and types of alkanes present. Further comparisons of profile 419 against Los Angeles area gasoline composition measured during summer 1996 (Norbeck et al., 1998) could be helpful.

Comment 5: HOT SOAK. Duplicate entries exist in the hot soak emission profile (420) for all 3 isomers of ethyltoluene (also called methyl-ethyl-benzene). ARB staff should consider deleting the entries for SAROAD codes 45211, 45212, and 98164 in profile 420, which duplicate entries for SAROAD codes 99915, 99912, and 99914, respectively. If this change is made, the profile will need to be renormalized to sum to 100%, and the hot soak profiles for other fuels (numbers 652, 662, and 672) should be rederived based on the revised profile 420.

The benzene content in hot soak emissions varies widely across fuels, from a low of 3.3% to a high of 4.9% by weight. Given the modest changes specified in fuel benzene content, the changes appear too large, and furthermore the highest hot soak benzene content is specified for the liquid fuel having the lowest benzene (profile 652). A large decrease in hot soak benzene occurs between profiles 662 and 672, while fuel benzene hardly changes.

Response to 2nd paragraph:

Four factors are involved in the benzene content:

- *Proportionality of evaporative emissions to fuel composition (e.g., Raoult's law).*
- *Use of MathPro's linear programming predicted fuels to derive adjustment factors for species in the various CaRFGs.*
- *ARB's model (like EPA's) that shows hot-soak benzene increasing when MTBE is removed.*
- *Normalization of each profile to total 100%, which alters the "raw" numbers.*

These have led to a complex set of benzene contents in the fuels and associated hot-soak profiles. Further consideration has led to a simpler approach that reduces the variation in the hot-soak profiles.

MathPro predicts 0.80 benzene content in both EtOH-blended and oxygen-free CaRFG vs. 0.67 percent benzene in MTBE-blended CaRFG. Per Raoults' law, the greater benzene content caused a 20% increase in the benzene content of the hot-soak profile compared to MTBE-blended CaRFG. However, both the 0.67 and 0.80 figures exceed the typical benzene content of current gasoline and probably will not be practical under upcoming changes to the ARB's gasoline regulations. Accordingly, there is no clear basis to predict any differences in the benzene contents of the various CaRFGs in the future. Therefore, it is advisable to fix the benzene contents of all CaRFGs at the value in the ARB's composition for MTBE-blended CaRFG.

This change leaves only the depressant effect of MTBE (6%) as the only factor to change the benzene content of hot-soak emissions. (It also changes some results for benzene in exhaust emissions as predicted with the Predictive Model.)

[Comment 5 resumed]

The composition of hot soak evaporative emissions may approach, in some cases, the composition of liquid gasoline, especially for older vehicles with carburetors. Large differences exist in the relative abundances of toluene (15.1% in profile 420 vs. 6.7% in liquid fuel), m-xylene (8.8% in profile 420 vs. 3.5% in liquid fuel), and 2,2,4-trimethyl-pentane (2.1% in profile 420 vs. 5.5% in liquid fuel).

Response:

We used the liquid fuel gasoline composition to represent hot soak evaporative emissions in the 2000 and 2003 scenarios.

Comment 6: DIURNAL. A gasoline headspace vapor profile (906) is used to represent the speciation of diurnal evaporative emissions. This profile was derived using vapor-liquid equilibrium theory and measured composition of liquid gasoline from the Bay Area in summer 1996 (see Kirchstetter et al., 1999). This profile is likely to describe the composition of displaced gasoline vapor emissions that occur during refueling (Furey and Nagel, 1986). For diurnal emissions from vehicles equipped with correctly-functioning activated carbon canister control systems, other factors such as differing uptake rates of individual VOC, canister carryover effects, and permeation of VOC through fuel system elastomers, can affect VOC composition (Urbanic et al., 1989; Burns et al., 1992). Therefore, an equilibrium headspace vapor composition profile may not represent all diurnal evaporative emissions correctly. Also the benzene levels in profile 906 were calculated from Bay Area liquid gasoline composition which included 0.58% benzene, as opposed to 1.00 wt% benzene in profile 419 (unburned fuel profile, RFG w/MTBE). Therefore profile 906 is likely to understate the benzene content of diurnal evaporative emissions relative to what is specified in the liquid fuel in profile 419.

The level of benzene in diurnal profile 651 (0.52% for RFG w/o oxygenate) is not consistent with benzene content in the liquid fuel, which is the lowest of all 4 fuels, whereas the corresponding diurnal profile has the highest benzene value.

Response to 2nd paragraph:

The response to the previous comment applies here, too; except that in the most recent version of the ARB model for evaporative benzene, MTBE is not a factor for diurnal benzene emissions.

[Comment 6 resumed]

The presence of ethanol in headspace vapor/diurnal evaporative emissions may not scale linearly with ethanol content in fuel, because ethanol exhibits non-ideal behavior in solution with non-polar gasoline hydrocarbons (Bennett et al., 1993), and the activity coefficient increases as ethanol content decreases. Therefore, decreases in ethanol in the liquid may be offset in part by increases in its activity coefficient. Further analysis of profiles 661 and 671 is recommended.

Response to 3rd paragraph:

We dropped these profiles from our analysis and used the headspace calculation provided by Professor Harley (see Attachment A1).

[Comment 6 resumed]

ARB staff should move isomers of ethyltoluene listed in the diurnal evap profiles to list them under SAROAD codes 99915, 99912, and 99914, for consistent labeling of these species across all 7 profiles for each fuel.

Response:

We made this change.

Comment 7: BUTADIENE. 1,3-butadiene is present in exhaust emissions, but is not present in any of the evaporative emissions profiles supplied by ARB. This is appropriate. At present there are only minor differences in butadiene weight fractions across the different fuels. Increases in olefin content in unburned fuel may increase butadiene emissions in vehicle exhaust (e.g., Table 3 of Gorse et al., 1991). Therefore, ARB staff should consider whether converting 80% of butane content to butene to construct profile 650 would lead to increased butadiene in the exhaust profiles for gasoline without oxygenate.

Response:

We have no information on the effects of specific olefins on butadiene emissions. However, as shown in Table 12, the Predicted Model predicts that the total olefinic content of the oxygen-free CaRFG (modeled by MathPro) would not cause higher butadiene emissions. The butane content in profile 650 was incorrect and has been dropped.

Comment 8: ACETALDEHYDE. Profiles 673-676 correspond to exhaust emissions for gasoline with 3.5% oxygen as ethanol. Given the higher fuel ethanol levels, emissions of acetaldehyde should increase compared to profiles 663-666 where ethanol is present at only 2% oxygen, yet the profiles are virtually identical in terms of acetaldehyde content.

Response:

We have changed the acetaldehyde contents to reflect the ethanol content of the fuels.

The dataset used to generate the species adjustments (ARB's MTBE-EtOH study) does not include multiple ethanol contents in the fuels; so other than the assumed linearity in the ethanol content of emissions, there has been no distinction in emission strengths of particular species according to the ethanol content of the fuel. However, ARB has developed oxygenate-specific aldehyde emission models (whereas the Predictive Model uses only oxygen content as an input). These new models produce the following emission predictions versus oxygen and oxygenate. In the final document, the emissions relative to emissions for 11% MTBE are combined with changes between fuels in hydrocarbon emissions to yield new values of the aldehyde contents of the profiles.

Table 2.1. Aldehyde Emission Predictions

	11% MTBE	*No Oxygen*	*EtOH, 3.9% O_2*	*EtOH, 3.5% O_2*	*EtOH, 2.0% O_2*
Formaldehyde					
rel. to 11% MTBE	*1.00*	*.90*	*.90*	*.91*	*.95*
rel. to 3.9% O_2	*xx*	*xx*	*1.00*	*1.01*	*1.05*
Acetaldehyde					
rel. to 11% MTBE	*1.00*	*.96*	*2.74*	*2.33*	*1.28*
rel. to 3.9% O_2	*xx*	*xx*	*1.00*	*.85*	*.47*

Comment 9: OTHER. There are errors in the molecular weights assigned to some of the chemical species in the speciation profiles that were sent to me. Recommended corrections are listed in the attached Table 1. Depending on the chemical mechanism and emission processing procedures used in air quality modeling, these errors in molecular weights could affect conversion of emission rates from mass to molar units. Also, in estimating headspace vapor composition from liquid fuel composition, accurate molecular weights are needed to convert between mass fractions and mol fractions. The most important change is likely methylcyclohexane (43261) where the molecular weight should be 98.2 rather than 85.2 g mol^{-1}.

Response:

We agree with the molecular weight changes and have changed our database.

D-3. Response to Public Comments

D-3.1. Public Comments on Work Plan

This section contains public comments and ARB staff responses on "ARB Work Plan for Conducting an Airborne Environmental Fate and Transport Analysis of Ethanol-Containing Gasoline" dated July 8, 1999 and "Development of Emission Profiles for CARFG W/o MTBE" dated July 12, 1999.

Comments were received from Dennis Hoagland of Shell, David A. Smith of ARCO, Jim White of White Environmental Associates, Gary Z. Whitten of ICF Consulting, and Gina Grey of the Western States Petroleum Association (WSPA). The comments are paraphrased below with the ARB staff responses in italics.

Emission Inventory Component

1. Comment: No consistent, comprehensive data set exists from which to derive the speciation profiles for all the fuels -- and emissions from these fuels -- which will be used by ARB. Given this lack of data, ARB is compelled to adjust existing profiles, using many assumptions, comparisons, arbitrary additions and deletions, etc. ARB's approach is described in a document entitled "Development of Emission Profiles for CaRFG w/o MTBE." While far from satisfying, this approach is probably the best that can be done, given the time constraints of the Governor's Executive Order. Nevertheless, we are concerned about the precedent this methodology sets--specifically that many tasks are fraught with subjective engineering judgement. We are also concerned that future policy could be made using results from this work. To address these concerns, we urge ARB to generate more experimental data in the future, using appropriate fuels and vehicle sets. (WSPA)

   Response: California Air Resources Board (ARB) staff agree that in the absence of the availability of production fuels, the airborne environmental fate and transport analysis of ethanol-containing gasoline relies on engineering judgement and should not be viewed as definitive. However, the approach should provide adequate information to allow evaluation of the use of reformulated gasoline with ethanol and non-oxygenated reformulated gasolines. It is preferable to use experimental data where possible, however, even in the best of circumstances engineering judgment must be exercised.

2. Comment: Assuming ethanol-blended fuels are precluded from pipeline distribution, surface transport of this gasoline component between manufacturing/refining locations to the distribution network will need to increase substantially. My estimate is a potential increase of tank truck traffic (depending upon locations rail cars do not work) by as much as 30%. Is the extent to which traffic accident and spills have been addressed in risk analyses? At present, and for our facility, this exposure would be minor. (Inasmuch as our receipts are by ship/pipeline and bulk of outgoing transportation is pipe). What steps would be necessary to assure this

impact is addressed in an Environmental Impact Report for an ethanol fuels requirement? (Hoagland)

What about the diesel emissions from trucks delivering all the ethanol to the terminals for blending into the gasoline? (Smith)

Response: *Emissions from diesel trucks are not pertinent to comparing the environmental transport and environmental fate of ethanol versus MTBE in gasoline. Any issues about extra diesel emissions and other risks will be considered by permitting authorities and California Environmental Quality Act (CEQA) lead-agencies when new facilities would under go CEQA and permit reviews.*

Spilled ethanol is pertinent to the current analysis in that it would become air emissions. However, the amount of ethanol would be trivial compared to the ambient burden of ethanol from vehicular emissions.

3. Comment: First we must all realize that the future is uncertain regarding just how the refineries will blend fuels to meet the emissions requirements of CaRFG without using MTBE. Given such uncertainty, the development of emissions profiles might best require that some attention first be given to some likely scenarios before heading off to analyze exiting data on emissions from vehicles using non-oxygenated or ethanol-containing gasolines.

For example, it is the understanding of this reviewer that a scenario with a high probability would have premium gasoline using ethanol and a large fraction of regular grade made without oxygen. The approach described in this draft ARB document appears to be based on some single average fuel containing either ethanol (at either 2 or 3.5% oxygen) or no oxygenate. Perhaps the final assessment of the air quality impact of removing MTBE can very readily incorporate some mixture of ethanol and neat gasolines using the fuels described in this document, but the present text and fuels chosen don't appear to have addressed such a possibility.

Some reasons supporting a mixture of oxygenated and non-oxygenated are as follows:

- MTBE in the present CaRFG market supplies about one grade of octane, 11% volume, between 10 and 20 points to T50, and about 11% dilution for sulfur, aromatics, benzene, and olefins. MTBE also adds a couple of tenths to RVP and it contains enough oxygen to meet the federal Clean Air Act requirement for reformulated gasoline, and this oxygen is known to reduce carbon monoxide which is known to be a significant ozone precursor.
- Ethanol blended to the 10% volume level essentially replaces MTBE except that the oxygen content exceeds the federal oxygen requirement, RVP increases nearly an additional psi and, according to the Predictive Model, NO_X emissions will increase unacceptably.
- Using only 10% ethanol to replace MTBE would require refinery adjustments mainly to reduce RVP and predicted NO_X emissions. A current draft Predictive Model (Beta 1) suggests that RVP levels above 7 psi will be possible if further refinery adjustments are made to reduce exhaust THC emissions. However, a full psi does not appear possible, and the Beta 1 Predictive Model appears to require extra refinery adjustments to bring predicted NO_X emissions into conformity.

- If pentanes are removed to reduce RVP for the ethanol blends, then these refinery streams might be used to replace MTBE (for dilution and T50) in the lower octane grades of gasoline.

The above points suggest that the regular-grade oxygen-free gasoline might be similar to current CaRFG with paraffins roughly replacing MTBE. At the same time the higher octane grades would contain ethanol in place of MTBE, but multiple adjustments may be necessary to meet the NO_X requirements of the Predictive Model. The sensitive parameters seem to be sulfur and T90 with some additional effects possible from minor adjustments in aromatics, olefins and T50. In the end, such adjustments may not significantly alter the balance of reactive components (i.e., olefins and higher aromatics) to render the profiles inappropriate for use in assessing the ozone chemistry of using ethanol blends. However, the ARB documentation should address the use of their proposed profiles in light of a mixed market of regular grade non-oxygenated gasoline with premium and some mid-grade fuels using ethanol. (Whitten)

Response: Given the very small differences in the results for single gasolines, there is no need to analyze a situation with multiple gasolines.

4. Comment: Are you trying to estimate the incremental emissions associated from using ethanol that might come from increased vapor emissions when Cleaner-Burning Gasoline with and without ethanol are mixed together in a car's tank? (Smith)

   I cannot remember hearing or seeing any mention of the CARB portion of the EtOH fate and transport analysis evaluating the impacts stemming from the consumer mixing of non-oxygenated gasoline with gasoline containing EtOH. As you know, this will create an increase in vapor pressure as the EtOH blends mix with the non-oxygenated gasoline. This phenomena is happening right now and will continue as refiners are making both non-oxygenated and EtOH

   blended gasolines. This should most certainly be a part of your analysis. (White)

   Response: The effect is probably real, but there are not now enough data on consumers' habits to allow an estimate of the increased emissions. Some analyses may be forthcoming in the future. As long as the federal oxygen mandate remains for federal RFG areas, the point is moot. If a waiver from the federal oxygen regiment is provided, the situation will have to be monitored and appropriate recommendations developed.

5. Comment: On page iv of the summary of the draft report it is clear that more paraffins are expected in the non-oxygenated fuel and that MTBE-related exhaust products (i.e., isobutylene and formaldehyde) would be reduced, but the reasons for less benzene are not clear. (Whitten)

   Response: The adjustments for each of the four toxic species have been made via the Predictive Model.

6. Comment: On page 2 of the report (in Table 2) the difference in octane of the Auto/Oil fuels is noted, but the text does not comment on this. Then on page 20 (Table 9) the proposed non-oxygen fuel is shown to have less aromatics than the MTBE-related fuels. And on the next

page (page 21) that the proposed profile is then to be further reduced by a factor of 21.7/27.1. In light of the above discussion, the octane of the proposed profile may be too low to be representative of the California market. (Whitten)

Response: The non-oxygenated A/O fuel described in Table 2 is not one of the fuels that are described in Table 9. The speciated emissions from the A/O fuel (in comparison to its baseline MTBE fuel) were used to make certain adjustments to the ARB's exhaust and evaporative profiles to create profiles for oxygen-free fuel. The fuels described Table 9 are those predicted by MathPro for CEC. Within that table, there is a decrease in the aromatic content between the MTBE-blended and oxygen-free fuels. That decrease was transferred to the ARB's profile for whole gasoline.

7. Comment: In light of the discussions on page 22, it is surprising that the EPA Complex Model was not used to test the impact of removing MTBE on benzene exhaust emissions. The EPA Complex Model actually predicts that benzene exhaust will increase by about 12% rather than the decrease of 12% shown in the unnumbered table on page 24. In fact the Complex Model also suggests that 1,3 butadiene will increase by 7% and acetaldehyde will increase 7.6% going from CaRFG flatline specifications to the same with 11% volume MTBE substituted by paraffins giving the same boiling and T50 specifications (i.e., all parameters at flatline except oxygen). (Whitten)

   Response: The ARB's regulation for RFG does not allow toxics to increase. In changing one fuel parameter, other parameters must be adjusted using the Predictive Model to preserve the emission benefits. The EPA program is not designed to do this.

8. Comment: As explained by ARB, each experimental study they used in deriving their speciation profiles has "imperfections that complicate its use." (These studies were conducted by ATL, the Auto/Oil Program, and internal ARB work.) The problems included the use of small and inconsistent sets of vehicles, non-representative fuels, failure to measure all emissions of interest, and incomplete characterization of the test fuels. Another problem--not mentioned by ARB--is that each study used different analytical techniques for determining the speciated emissions profiles. Lab-to-lab differences for speciation analyses are significant -- even when using identical procedures -- and are even more substantial when using different analytical procedures. (WSPA)

   Response: For each of the ethanol-blended and oxygen-free fuels, the emission profiles were based on the ARB study for ethanol and the A/O study for oxygen-free. This should minimize the problem.

   The incompleteness of data and the non-representativeness of the non-MTBE fuels in the studies is recognized. However, no alternatives were available when the inputs to the original model were being developed. For that reason, we recognize uncertainty in the quality of the inputs to UAS modeling, and we think that the slight differences in predicted ozone among fuel types may be well within the effects of that uncertainty.

9. Comment: The differences in analytical methodologies and reporting procedures make it very difficult to compare results from one experimental study to another for many individual species. A simple illustration of this is shown in ARB's Figure 5: "Hot Soak Profiles -- MTBE-Blended CaRFG." Here we see that ARB reported about 1% of 2,3-dimethylbutane, while ATL reported none. On the other hand, ATL reported about 1% of 2,3,3-trimethylpentane, while ARB reported none. It is likely that these differences are not real, but arise from the unique ways in which the two labs chromatographically distinguish and report these compounds. Under some chromatographic conditions, 2,3,3-trimethylpentane cannot be resolved from toluene. It is possible that ARB could not make this distinction, while ATL could (or ATL used some other method to estimate the split between toluene and 2,3,3-trimethylpentane). A similar resolution problem exists between 2,3-dimethylbutane and MTBE, and between numerous other pairs of compounds. The point here is that simply comparing lists of numbers, without an understanding of the chromatographic analyses that generate the numbers, may lead to incorrect conclusions. (WSPA)

   Response: See response to Comment 8.

10. Comment: Professor Rob Harley provided a good assessment of ARB's proposed speciation profiles, and identified a number of problems that should be corrected. We agree with the points made by Prof. Harley. In most cases, however, it is not clear how these problems have been addressed. It appears that some of Harley's suggestions have been followed. For instance, the ethanol fractions in ARB's updated catalyst exhaust profiles for the ethanol-blended fuels (dated 7/9/99) are now 2-3% as compared to <1% in the profiles Harley reviewed. On the other hand, the acetylene levels in ARB's updated profiles are still higher in catalyst stabilized emissions than in non-catalyst stabilized emissions. As pointed out by Harley, this seems incorrect. ARB should clearly explain how each of the issues raised by Harley has been addressed. (WSPA)

    Response: The responses to the comments by Prof. Harley on June 23, 1999, are in Section D-2. The acetylene content of ARB's MTBE profiles were not adjusted in "turning" those profiles into ethanol-blended or oxygen-free profiles

11. Comment: ARB's work plan indicates that Prof. Harley will "…calculate headspace vapors from the liquid fuel speciation profiles as a check on the ones developed in-house." It is not clear from Harley's letter of June 23 whether he has done this. However, he did point out that "…an equilibrium headspace vapor composition profile may not represent all diurnal evaporative emissions correctly." What is ARB planning to do to address this concern? (WSPA)

    Response: The main issue in the evaporative profiles is whether or not the ethanol content is linear with the ethanol in the fuel. We acknowledge that it probably is not linear and that the ethanol contents of the evaporative emissions from the 10% ethanol fuel are too high. However, the close similarity of photochemical modeling results among the fuels indicates no need to revise the ethanol contents downward.

Air Quality Modeling Component

12. Comment: The August SCAQS episode is an ozone episode--not CO, and consequently there was no previous need to develop CO model performance. Before spatial and temporal behavior of toxics emissions dispersion and reaction can be used and related to CO concentrations, acceptable model performance must be demonstrated. (WSPA)

    Response: The CO model performance was calculated for the August 26-28 SCAQS episode using the updated SAPRC97 mechanism and the Carbon Bond IV mechanism. We found that both photochemical mechanisms have similar CO model performance. As expected, the CO model performance exhibits underestimation. This is generally true for all primary emitted compounds (like CO and NO) which are volume averaged in the model. However, it is important to note that model estimated CO concentrations were not used to adjust concentrations of other compounds to the future year or to estimate the impact of alternate fuels on other compounds.

13. Comment: The UAM-FCM is a grid model that does not incorporate subgrid-scale treatment--consequently UAM is known to predict neighborhood scale concentrations--not microscale concentrations as measured by CO monitors. In other words, the grid resolution is not fine enough to adequately portray changing CO concentration gradients. This has been known and is one of the reasons the CAL3QHC model has been used to characterize subgrid-scale "hot-spot" CO concentrations, which are overlayed on UAM regional predictions. ARB's work plan describes using interpolation techniques with ambient measured CO concentrations to characterize annual exposure to the compounds of interest supplemented by UAM predictions. Critical uncertainties are how quickly CO hot-spot concentration gradients fall off with distance from a monitor, and how well UAM portrays these concentration gradients and population exposures. (WSPA)

    Response: The problem of comparing measured concentrations at a monitoring site against volume-average concentrations predicted by air quality models (the "incommensurability" problem) has been recognized in the past. The use of a finer grid resolution in the model could partially address this problem. However, it is important to note that the model is being used for this study in a relative sense, i.e., to estimate changes in species concentrations, not absolute values. While the use of predicted CO concentrations will not yield "hot spots" exposures, the study results provide an indication of the directional change in CO concentrations. As indicated in the previous response, it is also important to note that model estimated CO concentrations were not used to adjust concentrations of other compounds to the future year or to estimate the impact of alternate fuels on other compounds.

Data Analysis Component

14. Comment: Another concern arises about consistency of the relationship between CO and the toxic compound of concern between August episode temperatures and more moderate (e.g., wintertime temperatures). Both atmospheric reaction rates and primary emission rates differ as a function of temperature. (WSPA)

<u>Response:</u> We agree that atmospheric reaction rates and primary emission rates differ as a function of temperature. Although this comment seems to arise from a concern that a relationship between modeled CO and modeled toxic compound levels would be used in estimating future toxics levels, such was not the case. While these relationships were used to establish base year concentrations, only ratios of model predicted toxic compound levels were used to estimate future year toxics levels from base year toxics levels.

15. <u>Comment</u>: It is not clear how the 1-hour peak and the 24-hour average concentrations will be used to develop baseline concentrations. How well do the spatial and temporal relationships of these metrics represent annual average conditions? (WSPA)

    <u>Response</u>: Ratios of 2003 to 1997 model predicted one-hour maximum concentrations were multiplied by the maximum 1997 (measured or estimated) one-hour concentrations to estimate a maximum one-hour concentration in 2003, as described in Appendix 5 of the report. Similarly, the ratio of 2003 to 1997 modeled daily (24-hour average) concentrations was multiplied by the 1997 maximum daily average to calculate a maximum 2003 daily average.

    To estimate changes in population weighted annual average concentrations between 1997 and 2003 the ratio of the 2003 to 1997 modeled region population weighted daily average results were used. For formaldehyde and acetaldehyde, the ratio was applied separately to primary and secondary aldehyde components so as to better represent annual average conditions. When used in this way, the metrics are believed reasonably appropriate for the specific application.

16. <u>Comment</u>: Population exposure developed solely on spatial interpolative techniques assumes linear concentration gradients between monitoring sites. In fact, mobile source emissions occur between sites and change the gradients. Therefore, population exposure may be incorrect. (WSPA)

    <u>Response:</u> The current method for calculating population exposure has been in use for a long time and has been used extensively. It is the best technique available at this time. ARB will modify the technique, as a better method becomes available and data are available to drive the method.

17. <u>Comment</u>: Assuming a consistent emissions relationship of toxics species to CO for all vehicle types (light-duty autos, light-, medium- and heavy-duty gasoline trucks, and motorcycles) is erroneous--albeit necessary. We don't know the true effects of fuel changes on emissions from most of these vehicle types, and can only speculate whether the bias this assumption introduces is high or low. (WSPA)

    <u>Response:</u> The analysis approach only used a correlation between toxic compounds and CO to estimate 1997 toxics levels. This approach was only done where there was good correlation. Correlation was not used for estimating future concentrations for the various fuel scenarios.

General

18. Comment: With the layers of uncertainty in ARB's planned analyses, it is unclear whether the results can provide even directional guidance. Further work is necessary to bolster the credibility of any results to be released in December. (WSPA)

    Response: As mentioned in the report, the air quality impact study of ethanol-containing fuel relies on engineering judgement. Deliberate effort was made to solicit comments and improvements and investigate specific alternatives suggested. The approach to uncertainty generally encompassed the consideration and evaluation of such alternatives. Ranges of estimates are provided where the results are different using different approaches. It is believed that the open process and evaluation of alternative methods provides an adequate foundation to establish the credibility of results. We agree that additional work is beneficial and have outlined such work in our report. A fuel and vehicle testing program has been conducted (results still being gathered) and a field measurement program is planned to confirm that actual impacts are consistent with impacts estimated in this study.

D-3.2. Public Comments on Reactivity of Carbon Monoxide

D-3.2.1. Recent UAM Simulations On The "Reactivity" Of Carbon Monoxide

Gary Z. Whitten of ICF Consulting submitted this in a personal communication forwarded from Tom Koehler of Parallel Products, Inc. to Steve Brisby of ARB on September 23, 1999.

Previous evaluations of the "reactivity" of carbon monoxide (CO) have focused on the use of Maximum Incremental Reactivity (MIR) factors developed by W. Carter of the University of California at Riverside. These factors were developed using a 1-day moving box model. However, the rate of atmospheric decay for CO is an order of magnitude slower than the average hydrocarbon decay rate. While a 1-day model might be considered appropriate to evaluate the relative reactivities of various volatile organic compounds (VOC) to each other, the same 1-day model would not reflect the multi-day impact of CO. The Urban Airshed Model (UAM), on the other hand, is a far more appropriate tool for comparing the relative reactivity of CO to VOC.

Recent simulations for the year 2000 of the South Coast Air Basin, the Chicago area, and New York all point to a reactivity of CO that is about 65 percent greater than the 1-day approach used to develop the MIR factor for CO. That is, the Carter MIR for CO is 0.07 grams ozone per gram of CO, but using the UAM implies a value closer to 0.12 instead.

The base UAM simulations for the three cities have all been used in other projects. For the South Coast Air Basin the inputs were developed by the South Coast Air Quality Management District (SCAQMD). The Chicago and New York base simulations were originally developed for the Auto/Oil program (Guthrie et al, 1997, SYSAPP-96/31). In each case the on-road mobile CO emissions were set to zero and compared to one or more simulations where mobile-related VOC emissions were reduced. Also, simulations were performed where the initial and boundary conditions for CO were reduced according to the mobile-related emissions percentages (48 percent in Chicago and 35 percent in New York). Even for the Chicago case, which used the newer

UAM-V version with a five-day simulation covering a large region of the Lake Michigan area, the boundary conditions for CO proved to play a significant role. Tables 1, 2, and 3 list many of the detailed results, which show considerable variation. Nevertheless, the impact of on-road CO emissions are clearly significant compared to VOC emissions.

The base simulation for the South Coast Air Basin comes from the 1997 Air Quality Management Plan (AQMP). The main information on the use of the UAM in the AQMP can be found in Appendix 5, Chapter 3 of the AQMP documentation. The simulations reported here use the same input files (or input file preparation software) as were used in the AQMP for the control simulations for the year 2000 based on the meteorological episode on the 26th, 27th and 28th of August 1987.

The sensitivity simulations shown below illustrate the relative importance of the various parts of the gasoline-related mobile emissions inventory. For the most part these simulation scenarios involve setting a particular part of the gasoline-related inventory to zero. For carbon monoxide (CO), two sensitivity simulations were performed to bracket the impact of gasoline-related CO emissions. For one CO scenario the chemistry of CO was totally eliminated and for the other the gasoline-related emissions were set to zero. . Gasoline-related CO emissions are only 60 percent of the total CO emissions as seen in the AQMP emissions inventory. For convenience, 60 percent of eliminating CO chemistry from the UAM are represented in parenthesis in Table 1 for the peak impact values.

The CO chemistry was eliminated by setting the chemical reaction rate of CO with the hydroxyl radical to zero. Such a sensitivity test includes non-gasoline related emissions, off-road engines, secondary CO from VOC, carry-over from previous days, plus initial and boundary conditions. In the other test only the on-road gasoline-related emissions were set to zero; carry-over effects from first day emissions into the second and third days would still be included. The actual impact of the CO emissions would be expected to fall somewhere between these simulations because emissions both in the basin and in surrounding areas would affect initial and boundary conditions over a period of several days due to the month-long atmospheric lifetime of CO compared to the day-long lifetimes of urban VOC.

A potential update to the AQMP is included as a sensitivity scenario that uses a newer running-exhaust profile (#882) supplied by P. Allen of the ARB. The original AQMP profile had 57 percent methane; the new profile has 18 percent methane, and for reference the Caldecott tunnel data show 9.9 percent methane. The newer profile (#882) resulted from a special ARB workshop in the summer of 1998.

Table 1. 1-Hour Max Ozone (ppb) UAM Results, South Coast Air Basin, 2000

Scenario	**August 27th**	**Peak Impact**	**August 28th**	**Peak Impact**
Base	**129.0**		**148.3**	
CO Chem	**114.1**	**-14.9(-8.9)**	**132.4**	**-15.9(-9.5)**
CO Emiss.	**126.4**	**-2.6**	**143.3**	**-5.0**
Run Evap	**127.8**	**-1.2**	**146.9**	**-1.4**
Hot Soak	**128.1**	**-0.9**	**147.7**	**-0.6**
Diurnal	**125.4**	**-3.6**	**145.4**	**-2.9**
VOC Strt	**121.6**	**-7.4**	**143.9**	**-4.4**
VOC Rn	**125.3**	**-3.7**	**144.7**	**-3.6**
Rn Spec.	**132.0**	**+3.0**	**150.9**	**+2.6**

Table 2. 1-Hour Maximum Ozone (ppb) UAM-V Results for Chicago, 2000

Scenario	**June 26**	**Peak D**	**June 27**	**Peak D**	**June 28**	**Peak D**
Base	**124.6**		**122.1**		**116.7**	
CO emis	**123.0**	**1.55**	**120.6**	**1.53**	**115.6**	**1.11**
CO w.bc	**120.7**	**3.85**	**117.6**	**4.53**	**113.3**	**3.41**
VOC 4.7%road	**124.3**	**0.28**	**121.9**	**0.24**	**116.6**	**0.16**

Table 3. 1-Hour Maximum Ozone (ppb) UAM Results for New York, 2000

Scenario	**July 9**	**Peak D**	**July 10**	**Peak D**	**July 11**	**Peak D**
Base	**184.4**		**179.7**		**174.9**	
CO emis	**183.3**	**1.08**	**175.8**	**3.89**	**172.9**	**1.97**
CO w.bc	**182.1**	**2.28**	**174.0**	**5.69**	**170.9**	**3.97**
VOC 6.9%road	**184.3**	**0.12**	**178.9**	**0.79**	**174.5**	**0.33**

Carbon Monoxide Contribution to Ozone

The National Research Council (NRC) recently (National Academy Press, 1999, “Ozone-Forming Potential of Reformulated Gasoline”) stated that “CO in exhaust emissions from motor vehicles contributes about 20% to the overall reactivity [i.e., ozone-forming potential] of motor-vehicle emissions.” However, this statement is based on the use of Carter MIR factors. For comparison, the UAM sensitivity tests reported here can be expressed as overall contribution to ozone formation.

For the South Coast simulations the ozone sum of all mobile VOC tests shown in Table 1 is 19.8 ppb for the August 27th day and 15.5 ppb for the August 28th day. For the scenario eliminating CO chemistry the 60 percent ozone impacts (reduced to account for the on-road percentage of emissions) are 8.9 ppb and 9.5 ppb, respectively. These results indicate an upper limit contribution of CO to the combined VOC and CO ozone formation appears to be 31 percent on the August 27th day and 38 percent on the August 28th day. An increase from one day to the next is consistent with some carry-over of emissions. For the lower-limit estimate cutting just the emissions shows an even stronger apparent carry-over effect by going from an 11.6 percent impact on the 27th to a 24.4 percent impact on the August 28th day. Taking the average of the second of these days a contribution of 31 percent is estimated for CO to the total CO and VOC ozone formation.

For the Chicago simulations VOC emissions were reduced by 14.2 tons, which were 4.7 percent of the total 301 gasoline-related mobile inventory. The changes in ozone listed in Table 2 would be expected to increase to 6.0, 5.1, and 3.4 ppb, respectively for the three days if the full 301 tons were reduced. For the emissions only CO scenarios the percent contribution to total ozone for the three days would then be 20, 23, and 25 percent, respectively. Again these results are consistent with an accumulation due to day-to-day carry-over. For the upper-limit estimates with the boundary and initial conditions reduced by 32 percent CO to account for the on-road contribution (off-road would decrease this further), the estimated ozone contributions would be 39, 47, and 50 percent, respectively for the three days. The average of the two last day contributions is a 38 percent ozone conrtibution for CO.

For the New York simulations were reduced by 41.9 tons, which were 6.9 percent of the total 607 gasoline-related mobile inventory. The changes in ozone listed in Table 3 would be expected to increase to 1.7, 11.4, and 4.8 ppb, respectively for the three days if the full 607 tons were reduced. For the emissions-only CO scenario the percent contribution to total ozone for the three days would then be 38, 25, and 29 percent, respectively. For the upper-limit estimates with the boundary and initial conditions reduced by 50 percent CO to account for the on-road contribution (off-road would decrease this further), the estimated ozone contributions would be 57, 33, and 45 percent, respectively for the three days. The average of the two last day contributions is a 37 percent ozone contribution for CO.

In summary, when the UAM is used to estimate the carbon monoxide contribution to mobile VOC and CO ozone formation in three cities (Los Angeles, Chicago, and New York) for the year 2000, the average is 35 percent on the last day of the simulations. With the exception of the first day of simulation in New York, the estimated CO contribution appears to increase each day, which is consistent with the slow decay of CO leading to carry-over effects. In each of the cities the results were highly sensitive to adjustments in the boundary conditions assumed for CO, which is also consistent with the importance of carry-over effects resulting from the long atmospheric lifetime of carbon monoxide. The analyses used by the California Air Resources Board and the NRC have used the 1-day Carter MIR factor of 0.065 to 0.07 grams ozone per gram CO. The NRC used such a value to derive an overall CO contribution to urban VOC and CO ozone of 20 percent. Since the percent derived here is 35 percent, this implies that a UAM-derived MIR factor for CO would then be 1.75 (i.e., 35/20) times 0.07 or 0.12 grams ozone per gram CO. It might also be added that off-road CO emissions were not included in the present study, but these emissions could enhance the importance of CO to overall ozone formations. These multi-day UAM grid-model simulations all tend to show a considerably higher contribution to ozone formation from on-road mobile CO emissions than the one-day simulations used in the MIR factors which formed the basis of the NRC estimate.

D-3.2.2. Why Carbon Monoxide Grows in Importance on Multi-Day Smog Episodes

Gary Z. Whitten of ICF Consulting submitted this in a personal communication to Bart Croes of ARB on November 12, 1999.

Recent sensitivity results from photochemical grid modeling show a day-to-day progression in the contribution that carbon monoxide (CO) makes to urban ozone formation. Moreover, the contribution of CO exceeded that expected from Maximum Incremental Reactivity (MIR) factors. An explanation for such a progression and the appropriateness of using a higher factor for CO relative to organic emissions is discussed here.

The Urban Airshed Model was used with base case simulations that had been prepared for State Implementation Plans (SIP). The sensitivity simulations compared mobile CO emissions reductions with and without boundary condition adjustments against volatile organic compound (VOC) emissions reductions for three cities: Los Angeles, Chicago, and New York. In one simulation the chemistry of CO was deleted to provide an upper bound estimate to the overall importance of CO (this is more than the contribution from emissions of CO because CO is an intermediate product of many VOC). Using an average of the emissions-only and emissions plus boundary adjustment simulations it was found that over two or three days the contribution to ozone relative to VOC tended to increase.

The causes of this observation appear to relate to the fundamental characteristics of how carbon monoxide contributes to ozone formation. The most frequent pathway for either CO or VOC to begin the atmospheric chemistry leading to urban ozone formation is through reaction with the hydroxyl radical (OH). However, carbon monoxide yields only one intermediate peroxy radical, namely the hydroperoxyl radical (HO2) and no other products that might contribute to ozone formation. On the other hand, VOC usually yield not only two intermediate peroxy radicals (RO2 and HO2), but secondary organic products that can either react as a VOC themselves or can contribute new free radicals to the overall process through photolysis. These new free radicals and secondary VOC products can be especially important under VOC-limited conditions like those used by W.P.L Carter in the development of the MIR factors.

Even under conditions that lead to peak ozone formation under NOx-limited conditions, the mixture of smog-forming precursors can be VOC-limited during the morning and mid-day hours. Because the decay of NOx tends to be faster than VOC decay on average, this progression from early VOC-limited chemistry (that is enhanced by new free radicals) can occur not only over a single day, but over a multi-day episode as well. At the time when ozone might be peaking under NOx-limited conditions the addition of new free radicals can actually reduce ozone because these new radicals tend to remove NOx even faster. Because CO contributes neither secondary VOC nor new free radicals, the importance of CO relative to VOC will become greater under such conditions relative to the strongly VOC-limited conditions used to develop the MIR factors.

Although previous airshed studies have tended to show that the MIR factors correlated well with exposure estimates, exposure estimates emphasize the period of the day when ozone is rapidly forming (still during the VOC-limited part of the day) in highly populated areas. Peak ozone (by definition, slowly forming) often tends to form further downwind in less populated regions later in the day under more NOx-limited conditions. However, as an airshed becomes closer to attainment the only exposures to high ozone will be near the downwind peaks and, further, it is these peaks which drive the SIP strategies. Hence, it is appropriate to consider a higher reactivity factor for CO relative to other VOC.

Carter in 1994 (published in the *Journal of Air and Waste Management*), developed a series of reactivity factors. This series of three reactivity sets (MIR, MOIR for maximum ozone, and EBIR for equal benefit) were developed by reducing the NOx inputs to progress towards more NOx-limited conditions. Others, including Carter, have noted that the three sets of factors in this series show surprisingly similar relative reactivities between the various VOC. A notable exception, of course has been toluene which has secondary chemistry that removes NOx so that "reactivity" can actually become negative under NOx-limited conditions. However, a new look at this series of factors is presented here which shows that the reactivity of CO consistently increases relative to VOC as the series (with reduced NOx) progresses. Hence, the progressive series published by Carter is consistent with the progressive trended observed in the recent UAM sensitivity simulations using SIP-like conditions.

Table 1 compares the reactivity factors published by Carter (1994) in their original form relative to the base VOC mixture. A group of VOC were chosen to be representative of various types. In the last two columns the percent increase of CO reactivity to each VOC is given relative to the MIR factor of CO relative to each VOC. It is seen that the relative reactivity of CO consistently increases relative to all VOC as the series progresses toward more NOx-limited conditions. Also it is noteworthy that for VOC which are known to supply significant secondary new free radicals (e.g., formaldehyde and methyl glyoxal) the relative increase of CO reactivity is especially large as would be expected from the fundamental explanation given above. Finally, it is perhaps coincidental but the average increase in CO reactivity seen in the UAM simulations is consistent with the average seen in Table 1. That is, the reactivity of CO appears to be approximately 65 percent more, on average, than the MIR estimate relative to other VOC under multi-day airshed episodes and in the Carter progressive series of reactivity factors.

Table 1. Reactivity Relationships from Carter (1994)

Compound	MIR	MOIR	EBIR	% MIR to MOIR	to EBIR
CO	0.018	0.032	0.044		
Methane	0.005	0.008	0.01	11.1	22.2
Ethane	0.079	0.14	0.18	0.3	7.3
Propane	0.16	0.27	0.33	5.3	18.5
n-Butane	0.33	0.57	0.7	2.9	15.2
n-Pentane	0.33	0.58	0.71	1.1	13.6
i-Pentane	0.39	0.63	0.8	10.1	19.2
3-M-Pentane	0.48	0.8	0.99	6.7	18.5
2,2,4-TM-Pe	0.51	0.78	0.94	16.2	32.6
Cyclopentan	0.76	1.19	1.46	13.5	27.2
Ethene	2.4	2.8	3.2	52.4	83.3
Propene	3	3.2	3.7	66.7	98.2
1-Butene	2.9	3	3.4	71.9	108.5
Isobutene	1.7	1.6	1.9	88.9	118.7
trans-2-but	3.2	3.2	3.6	77.8	117.3
2-Heptene	1.8	1.8	1.9	77.8	131.6
1,3-Butadie	3.5	3.5	4.1	77.8	108.7
Benzene	0.135	0.114	0.051	110.5	547.1
Toluene	0.88	0.53	-0.023	195.2	
m-Xylene	2.6	2.1	1.7	120.1	273.9
1,3,5-TM-Be	3.2	2.6	2.4	118.8	225.9
Methanol	0.18	0.23	0.28	39.1	57.1
Ethanol	0.43	0.61	0.72	25.3	46.0
t-Butyl Alc	0.132	0.21	0.27	11.7	19.5
Formaldehyd	2.3	1.8	1.7	127.2	230.7
Acetaldehyd	1.8	1.8	2.2	77.8	100.0
Methyl Glox	4.7	4	3.9	108.9	194.6
Acetone	0.18	0.17	0.18	88.2	144.4
Average & increase from MIR				**59.4**	**106.9**

D-3.2.3. Response

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

Our review of the literature indicates the reactivity of CO is well established. 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 ARB's 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 airshed 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.

On a per-mole basis, the atmospheric reactions of CO create a minimal amount of ozone. Literature values for the incremental reactivity of CO are given in Table 3.1. The latest version of SAPRC (Carter, 1999) calculates the MIR for CO as 0.066 g O_3/g CO. Earlier work by Carter (1994) reports a slightly lower value of 0.054 g O_3/g CO. Bowman and Seinfeld (1994a) report incremental reactivities in units of ppb O_3/ppbC but a comparison of CO and CH_4 in the two scale allows an estimate of relative reactivity of CO. The stability of the MIR for CO is consistent with Carter's estimate of the uncertainty of the value. In both the 1994 and 1999 work, Dr. Carter lists the uncertainty of CO's reactivity in the least uncertain category. The peer review of SAPRC99 (Stockwell, 1999) found that the relative rank of CO in terms of reactivity for the compounds common to both works did not change at all between 1994 and 1999.

Table 3.1. Comparison of Incremental Reactivities for CO and CH_4

Compound	Carter (1994)	Carter (1999)	Bowman (1994a)
CO	0.054	0.066	0.005
CH_4	0.015	0.0153	0.001

[a]Units of gO_3/g CO.

[b]Units of ppb O_3/ppbC with VOC to NO_X ratio of 8.2.

Dr. Whitten's analysis of the reactivity of CO using the Urban Airshed Model (UAM) focuses on the changes in the maximum ozone concentration. Maximum ozone concentration is the reactivity metric used in the MIR scale; however, the model used to calculate MIR values is a simple zero-dimensional box model. The UAM is a more complex, three-dimensional, Eulerian model. As such, it allows the calculation of ozone concentrations as a function of spatial distribution. Using the spatial distribution and population data, the UAM can generate three ozone metrics; peak ozone, population-weighted ozone exposure, and spatial exposure. Peak ozone corresponds to the maximum ozone concentration used in the MIR values. Population-weighted exposure multiplies the ozone concentrations greater than a selected threshold by the population in that grid cell and sums over all the grid cells. The spatial exposure weights the ozone concentration by the grid cell area and, again, sums over all the grid cells. The three reactivity metrics can provide significantly different estimates of reactivity. An analysis (Bergin *et al.*, 1998) of the effects of uncertainties in the rate parameters used in the chemical mechanism found that the use of different metrics in determining compounds reactivities as well as the differences between single-cell and airshed model predictions have a larger impact on relative reactivity predictions than do rate constant uncertainties for the compounds and reactions examined. For this reason, care should be taken to select the most appropriate metric to compare with MIR values.

Several comparisons of reactivity calculated with a three-dimensional airshed model and Dr. Carter's MIR scale have been published (Bergin et al., 1998; Bergin et al., 1995; Russell et al., 1995). Bergin et al. (1998) calculated composite normalized reactivities for CO. The results for the three-dimensional model are peak ozone = 0.05, population exposure = 0.02, spatial exposure = 0.03. The MIR value for CO in the same normalized scale = 0.02, (Bergin, 1995). The peak ozone value which is most similar to the metric used in Dr. Whitten's analysis is significantly higher than the values for population and spatial exposures. The agreement between the three metrics calculated with the three-dimensional model and the MIRs for 25 compounds was quantified by calculating the normalized bias. The normalized bias was greatest for MIR to peak ozone, 0.26, while MIR to population exposure and MIR to spatial exposure had smaller biases of –0.16 and 0.05 respectively (Bergin, 1998).

California's reactivity regulations (LEV/CF, CLEAR) are based on the MIR scale. The choice of this particular reactivity scale was made for several reasons. Carter suggested it as the single scale most appropriate for regulations due to the robustness of its response to variations in NO_X concentrations (Carter, 1994). Additionally ARB determined it to be the most appropriate reactivity scale to complement California's NO_X control program. As the choice of reactivity scale was made for specific reasons and is codified in the California Code of Regulations, it is inadvisable to change scales or metrics without serious consideration. Of the three reactivity metrics calculated with a three-dimensional airshed model, peak ozone shows the greatest bias when compared with the MIR scale; while population and spatial exposure demonstrate better correlation. This supports the choice of one of the latter metrics as the appropriate metric to evaluate three-dimensional simulations. Health-based concerns support the population exposure metric. Both the Federal and State ozone standards were designed with the goal of protecting public health. The population exposure metric more clearly evaluates the public health effects by providing an estimate of public exposure to ozone concentrations above a threshold value.

The conclusion of Dr. Whitten's analysis based on peak ozone values suggests that the reactivity of CO, as measured by MIR, should be multiplied by 1.65. The values of the population and spatial metrics cited above can not be directly compared to MIRs. "The absolute reactivities calculated with box models (g of O_3/g of VOC) are not directly comparable to the more complex metric used here." (Bergin, 1995). However, a comparison within the three metrics suggests that peak ozone reactivity is significantly higher than population exposure. The population exposure result of 0.02 is identical to the composite normalized MIR. This suggests three-dimensional models do not justify a significant increase in the reactivity of CO.

Use of a different chemical mechanism within a 5-day trajectory model actually calculates CO's reactivity as less than that of CH_4. Derwent et al. (Derwent, 1996) used a predecessor to the Master Chemical Mechanism and a trajectory model to calculate photochemical ozone creation potentials (POCP). A POCP is defined as the change in ozone caused by a compounds relative to the change in ozone caused by ethene. In this study, the POCP of CO = 2.7, CH_4 = 3.4, and C_2H_6 = 14.0 (Derwent, 1999). The most recent MIRs values are CO = 0.066, CH_4 = 0.0153, and C_2H_6 = 0.35.

In summary, California's reactivity regulations are based on the MIR scale. Changes to the scale should only be undertaken after careful analysis and only when the scientific evidence warrants a change. Dr. Whitten's suggestion that the reactivity of CO is underestimated is based on his analysis of three-dimensional airshed simulations. However his analysis is based on the peak ozone metric. Other works indicate poor agreement between peak ozone values as calculated with a

3D airshed model and MIRs values. A comparison of population exposure and MIR indicate identical reactivities. Additionally, the MIR of CO is well established and regarding as having a low uncertainty. Taken together, these recommend against any increase in the reactivity of CO.

D-3.3. Public Comments on Carbon Monoxide Emissions

D-3.3.1. The Impact of Fuel Oxygen on Carbon Monoxide in California Cleaner Burning Gasoline

Gary Z. Whitten of. ICF Consulting submitted this in a personal communication forwarded from Tom Koehler of Parallel Products, Inc. to Bart Croes of ARB on October 26, 1999.

The California Air Resources Board (CARB) is considering a credit for reducing carbon monoxide (CO) in the cleaner burning gasoline (CBG) regulations. The ozone forming chemistry of CO has been known for many years, but due to its low reactivity relative to hydrocarbons and due to its own health hazards, carbon monoxide has been regulated only for the latter. Also CO is reduced by the same vehicle emissions control technology used to meet regulatory requirements for hydrocarbons (some recent on-board computer chips can “fine tune” between more hydrocarbon control relative to CO control). However, fuel oxygen is widely known to provide additional CO reductions, and during winter months when CO levels can still exceed air quality standards, fuel oxygen is often required. In the California CBG summer ozone program fuel oxygen is not required except in areas such as the South Coast Air Basin and Sacramento where the Federal requirements of the 1990 Amendments to the Clean Air Act mandate a minimum average level of 2 weight percent.

Although fuel oxygen can reduce hydrocarbon emissions in parallel with its ability to reduce CO, the amount of hydrocarbon reduction is typically less than the CO reductions that are possible from this fuel effect. Other fuel effects appear to be parallel as well, but some, like T90 can be opposite when comparing the emissions impacts on hydrocarbons relative to CO impacts. For sulfur and T50 the impacts appear to be parallel, but the relative magnitudes are revered compared to fuel oxygen. That is, fuel sulfur and T50 tend to reduce hydrocarbon emissions more that they can reduce CO emissions. Hence, for neither vehicle control technology impacts nor for fuel parameter effects does it appear that hydrocarbon impacts might serve as an accurate surrogate for predicting carbon monoxide impacts. Nevertheless, the California Air Resources Board has indeed suggested that other fuel parameters that might be adjusted to reduce hydrocarbon emissions would similarly impact CO emissions. In particular the ARB has suggested that the CO debit between 2 percent oxygen and zero oxygen would be less in magnitude (per percent fuel oxygen) than the credit for increasing fuel oxygen from 2 percent up to the cap limit of 3.5 percent oxygen.

The ARB has currently suggested that a credit for increasing fuel oxygen to 3.5 from the standard CBG level of 2 percent be based on a CO reduction of 7.5 percent. This is close to the approximately 5 percent linear CO reduction per percent fuel oxygen recommended by the OSTP study (1997). For reducing fuel oxygen from 2 percent to zero the ARB has suggested that a debit be based on only a 5 percent CO increase, which is less than half the OSTP recommendation. While it can be argued that even the OSTP recommendation is low (which is another issue not discussed here), the “non-linear” relationship suggested by the ARB between reducing fuel oxygen and increasing it, is the issue to be discussed here.

The ARB has suggested that, according to the Predictive Model, reducing fuel oxygen will increase hydrocarbon emissions, and to restore hydrocarbons to their original level other fuel parameters will have to be adjusted which will, in turn, reduce CO also. The ARB then concludes that the actual CO increase will be less (by half) than the 10 percent expected from a linear application of their recommended impact for increasing fuel oxygen. Unfortunately, there is only one study where a non-oxygenated fuel intended to meet the CBG regulations was tested against an oxygenated CBG gasoline (see Auto/Oil Technical Bulletin No. 17). Nevertheless, even in this widely quoted study the CO emissions difference in Tech 4 vehicles (actually model year 1989 and known as "current fleet" in the Auto/Oil program) turned out to be 11 percent, close to what was predicted from the OSTP (1997) recommendation[1]. However, the fuel made without oxygen did not quite meet CBG requirements and it was a full grade in octane lower than the oxgenated fuel. The hydrocarbons for the non-oxygen fuel (according to the Predictive Model) were too high by 2.12 percent compared to flatline requirements in the CBG program. As noted above the Auto/Oil data for the non-oxgenated fuel indicated an 11 percent carbon monoxide increase; it is not known what the CO changes might have been had the octane been increased to match that of the oxygenated fuel and had it been further changed to fully meet the CBG requirements. Furthermore, as noted above and discussed in more detail below, there are other parameters (like T90) that might have been adjusted instead of those used to reduced hydrocarbons when oxygen is absent and some of these (especially) T90 might conceivably have increased CO beyond the observed 11 percent.

A review of Auto/Oil studies and an earlier version of the California Predictive Model indicate a variety of responses between fuel parameters and CO emissions that seems quite different that the responses for hydrocarbons, NOx, and toxics. A summary of this review is presented in Table 1.

The earlier version of the Predictive Model did contain CO estimates, but the final version of 1994 did not. Both model predictions are included for reference. While the earlier version provides a relative reference between CO and THC, the final version provides a relative reference between the two model versions for THC. The database (even with the latest additions) does contain CO along with THC and NOx, so it would be possible to construct and updated Predictive Model that includes CO.

In summary it has been shown that several fuel parameters might be adjusted to compensate for the loss of oxygen in California CBG and there is little if any evidence to support the ARB claim that these compensating adjustments would consistently reduce the expected increase in CO. Therefore, it is recommended that a linear relationship be used to estimate the CO impacts associated with fuel oxygen content.

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[1] Ironically, the Auto/Oil study reported in Technical Bulletin No. 21 does recommend a difference of about 5 percent between these fuels for the Los Angeles emissions inventory for the years 2000 and 2010. However, this recommendation is based on future fleet assumptions that weight new technologies that might have low to zero impact from fuel oxygen. That is, the 5 percent impact is derived, not from fuel adjustments as the ARB claims, but from fleet-weighting assumptions.

Table 1. Summary of Auto/Oil and Predictive Model impacts on CO and hydrocarbons from various fuel parameters.

	Sulfur[2]		**Aromatics[3]**		**Olefins**		**T90**		**T50**	
	CO	**HC**	**CO**	**HC**	**CO**	**HC**	**CO**	**HC**	**CO**	**HC**
Auto/Oil #2	**-13**	**-16**								
Auto/Oil #1			**-13.6**	**-6.3**	**+1.5**	**+6.1**	**+0.8**	**-21.6**		
Pred Mdl #6	**-0.88**	**-0.82**	**-2.6**	**+0.2**	**0.0**	**+0.6**	**+2.5**	**-1.1**	**-0.9**	**-3.2**
Pred Mdl fnl	**----**	**-1.44**	**----**	**0**	**----**	**-0.74**	**----**	**-0.1**	**----**	**-5.9**

D-3.3.2. Response

The 7.5% increase for the higher oxygen content has been derived from data taken by ARB under the REPO5 test cycle (ARB, 1998b). According to FTP testing, the decrease in the CO inventory would be about 2.5% if oxygen were increased from 2.0 to 3.5 wt% of gasoline. However, the REPO5 data indicate that under "off-cycle" (non-FTP) operation, CO emissions are reduced much more. The staff has estimated the actual CO inventory reduction as 2.8 times the value calculated from FTP data. In contrast, available data do not show a difference between FTP and off-cycle testing in the effect of eliminating oxygen from gasoline. Therefore, the increase in the CO inventory estimated from FTP data, 5%, has been applied for the oxygen-free fuel.

We are not simply taking oxygen out of gasoline. The linearity assumption is generally based on the addition of oxygen to gasoline without significantly changing other parameters. This is not the case here. A CaRFG without oxygen has to make up the hydrocarbon loss from the removal of the oxygen. In reducing hydrocarbons, there is also a reduction in CO due to the other changes in the CaRFG. Adding oxygen results in increases in NO_X which need to be mitigated by adjusting other fuel parameters. Offsetting NO_X does not result in decreases in CO.

D-3.4. Public Comments on Peer Review Draft Report at ARB Hearing

This section contains the written comments and oral testimony at the public hearing of the Air Resources Board on December 9, 1999 to consider the November 18, 1999 version of the main report and versions of Appendix A through Appendix D dated November 10, 1999. The written comments are included with the ARB staff responses in italics. A transcript of the oral testimony is

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[2] In this Auto/Oil study (#2) sulfur was reduced from 466 ppm to 49 ppm. For the Predictive Model results sulfur was reduced from 40 ppm to 20 ppm with the other parameter set at current flatline.

[3] In the Auto/Oil study (#1) aromatics were reduced from 45 to 20 percent, olefins from 20 to 5 percent, and T90 from 360 to 280 degrees F. For the Predictive model results aromatics were reduced from 30 to 25 percent, olefins from 10 to 6 percent, T90 from 300 to 280 degrees F, and T50 from 210 to 190 degrees F, with the base parameters set to 7 RVP, 20 ppm S, 0.8 benz, 25 aromatics, 6 olefins, 210 T50, 300 T90, and zero oxygen.

included in full as ARB staff addressed all public comments at the hearing. The transcript has been slightly modified to remove banter and to correct obvious transcription errors.

D-3.4.1. Written Comments

Letter from Larry Pearce of the Governors' Ethanol Coalition

On behalf of the coalition, I am pleased to submit the enclosed study, entitled *The Fate and Transport of Ethanol-Blended Gasoline in the Environment: A Literature Review and Transport Modeling*. We hope the study is helpful in your deliberations under Governor Davis's Executive Order D-5-99 and ask that the study be made part of the hearing record. The study is also available on the coalition's home page at http://www.ethanol-gec.org/publicat.htm

Response: This study is summarized in the main report. It 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. Our analysis addresses this recommendation. We have provided the report to the Lawrence Livermore National Laboratory, who is performing the water quality analysis for the State Water Resources Control Board.

Letter from Gina D. Grey of the Western States Petroleum Association

The Western States Petroleum Association (WSPA) has reviewed ARB's revised Staff Report (dated November 18, 1999) on the "Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline," and was pleased to find that several of our criticisms from earlier this year have been addressed. Our comments initially delineate the areas where revisions by staff have improved the results, and then we outline several areas where corrections and clarifications are still needed.

Most significantly, ARB has developed more realistic speciated profiles for the fuels and emissions used in the air quality modeling assessments. The striking inconsistencies observed earlier between the fuel and emissions profiles for the 2003 non-oxy fuel case are no longer evident. As a consequence of these profile changes, identical ozone results are now obtained from modeling of all four fuel cases in 2003. Previously, the non-oxy fuel case had shown slightly higher ozone levels. More reasonable benzene results are also evident, with the non-oxy fuel now showing slightly lower ambient benzene concentrations compared to the other three fuels, as would be expected based upon the gasoline benzene levels.

The emissions profiles for the ethanol fuels now include higher levels of ethanol itself, and the modeled ambient concentrations seem more believable, showing 40-60 ppb increases in ethanol compared to the baseline case. This change is now similar in magnitude to the approximate 50 ppb reduction in ambient MTBE resulting from removal of 15% MTBE from the base case fuel.

The CO emissions impacts of the four fuels considered in 2003 are also modified. Previously, staff assumed a 5% CO increase for the non-oxy fuel compared to baseline, and a 15% CO decrease for the high ethanol fuel (3.5% oxygen). In the revised assessment, ARB still uses a 5% CO increase for the non-oxy fuel, but the CO decrease from the ethanol fuel has been reduced from 15% to 7.5%. This smaller CO benefit is more consistent with our expectations.

The modified emissions profiles have also led to more reasonable specific reactivity values. Previously, emissions from the non-oxy fuel (hot-soak, headspace, and exhaust) had higher specific reactivity than did emissions from the other three fuels, although when considering the liquid fuels themselves, the non-oxy gasoline had the lowest reactivity. Now, emissions from the non-oxy fuel have reactivity as low, or lower than emissions from the other fuels.

Finally, WSPA would agree with ARB's proposal to redo certain analyses once the new mobile source emissions model, EMFAC2000, is officially released, and the Phase 3 gasoline specifications are finalized. Also, we encourage ARB to conduct a robust vehicle emissions testing program using authentic Phase 3 gasoline formulations, to eliminate certain assumptions and obtain more reliable emissions profiles.

Response: *The new upper-bound modeling simulations bracket the effect of EMFAC2000. The Phase 3 regulations preserve the air quality benefits of Phase 2 gasoline, and apply equally to ethanol-blended and non-oxygenated gasolines, consideration of Phase 3 will not affect our overall conclusions. We will consider further vehicle testing as warranted.*

Despite all these improvements, there are still a few minor corrections, clarifications, and other considerations:

- In describing the development of emissions inventories for modeling (page 19 of ARB's revised report) it is stated that "Stationary source emissions were assumed to be the same for all scenarios." Does this mean that no changes in stationary source emissions were applied between the 1997 and 2003 scenarios? If so, this clearly is an erroneous assumption, which would affect the air quality modeling results.

Response: *Stationary source emissions were different for 1997 and 2003. The main report now clarifies that stationary source emissions were assumed to be the same for all 2003 scenarios.*

- It is not clear how the annual average exposure estimates were derived for specific pollutant species. On page 26 it is stated that "For the population-weighted annual-average exposure estimates, we normally used the region-wide population-weighted average of the daily-average model results." Does this mean that only concentrations from the modeled August 26-28, 1987 episode were used? If so, wouldn't this overestimate the annual averages for many species, since this period represents a high pollution episode, rather than an average situation?

Response: *The population weighted concentrations predicted by the model were not the only basis for the estimated 2003 air quality concentrations for the various fuel scenarios. The method for calculating future year air quality concentrations used both model results and 1997 base year concentrations. Basically, the relative change in the model results between 1997 and the various 2003 fuel scenarios was used to scale the 1997 baseline concentrations to the future. Details of the procedures are contained in Section C-4 of Appendix C. Regarding the question of overestimate, the procedures protect against this. For secondary dominated pollutants (e.g. acetaldehyde and formaldehyde) which may have their highest concentrations in summer or fall, annual concentrations are lower than summer concentrations, as suggested. However, for primary pollutants (e.g. CO, benzene, 1,3-butadiene, MTBE, ethanol) which have their highest concentrations in winter, annual concentrations are higher than summer concentrations.*

- The approach used to estimate future-year air pollutant concentrations is unclear, and should be explained in more detail. The ARB report indicates that photochemical modeling results were used to scale the 1997 baseline results to 2003 (page 26). What is the justification for this scaling approach? How was this scaling done?

Response: The details on the procedures for estimating future year concentrations are in Section C-4 of Appendix C. The scaling approach combines model results for 1997 and 2003 with 1997 base year concentrations for the various averaging times of interest to estimate future year air quality concentrations. This scaling procedure was done for all pollutants. Special adjustments are made for primary pollutants (whose highest base year value occurred at Lynwood) and annual exposure estimates for the aldehydes (which required separate treatment of primary and secondary components). The scaling approach is justified because it provides better concentration estimates (particularly for times of the year not represented by the modeled episode), than is provided directly by the modeling results.

- As shown in Table 4.1 (page 21), NOx emissions were assumed to be identical for all four fuel cases considered in 2003. This is inconsistent with experience and Predictive Model projections showing that NOx emissions increase with increasing oxygen level.

Response: The Phase 2 and Phase 3 regulations require that any NO_X emission increases due to increasing oxygen content be offset by adjusting other fuel parameters in the Predictive Model.

D-3.4.2. Oral Testimony

CHAIRMAN LLOYD: Good to have a professor here. First we have Dr. Don Lucas from the Lawrence Berkeley National Lab, who was one of our peer reviewers.

DR. LUCAS: Morning, Mr. Chairman. My name is Donald Lucas. I'm a staff scientist at the Lawrence Berkeley National Laboratories. I'm a researcher in the School of Public Health at UC Berkeley. I have a Ph.D. in physical chemical from UC Berkeley. My research interests include combustion-generated air pollutants, and developing new diagnostic methods. I was an investigator on the UC MTBE report requested by Senate Bill SB 521. We reviewed previous data on the combustion byproducts of MTBE in laboratory and vehicle studies, and performed laboratory experiments and flow reactivity. I also reviewed last year's ARB report on the RVP waiver for ten percent ethanol fuels. I've also read previous studies relating to this subject and comments and reviews made by other interested parties and the subsequent responses of ARB staff. I also served as a reviewer for the reformulated gasoline regulations that will be discussed later today. The review of this work was done by four individuals, Professor John Seinfeld, Cal Tech; Professor Barbara Finlayson-Pitts of UC Irvine; Professor Roger Atkinson of UC Riverside; and myself. Each of us reviewed the executive summary and the sections relating to our areas of expertise.

My comments today are a short summary based on all the reviews and some communications we have had. However, my comments have not been reviewed or approved by the other reviewers. The predicted changes in the emissions expected from using ethanol in gasoline appear reasonable, both in the direction and magnitude of the changes. The calculations presented appear to be consistent and are well documented.

Professor Atkinson states that the findings of the report are supported by the evidence presented, indicate that vehicle exhaust emissions and their impact on ozone formation will not be significantly affected by replacing MTBE with ethanol. The results are also consistent with previous studies, the reviews regarding the impacts of oxygenated and reformulated fuels.

Professor Seinfeld states that the photochemical modeling is consistent with current practices and there are no evident danger signals associated with the results. The model performance could be better in an absolute sense, but using the simulations in a relative sense should bypass many of the problems. It is noteworthy that the predicted differences in ozone between MTBE and ethanol cases are small.

Professor Finlayson-Pitts used the report as a good initial approach to addressing air quality impacts from the use of ethanol in reformulated fuels. Her major concern is that this report will be taken by many as the final assessment and could be cited as such in a widespread manner.

The calculations presented in the report are very complicated and there are many assumptions made regarding the emissions. The reviewers and the ARB staff recognize that the results rely on engineering judgments and that additional modeling and testing needs to be done.

There were concerns expressed about several issues. There was a large, complex report that was conducted at the same time as the Phase 3 reformulated gasoline and the EMFAC 2000 studies. They're all related and all have time constraints. The timing of these studies make it difficult to use information generated in the other reports. While I do not think the results from this study would change significantly if more time were allowed, care must taken in balancing the need for timeliness issues with the effort and time needed to produce sound scientific results.

Professor Finlayson-Pitts and I are concerned about the potential for increased evaporative emissions. The increase could be from an increase in the RVP allowed, from commingling of fuels, decreased canister performance and/or increased permeability of the fuels. I was disappointed that the vehicle testing done in this study did not include testing of the evaporative emissions from vehicles. These issues need to be clarified as they could have significant impact on real-world emissions.

Professor Seinfeld and I agree that the ARB should not change the way it calculates the importance of CO in ozone formation. The value of examining issues such as these should not be underestimated and continued input from outside experts such as Gary Whitten and others should be encouraged. They are also a number of changes and corrections suggested by the reviewers, such as adding additional chlorine chemistry, revised rate constants and also boundary conditions. As mentioned, ARB staff has responded to these and made many changes in the report.

In summary, conclusions reached by the ARB staff appear correct and are justified by the data and analysis performed. The emissions are calculated in a consistent and defendable manner and the assumptions made in reaching the conclusion are reasonable.

Thank you.

CHAIRMAN LLOYD: Thank you very much. Questions from the board? Thank you very much also for responding, and I realize on a very short time frame on a lot of information to assimilate. Thank you very much.

By the way, the witness list is growing, so I guess somebody heard that I'm not going to keep it to five minutes, so I guess we have two more, so now we have four people.

The next one is Dr. Gary Whitten, from ICF Consulting.

DR. WHITTEN: Good morning. My name is Gary Whitten. I'm the chief scientist with ICF Consulting in San Rafael, California, here to talk about the assessment in terms of airshed modeling that was done. And I want to applaud the staff for the work that they did in the past year or even less than that. It was a lot of work and I think it was quite well done.

I agree with most of the peer review comments that the urban airshed model that was used is a good tool for assessing things on a relative basis and that the overall main conclusion that was the beginning of this was the impact of use of ethanol fuels on PAN and acetaldehyde. I believe that the comments and suggestions that I have today will not appreciably affect that in any way whatsoever. But I do believe that the results that one gets from a model such as the urban airshed model depend very strongly on the inputs that are used and the quality of those inputs. And the peer review did not comment on the fact that the initial modeling efforts were quite a bit different than the final modeling efforts. And it was not clear to me from our interactions with the staff what was done to the inputs to make these changes.

And I also agree with the peer reviewers that the impending inputs from EMFAC2000, which have now been postponed to March for full approval, could change some of the results substantially.

The main things that I wish to bring in at this point that are new are, first of all, that the speciation profiles, the representation of the gasoline components needs to, I think some more work in terms of, especially in terms of the area of aromatics. And then also wish to comment on some of the formaldehyde importance as you've been hearing already. I can talk without slides, I think.

The point I'd like to make is that the results of this modeling study have changed dramatically during the one-month period between October and November. The initial results showed a spread in ozone formation between the 3.5 or full 10 percent volume ethanol fuel and the non-oxygenated fuel, a difference of six ppb in ozone. Now, this is a phenomenal large difference. The newest results show a difference of only three-tenths of a 22 ppb between these two fields. So the fact that this change from a six ppb spread to three-tenths of a ppb spread is something that I think it needs some explanation and would like to hear what that is. A six ppb spread between these two fuels is comparable from other modeling that we've done at ICF, is comparable to removing all of the evaporative emissions from the model. So this is a large difference, six ppb. And the fact that it's diminished to only three-tenths is something that's not clear.

The next thing I'd like to talk about is higher aromatics that may be possible from non-oxygenated fuels. In 1994 there was a introduction of oxygen, the MTBE that was the beginning of the use of MTBE in the fall of 1994, and Professor Harley and his group did, I think, a seminal measurement in the Caldecott Tunnel where there was enough -- no regulations towards performance of these fuels except that they must have oxygen. And what the oil companies did was add this oxygen at about the two percent level where it was required at, the same time they reduced aromatics.

So now we're at the, if you will, the flip side of that situation where we're talking about not making appreciable changes to the regulations, but removing MTBE and in some case removing the oxygenate, and so without --it seems to me that you would expect aromatics then to go back up, because both MTBE and ethanol are very powerful octane enhancers, and this sensitivity to aromatics and various toxins and things like that that might be involved, especially ozone, has not been addressed, I believe, in the study to date.

On the carbon monoxide issue, the point I'd like to make here is that it is a very important part of the overall ozone-forming process. The ARB staff did do a sensitivity analysis when they were looking at the three times the emissions to take into account the EMFAC 2000, and the six ppb spread then spread to 22 ppb between full ethanol fuel and the non-oxygenated fuel. And the sensitivity that they did for CO was, I think, was very good and that they set the CO the same between these two and they found that a seven ppb of the 22 ppb was accounted for by the CO. That's one-third of the difference between these fuels. And seven ppb, just a CO adjustment to make them the same, I think attests to the fact how important CO is towards the ozone-formation process.

I would add that in the analysis that we have done and commented on earlier this morning, that we also had changed boundary conditions and found that boundary condition for CO could also play a factor, and I suggest a sensitivity analysis of that be done as well. So one of the things that did occur between the six ppb spread that I told you about and the three-tenths of a ppb in the new staff analysis was a reduction in the amount of CO.

And later today in the reformulated gasoline regulations I will talk more about the amount of CO that might be adjusted. But that was one of the things that was reduced in the final analysis.

So thank you. That's my comments at this time.

CHAIRMAN LLOYD: Thank you very much, Gary. Maybe we could ask staff to respond.

MR. SIMEROTH: Chairman Lloyd, maybe I can start. The tunnel study in 1994 was done before implementation of Phase 2 gasoline vapor recovery. With that the aromatic content with gas control for 1994, premium gasolines could be found that added up to 60 percent aromatics. So putting something in to give the aromatic --or the octane and reducing aromatics is fairly logical. The Phase 2 aromatics were capped at 30 percent and the average has been around 24 or 25, so there are two entirely different situations, so the logic that oxygenates are going to cause a significant decrease in aromatics by our program doesn't hold because of the way our program is structured. There will be some shifts that it's going to be relatively minor, one or two percent.

In terms of the changes of what happened from the first draft to the second draft, at the workshop I indicated that there was some errors in the analysis and we were working on correcting. Subsequent to that statement we found what the errors were, we found that staff had simply taken the oxygenate out and grown the remaining compounds there to fill the void, so to speak, so you saw an increase in aromatics and olefins and everything else. In real life, it won't happen that way. Something will replace the oxygenate, whether it be ethanol or alkylates, and they have different characteristics than what staff assumed. Staff corrected that assumption and published the corrections. We think we're now correct and the previous one was simply incorrect.

We also corrected -- we made the same mistake on the two percent ethanol fuel as well and we corrected that one as well.

CHAIRMAN LLOYD: I think on the speciation profiles, we probably all agree that we can do better there and get those as time goes on. And again, with all due respect to Dr. Whitten, I don't think there's anybody, by the way, who's probably done more modeling runs than Gary throughout the years. He started this, pioneered a lot of the work. But I don't think probably, Gary, you would admit it's unusual for some of the air modeling results to change, not only by the month, but probably by the day, depending on what's done there. So I think again I think we understand the issue in this case that staff has changed some of the results, but I think we understand that part of it. But clearly we will continue to refine the modeling. But I'm not sure the bottom line here is that we don't see a major show stopper for ethanol from an air quality perspective, and that's what we were trying to do in terms of the Governor's Executive Order.

DR. WHITTEN: My comments were more directed to the non-oxy fuel and that the direction of aromatics was down rather than up, and that's contrary to what we would expect.

CHAIRMAN LLOYD: Dean, I'm sure you can respond.

MR. SIMEROTH: Dr. Lloyd, I think the direction was correct and it was wrong initially, and we spent a lot of time working on that correction. We also found that we made a similar error on the two percent ethanol or 5.7 percent ethanol fuel and corrected that one as well.

DR. WHITTEN: We'll have more comments later.

CHAIRMAN LLOYD: I'm sure. Dee Dee, sorry. Ms. D'Adamo. Sorry.

BOARD MEMBER D'ADAMO: Yes. Just one other question then of staff. So initially a non-complying fuel was used and then you made a change so that you used a fuel that would comply with the proposal?

MR. SIMEROTH: It was an error made on how we were assessing what the exhaust emissions would be. And also it would have been a non-complying if we simply had done it that way, backing it back up in the liquid gasoline. I think the corrections were necessary and appropriate and are consistent with what we expect in the future under Phase 3 reformulated gasoline.

BOARD MEMBER D'ADAMO: And the problems that you saw with the first set of data disappeared once you did the run a second time with fuels that would comply?

MR. SIMEROTH: Yes. We found all the mistakes, corrected them and gave the results that you see in the report today that's been peer reviewed, and we've listed every single assumption that we've made and referenced what the source of those assumptions was.

BOARD MEMBER D'ADAMO: Great.

MR. SCHEIBLE: I just want to note that we actually identified the problem with the emissions input prior to putting out the draft report, judged that since the major results in the report about how ethanol substitution affected toxics and PAN needed as much time as possible for review, so we put that advisory in the report when it went out, noticing people that we would be revisiting that particular section.

CHAIRMAN LLOYD: Thank you. Thank you very much, Gary. Look forward to seeing you later. Next witness is Janet Hathaway from NRDC.

MS. HATHAWAY: I'm Janet Hathaway from Natural Resources Defense Council. I did want to make one just brief comment about this segment of the proceedings today. First of all, I recognize that this is an extraordinarily complex issue that the board and the staff have had to deal with in a very short time because of the Governor's order. But I do think that it's important to just pay attention to a couple of possible concerns that need further addressing, and although I know that the Water Resources Board is chiefly designated to be looking at some of these questions, I think part of the problem that happened in our last round with RFG is having two segmented and segregated series of reviews, so I just want to draw attention to these issues and hopefully they will get resolved fully as we move forward.

One is the fact that we still don't really understand enough, I think, about the effect of ethanol blends on the environmental persistence of the other toxic compounds in gasoline. That is very problematic, precisely because we know that many of the contamination places that are most likely to see ethanol spills, places around refineries, around distribution centers, near gas delivery systems, already are contaminated with BTEX compounds, with the benzene, toluene, xylene, ethylene compounds. And because there is reason to believe that there is an effect on making those compounds more soluble, making them migrate more through soil, I just think we need to be very concerned to have those answers before we actually do wide-scale introduction of an ethylene -- I mean of a ethanol-blended gasoline in this state.

Now, many people will say, oh, well, there's no reason to worry, because other states have already done this. But there is reason to worry, because this is from the peer reviewed report. None of the states require ethanol concentrations to be measured in groundwater. So we wouldn't know, even if there were indeed problems going on. We do know from laboratory scale experimentation that ethanol can change the structure of clay lenses, which are known or at least believed to help protect our groundwater sources by sort of capping them and providing a barrier that is usually impenetrable to the usual gasoline compounds, the BTEX compounds. That can be affected by ethanol, so that's a reason for concern, in addition to the co-solvency effect, the effect of -- not melting -- the solvency that occurs that allows the BTEX compounds to move more rapidly through soil. And then finally some of the studies that have been done to date show that the hydraulic activity or the moving of the water through soils that have ethanol blends in them is increased by an order of magnitude or in some cases even two. So, again, reason just to flag that, make sure we have the answers and that we know how to respond if indeed there are changes in how gasoline and ethanol would move through soil.

Now, this is not to say at all that ethanol is something more problematic than MTBE. It is widely and, I think, probably universally acknowledged that ethanol itself will break down in soils pretty rapidly. And that is very reassuring. Whether there's air in the soil or not, ethanol is very likely to break down. The only concern here that I'm raising is the transport of other possibly even more toxic substances through our soil systems into groundwater and that we have to be very careful about. And keep in mind that we already have thousands and thousands of MTBE-contaminated sites. The effects should be looked at not just in terms of BTEX, these benzene, toluene, xylene compounds, but also in terms of the co-solvency effect that might move more of the MTBE already in the soil. Not wanting to rain on any parades or anything, I just wanted to make sure that we are very careful about this approach. I do think that the staff has been extraordinarily conscientious at looking at all the air quality impacts. But this board and I think every agency has to keep in mind the cross-media issues, because it's easy for them to sort of slide into somebody else's domain and not get fully addressed.

Any questions?

CHAIRMAN LLOYD: Thank you very much, Janet. And I think we take your comments to heart. And I hope that you passed those on to the State Water Resource Control Board, and also make comments at the October 18th first meeting of the Environmental Council. And, as you know, Senator Bowen has made sure that we will not in the future forget cross-media, inter or intramedia interactions, as well as the Governor and Secretary Hickox.

MS. HATHAWAY: Absolutely. I'll be attending those.

CHAIRMAN LLOYD: And that's an issue. See if any board members have any comments or questions.

BOARD MEMBER C.H. FRIEDMAN: I have a quick question. Does our report explicitly raise this issue?

MR. CROES: Our report does not raise any issues on surface or groundwater impact.

BOARD MEMBER C.H. FRIEDMAN: I know we didn't investigate it, I take it, but do we point out that we -- that we raised this concern and so that it --

MR. CROES: Our report is one chapter of a three-chapter report that is going to the Environmental Policy Council. The chapter being written by the State Water Resources Control Board and their contractor, Lawrence Livermore National Lab, will completely address these issues.

BOARD MEMBER C.H. FRIEDMAN: So we say at the end, if not the beginning of our report, that this is one in three chapters?

MR. CROES: Yes.

BOARD MEMBER C.H. FRIEDMAN: And be sure to read the others?

MR. CROES: Yes.

CHAIRMAN LLOYD: Last witness on this particular item is Tom Koehler, representing the ethanol industry.

MR. KOEHLER: Good morning. Thank you. My name is Tom Koehler. I'm here today representing Parallel Products, the only current ethanol producer in the State of California. And hopefully after these and other proceedings are over, we will be joined by many others.

I'd like to just briefly touch on Janet's comments. I mean, her questions are absolutely appropriate, and I believe that that discussion has been reviewed extensively by the Water Board and a study with Lawrence Livermore Lab and perhaps, I notice there are people from the Water Board here today, they may want to just clarify issues. My understanding is that ethanol biodegrades at warp speed and in fact the water issue is not an issue.

I would like to thank staff for their work on the urban airshed modeling. I think it was a very good piece of work. Staff was extremely responsive. And I think, Dr. Lloyd, you're correct when you look at the analysis, both the previous analysis and the current analysis, what it says is that the fate and transport of ethanol gives you air quality benefits as good, if not better, than what we currently receive from the California reformulated gasoline program, which in itself is very good air quality benefits. I guess I would encourage if there's other runs to be done to include some ancillary benefits of the use of ethanol here in California, like the reduction of rice straw burning that affect on air pollution, the reduction of other potential wildfire burning that can be all turned into and will be turned into ethanol. I think that would be appropriate to include in further analysis.

I think you'll find that the use of ethanol on an air quality issue alone will provide multi benefits for the environment. Just one comment, there has been talk about the aromatic level of the non-oxygenated gasoline versus ethanol, and I agree, Dr. Lloyd, and with Bart that these are assumptions and over time they change. I would like to point out that the non-oxygenated fuel that was actually measured by the ARB staff in the field versus the actual ethanol fuel that was measured in the field, the non-oxy had twice the amount of aromatics. So just wanted to point that out.

And lastly wanted to follow up on the peer review by Dr. Seinfeld. And in his analysis, I'll quote, Dr. Whitten's analysis of the effect of carbon monoxide on ozone formation is correct. And essentially what Dr. Whitten has been saying is the carbon monoxide is extremely important to the formation of ozone, and is in fact underrepresented by the MIR scale. Now, Dr. Seinfeld goes on to say it's not appropriate to change the MIR for CO alone, but that it would be appropriate to go back, and in fact I believe he is recommending to go back and revisit this issue, and change all of the species based upon the more accurate 3D modeling. And I would encourage the board possibly to direct staff in that direction, and that would be appropriate, would be appropriate action. I believe that's all I have.

CHAIRMAN LLOYD: Thank you very much, Tom. Any questions from the board? Mr. Calhoun.

BOARD MEMBER CALHOUN: I think Dr. Lucas made some remark, I'd like to get staff's reaction to the suggestion about changing the reactivity scale, in particular as it pertains to CO.

MR. CROES: The comments from both Donald Lucas or Dr. Lucas and Professor Seinfeld were that the -- that it would be desirable to base the reactivity scales on state-of-the-science airshed models. MIRs are currently based on models with simple physics with complex chemistry. And the reason that was done a number of years ago was because those were the models that best represented a range of conditions that you would expect around California and throughout the country.

We recognize when we adopted the reactivity scales that as we developed better information with more complex models that we would eventually go to using those as the basis for the reactivity scales. And there's been a long-term research program that has begun since the early '90s to eventually go toward that objective.

The staff feels that we aren't there yet, and I believe that the Reactivity Scientific Advisory Committee would agree with that as well, but it's something that we're going towards.

BOARD MEMBER CALHOUN: Thank you.

CHAIRMAN LLOYD: Dean.

MR. SIMEROTH: Chairman Lloyd, I'd like to indicate the liquid fuels used in the test program that ARB conducted, the total aromatics ranged from 24 percent to 28 percent in liquid fuels.

CHAIRMAN LLOYD: Okay. That range. I'd like to make two comments. One I think that Bart is correct, I think in heading towards the urban airshed model to look up the reactivity, but on the other hand, I think that's a huge exercise when you look at the fact that we still have tremendous degrees of freedom outside the chemistry when we do that. So I understand staff and the scientific community's concerns, but on the other hand I think the -- you should be congratulated for supporting a lot of Dr. Whitten's work which actually has consistently actually pushed the issue that we have to look at CO as an ozone precursor. And I think that significant strides have been made in that, and I've seen that evolve over the last ten years, and clearly as we've pushed the hydrocarbons down in the atmosphere, then CO acting as a hydrocarbon has been recognized. So I think the investment you've made on that, we're reacting and putting that in there, so I congratulate you for supporting that work.

MR. KOEHLER: I think the environment is the winner, and the peer reviews essentially note that CO is an essential component of ozone, and I think that's an important issue to remember as we go into the next board item as well. Thank you.

CHAIRMAN LLOYD: Thank you. I think that's the last witness we have. Mr. Kenny, are there any written comments on that item?

MR. CROES: Yes. We received three letters in response to this item. The first two letters were from the Western States Petroleum Association. There's a letter dated December 3rd, which actually was addressed to Dr. Bill Vance from the California Environmental Protection Agency. And I clarified this letter with WSPA, but apparently he was commenting on the earlier draft of the report from late September. And then it's superseded by a letter dated December 7th, which is actually fairly complimentary that several of our criticisms from early this year have been addressed. And the letter primarily describes the revisions that WSPA agrees have improved the results. And then they outline four areas of minor corrections, clarifications, and we will certainly address those in the final version of the report and feel these are fairly minor issues and just explains what we did.

We also got a letter from the Governor's Ethanol Coalition signed by Larry Pearce, and it just wanted to submit a report that they funded, titled, "The Fate and Transport of Ethanol-Blended Gasoline in the Environment: A Literature Review and Transport Modeling." We had actually included a review of this report. It was one of the seven reports that we reviewed in our assessment of prior work. And the report is almost completely focused on groundwater impacts, so we have passed this report on to the State Water Resources Control Board.

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Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate

Report to the Governor
of the State of California
in response to
Executive Order
D-5-99

VOLUME 4

Potential Ground and Surface Water Impacts

STATE WATER RESOURCES CONTROL BOARD
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Volume 4: Potential Ground and Surface Water Impacts

Chapter 1: Potential Scenarios for Ethanol-containing Gasoline Released into Surface and Subsurface Waters

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Table of Contents

List of Figures

List of Tables

1. Potential Scenarios for Ethanol-containing Gasoline Released into Surface and Subsurface Waters

1.1. Introduction

If California introduces the use of ethanol as a fuel oxygenate, a variety of scenarios may be anticipated in which either bulk fuel-grade ethanol or gasoline blended with ethanol (gasohol) may be released into the environment during its production, distribution, and use. The purpose of this chapter is to use a life-cycle approach (that is, the production, distribution, and use of ethanol) to review systematically the potential release scenarios that may impact California's surface and subsurface waters. The discussion of these scenarios includes field studies wherever possible to identify potential surface and groundwater impacts associated with a scenario.

Figure 1-1 summarizes the life-cycle phases of production storage, blending, distribution, and use of ethanol and gasohol. Table 1-1 summarizes the various potential release scenarios. The table includes a brief description of each release site assumptions and risk assessment issues that may be important during the consideration of each scenario. Also included in the table are qualitative descriptions of the likelihood of occurrence for the scenario, risk-management options, and other release considerations.

1.2. Production

Currently, ethanol is produced primarily in the Midwest from domestic grain. (California has the potential in the future to produce ethanol from recycled biomass [California Energy Commission, 1999]). Most large ethanol producers use a process called "wet-milling" to separate the starch from the grain prior to fermentation of the starch. The highly purified starch is used as the feedstock for ethanol (American Coalition for Ethanol [ACE], 1999). Small processors, however, still use whole-grain fermentation processing which does not first separate out starch through wet-milling and leaves more impurities in the final ethanol product which are not removed.

During the production of ethanol, bulk fuel-grade ethanol (that is, fuel ethanol) is typically stored in large-capacity, above-ground storage tanks (ASTs). Bulk fuel ethanol releases from ASTs and associated piping may also contain other compounds that are byproducts of the fermentation and the subsequent distillation process, or that have been added as amendments.

1.2.1. Trace Compounds Introduced during the Production of Fuel-grade Ethanol

1.2.1.1. Process Impurities

When purified starch is used to produce ethanol, the recovered bulk fuel ethanol is relatively free of production byproducts except for glycerol and fusel oil. Glycerol is a major byproduct (about 5–10% of the quantity of ethanol) of fermentation (Karaosmanoglu *et al.*, 1996); however, glycerol has a boiling point higher than 200°C and is an unlikely contaminant in the final distilled ethanol product.

Another byproduct of the industrial fermentation process is “fusel oil,” an alcohol mixture with a boiling range of 80–132°C. The amount and the composition of fusel oil produced in the fermentation process depend on the raw materials used. A typical fusel-oil production ratio during the fermentation process is 0.2–0.7% (wt) on the basis of pure ethanol (Karaosmanoglu *et al.*, 1996). Although 50 different compounds have been identified in fusel oil, its major components are fermentation amyl alcohols, such as 2-methyl-1-butanol and 3-methyl-1-butanol (Karaosmanoglu *et al.*, 1996).

There are also other compounds, such as acetaldehydes and ethyl acetate, present as process impurities. However, the concentration of these byproducts in fuel ethanol is only in the milligrams-per-liter (mg/L) range when purified starch is used as the feedstock.

Fuel ethanol produced from whole grain contains substantially more impurities (Karaosmanoglu *et al.*, 1996). These byproducts are derived from the non-starch portions of the whole grains, such as hemicellulose and pectin, which contain methyl and acetyl groups. Upon hydrolysis, methanol and acetic acid are formed. These byproducts are subsequently distilled together with ethanol. Whole-grain processing also produces a higher quantity of fusel oil in fuel ethanol. These byproducts are not separated out of fuel ethanol by distillation and so are delivered with the final product.

Methanol is another common process impurity in fuel ethanol. Typically, fuel ethanol consists of the following: 95.1 wt% ethanol, 4.8 wt% water, and 0.1 wt% higher alcohols (Paul, 1978). At the time of blending, fuel alcohol must meet the criteria in Table 1-2.

1.2.2. Additives

Denaturants—toxic or noxious materials used to make the ethanol unfit for human oral consumption—must be added to fuel ethanol directed to storage. Commonly used denaturants for fuel ethanol are unleaded gasoline or rubber hydrocarbon solvent. These are added to ethanol at a minimum of 2% by volume, as defined by formula CDA 20 of the Bureau of Alcohol Tobacco and Firearms of the U.S. Treasury Department (American Society of Testing and Materials [ASTM], 1995). This specification prohibits the use of hydrocarbons, such as kerosene, with a boiling point higher than 225°C. Thus, only hydrocarbons in the gasoline boiling range can be used as denaturants (ASTM, 1995).

Denatured fuel ethanol may contain other additives, such as corrosion inhibitors and detergents (ASTM, 1995). Various blending agents also have been used in fuel alcohol-gasoline mixtures to lower the phase-separation temperature of the blends to below ambient temperatures experienced during the winter season (Karaosmanoglu *et al.*, 1996). These blending agents can be grouped as aromatic compounds, higher aliphatic alcohols, and aromatic alcohols. The addition of other materials is prohibited.

In the final product, the ethanol component of denatured fuel ethanol, excluding water, must comprise at least 98% by volume and must not contain more than 0.5% by volume of methanol or total ketones, or both. Furthermore, the total ethanol content of denatured fuel ethanol, including impurities, must be no less than 95% by volume (ASTM, 1995). A summary of the trace compounds created or introduced during production and processing of fuel ethanol is shown in Table 1-3. This table shows no additional trace elements that are noteworthy of concern due to their solubility and associated toxicity compared to other common gasoline components. None of these trace compounds is substantially less biodegradable than other common gasoline components.

1.3. Distribution

1.3.1. Distribution of Bulk Fuel Ethanol

Shipments of ethanol to California could average about 46 million gal per month and could be as high as 50 million gal per month during the summer peak driving season. A combination of rail transport and marine cargo is likely to be used to distribute bulk ethanol to the California market. Initially, approximately 80% of the bulk ethanol destined for California will be shipped in railroad tanker cars that typically contain about 29,000 gal. Approximately 1600 rail car movements per month would be needed to meet demand (Downstream Alternatives, Inc., 1999). Strings of railroad tankers may be piped together to form a unit train “rolling pipeline.” This arrangement allows a string of tanker cars to be emptied quickly, permitting transport turnaround times of about two weeks between production facilities in the Midwest and distribution terminals in California (Jaffoni, 1999).

Initially, about 20% of the bulk ethanol will be transported as marine cargo. In this scenario, 10,000-barrel tanker barges would float the bulk fuel ethanol down the Mississippi River to New Orleans where it would then be transferred to large-capacity marine tankers for transport to Pacific coast terminals. Marine tanker cargoes most likely would be about 4–5 million gal but may be as large as 10–12 million gal (Downstream Alternatives, Inc., 1999; Jaffoni, 1999).

According to a California Energy Commission analysis (Schremp, 1999), two distribution hubs—one in Northern California and one in Southern California—would receive the bulk fuel ethanol. The volume of bulk fuel ethanol entering California as marine cargo is expected to increase over time to as much as 80% because distribution terminals prefer receiving single shipments of large quantities to minimize the labor- and time-intensive handling of rail cars (Jaffoni, 1999).

Presently, refiners and pipeline operators are reluctant to distribute bulk fuel ethanol through a pipeline because of concerns regarding ethanol’s affinity to water. Water is often present in association with unblended gasoline transported through the pipelines (Center for Transportation Research, no date). If this issue can be addressed, more pipeline use can be anticipated.

1.3.2. Blending of Ethanol with Gasoline

Because of the limitations in pipeline use, about 77% of the bulk fuel ethanol would be distributed by tanker trucks from the distribution hubs to blending terminals. It is expected that truck traffic would increase in proximity to the distribution hubs (Schremp, 1999). Pipelines will continue to be used to deliver a base gasoline to blending terminals for blending with fuel ethanol. The bulk fuel ethanol and base blending gasoline will be stored in separate tanks and blended just prior to shipment to gas stations. Several blending processes are available (Downstream Alternatives, Inc., 1999):

- **Tank Blending:** This alternative requires a recirculation capacity within the storage tank. This is the least preferred method because of the possibility of water contamination of the blended fuel which may lead to separation during distribution.
- **Top-off/Splash Blending:** In this blending process, ethanol and base gasoline are delivered separately into a tanker truck. The mixing during loading and transport accomplish the blending process. This process is widely and successfully used and is the preferred method for developing distribution systems.
- **In-line/Injection Blending:** Ethanol and gasoline are blended in-stream as the mixed fuel is delivered to a tanker truck. This is the preferred method of blending for established distribution systems because of better quality control and fewer blending errors.

1.3.3. Transportation and Storage of Blended Gasohol

Tanker trucks will transport the gasohol (that is, gasoline blended with ethanol) much as it is currently done. The typical gas station operates at least two underground storage tanks of between 10,000 and 20,000 gal each. High-throughput gas stations may receive a tanker-truck delivery at least once a day. If only two tanks are operated, mid-octane gas is often dispensed by blending a lower- and a higher-octane gasoline at the pump.

Monoaromatic hydrocarbons such as benzene, toluene, ethylbenzene, and the three isomers of xylene (BTEX) are ubiquitous groundwater pollutants commonly associated with petroleum product releases from underground storage tanks (USTs). All six BTEX compounds are powerful depressants to the central nervous system, and chronic benzene exposure can cause leukemia (*Federal Register,* 1985). Thus, BTEX contamination of potential drinking water sources represents a serious threat to public health. To put the magnitude of this problem in perspective, 370,000 fuel releases from leaking underground storage tanks (LUST) have been confirmed in the United States (U.S. Environmental Protection Agency [U.S. EPA], 1998). The actual number of tank releases could be as high as 600,000 (Flatham, *et al*., 1994).

In December 1998 federal regulations were placed into effect requiring improved, leak resistant underground gasoline storage tanks (Herman and Fields, 1998). California gas stations are required to have USTs and piping that are double-walled with leak-detection systems capable of detecting line leaks of 3 gal per hour and tank leaks of 3 gal per day (*California Code of Regulations,* Title 23, sections 2610–2728).

Use of a 10% by volume (or less) ethanol blend requires no vehicle engine or fuel tank modification (Canadian Renewable Fuels Association [CRFA], 1999). Currently, retail gasoline dispensing equipment is designed to handle 10% by volume ethanol gasolines although attention should be given to the use of alcohol-resistant materials in the pumps, line leak detectors, hoses, seals, and nozzles (Center for Transportation, no date). Gas stations that convert to dispensing gasohol will need to replace or recalibrate meters, conduct storage tank cleaning and drying, and check storage tank and piping capability for use with ethanol fuels.

1.4. Use

1.4.1. Present Extent of Gasohol Use

Gasohol has been used extensively in the corn-growing states of the Midwest for several years. It can be found as an option at most gasoline stations in Iowa and Nebraska. At present, 60% of gasoline sold in Illinois and 90% of the gasoline sold in the Chicago area contains 10% by volume ethanol (Renewable Fuels Association [RFA], 1999). Between the Chicago and Milwaukee areas, approximately 450 million gal of ethanol are consumed in gasoline annually (Hord, 1999). Gasohol has also been sold in Kansas through independent stations although its availability has declined in the last couple of years because major distributors have bought many of the independent stations (Winn, 1999). Throughout the United States, consumers use more than 15 billion gal of ethanol-blended gasoline each year (ACE, 1999).

In July 1998, there were approximately 950 retailers of ethanol-blended fuels across Canada, excluding those who were not listed with the CRFA (1999). The ethanol-gasolines were distributed by most major petroleum companies (for example, Mohawk Oil; Sunoco, Inc., and MacEwen Petroleum, Inc.) and several other independent retail outlets (Mr. Gas, Pioneer Petroleum, Frances Fuels, Stinson Petroleum, and Sunys). This gasohol was available in all grades of gasoline, and also for on-farm delivery.

During the use of gasohols in vehicles and watercraft, two types of emissions are released: exhaust and evaporative. Exhaust emissions are those exiting the tailpipe during the combustion of gasohols. Evaporative emissions occur while the vehicle is sitting as well as operating. Heat from the engine or from ambient weather conditions can cause volatile components of the fuel, including ethanol, to boil off and leak into the air. The California Air Resources Board has developed emission profiles for proposed 5.8% and 10.1% ethanol blends of motor vehicle fuel (Allen *et al.*, 1999). These emission profiles have been used during our evaluation of potential releases to groundwater from the rainout of these emissions.

Releases of ethanol and blended gasohol during production and distribution are typically point source releases (that is, the extent of the release is a localized area). The environmental concentrations of ethanol or gasoline components associated with point source releases often are, initially, relatively high. On the other hand, the area extent of releases during the use of gasohol is typically quite large, for example, an entire lake, watershed, or air basin. These types of releases associated with the use of gasohol are referred to as non-point source releases, and the environmental concentrations of ethanol and gasoline components associated with these types of release typically are relatively low.

1.4.2. Releases from Watercraft Exhaust Emission into Surface Waters

One of the unexpected surface-water impacts resulting from the use of MTBE in gasoline was MTBE entering surface water in reservoirs and lakes in California (see Malcolm-Pirnie, Inc., 1998; McCord and Schladow, 1998). The principal source of this contamination is recreational boating, with the largest source attributed to two-stroke carbureted marine engines used in jet skis (Allen *et al.*, 1998). Recreational watercrafts typically discharge exhaust below the water surface. Often this discharge is through the watercraft propeller or propulsion jet, which promotes a thorough mixing of the discharged compounds with surface waters.

Effective June 1, 1999, the Tahoe Regional Planning Agency imposed a ban on certain two-stroke marine engine technologies. Previous studies had shown that while two-stroke carbureted engines accounted for only 11–12% of the total fuel used by watercraft on Lake Tahoe, they were responsible for approximately 90% of the MTBE emissions to the lake (Allen *et al*, 1998). While recent data strongly suggests that the ban on certain types of two-stroke engines at Lake Tahoe was very successful in reducing both MTBE and BTEX (Allen and Reuter, 1999: Appendix C of Chapter 5 of this report), exhaust releases of gasoline containing ethanol can be expected to continue.

1.4.3. Releases from Washout of Automotive Tailpipe Emissions and Combustion Products to Surface Waters

Tailpipe and combustion products generally enter the atmosphere in the vapor phase. In the case of ethanol and methyl tertiary butyl ether (MTBE), these vapors preferentially partition into water present in the atmosphere. During precipitation events, such as rain storms or the formation of dew, the ethanol or MTBE is washed out of the atmosphere and deposited onto the ground surface or surface bodies of water and eventually infiltrates into groundwater. Although the concentrations washed out often are relatively low, the depositions occur over a large area and will continue to be deposited as long as the fuel is used. For these reasons, it is important to consider any cumulative impacts that may result from the ongoing deposition of tailpipe emissions and combustion products.

1.5. Field Studies

1.5.1. Bulk Fuel Ethanol Releases with Fuel Hydrocarbons Absent

Releases of liquid bulk ethanol to soil and water can result from leaks or spills from ASTs at the production site. Few studies have documented the release of bulk ethanol to soils where fuel hydrocarbons are absent. Concentrations of ethanol as high as 2600 parts per million (ppm) were detected at the site of a 30,000-gal spill of denatured alcohol (Chambers, 1999).

Although we found few field studies that deal with bulk releases at ethanol production sites, there was a study of Savasol, a solvent comprised almost entirely of ethanol, that leaked from an UST at an industrial facility in Salem, Massachusetts, in the early 1990s (Schaffner, 1999). The volume of ethanol leaked was unknown. Although initial concentrations were high, ethanol concentrations were non-detectable within six to eight months after the spill event. The groundwater table was near the ground surface in the vicinity of the spill site. It is likely that volatilization in combination with rapid biodegradation were important mechanisms in the rapid natural attenuation of the bulk ethanol at this site.

1.5.2. Bulk Fuel Ethanol Releases with Fuel Hydrocarbons Present

A 1994 American Petroleum Institute (API) survey found that 85% of the monitored AST farms reported groundwater contamination. In view of this fact, bulk ethanol releases at distribution and blending terminals could reasonably be expected to impact already existing fuel hydrocarbon releases. Indeed, as described below, there have been such incidents in states that use gasohol.

Our review of field studies found a few instances in which ethanol was released at sites where fuel hydrocarbons were known to be present. One such study concerned bulk ethanol that was released in the early 1980s from a gasoline distribution terminal owned by Zephyr, Inc., in Leelanau County, Michigan (Skipper, 1999). It is believed that the spill occurred when either a valve or pipe failed during a transfer at the blending rack. The less-than-500-gal spill of ethanol was onto soil which already had a high degree of prior contamination by other petroleum hydrocarbons. Although the distribution of sampling wells at this site was sparse, groundwater samples were analyzed for a very comprehensive suite of petroleum hydrocarbons. Technical reports written about this site did not note any increase in the concentration of petroleum hydrocarbons following the ethanol spill. The ethanol- and petroleum-contaminated soil has since been excavated and landfilled, preventing any long-term analysis of the fate of these contaminants.

An estimated 17,740 gal of denatured ethanol was released in September 1992 from an AST at a bulk storage terminal in Tacoma, Washington (Hooton, 1999). The leak was attributed to a faulty water draw valve. The area surrounding the spill site had previously been contaminated by a variety of petroleum products. Free-product and groundwater recovery, and soil vapor extraction remediation measures were ongoing at the site before the ethanol spill.

Groundwater and soil sampling efforts at the Tacoma, Washington, site were not initially implemented due to the lack of regulatory concern by the Washington state Department of Ecology (O’Hara, 1993). In August 1994—almost two years after the initial spill event—groundwater samples were collected and analyzed for ethanol. Concentrations of ethanol in the immediate vicinity of the tank that leaked ranged from 5,600 to 81,000 ppm (about 8% ethanol by mass) (EMCON, 1997). However, no ethanol was detected in these same wells in May 1997, approximately five years after the spill.

While data in this case are insufficient to thoroughly assess the overall impact of ethanol on the existing light nonaqueous phase liquid (LNAPL) contamination, or benzene, toluene, ethyl benzene, and xylene (BTEX) concentrations, evidence suggests that benzene concentrations increased in the immediate vicinity of the tank as a result of high ethanol concentrations. Data quantifying benzene concentrations before and after the ethanol spill are only available for one well. Benzene concentrations two to five years after the spill (10–20 mg/L) were more than an order of magnitude higher than that three years before the spill (0.88 mg/L) (Dalton, 1998). Although the lack of data prevents a thorough analysis of the effects of ethanol, it can be concluded that the area within 20 ft of the ethanol spill generally has significantly higher benzene concentrations than at other areas at the bulk petroleum distribution terminal.

The impact of the ethanol spill on the distribution of light non-aqueous phase petroleum hydrocarbons (free product) at the Tacoma, Washington, site is unclear. Professionals who have studied this site conflict in their assessment of the amount of free product at the site before the ethanol spill (Dalton, 1998; EMCON, 1997). Because of these conflicting interpretations of the initial conditions, changes in the nature of the free product cannot be quantified.

In March 1999, an unknown amount of ethanol was released from an AST at a bulk fuel ethanol terminal in the Pacific Northwest where petroleum hydrocarbons were also present. The volume of the bulk fuel ethanol released is estimated to be greater than 10,000 gal (Buscheck, 1999). Groundwater sampling data from this site is much more extensive than that available at other sites. At least ten additional wells were installed to monitor the fate of ethanol and BTEX at this site; however, analysis of the database of groundwater concentrations has not yet been completed. Groundwater was sampled in June and August 1999, with additional rounds of sampling possible in the near future. Shortly after the spill event, concentrations of ethanol in the groundwater ranged from 0.2 to 20,000 mg/L. Preliminary interpretation suggests that by the August 1999 sampling period, less than five months after the spill itself, ethanol concentrations in the groundwater were below detection limits.

Significant petroleum contamination existed at this site prior to the ethanol spill. BTEX and total petroleum hydrocarbons (TPH) had been detected in soil samples although no free product had been observed in the immediate vicinity of the ethanol tank. Preliminary analysis of the groundwater concentration data suggests that BTEX concentrations are on the order of a factor of two greater than before the ethanol spill.

1.5.3. Releases of Gasohol from Tanker Truck

Recent spills of gasohol from tanker trucks are treated as emergency response actions and generally the site of these spills receive no long-term environmental monitoring. Therefore, there is little data about residual impacts from such releases.

1.5.4. Gasohol Releases from Gas Station Underground Storage Tanks

With the current widespread use of gasohol, it is expected that there would be numerous releases of gasohol from LUSTs. As part of the review conducted for this chapter, information was gathered on the extent and knowledge base available about such sites. The data collection methods included telephone interviews with state and US EPA personnel in Midwestern states who investigate and remediate LUSTs, contact with Bruce Bauman of the API, and a general request for information through an electronic mailing list to groundwater professionals.

From these contacts, it appears that there is inadequate information available to identify and investigate the impact of ethanol on the fate of BTEX species from LUST sites at gasoline stations. Although the persons who were interviewed acknowledged that there must be gasohol spill sites in each of the Midwestern states, there is no knowledge base associated with potential differences in the nature or extent of groundwater contaminated by gasohol versus gasolines not containing ethanol.

David Chambers of the Nebraska Department of Environmental Quality (NDEQ) searched the NDEQ database for spill sites related to “gasohol,” “alcohol,” or “ethanol” (Chambers, 1999). Of the 39 entries found, 11 were associated with gasohol or ethanol-diesel mixtures (see

Appendix A for database search results). For the one railroad accident involving a 114,000-gal alcohol diesel release, no ethanol was detected in the groundwater.

1.5.5. Summary of Knowledge Gained from Field Studies

In general, the information presently available on the fate of BTEX and ethanol at field sites confirms the expected behavior based on the literature reviews presented in Chapters 2 and 3 of this volume. Although the information is sparse, it appears that when neat ethanol is spilled, the ethanol concentrations drop quickly in the subsurface via natural attenuation mechanisms. There is, however, a risk of elevated BTEX concentrations in groundwater following the release of bulk ethanol into soil previously contaminated with petroleum products. A significant opportunity exists to learn more from the ethanol spill site in the Pacific Northwest. Substantial data was collected in a timely fashion at that site and further analysis could prove extremely valuable. An effort to rigorously interpret this data could lead to substantial improvements in our understanding of the fate of ethanol and BTEX in the subsurface.

For gasohol spills or LUFT releases at gasoline stations, much of the lack of information stems from the regulatory environment controlling the investigation and remediation of gasoline leaks and spills. None of the states requires that ethanol concentrations be measured in groundwater samples because ethanol is not a regulated pollutant. Similarly, databases used for tracking release sites do not include a mechanism to identify or sort releases of gasohol versus non-ethanol gasolines. This is due in part to the perception that there are no important qualitative differences in environmental impact between the two types of gasoline. Further, there is no means of ascertaining the type of gasoline released at many sites. Perhaps, as was the case with MTBE less than a decade ago, regulators and groundwater professionals are not yet looking for any impacts because they do not perceive nor systematically evaluated gasohol as having an important effect on impacts due to groundwater contamination.

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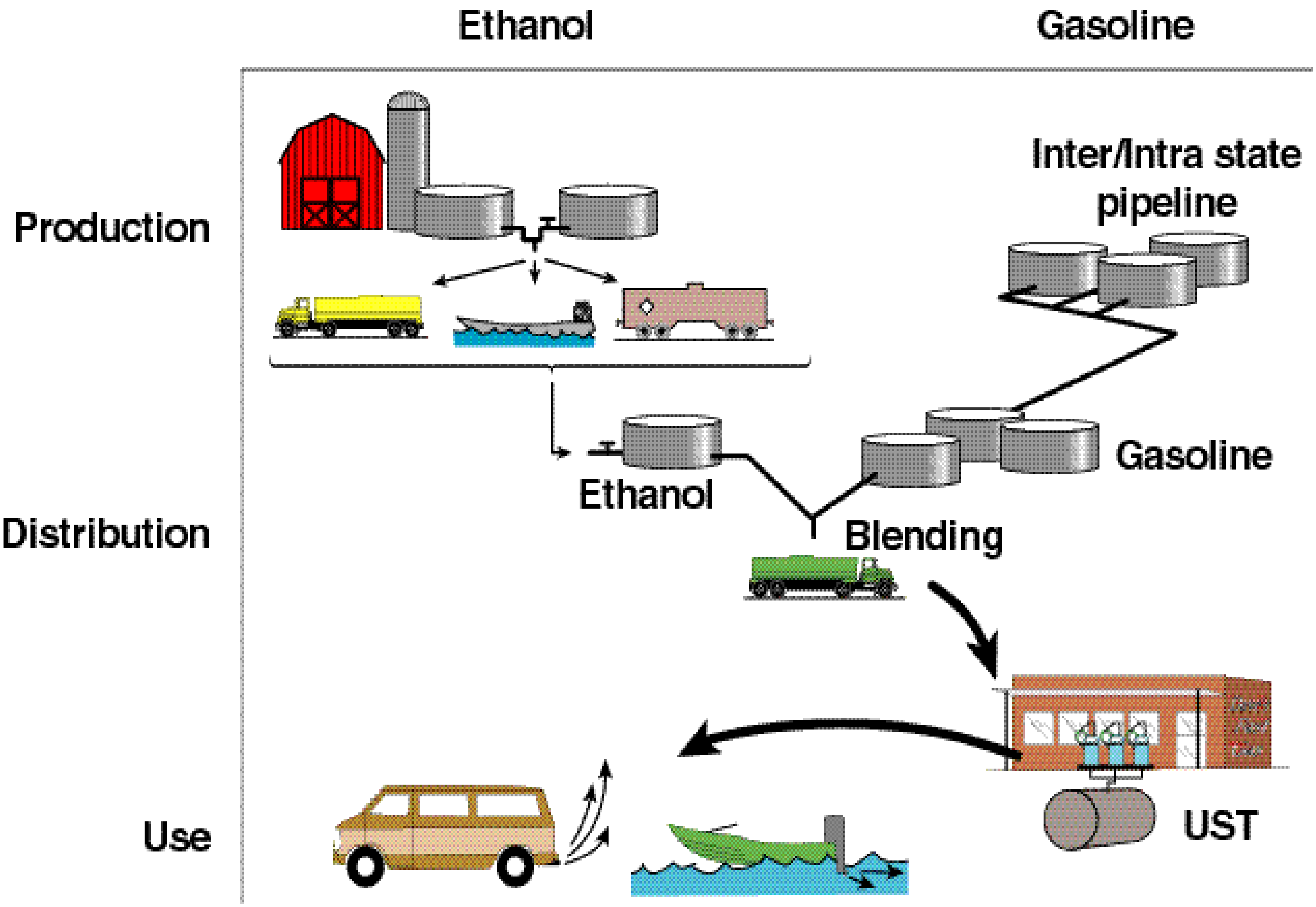


Figure 1-1. Life-cycle of fuel ethanol.

Tables

Table 1-1. Life-cycle assessment of ethanol releases.

Release scenario	Release assumptions	Site assumptions	Likelihood of occurrence	Risk assessment issues	Risk management options
Production					
Release from an aboveground storage tank (AST) at production site	*Assumes a large-volume (>30,000 gal) bulk ethanol release to soils and groundwater from a high-volume AST or associated piping at an ethanol-manufacturing site.*	*Assumes bulk ethanol release into relatively pristine subsurface conditions. Fuel hydrocarbons are assumed to be historically absent.*	*Small likelihood of occurrence.* *Because California currently has few ethanol production facilities, this scenario represents a release that could occur only once biomass ethanol production facilities are constructed in the state in the future.*	*Toxicity to ecological receptors in direct contact with the release. Case studies indicate that ethanol is relatively rapidly lost in the subsurface environment.*	*Engineered containment to control potential release, e.g., double-walled tanks and piping. Spill prevention and containment contingency (SPCC) Plans typically in place.*
Distribution					
Release during bulk ethanol transport by rail or highway	*Assumes that a rupture of a rail tank car or a tanker truck releases a large volume of bulk ethanol (10,000–30,000 gal) to soils and groundwaters or surface waters.*	*Assumes a relatively pristine surface and subsurface conditions where fuel hydrocarbons are historically absent.*	*Moderate likelihood of occurrence. Because California currently has few ethanol production facilities, most ethanol used will initially be imported into the state by way of rail tank car or tanker truck.*	*Toxicity to ecological receptors in direct contact with the release. Potential to impact surface aquatic ecosystem. It is likely that volatilization as well as biodegradation will be important mechanisms in the rapid natural attenuation of the bulk ethanol.*	*Rail car and truck tanker releases are typically treated as an emergency response action and generally require no long-term monitoring.*

Table 1-1. Life-cycle assessment of ethanol releases (Cont.).

Release scenario	Release assumptions	Site assumptions	Likelihood of occurrence	Risk assessment issues	Risk management options
Distribution (Cont.)					
Release during bulk ethanol transport by marine cargo tanker	*Assumes that a rupture of a marine tanker ship releases a large volume of bulk ethanol (>100,000 gal) into marine surface waters. While ethanol is infinitely soluble, it will tend to distribute near the water surface because it is less dense than water.*	*Assumes a bulk ethanol release into the near-shore coastal marine environment.*	*Low likelihood of occurrence.* *However, the shipment of ethanol as marine cargo will increase because distribution hubs will prefer to receive larger quantities to minimize the handling of rail cars.*	*Toxicity to ecological receptors in direct contact with the release; potential to impact surface aquatic ecosystem. It is likely that volatilization, dispersion, and dilution as well as biodegradation will be important mechanisms in the rapid natural attenuation of the bulk ethanol.*	*Requires bulk ethanol to be shipped in marine tankers with double-walled construction.*
Release of bulk ethanol at a distribution terminal	*Assumes a large volume bulk ethanol release to soils and groundwater at a distribution hub or terminal. The release is assumed to be from a high volume AST or associated piping. ASTs at a distribution hub may contain >150,000 barrels of ethanol.*	*Fuel hydrocarbons are assumed to be historically present and may be present as free product trapped in the subsurface. MTBE may be present in the free product.*	*Moderate likelihood of occurrence.*	*The ethanol is assumed to interact with soils contaminated with existing fuel hydrocarbons. Previously immobile hydrocarbons may now be mobilized to the groundwater. An existing fuel hydrocarbon groundwater plume may be expanded.*	*Engineered containment to control release, e.g. double-walled tanks and piping. SPCC Plans typically in place. Manage the location of ethanol ASTs to avoid known areas of fuel hydrocarbon releases. Remediate the fuel hydrocarbon releases.*

Table 1-1. Life-cycle assessment of ethanol releases (Cont.).

Release scenario	Release assumptions	Site assumptions	Likelihood of occurrence	Risk assessment issues	Risk management options
Distribution (Cont.)					
Release of blended gasohol during transport from a California distribution terminal	*Assumes that ethanol is blended with gasoline at a distribution terminal or refinery and transported by tanker truck to a gas station. Assumes a large volume (~5000 gal) of blended gasoline/ ethanol (10% or 6% gasohol) released from tanker truck to soils and groundwaters or surface waters.*	*Assumes release occurs into roadside environments where fuel hydrocarbons are historically absent.*	*Moderate likelihood of occurrence.*	*If any gasohol infiltrates into the subsurface, it will act as a source of groundwater contamination. Concentrations of BTEX in groundwater may initially be somewhat higher than for standard gasoline spill. Potential for a release to streets and urban storm drains.*	*Tanker cars and truck releases are typically treated as an emergency response action and generally require no long-term monitoring*
Release at gas station during underground storage tank (UST) filling	*Assumes that gasohol is spilled during UST filling at a gas station. A low-volume (< 50 gal) of blended gasoline/ ethanol (10% or 6% gasohol) released to soils and groundwater.*	*Assumes small masses of fuel hydrocarbons are historically present in the subsurface.*	*A likely and common release scenario.*	*The ethanol is assumed to interact with soils contaminated with existing fuel hydrocarbons. MTBE may be present.*	*UST over-fill buckets associated with upgraded USTs should minimize these releases.*

Table 1-1. Life-cycle assessment of ethanol releases (Cont.).

Release scenario	Release assumptions	Site assumptions	Likelihood of occurrence	Risk assessment issues	Risk management options
Distribution (Cont.)					
Release at a gas station from a small UST puncture	*Assumes a small puncture of the UST or associated piping resulting in a low-volume release of blended gasohol (~<3 gal per day).*	*Assumes release may occur into sub-surface environ-ments with or without historic fuel hydrocarbon contamination. MTBE may be present.*	*A likely and common release scenario. Evaluation of this scenario will be important to estimating potential impacts to groundwater resources.*	*This scenario has the potential to release a large cumulative mass of gasohol because of the large number of USTs in operation and the potential for small leaks to go undetected.*	*Current requirement for USTs to use double-walled containment reduce the likelihood of this scenario's occurrence. There remain some issues with materials compatibility with ethanol.*
Release at a gas station from large UST puncture	*Assumes a large puncture of the UST or associated piping resulting in a high-volume release of blended gasohol (~<10 gal per day).*	*Assumes releases may occur into subsurface environments with or without historic fuel hydrocarbon contamination. MTBE may be present.*	*Moderate likelihood of occurrence.*	*Typically, larger UST leaks are rapidly detected, and corrective action is initiated.*	*Current requirement for USTs to use double-walled containment reduce the likelihood of occurrence. Some issues with materials compatibility with ethanol remain.*

Table 1-1. Life-cycle assessment of ethanol releases (Cont.).

Release scenario	Release assumptions	Site assumptions	Likelihood of occurrence	Risk assessment issues	Risk management options
Use					
Release from watercraft emissions into surface waters.	*Assumes a significant percentage of fuel released through exhaust as uncombusted free product.*	*Assumes pristine freshwater lakes and rivers.*	*A likely and common release scenario*	*The biodegradation and volatilization of ethanol in surface waters is expected to be rapid. Low increases in nutrient loading and decreases in dissolved oxygen concentrations may occur.*	*Increase engine combustion efficiency.*
Release due to rainout of tailpipe emissions and combustion products to surface soils and waters.	*Assumes ethanol vapors and combustion products will partition into atmospheric moisture.*	*Assumes widespread nonpoint source deposition with various amounts of recharge to groundwaters and runoff to surface waters.*	*A likely and common release scenario.*	*Ethanol emissions preferentially partitions into water and will be expected to rainout. The biodegradation of ethanol in surface waters is expected to be rapid.*	

Table 1-2. Summary of fuel-grade alcohol at time of blending as specified by ASTM Specification D4806-95.[a]

Description of trace compound	Maximum content
Water content, max, mass %	*1.25*
Existent gum, max, mg/100 mL	*5*
Chloride ion content, max, mass ppm	*40*
Copper content, max, mg/kg	*0.1*
Acidity (as acetic acid), max, mass %	*0.007*
Appearance	*Visibly free of suspended or precipitated contaminants (clear and bright)*

[a] *Source: American Society of Testing and Materials (ASTM), 1995.*

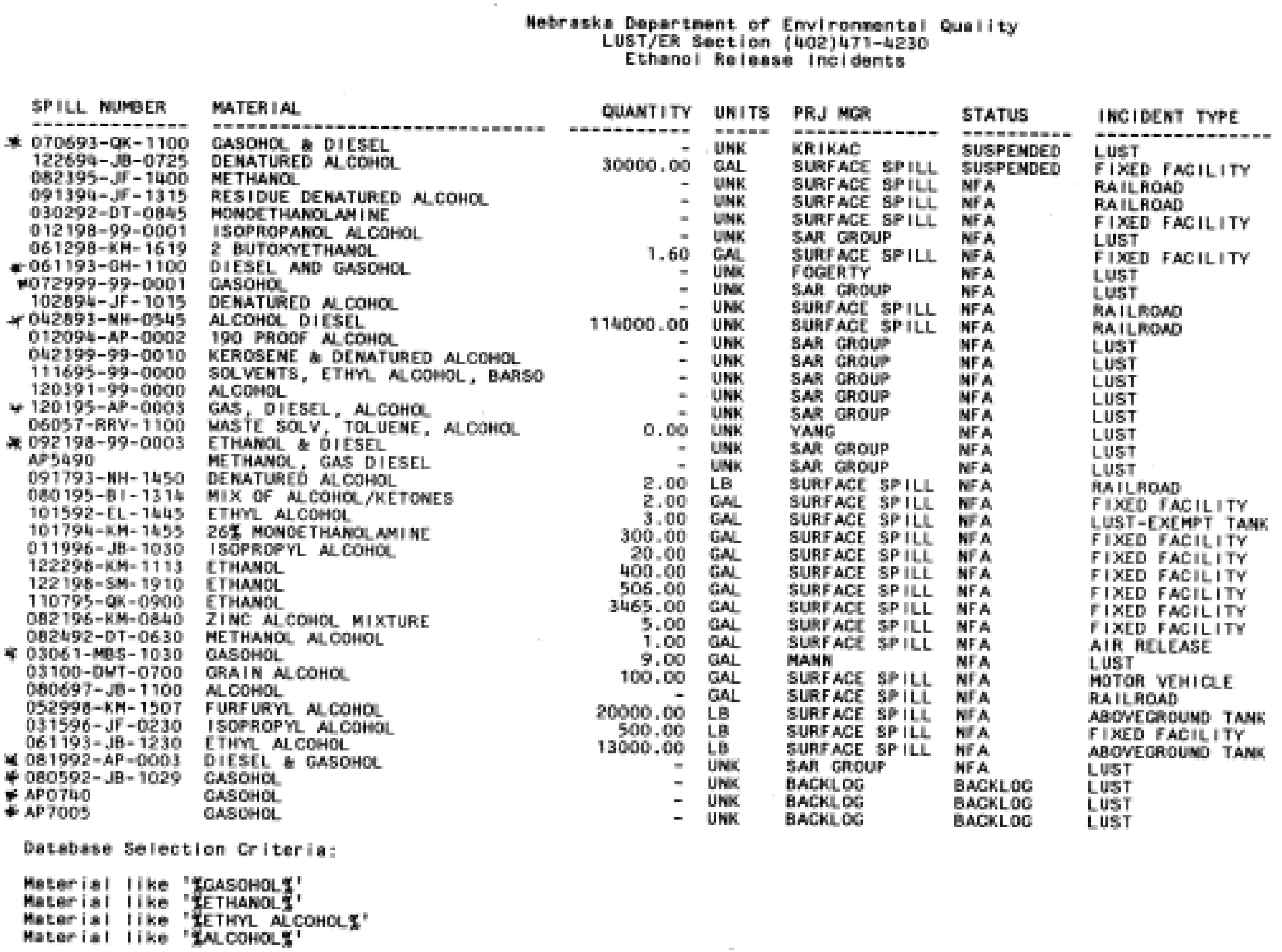
Table 1-3. Trace compounds introduced during production of fuel-grade ethanol.[a]

Impurities	Denaturants	Blending agents	Additives
Methanol *Fusel oil: amyl and isoamyl alcohols*	*Unleaded gasoline* *Rubber hydrocarbon solvent; hydrocarbons with end boiling point <225°C (437°F)*	*Aromatic compounds* *Aromatic alcohols* *Higher alcohols*	*Corrosion inhibitors* *Detergents*

[a] *The total content of impurities, denaturants, blending agents, water, and additives must be less than 5% (by volume) of fuel alcohol (ASTM, 1995).*

Appendix A
Results of Search of NDEQ Spill Database

Appendix A
Results of Search of NDEQ Spill Database[1]



Nebraska Department of Environmental Quality
LUST/ER Section (402)471-4230
Ethanol Release Incidents

SPILL NUMBER	MATERIAL	QUANTITY	UNITS	PRJ MGR	STATUS	INCIDENT TYPE
* 070693-QK-1100	GASOHOL & DIESEL	-	UNK	KRIKAC	SUSPENDED	LUST
122694-JB-0725	DENATURED ALCOHOL	30000.00	GAL	SURFACE SPILL	SUSPENDED	FIXED FACILITY
082395-JF-1400	METHANOL	-	UNK	SURFACE SPILL	NFA	RAILROAD
091394-JF-1315	RESIDUE DENATURED ALCOHOL	-	UNK	SURFACE SPILL	NFA	RAILROAD
030292-DT-0845	MONOETHANOLAMINE	-	UNK	SURFACE SPILL	NFA	FIXED FACILITY
012198-99-0001	ISOPROPANOL ALCOHOL	-	UNK	SAR GROUP	NFA	LUST
061298-KM-1619	2 BUTOXYETHANOL	1.60	GAL	SURFACE SPILL	NFA	FIXED FACILITY
* 061193-GH-1100	DIESEL AND GASOHOL	-	UNK	FOGERTY	NFA	LUST
* 072999-99-0001	GASOHOL	-	UNK	SAR GROUP	NFA	LUST
102894-JF-1015	DENATURED ALCOHOL	-	UNK	SURFACE SPILL	NFA	RAILROAD
* 042893-NH-0545	ALCOHOL DIESEL	114000.00	UNK	SURFACE SPILL	NFA	RAILROAD
012094-AP-0002	190 PROOF ALCOHOL	-	UNK	SAR GROUP	NFA	LUST
042399-99-0010	KEROSENE & DENATURED ALCOHOL	-	UNK	SAR GROUP	NFA	LUST
111695-99-0000	SOLVENTS, ETHYL ALCOHOL, BARSO	-	UNK	SAR GROUP	NFA	LUST
120391-99-0000	ALCOHOL	-	UNK	SAR GROUP	NFA	LUST
* 120195-AP-0003	GAS, DIESEL, ALCOHOL	-	UNK	SAR GROUP	NFA	LUST
06057-RRV-1100	WASTE SOLV, TOLUENE, ALCOHOL	0.00	UNK	YANG	NFA	LUST
* 092198-99-0003	ETHANOL & DIESEL	-	UNK	SAR GROUP	NFA	LUST
AP5490	METHANOL, GAS DIESEL	-	UNK	SAR GROUP	NFA	LUST
091793-NH-1450	DENATURED ALCOHOL	2.00	LB	SURFACE SPILL	NFA	RAILROAD
080195-BI-1314	MIX OF ALCOHOL/KETONES	2.00	GAL	SURFACE SPILL	NFA	FIXED FACILITY
101592-EL-1445	ETHYL ALCOHOL	3.00	GAL	SURFACE SPILL	NFA	LUST-EXEMPT TANK
101794-KM-1455	26% MONOETHANOLAMINE	300.00	GAL	SURFACE SPILL	NFA	FIXED FACILITY
011996-JB-1030	ISOPROPYL ALCOHOL	20.00	GAL	SURFACE SPILL	NFA	FIXED FACILITY
122298-KM-1113	ETHANOL	400.00	GAL	SURFACE SPILL	NFA	FIXED FACILITY
122198-SM-1910	ETHANOL	506.00	GAL	SURFACE SPILL	NFA	FIXED FACILITY
110795-QK-0900	ETHANOL	3465.00	GAL	SURFACE SPILL	NFA	FIXED FACILITY
082196-KM-0840	ZINC ALCOHOL MIXTURE	5.00	GAL	SURFACE SPILL	NFA	FIXED FACILITY
082492-DT-0630	METHANOL ALCOHOL	1.00	GAL	SURFACE SPILL	NFA	AIR RELEASE
* 03061-MBS-1030	GASOHOL	9.00	GAL	MANN	NFA	LUST
03100-DWT-0700	GRAIN ALCOHOL	100.00	GAL	SURFACE SPILL	NFA	MOTOR VEHICLE
080697-JB-1100	ALCOHOL	-	GAL	SURFACE SPILL	NFA	RAILROAD
052998-KM-1507	FURFURYL ALCOHOL	20000.00	LB	SURFACE SPILL	NFA	ABOVEGROUND TANK
031596-JF-0230	ISOPROPYL ALCOHOL	500.00	LB	SURFACE SPILL	NFA	FIXED FACILITY
061193-JB-1230	ETHYL ALCOHOL	13000.00	LB	SURFACE SPILL	NFA	ABOVEGROUND TANK
* 081992-AP-0003	DIESEL & GASOHOL	-	UNK	SAR GROUP	NFA	LUST
* 080592-JB-1029	GASOHOL	-	UNK	BACKLOG	BACKLOG	LUST
* AP0740	GASOHOL	-	UNK	BACKLOG	BACKLOG	LUST
* AP7005	GASOHOL	-	UNK	BACKLOG	BACKLOG	LUST

Database Selection Criteria:

Material like '%GASOHOL%'
Material like '%ETHANOL%'
Material like '%ETHYL ALCOHOL%'
Material like '%ALCOHOL%'

---

[1] Provided by David Chambers, NDEQ (Chambers, 1999).

Reference

Chambers, D. (1999). (Nebraska Department of Environmental Quality). Personal letter to S. E. Powers, September 13.

Table 1-2 & 3

UCRL-AR-135949 Vol. 4 Ch. 2

Volume 4: Potential Ground and Surface Water Impacts

Chapter 2: A Critical Review: The Effect of Ethanol in Gasoline on the Fate and Transport of BTEX in the Subsurface

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Table of Contents

List of Figures

List of Tables

Appendices

2. A Critical Review: The Effects of Ethanol Gasoline in the Fate and Transport of BTEX in the Subsurface

2.1. Overview of Processes Affecting Ethanol and Gasoline in the Subsurface

Following a spill or leak, the presence of oxygenate chemicals in gasolines can potentially impact the migration and fate of the gasoline in the subsurface. In general, public health concerns with gasoline in the subsurface arise from the presence of dissolved species (monoaromatic hydrocarbons, such as benzene, toluene, ethyl benzene, and the three isomers of xylene [BTEX]) in groundwater that could be used for drinking purposes. There are numerous processes that affect the ultimate concentrations of chemicals in groundwater (Figure 2-1). Generally, these processes include:

- Infiltration of the gasoline through the unsaturated zone of the subsurface.
- Spreading of the gasoline pool at the water table.
- Dissolution of slightly soluble species from the gasoline into the water.
- Transport of these chemicals with the groundwater towards a potential point of contact, such as a groundwater well.

Because of the differences between the hydrophobicity of standard gasoline and hydrophilicity of alcohols, the presence of alcohols in gasoline has the potential to affect each of these fate-and-transport mechanisms.

Table 2.1 summarizes the potential impacts of ethanol on mechanisms controlling the ultimate concentration of hazardous chemicals in groundwater. As summarized briefly here and documented more fully throughout this report, ethanol has the potential to increase the concentration of BTEX species in groundwater. Based on current levels of understanding, it is known that equilibrium concentrations of BTEX increase in the presence of ethanol and that losses due to adsorption and biodegradation are reduced. However, the significance of these impacts in a subsurface setting are not known and the potential impacts of many of the mechanisms and variables identified in Table 2.1 are poorly understood at the present time. Changes in the fate of gasohol and BTEX concentrations in groundwater are attributable to the cosolvent effect associated with high ethanol concentrations in the aqueous phase. Essentially, the presence of the organic ethanol molecules in the aqueous phase makes this phase less polar and therefore more compatible with organic molecules. This and other specific mechanisms and variables that have the greatest potential impact on groundwater contamination are discussed and research needs are identified in this report following a thorough review of the present state of knowledge.

2.2. Subsurface Transport of Fuel Hydrocarbons in the Presence of Ethanol

2.2.1. Overall Phase Partitioning Behavior

Standard-formulation gasolines and water are almost completely immiscible. For example, Polak and Lu (1973) measured the aqueous solubilities of 21 gasoline compounds. The reported values ranged between 0.54 milligrams per liter (mg/L) (or parts per million [ppm]) for 2,2,5-trimethylhexane at 25°C and 1800 mg/L for benzene. Solubilities of water in gasoline compounds were reported by Polak and Lu (1973) to range between 74 mg/L for water in 2,3,4-trimethylpentane and 690 mg/L for water in benzene. The reported solubilities do not include the effects of surface-active agents or other additives to gasoline that may contain polar components in the molecular structure.

In contrast, ethanol is completely miscible in both gasoline and water at all concentrations. When ethanol is present with both gasoline and water, the phase behaviors of water and gasoline are modified in such a way that:

- Solubilities of gasoline hydrocarbons in water increase.
- Solubility of water in gasoline increases.
- Ethanol partitions preferentially into the aqueous phase.
- Interfacial tension (IFT) between the water and the gasoline phases is reduced.

When ethanol content of gasoline is increased, the mutual solubilities increase, and the IFT becomes further reduced. However, ethanol partitions less preferentially into water with the introduction of more ethanol. With a sufficiently large proportion of ethanol, gasoline and water become completely miscible with each other and merge into a single phase. Conversely, at lower ethanol concentrations, gasoline may separate into two phases if water is added to the blend. Gasoline- and water-rich phases generally merge for ethanol fractions exceeding about 70% by weight and separate when ethanol fractions fall below this value. However, as will be shown below, ethanol fractions that bound single- or two-phase behavior depend upon the composition of the gasoline and the water content.

2.2.1.1. Ternary-phase Diagrams

Ethanol partitioning and the effects of ethanol on solubility are illustrated on a ternary-phase (gasoline-water-ethanol) diagram (Figure 2-2). Note that the diagram assumes a completely mixed system that has reached equilibrium and thus ignores complex transport phenomenon that exists in the subsurface. The diagram is not intended to convey actual phase behavior in the subsurface but instead is intended to illustrate general equilibrium phase behavior that will govern phase behavior in the subsurface. Using the three axes, one can determine the overall system mass fractions of gasoline, water, and ethanol for any point on the interior. The shaded region indicates the range of water, gasoline, and ethanol fractions where the three components exist as two separate phases while the unshaded region indicates the composition range where these components exist as a single phase. The curve separating the two regions is called the binodal curve. On Figure 2-2 the binodal curve indicates that gasoline, ethanol, and water will exist as a single phase in all relative combinations of water and gasoline provided that the ethanol present in the entire system exceeds 70% by weight.

Tie lines transect the two-phase region and join water-rich and gasoline-rich segments of the binodal curve. These tie lines indicate the equilibrium compositions of the two phases. The points connected by the lines define the composition of the water-rich phase (on the left side of the two-phase region) and the gasoline-rich phase (on the right side of the two-phase region). The preferential partitioning of ethanol into water is indicated by the downward, left-to-right slope of the tie lines.

For example, if a gasoline initially contained 10% ethanol, its composition would be indicated by point A on Figure 2-2. If that gasoline came into contact with an equal volume of water and if the gasohol and water were allowed to equilibrate, nearly all of the ethanol would migrate into the aqueous phase. At equilibrium, the gasoline-rich phase would then have a composition indicated by point A` and the water-rich phase by point B`.

2.2.1.2. Effect of System Composition

The phase behavior of ethanol is compared with that of methanol on Figure 2-3. Ternary-phase diagrams, adapted from Letcher *et al.* (1986), are shown for three-component systems comprised of water, gasoline, and an alcohol. A comparison of the ethanol and methanol systems indicates that methanol produces a smaller single-phase region than does ethanol. Thus, less water is required to cause phase separation in a gasoline containing methanol than in a gasoline containing ethanol.

Because gasoline is a highly complex mixture of alkane, cycloalkane, alkene, and aromatic compounds, changes in gasoline composition may affect the phase behavior. To illustrate this, ternary-phase diagrams for two individual components compounds found in gasoline—2,2,4-trimethylpentane (an alkane) and toluene (an aromatic hydrocarbon)—are illustrated on Figure 2-4. A lower ethanol fraction would be required for phase separation if toluene were the hydrocarbon than if 2,2,4-trimethylpentane were the hydrocarbon. Additionally, the slopes of the tie lines in Figure 2-4a indicate that ethanol partitions less preferentially into water from toluene than from 2,2,4-trimethylpentane. Assuming that toluene is representative of the general phase behavior of the aromatic hydrocarbons and that the 2,2,4-trimethylpentane represents the properties of the alkanes, cycloalkanes, and alkenes, then one could generalize that, if the fraction of aromatics in the gasoline were increased, the single-phase region would expand; and upon phase separation, the gasoline would contain slightly more ethanol. Published phase relationships for water and ethanol in combination with a number of individual gasoline components may be found in Stephenson (1992), Letcher *et al.* (1986), and Letcher and Siswana (1992).

2.2.2. Unsaturated Zone: Infiltration and Spreading at the Water Table

Gasoline typically enters the subsurface following the corrosion or rupture of storage tanks or pipelines. Relatively small-scale releases are associated with gasoline stations, construction facilities, truck rental agencies, etc. Much larger-scale releases are commonly associated with petroleum refineries, petroleum distribution centers, industrial facilities, and civilian and military airports. Following its release into the subsurface, gasoline flows predominantly downward toward the water table in response to gravitational forces. A fraction of the gasoline is retained as lenses or films between the air and water in the unsaturated zone. Once the bulk volume of gasoline reaches the capillary fringe, gasoline spreads laterally under a combination of gravitational and capillary forces, forming a body typically characterized by a lensoidal geometry. The capillary fringe is not completely saturated with gasoline but shares the zone with residual water and possibly air. Where air, water, and gasoline coexist at a given elevation, the air predominantly fills the largest pores; the smallest pores are generally filled with water; and gasoline fills the pores of intermediate diameter.

The introduction of ethanol affects the migration and distribution of gasoline in the subsurface in two primary ways: the capillary forces are reduced, thereby changing the multiphase flow characteristics; and, the pore structure of some mineral types is altered by chemical interactions with the alcohol. Information on the specific mechanisms is summarized below although the overall importance of these factors on the net impact of ethanol-gasolines in the subsurface has not been quantified. In fact, the few major studies on the effects of oxygenated gasolines on groundwater contamination (Malcolm Pirnie, Inc., 1998; Blue Ribbon Panel [BRP], 1999) have not even addressed the potential differences in the nature of the multiphase flow process between standard gasoline formulations and ethanol gasolines.

2.2.2.1. Change in Capillary Forces and Multiphase Flow in the Presence of Ethanol

The addition of oxygenates to gasoline changes the nature of the capillary phenomena affecting gasoline infiltration and distribution at the water table because of a reduction in the surface and interfacial tensions (IFT) between the phases. Figure 2-5a illustrates the extent of decrease in these values. Much of these data were collected for real gasolines equilibrated with water and ethanol (Kowles and Powers, 1997). The “C2” gasoline is a reformulated gasoline (RFG) containing 5.8% ethanol by volume that was developed by Phillips Chemical Company and is certified for testing in California. Ethanol contents were varied by altering the gasoline-water volume ratio or by adding additional ethanol to the system.

The IFT of the C2 system decreased in an almost perfectly linear way from 26.3 dynes/cm at 0% ethanol to 7 dynes/cm at 50% ethanol—a decrease of about 75%. In contrast, neat solvents and a surrogate gasoline comprised of xylene (20% by volume) and isooctane had a much more significant decrease in the IFT with the addition of small volumes of ethanol (less than 10%) to the aqueous phase. These differences suggest that some of the other components of the C2 gasoline also strongly affect the IFT, and that surrogate mixtures of monoaromatics and alkanes are not representative surrogates for gasoline in studies of the gasoline migration and distribution at the water table.

Data for the surface tensions (liquid-air) are available for water and organic phases in the presence of ethanol. Figure 2-5b illustrates the surface tension of water after equilibration with a variety of organic phases in the presence of ethanol. The surface tension drops for all cases substantially with the increase in ethanol, although there is very little difference among the waters equilibrated with different organic phases. These results illustrate that ethanol has a much greater effect on the surface tension of water than the presence of other gasoline constituents. In contrast, surface tension of the C2 gasoline following equilibration with water and added ethanol was 19.7 ± 0.25 over a wide range of ethanol contents (Kowles and Powers, 1997). Other researchers have also noted the same lack of change for the surface tensions of neat solvents in ternary (organic-ethanol-water) systems (e.g., Ross and Paterson, 1979). The independence of the gasoline-air surface tension can be explained by the near complete partitioning of the ethanol into the aqueous phase.

Because of the reduction in capillary force associated with the changes in interfacial and surface tensions, the height of the capillary fringe is reduced and the depth of the gasoline pool altered. The gasoline can also enter smaller pore spaces (Demond and Roberts, 1991), potentially affecting its distribution in the vadose zone and in the gasoline pool. Ostendorf *et al.* (1993) presented a model for estimating the depth of a gasoline pool based on hydrodynamics and capillary forces. The resulting equation expresses the depth in terms of the densities of the gasoline and water, nonaqueous phase liquids (NAPL) surface tension and NAPL-water IFT, maximum saturation of the mobile gasoline phase, and a parameter that characterizes the pore-size distribution (the *n* value in the capillary pressure-saturation model of van Genuchten [1980]). Assuming that this equation can also be applied to ethanol-gasoline, we can evaluate the expected trends in the depth of the gasoline pool. Variations in the density between the C2 gasoline that has been stripped of ethanol ($\rho = 0.733$ grams per milliliter [g/mL]) and C2 gasoline with 10% ethanol by volume ($\rho = 0.738$ g/mL) have an insignificant effect on the calculated depth of the pool. The maximum saturation of the mobile form of the gasoline is unknown, but it is not expected to vary substantially. With the small variations in these properties between standard gasoline and ethanol-gasoline, the Ostendorf *et al.* (1993) equation is reduced to a direct dependence of gasoline-pool depth on the NAPL-water IFT. Thus, a reduction in the IFT would result in a decrease in the thickness of the gasoline pool and a larger areal extent of the gasoline pool. No data or modeling efforts exist to predict the extent or significance of this impact.

Although these general trends are based on theory and experimental observations from other systems, few papers in the literature are available that specifically addressed the impacts of alcohols on multiphase flow processes pertinent during gasoline infiltration and spreading at the water table. Results of the most closely related studies are described below.

Researchers at the University of Waterloo (Donaldson *et al.*, 1994) conducted the most extensive study addressing the impact of alcohol as an oxygenate in gasoline on the behavior of the gasoline in the subsurface. They observed the dynamics of M85—a mixture of 85% methanol and 15% standard gasoline—infiltration and migration in both saturated and unsaturated systems. The very high alcohol content of this gasoline resulted in a change from the immiscible displacement phenomena associated with standard gasolines to a miscible displacement process. Differences in density and viscosity become more important in miscible displacement processes than IFT. Based on the unsaturated zone infiltration experiments, the behavior of the M-85 gasoline relative to the standard gasoline used for comparison can be characterized by:

- Less lateral spreading in the unsaturated zone.
- A decrease in the height of the capillary fringe, which resulted in the formation of the gasoline pool at a lower elevation (the depth of the capillary fringe returned to its original position after the methanol was flushed from the system).

- The formation of a gasoline pool at the water table with a smooth and regular geometry that was smaller in lateral extent.
- The formation of air bubbles in the area where the M-85 displaces water due to non-ideal mixing of the methanol and water that causes a reduction in the volume of the mixture.
- The formation of a “halo” of droplets of gasoline around the periphery of the gasoline pool and infiltration zone due to reduced methanol concentrations and reduction in the effective solubility of the gasoline constituents.

The formation of residual droplets of gasoline in the saturated zone is significant because it substantially increases the NAPL-water contact area for dissolution. In addition to the formation of these droplets by precipitation when the alcohol concentration drops, they can also be formed by multiphase displacement mechanisms as the water-table elevation changes. Ryan and Dhir (1996) studied the changes in hydrocarbon entrapment at the bottom of a pool as the water table fluctuates. They found that by reducing the IFT from approximately 40 to 10 dynes/cm with the addition of isopropyl alcohol, the volume of the hydrocarbon entrapped in the saturated zone was reduced from 11 to 6% of the total pore space. Thus, trends associated with the generation of these droplets are opposite depending on the mechanism involved. High alcohol concentrations tend to increase the probability of precipitation but reduce the probability that droplets are formed during multiphase displacement.

Researchers at the University of Florida at Gainesville (for example, Rao *et al.,* 1997) recently completed a large research project on the use of ethanol as a flushing agent to enhance the dissolution and recovery of NAPLs entrapped in the subsurface. Although the researchers did not investigate the multiphase flow characteristics of the NAPLs, they did make an effort to understand the effects of ethanol on the capillary forces at the capillary fringe. Jawitz *et al.* (1998) conducted miscible displacement studies, using ethanol-water solutions to displace pure water in a small, two-dimensional sandbox that represented an unconfined aquifer. The displacing fluid was introduced through an injection well rather than through the unsaturated zone. The study made two primary observations:

- The ethanol solution preferentially stayed near the top of the sandbox because of its lower density than that of clean water.
- The capillary fringe was reduced in height by approximately 50%, the same percentage as the decrease in the air-water surface tension of the ethanol solution.

The studies were limited to the miscible displacement dynamics expected with neat ethanol displacing water.

One significant effect associated with a reduction in the IFT of water in the unsaturated zone is a reduction in the field capacity. Smith and Gillham (1994) noted that drainage of water from the unsaturated zone occurred with decreasing IFT, thereby increasing the rate of contaminant transport from the vadose zone to the saturated zone.

It is very difficult to predict how the effects described above would compare with the spill of an ethanol gasoline containing 10% or less ethanol by volume. If mass transfer of the ethanol to the aqueous phase is rapid relative to the rate of gasoline infiltration, it is possible that some miscible displacement dynamics could dominate the overall behavior of the infiltrating gasoline. Most of the ethanol in this case could partition into the aqueous phase, causing a change in the relative permeability of fluids in the vadose zone as the aqueous phase swells. Drainage of the ethanol-laden aqueous phase at a later time could dissolve BTEX compounds from the gasoline in a manner different than anticipated from a pool of gasohol. It is clear that changes in the retention of gasohol in the vadose zone, and the size and shape of a gasoline pool at the water table would occur due to the partitioning of ethanol into the aqueous phase and resulting reduced surface and IFTs and the reduced height of the capillary fringe. The extent of these effects is not known although this would be of particular interest in defining the overall exposure and risk potential stemming from subsurface releases of oxygenated gasolines.

2.2.2.2. Changes in Pore Structure

In addition to the impacts described above that are caused by changes in the IFT, the presence of ethanol can also change the pore structure of clay lenses, further affecting the migration of gasoline through the subsurface. Clay lenses are generally presumed to be essentially impermeable to infiltrating light nonaqueous phase liquid (LNAPL), such as gasohol. The LNAPL would typically accumulate above the clay lens, increasing the lateral extent of soil contamination in the unsaturated zone. If the spill is of sufficient volume, the LNAPL would continue to migrate vertically when the LNAPL pool reached the lateral extent of the clay lens. Changes in the pore structure that would increase the permeability of the clay lens to the gasohol would reduce the pooling of the gasohol above the lens, potentially allowing for faster infiltration to the water table and less lateral migration in the unsaturated zone. Gasohol entrapped within the clay lens represents an LNAPL source that would be difficult to remediate.

Fernandez and Quigley (1985) measured changes in the hydraulic conductivity of compacted, naturally occurring, silty clays. The hydraulic conductivity of ethanol in this soil was two orders of magnitude higher than that measured with water. Experiments with ethanol displacing pore water, followed by the introduction of a non-polar hydrocarbon, resulted in a four-order of magnitude increase in the hydraulic conductivity of the hydrocarbon. It was not clear if these changes were due to cosolvent effects or changes in the pore structure.

Stallard *et al.* (1997) studied these impacts further with ethanol and ethanol-gasoline in kaolinitic (clay) soils. Gasoline containing 10% ethanol displaced the water and entered the clay under a relatively high applied head although a standard formulation gasoline was not able to imbibe into this clay. The final permeability of the clay after the imbibition of ethanol-gasoline was 20 times greater than that of water. Magnetic resonance imaging (MRI) techniques revealed that these results occurred because of a vertical crack developed in the clay as the clay was dehydrated upon contact with ethanol. Other experiments with neat ethanol indicate that, like the results of Fernandez and Quigley (1985), ethanol displaced water at a much faster rate than water alone.

During the dehydration of clays upon contact with ethanol, some regions of the clay become more dense as the clay particles flocculate, leading to the development of other areas within the clay strata that have significantly increased porosity (Stallard *et al.*, 1997). This generation of micro- and macro-scale cracks and associated increases in permeability will greatly affect the potential for the entry of ethanol-gasoline into regions of the subsurface that a standard gasoline could not enter.

2.2.2.3. Summary of Impacts of Ethanol in the Unsaturated Zone

The material discussed above identified potential impacts of ethanol spills or ethanol-gasoline spills on the migration of the gasoline in the subsurface. None of these studies, however, is directly applicable for predicting the impacts of a spill of ethanol-gasoline at the concentrations required for California's RFG program. Direct measurement do, indeed, show that the surface tension of water with ethanol and gasoline-water IFTs drops with increasing ethanol content in the aqueous phase. The significance of these changes on the distribution of gasoline in the unsaturated zone and its spreading on the water table has not been directly studied. Based on related studies, the following processes may be of importance:

- Capillary forces
  - Reduction of the height of the capillary fringe and possible recovery of the original height could entrap gasoline droplets in the region below the water table.
  - Reduced entrapment of gasoline in the unsaturated zone.
  - Changes of unknown direction or extent in the shape and size of the gasoline pool due to reduced capillary forces around the periphery of the pool. Theoretical calculations that indicate a reduction in pool depth are inconsistent with the observed smaller pool area for the M85 versus a standard gasoline. It is possible that significant losses of methanol to the aqueous phase could have resulted in the comparison of substantially different volumes of "gasoline" in these pools.
- Effective permeabilities
  - Significant partitioning of ethanol into the aqueous phase in the unsaturated zone could affect the relative permeability of the gasoline and alter migration pathways during infiltration.
  - Dehydration and cracking of clay strata could allow ethanol-gasoline to penetrate aquitards that were previously impermeable. Mass transfer of ethanol and BTEX from cracks in a clay lens would be slower than from an unconsolidated medium.

Further study is required to understand and quantify the significance of these effects on the overall risk associated with ethanol-gasoline versus standard blend gasolines.

2.2.3. Gasoline-water Interface: Interphase Mass Transfer

2.2.3.1. Overview

Environmental releases of NAPLs, such as gasoline, contribute to the degradation of groundwater quality as the more soluble components in the organic phase are slowly leached into the aqueous phase and transported with the groundwater. With gasoline, the more highly soluble monoaromatic compounds dissolve into the aqueous phase, creating a long-term source of these hazardous constituents. This mass-transfer process is dependent on hydrodynamic conditions, chemical composition of both phases, molecular diffusion of the species, and the specific surface area between phases. The net exchange of chemical species across an interface between two phases continues until an equilibrium condition has been achieved.

The most complete study associated with mass transfer of soluble species from an alcohol-gasoline mixture was completed as a series of studies conducted for the American Petroleum Institute (API). These studies focused on the fate and transport of monoaromatic petroleum hydrocarbons from a standardized gasoline containing 85% methanol by volume (that is, M85) (Barker *et al.,* 1991; Donaldson *et al.,* 1994; Hubbard *et al.,* 1994). This M85 blend has been used to a limited extent to meet the stringent California emission requirements. Computer simulation and laboratory experiments showed that the methanol in a gasoline pool at the water table quickly dissolved into the groundwater. High aqueous-phase concentrations of benzene, toluene, ethyl benzene, and xylenes (BTEX) were also associated with the initial period of contamination because the cosolvency effect of the methanol created a slug of highly contaminated groundwater which was transported downgradient by advection. Once the methanol source was depleted from the gasoline, however, the BTEX concentrations were also reduced. While these experiments serve to help understand the possible behavior of gasoline containing ethanol, there are differences between ethanol and methanol biodegradation rates. Ethanol degrades at a rate approximately 10 times faster than methanol (Alvarez and Hunt 1999). Similar experiments with gasoline containing MTBE as an oxygenate showed negligible effects of this oxygenate on the dissolution characteristics of the BTEX compounds.

2.2.3.2. Equilibrium Partitioning

Thermodynamic equilibrium conditions for NAPL dissolution processes are often defined by Raoult's law, which enables the equilibrium aqueous-phase concentration, C^{*w}_i, to be estimated in terms of the pure liquid phase solubility, C_{s_i}, and the mole fraction, x_i^n, in the organic phase (Mackay *et al.*, 1991):

$$C^{*w}_i = C_{s_i} x_i^n \tag{2-1}$$

Raoult's law assumes that the organic phase is comprised of a mixture of similar types of organic chemicals and can, therefore, be assumed to be chemically ideal. Under ideal conditions, NAPL activity coefficients are unity, while activity coefficients for dilute concentrations of solute in the aqueous phase can usually be assumed to be constant.

Alternatively, the linear relationship can be represented with a NAPL-water partition coefficient, K^{nw}, to relate the mass concentration of a constituent in the organic phase to that in the aqueous phase:

$$K_i^{nw} = \frac{C_i^n}{C^{*w}_i} \tag{2-2}$$

Under ideal conditions, the partition coefficient is constant, making it relatively straightforward to estimate concentrations in the aqueous phase that would be in equilibrium with an organic phase.

2.2.3.2.1. Cosolvency. The polar oxygenates, such as ethanol or MTBE, are hydrophilic and can, thus, occur in high concentrations and be highly mobile in groundwater. The aqueous-phase concentration of oxygenates can, in fact, be high enough to affect the groundwater concentrations of other constituents leached from the gasoline. Of most concern are the monoaromatic hydrocarbons, especially benzene, which is a known carcinogen. Studies of the equilibrium concentrations of gasoline constituents in water have shown that the alcohols increase solubility, and that the ethers have little effect on the solubility of carcinogenic aromatic hydrocarbons (Groves, 1988; Cline *et al.*, 1991; Poulsen *et al.*, 1992; Lojkásek and Ruzicka, 1992; Stephenson, 1992). These analyses are, however, based only on equilibrium partitioning calculations and experiments. Many processes that affect the rates of mass transfer could limit the concentrations of both the ethanol and BTEX.

The addition of oxygenates to gasoline affects the ideal equilibrium partitioning relationships by the “cosolvent effect,” which is caused by the presence of high concentrations of organic compounds, such as alcohols, in the aqueous phase. These cosolvents reduce the polarity of the aqueous phase, causing a reduction in the aqueous-phase activity coefficient and allowing higher concentrations of hydrophobic organic compounds in the aqueous phase (Groves, 1988). This effect can also be explained in terms of changes in the Gibbs excess free energy associated with molecules of hydrophobic organic compounds (HOCs) in water being surrounded by cosolvent molecules as well as water molecules (Schwarzenbach *et al.*, 1993).

The significance of a cosolvent effect is dependent on the aqueous-phase solubility of the cosolvent (Pinal *et al.*, 1990). For oxygenates added to gasoline, alcohols partition preferentially to the aqueous phase, while ethers remain predominantly in the organic phase (Groves, 1988; Stephenson, 1992; Poulsen *et al.*, 1992). Thus, alcohols have a greater cosolvent effect than ethers (Cline *et al.*, 1991; Stephenson, 1992). Cline *et al.* (1991) conclude that the cosolvent effect from alcohols in gasoline will not be significant at the concentrations and residual saturations expected in subsurface systems. However, a study by Poulsen *et al.* (1992) shows that the preferential leaching of methanol during the early stages of dissolution of M85 gasoline will produce concentrations of hazardous aromatic hydrocarbons at levels that are orders of magnitude higher than without the alcohol. Rixey (1994) extended this sort of analysis to gasolines containing only 15% methanol. He concluded that significant aqueous-phase concentrations of BTEX would be present during the early stages of the dissolution process. Methanol, like ethanol, is completely miscible in water and partitions preferentially into the aqueous phase. For these reasons, its behavior as a cosolvent emulates that of ethanol.

Many of the studies that have considered the cosolvency effect of alcohols (Groves, 1988; Mihelcic, 1990; Stephenson, 1992; Peschke and Sandler, 1995; Hellinger and Sandler, 1995) utilized single HOCs as surrogates for gasoline and neglected the complexities associated with multicomponent aspects of this organic phase. Others (Letcher *et al.*, 1986; Lojkásek *et al.*, 1992) focused on the potentially detrimental hygroscopic nature of oxygenated gasolines in automobile engines. These studies provide information on the partitioning of “gasoline” but not on individual BTEX compounds. Thus, they have less utility in environmental applications.

The work by Poulson *et al.* (1992) provides much more substantial information on the partitioning of BTEX compounds from multicomponent gasolines. Methanol and MTBE were the oxygenates added to the PS-6 standard API gasoline in this work. They found that, for a given volume of gasoline, increases in the BTEX concentrations from a cosolvent effect were balanced by the reduced mass of these species in the gasoline because of the initial presence of the oxygenate. They observed significant increases in aqueous benzene concentrations only when the volume of gasoline-to-water was high.

Fernandes (1997) evaluated the effective solubilities of benzene, toluene, and xylenes (BTX) compounds in water equilibrated with a Brazilian commercial gasoline containing 22% ethanol. A range of ethanol concentrations in the aqueous phase was achieved by varying the volume ratio of water to gasoline (20:1 to 1:1) in the batch experiments. (Data collected for the Brazilian gasoline is presented in Figure 2-6.) Even with this wide range of water-to-gasoline ratios and the relatively high volume fraction of ethanol in the Brazilian gasoline, the maximum volume fraction of ethanol in the aqueous phase was on the order of 15%. These results showed that even a small concentration of ethanol in the aqueous phase (equivalent to 1%) increased the solubility of BTX compounds.

Heermann and Powers (1998) conducted an extensive study of the cosolubility effects associated with the use of ethanol in gasolines. They established BTEX and ethanol partitioning relationships by performing batch equilibrium experiments using both simple and complex "gasolines." To ensure that the entire system was well characterized, they utilized three organic solutions incorporating surrogates for the aromatic and alkane compounds comprising the majority of gasoline. They performed additional experiments with more complex commercial RFGs containing ethanol to verify results with the surrogate-compound gasolines. They measured equilibrium BTEX and ethanol concentrations in both phases, and computed the partition coefficients as a function of the aqueous-phase ethanol volume fraction.

The two commercial gasolines included a RFG containing 5.8% ethanol by volume that was obtained directly from the Phillips Chemical Company, and a generic gasoline, also containing ethanol, obtained from a local service station. The RFG obtained from Phillips Chemical Company is a certified gasoline marketed for automobile emissions testing under the California Phase II air-quality program and is here designated as the C2 gasoline. The generic gasoline was purchased from a Gas Bar station in Cornwall, Ontario, Canada. Ethanol content in that gasoline was measured to be 3.4% by volume. Additional ethanol was added to the water-gasoline mixtures to achieve a range of ethanol volume fractions in the aqueous phase.

Experimental measurements quantified the extent of BTEX partitioning from RFGs containing ethanol. The aqueous-phase concentrations displayed an approximate linear trend when they were plotted on semi-log scale at ethanol volume fractions greater than approximately 0.2 (Figure 2-7). At lower concentrations, however, there was a distinctly different trend. These differences are attributed to the hydration of the cosolvent molecules at low concentrations (Banerjee and Yalkowsky, 1988). Over the range of the maximum aqueous-phase ethanol volume fractions observed by Fernandes (equivalent to 15%), BTX concentrations in the aqueous phase that was equilibrated with the C2 gasoline generally increase by less than 50% (Table 2-2). As observed by others (Munz and Roberts, 1986), the cosolvency effect results in greater percent increases in the concentrations of the more hydrophobic xylene versus the less hydrophobic benzene. The extent of the cosolvent effect is often quantified by a cosolvency factor, which is the slope of the logarithm of the concentration versus the volume fraction of cosolvent (Banerjee and Yalokowski, 1988). The cosolvency effect measured by Fernandes (1997) and Heermann and Powers (1998) for gasohol is greater for the more hydrophobic xylene versus the less hydrophobic benzene. This trend is consistent with theory and the observations of others (e.g., Munz and Roberts, 1986).

2.2.3.2.2. Modeling Cosolubility Effects. A cosolvent present in the aqueous phase changes the partitioning of slightly soluble organic species between the organic and aqueous phases. Quantification of this cosolvency effect requires a more sophisticated equilibrium relationship than provided by Raoult's law (Equation [2-1]) due to the non-ideal solutions formed in the presence of the polar oxygenate. There are two general approaches to deal with these non-ideal behaviors. An empirical relationship based on experimental measurements can be used to directly estimate the distribution of an organic compound between the two phases, or a more general and rigorous thermodynamic approach can be employed to estimate activity coefficients. The use of both of these methods is complicated by the complex and unknown composition of the organic phase-commercial gasolines. A detailed discussion of these approaches is included in Appendix A with highlights included below.

2.2.3.2.3. Empirical Cosolubility Models. The empirical models for the solubility of HOCs in non-ideal systems involve the use of both linear and log-linear equations. These equations were originally used for the solubility of pharmaceuticals but have also been applied to environmental systems (Banerjee and Yalkowsky, 1988). In general, cosolvents in water generate a logarithmic increase in HOC solubility with increasing cosolvent concentration (Pinal *et al*., 1990):

$$log(C_i^m) = log(C_{si}{}^w) + \sigma_s f^c \qquad (2\text{-}3)$$

where C_i^m is the equilibrium concentration of HOC i in the cosolvent mixture, $C_{si}{}^w$, is the solubility of HOC i in pure water, f^c is the volume fraction of the cosolvent in the aqueous phase, and σ_S is termed the *cosolvency power*.

Deviations from the log-linear cosolubility relationship (Equation [2-3]) have been observed in studies of the solubilization of non-polar drugs in a variety of cosolvent solutions (Rubino and Yalkowsky, 1987), PCBs in water-miscible alcohols (Li and Andren, 1994), and BTEX species in gasoline-methanol-water (Poulson *et al.*, 1992), and gasoline-ethanol-water (Heermann and Powers, 1998) systems. For short-chained alcohols, these deviations have been attributed to changes in the interactions between water and the cosolvent molecules (Rubino and Yalkowsky, 1987).

Because the log-linear cosolubility model (Equation [2-3]) does not incorporate the influence of interactions between the water and cosolvent molecules, this equation is only valid at higher cosolvent concentrations. Incorporating the observed linear relation at lower cosolvent concentrations (for example, Figure 2-7), two equations can be written to reflect differences in solubilization mechanisms at low versus high cosolvent concentrations (Banerjee and Yalkowsky, 1988).

$$C_i^m = \left(1 - \frac{f}{b}\right) C_i^w + f\,C_i^{\beta} \qquad \text{for } f < \beta \qquad (2\text{-}4a)$$

$$lnC_i^m = \left(1 - \frac{f-\beta}{1-\beta}\right) lnC_i^{\beta} + \left(\frac{f-\beta}{1-\beta}\right) lnC_i^{c} \qquad \text{for } f \geq \beta \qquad (2\text{-}4b)$$

where β is the volume fraction of ethanol in the aqueous phase at the breakpoint between the two segments of the model, and C_i^β is the concentration of *i* in the cosolvent mixture at this ethanol volume fraction. These model equations are referred to as the linear/log-linear model.

2.2.3.2.4. Models for Estimating Activity Coefficients. Chemical equilibrium between two phases is defined when the chemical activity of a species is equal in the two phases. This condition provides a thermodynamic basis for estimating equilibrium concentrations based on estimates of the chemical activity of each species in the two phases. The UNIQUAC (Universal quasi chemical) model is used most frequently for multicomponent liquid-liquid equilibrium problems (Smith and van Ness, 1987). This type of model requires a significant amount of data for the system of interest. The UNIFAC (UNIQUAC functional activity coefficients) model provides the same theoretical basis as UNIQUAC although necessary binary interaction parameters are estimated from the number and type of functional groups that comprise the chemical species. Because this model does not require extensive data, it is more easily implemented than UNIQUAC although the estimation of binary interaction parameters introduces additional uncertainty in the quality of the results.

2.2.3.2.5. Application of Cosolubility Models to Alcohol-HOC Systems. Models for describing the effects of cosolvents on HOC solubilities in environmental systems have been presented by several researchers (for example, Fu and Luthy, 1986a; Groves, 1988; Pinal *et al.*, 1990). These studies generally considered the cosolvent effect where the organic phase was comprised of a single HOC. Gasoline, however, represents a highly complex mixture of organic compounds. Poulson *et al.* (1992) applied cosolvent models to describe BTEX partitioning from their experiments with PS-6 gasoline and methanol. The models appeared to provide reasonable predictions of aqueous-phase concentrations although the sparse data set available was not sufficient to adequately verify the accuracy of these models.

UNIFAC has been used fairly extensively in environmental applications. Numerous researchers have used this model to estimate the aqueous-phase solubility of HOCs in organic phase-water systems, both with and without cosolvents. Reasonable prediction capabilities in these two to three component systems—generally within a factor of two relative to experimental data—have been reported (Banerjee, 1985; Arbuckle, 1986; Fu and Luthy, 1986a; Groves, 1988; Pinal *et al.*, 1990; Mihelcic, 1990). In an effort to improve the predictive capabilities of UNIFAC for HOCs, Chen *et al.* (1993) evaluated a database of published aqueous-phase solubilities and octanol-water partition coefficients to develop a new set of binary interaction parameters better suited for environmental applications.

Kan and Tomson (1996) recently completed a comprehensive evaluation of the applicability of UNIFAC for predicting aqueous solubilities of environmentally significant HOCs. With several different sets of published values of the vapor-liquid functional group binary interaction parameters, they found excellent agreement between experimentally measured and predicted solubilities of pure chemicals in water. In general, the predictions were within one order of magnitude of the measured solubilities with the greatest discrepancies observed for high molecular weight or chlorinated hydrocarbons. However, as with most other applications, the analysis of Kan and Tomson (1996) involved systems with only two to three components.

Hellinger and Sandler (1995) examined the quality of both UNIQUAC and UNIFAC to model their measured gasoline-water-oxygenate solubility data. In both experimental and modeling aspects of their work, they considered single alkane species as surrogates for all species in the gasoline and *t*-amyl methyl ether or *t*-amyl alcohol as the added oxygenates. Both UNIFAC and UNIQUAC provided qualitative descriptions of trends in the ternary diagrams representing equilibrium compositions of the two phases. However, neither was accurate in a quantitative sense, especially for the solubility of the alkane in the aqueous phase.

Three mathematical models were applied to the experimental results obtained by Heermann and Powers (1998). These models were applied in a true predictive manner based on the volumes of gasoline and water equilibrated and the initial concentration in the gasoline. Figure 2-8 shows representative results of these predictions. The log-linear and UNIFAC models were capable of representing the overall increase in concentration as a function of increasing ethanol content in the aqueous phase. However, neither of them mimicked the observed two-part curve. A piecewise model comprised of a linear relationship for low ethanol volume fractions and a log-linear model for higher concentrations was fit to data for a surrogate gasoline comprised of seven compounds. These parameters were then used to predict BTEX concentrations in the aqueous phase equilibrated with commercial gasolines. This model was superior to the UNIFAC predictions, especially at the low ethanol concentrations expected when gasolines presently sold are spilled in the environment. Thus, the linear/log-linear model presented by Heermann and Powers (1998) can be utilized to best predict groundwater contamination by gasolines containing ethanol when the relative volumes of the two phases and the gasoline composition can be estimated.

2.2.3.3. Rate-limited Interfacial Mass Transfer

2.2.3.3.1. General Concepts. The interphase mass transfer of ethanol and hydrocarbons between gasoline and groundwater can be most simply expressed as a product of a mass-transfer coefficient and a concentration difference (Cussler, 1984)

$$N_i = k_i \left(\frac{C_i^n}{K_i^{n,w}} - C_i^w \right) \qquad (2\text{-}5)$$

where N_i is the flux of compound *i*; k_i is the mass-transfer coefficient; C_i^w and C_i^n are the concentrations of compound *i* in phases *a* and *b*, respectively; and $K_{i,}^{n,w}$ is a partition coefficient describing the equilibrium partitioning relationship of the compound between the two phases (Equation [2-5]).

The mass-transfer coefficient, k_i, reflects rate limitations to interphase mass transfer resulting from the noninstantaneous transport of compounds to and away from the phase boundary. Thus, for a gasoline pool, ethanol and hydrocarbons must be transported through the gasoline to the phase boundary separating the gasoline and groundwater and must be transported away from the boundary with the groundwater. Appendix B provides additional details addressing the mass-transfer rate coefficient.

In most interphase mass-transfer models, the boundary is conceptualized as a two-dimensional surface with no thickness. Therefore, mass cannot accumulate at the boundary; and the physical constraint exists that the rate of transport to the boundary equals the rate of transport away from the boundary (Taylor and Krishna, 1993). Because of the sequential nature of the mass transfer and the constraints on the transport rates, a single transport process will often govern the overall interphase mass-transfer rate. That process, which typically exhibits the slowest rate of transport, is, thus, rate limiting.

The rate at which ethanol is transported from gasoline to groundwater will largely determine the magnitude and the duration of the cosolvency effect. Very rapid rates of ethanol mass transfer would lead to greater ethanol concentrations in groundwater that would further lead to increased hydrocarbon concentrations because of cosolvency. The rate of mass transfer would govern the duration of the cosolvency effect as a result of a more rapid depletion of ethanol.

Transport processes differ greatly between gasoline and groundwater. For example, a gasoline-phase pool is held largely motionless by capillary forces while the groundwater moves beneath it at a relatively steady rate. Some of the most important transport processes are described below, first for the gasoline, and then for the groundwater.

2.2.3.3.2. Rate Limitations in the Gasoline Phase. The vast majority of both analytical and numerical mathematical models of mass transfer from NAPL pools assume that the interphase mass transfer of HOCs is limited by the rate of groundwater transport away from the NAPL-groundwater boundary. Inherent in these models is the assumptions that the composition of the NAPL phase is homogeneous and remains constant over time. For standard formulation gasolines, these assumptions may be reasonable because the gasoline composition changes very gradually as a result of low solubilities and dissolution rates.

The presence of ethanol in gasoline, however, will likely invalidate the above assumptions. Because ethanol partitions preferentially into water, it may be nearly depleted from the gasoline at the boundary. For very slow rates of ethanol transport to the boundary, an ethanol concentration gradient develops through the gasoline, invalidating the assumption that the chemical composition is homogeneous over the depth of the pool. For a sufficiently slow ethanol transport, the net interphase mass-transfer rate will approximately equal the rate of ethanol transport through the gasoline. In contrast, for very rapid rates of ethanol transport, concentration gradients will be small, but the ethanol will be rapidly depleted from the gasoline invalidating the assumption that concentrations do not vary over time. For sufficiently fast ethanol transport through the gasoline, transport via groundwater will define the mass-transfer, rate-limiting process.

Two transport processes—molecular diffusion and free convection—have been identified that contribute to the transport of ethanol and other hydrocarbons through the gasoline. Molecular diffusion, which describes the net movement that occurs when molecules undergoing random motion are subjected to a concentration gradient, is a generally well understood process and is fairly easily modeled (for example, Cussler, 1984; and Taylor and Krishna, 1993). Free convection refers to the process where bulk-fluid flow occurs as a result of an unstable condition created when the fluid density increases vertically upwards. It has only recently been studied with respect to gasoline (Heermann and Powers, in preparation) and is a much more difficult process to model.

2.2.3.3.3. Molecular Diffusion. Molecular diffusion in a subsurface gasoline pool can be described mathematically by Fick's law:

$$J_i = -\frac{D_i}{t}\frac{\partial C_i}{\partial z} \tag{2-6}$$

where J_i is the diffusion flux of compound i, D_i is the diffusion coefficient, τ is the tortuosity, C_i is the concentration, and z is the vertical dimension. For simplicity, diffusion in Equation (2-6) is considered to occur only in the vertical (z) direction within the gasoline pool but may be generalized to include diffusive transport in all directions.

Holman and Javandel (1996) utilized the assumption that molecular diffusion of ethanol and hydrocarbons through a NAPL is the primary rate-limiting process governing interphase mass transfer to a groundwater body. They published a semi-analytical solution for time-dependent transport in an aquifer from an LNAPL pool with interphase mass transfer being controlled by diffusive transport in the LNAPL. Molecular diffusion in gasoline to a groundwater boundary could also be modeled using multicomponent multiphase numerical models. One model, MOFAT (Katyal *et al.,* 1991), is in the public domain, but numerous other such computer models exist in universities or can be acquired commercially. Both the semi-analytical and numerical models consider depletion of the compound from the gasoline as well as concentration gradients that develop in the gasoline due to the removal of ethanol and other gasoline hydrocarbons at the groundwater boundary

2.2.3.3.4. Free Convection. Free convection occurs when a density gradient exists within a single fluid. If the gradient is such that the fluid is less dense near the bottom, a physically unstable fluid profile is created. As a result, a convective flow is established within the fluid, typically as “fingers,” thereby blending the high- and low-density portions of the fluid. Figure 2-9 illustrates this concept.

Most gasoline has a density less than that of ethanol because the alkanes, cycloalkanes, and alkenes comprising the majority of most gasolines have densities less than the density of ethanol (ρ_{etoh}=0.789 g/mL). Therefore, gasoline with ethanol generally has a greater density than gasoline without ethanol. For example, the Phillips Chemical Company C2 gasoline contains 5.8% ethanol by volume and has a specific gravity of 0.741 at 20°C. When the ethanol is removed from the C2 gasoline, its density falls to 0.738 g/mL.

In the subsurface, as the ethanol is removed from the gasoline at the gasoline-groundwater interface, the density of the gasoline at the boundary becomes less than its density in the region above the boundary. As a result, the high- and low-density gasoline regions become unstable with respect to each other; and, consequently, the gasoline with the higher ethanol content and greater density flows downwards to the phase boundary while the less dense, ethanol-depleted gasoline moves upwards. In a series of column experiments, Heermann and Powers (in preparation) found that free-convective flow greatly increased the rate of ethanol transport to the boundary relative to diffusional transport.

The higher rate of interphase mass transfer resulting from free convection will likely lead to greater ethanol concentrations in groundwater and, therefore, to a greater cosolvency effect. However, the higher mass-transfer rate will yield a more rapid depletion of the ethanol in the gasoline.

Because all of the BTEX compounds have densities greater than ethanol, a gasoline with very high fractions of BTEX compounds could have a density greater than ethanol. Heermann and Powers (in preparation) demonstrated that, when the density of the bulk gasoline exceeds that of ethanol, the ethanol is transported primarily by the much slower molecular-diffusion mechanism.

2.2.3.3.5. Rate Limitations in the Groundwater. The net rate of transferring ethanol and hydrocarbon species from the gasoline to the groundwater may also be limited by mechanisms controlling the transport of these species via groundwater away from the gasoline-water interface. Mass transport in groundwater is largely controlled by the processes of advection and hydrodynamic dispersion. Advection is the principal means of transporting hydrocarbons horizontally away from the gasoline-pool boundary with the flowing groundwater while hydrodynamic dispersion is the principal means for vertical transport away from the gasoline pool. The net rate of interphase mass transfer increases with increased groundwater flow rates and dispersion because these processes reduce the concentration of solute near the interface.

2.2.3.3.6. Net Rate Limitations. Molecular diffusion in gasoline is generally a very slow transport process in comparison to the groundwater transport processes of advection and dispersion. Thus, if diffusion were the only transport process in the gasoline, it would likely be the rate-limiting step under most subsurface conditions.

Free convection is apparently a much more rapid transport process that exists, in theory, for all ethanol-bearing gasolines except those with very high aromatic fractions. With the higher rates of mass transfer associated with free convection, the concentrations of both ethanol and BTEX species in the groundwater are expected to be higher in comparison with those resulting solely from diffusion. The ethanol, however, will be depleted from the gasoline source more rapidly when free convection is the dominant process, reducing the period of time that the ethanol influences BTEX dissolution rates. Following the depletion of ethanol from the gasoline, the remaining pool of gasoline would behave as a standard blend gasoline. However, there is insufficient knowledge about free convection in subsurface gasoline lenses to determine whether this process would likely define the rate-limiting process or whether it is sufficiently fast such that advective/dispersive transport via groundwater would become the rate-limiting process.

2.2.4. Transport with the Aqueous Phase

2.2.4.1. Modeling Groundwater Transport

The transport of dissolved hydrocarbons in the groundwater via advection and hydrodynamic dispersion may be modeled using one or more of the numerous solutions available for the advection-dispersion equation. The advection-dispersion equation is a generalized differential equation describing the advective and dispersive transport and the addition and removal of dissolved compounds in groundwater.

The primary source of ethanol and gasoline hydrocarbons is the overlying gasoline pool. These compounds enter the groundwater domain via the interphase mass-transfer mechanisms discussed above. Examples of analytical models developed for the transport from NAPL sources by groundwater include those of Hunt *et al.* (1988); Johnson and Pankow (1992); Voudrias and Yeh (1994); Holman and Javandel (1996); Chrysikopoulos and Lee (1997); and Chan and Javandel (1998). All of these except for Holman and Javandel (1996) and Chrysikopoulos and Lee (1997) assume that the chemical composition of the NAPL source is homogeneous throughout the depth of the pool and remains invariant with time. The analytical solution of Chrysikopoulos and Lee (1997) permits the composition of the NAPL pool to vary over time; and, as discussed above, the solution of Holman and Javandel (1996) permits the composition of the NAPL to vary spatially and temporally. Potential sources of hydrocarbons in the groundwater are the organic-phase blobs that may form below the gasoline pool as a result of water-table fluctuations or due to phase separation that may occur when ethanol concentrations are reduced (Section 2.2.4.3).

Two critical hydrocarbon-removal processes include the adsorption of the hydrocarbons to sand, clay, or other solid materials in the subsurface, and the biologically mediated chemical transformation of the ethanol and hydrocarbons. Adsorption is reversible to varying degrees so that when concentrations of dissolved hydrocarbons decrease, the adsorbed hydrocarbons may be released back into the aqueous phase. Biologically mediated chemical transformations are generally not reversible and, thus, serve only as a removal mechanism for hydrocarbons. However, because these processes generate new compounds, biochemical transformations may act as sources and/or sinks for compounds other than BTEX.

The presence of ethanol in groundwater may potentially alter the processes of adsorption and biodegradation. It may reduce the adsorption of other petroleum hydrocarbons due to reductions in the aqueous-phase chemical activities of those hydrocarbons. Ethanol may also affect biodegradation. A discussion of the role of ethanol on subsurface biodegradation is presented by Alvarez and Hunt (1999).

2.2.4.2. Adsorption with Reduced Chemical Activities

Adsorption may be described by a number of “isotherms,” or mathematical relations between the concentration of a compound dissolved in water and its equilibrium concentration sorbed to a solid. One widely used isotherm is the Freundlich isotherm (Fu and Luthy, 1986b) which relates the equilibrium aqueous-phase concentration of compound *i*, C_i^w, and the concentration of *i* sorbed to the solid phase:

$$S_i = K_p C_i^{wn} \tag{2-7}$$

The partition coefficient, K_p, which describes equilibrium partitioning between the aqueous phase and the surface of the solid material, and the exponent n are empirical fitting parameters. In environmental analyses, S_i, is generally expressed in units of mass per unit-mass of soil; so K_p correspondingly has units of volume per unit-mass.

When a cosolvent is present in the aqueous phase, the partition coefficient, K_p, decreases. This has been documented by a number of researchers, including Rao *et al.* (1985), Nkedi-Kizza *et al.* (1985), Fu and Luthy (1986b), Rao *et al.* (1990), Kimble and Chin (1994), Barrett *et al.* (1994), and Errett *et al.* (1996). Nkedi-Kizza *et al.* (1985) demonstrated that log-linear cosolvency relationships similar to Equation (2-3) could be applied to adsorption and showed that K_p decreased in an approximate logarithmic manner with increasing volume fraction of cosolvent in the aqueous phase:

$$log \frac{K_{p_i}^m}{K_{p_i}^w} = -\alpha\sigma_s f^c \tag{2-8}$$

In Equation (2-8), K_{pi}^m and K_{pi}^w are the adsorption partition coefficients for compound *i* with the superscripts indicating equilibrium with a water-cosolvent mixture (*m*) and with pure water (*w*). Rao *et al.* (1985) and Fu and Luthy (1986b) provided theoretical explanations for the observed behavior analogous to those developed for the liquid aqueous-organic phase partitioning in the presence of a cosolvent. Using methanol as a cosolvent, Fu and Luthy (1986b) showed that the adsorption partition coefficient decreased in a log-linear manner, much the same as the solubility increases with cosolvent fraction. They compared the effects of cosolvency on adsorption and solubility and found that the slope of the log-linear plot for adsorption was about half that for solubility. Letting the cosolvency factor σ_s be equal for the solubility and adsorption partition coefficient, then α in Equation (2-8) would have a magnitude of about 0.5. The authors explained the difference was from the swelling of the organic carbon associated with the soil to which the HOCs sorb. Brusseau *et al.* (1990) showed that the log-linear model could be extended to include the kinetic parameters describing desorption rates.

As an alternative to the empirical log-linear approach, one may estimate the effect of ethanol on the partition coefficient, using aqueous-phase activity coefficients. This was demonstrated earlier for computing liquid-phase partitioning with the activity coefficients computed, using a thermodynamic model, such as UNIFAC or UNIQUAC (see a more thorough description in Appendix A). Assuming that the ethanol effects only the aqueous-phase hydrocarbon activities and has no effect on the solid surfaces upon which adsorption takes place, then one may simply scale the adsorption partition coefficient:

$$K_{p_i}^{w,c} = \frac{\gamma_{p_i}^{w,c}}{\gamma_{p_i}^{w}} K_{p_i}^{w} \qquad (2\text{-}9)$$

where $\gamma_{p,i}^{w,c}$ is the activity coefficient of compound *i* in a water-cosolvent solution, and $\gamma_{p,i}^{w}$ is the activity coefficient of compound *i* in pure water (Rixey, 1994).

One of the chief effects of adsorption is the retardation of hydrocarbons in such way that their effective velocities become less than the groundwater that is transporting them. In a one-dimensional modeling study to compare BTEX concentrations downgradient of an M85 gasoline release, Rixey (1994) showed that when cosolvent dependent adsorption was incorporated into the model, the BTEX compounds moved more rapidly through the porous medium. The methanol and BTEX were assumed to be added instantaneously to the aqueous phase, and so the downgradient concentrations appeared as discrete peaks. The effect was more pronounced for benzene than the other BTEX compounds because benzene is the least hydrophobic of the BTEX compounds and so moved through the porous medium with nearly the same velocity as the methanol and water. Because toluene did not move synchronously with the methanol, the cosolvency effect of the methanol was less than for benzene. Rixey (1994) also found that cosolvency effects were only significant where downgradient aqueous methanol concentrations exceed 10–13 wt%.

2.2.4.3. Phase Separation Due to Dilution of Ethanol Concentrations

In the aqueous phase, because ethanol and gasoline hydrocarbons mix with uncontaminated groundwater and biodegrade, ethanol and gasoline hydrocarbons concentrations will generally decrease with increasing distance from the NAPL source. As a result of the approximate log-linear relation between aqueous HOC solubility and ethanol concentration, the aqueous phase may become supersaturated with respect to the hydrocarbons, resulting in the formation of a liquid organic phase. The general concept of phase equilibrium and phase separation was addressed in Section 2.1 for ethanol-bearing gasolines.

Rixey and Dortch (1992) and Donaldson *et al.* (1994) investigated the phenomenon of phase separation for alcohol gasolines, using a pulse injection of gasoline comprised of 85% methanol (M85). Given a release of M85 gasoline into the subsurface, the gasoline would initially be completely miscible with water; and a NAPL would not form. However, as the fraction of water in that initial mixture increases due to dispersion and biodegradation, the ethanol fraction decreases, and the gasoline becomes immiscible with water. Donaldson *et al.* (1994) observed the process leading to the formation of a separate phase, primarily via column and pore-scale visualization models. The pore-scale visualization studies of Donaldson *et al.* (1994) revealed the formation of NAPL droplets on sand grains. These droplets became entrapped in the pore structure and consequently reduced the permeability of the porous medium to water. Rixey and Dortch (1992) also observed the formation of a separate NAPL phase when the methanol content dropped to below 77%. They used a numerical modeling approach to estimate the distribution of residual organic NAPL that precipitated as a result of a decrease in methanol concentrations.

If the composition of the aqueous phase becomes undersaturated with respect to the hydrocarbon concentrations (that is, if the chemical activities in the NAPL are greater than in the aqueous phase), the residual phase may re-dissolve into the groundwater. Thus, the precipitated gasoline droplets will act as a latent source of hydrocarbons. If the residual phase exists as well-dispersed droplets below the gasoline pool, then their higher surface areas will increase the rate of mass transfer, ultimately resulting in higher aqueous-phase hydrocarbon concentrations. The dissolution of entrapped NAPL has been investigated extensively by others (for example, Hunt *et al.,* 1988; Powers *et al.*, 1992, 1994; Geller, 1990).

The phase-separation studies discussed above considered only M85 gasolines that are initially miscible with water. It has not been determined whether hydrocarbons that solubilize in groundwater from a lens of gasoline containing much smaller quantities of ethanol are likely to form a separate organic phase as the ethanol concentration decreases.

2.2.5. Special Considerations

2.2.5.1. Neat Ethanol Dissolving Prior Contaminants

Because of ethanol’s hygroscopic nature, ethanol and gasoline are transported and stored separately until the final stages of the distribution process (Section 2.1). The potential, therefore, exists for neat ethanol to be released into the subsurface primarily from storage tanks or shipping containers. Where NAPLs already exist in the subsurface, the release of pure ethanol may influence the subsurface distribution of these NAPLs and enhance the transport of its constituents via groundwater.

The influence of neat ethanol on subsurface processes is expected to be nearly identical to those of gasohol except that its influence may be magnified. Two differences are important:

- The quantities and concentrations of ethanol will be greater; and
- The elimination of rate-limiting interphase mass transfer of ethanol from the gasoline to vadose-zone water or groundwater.

Increases in the aqueous phase solubilities would affect both BTEX and MTBE species that were initially present in the gasoline pool. The potential increase would depend mostly on the ethanol concentration in the aqueous phase. As described in Section 2.2.3.2, BTEX concentrations could increase by a few orders of magnitude right at the spill zone. There have been no studies conducted to predict increases in MTBE concentrations. Cosolvency effects depend greatly on the hydrophobicity of the organic species. Because MTBE is much more hydrophilic than BTEX, the cosolvency effect will be much less. This means that the percent increase in the aqueous phase concentrations of MTBE will not be as great as for BTEX species.

Based upon the understanding of the influence of ethanol on subsurface flow and transport processes (Sections 2.1–2.4), releases of neat ethanol are expected to (1) increase the aqueous solubility and, hence, the dissolution rates of NAPL compounds; (2) reduce the mass of organic compounds sorbed to the solid phase; and (3) reduce the IFT between NAPL and the aqueous phase and, thereby, potentially enable the NAPL to migrate.

Increased solubility and decreased adsorption were the subject of a laboratory investigation by Chen and Delfino (1997), who studied the effects of fuels containing 85% ethanol or methanol on HOC solubility. Solubilities and adsorption partition coefficients of 18 polynuclear aromatic hydrocarbons (PAHs) were determined for a soil contaminated with coal tar. The study demonstrated that the PAH solubilities increased in an approximate log-linear manner with increasing fractions of ethanol (Equation [2-3]), while the adsorption partition coefficients decreased in an approximate log-linear manner (Equation [2-8]).

The effects of high concentrations of ethanol on NAPL dissolution were investigated in two field studies that focused on the use of ethanol as a method to accelerate the removal of NAPLs during subsurface remediation. In one study, researchers injected 40,000 L (11,000 gal) of a solution comprised of 70% ethanol, 12% *n*-pentanol, and 18% water into the subsurface to determine the extent to which the alcohol solution would dissolve entrapped NAPL, consisting of jet fuel and chlorinated solvents (Rao *et al.*, 1997). The alcohol solution and the dissolved NAPL constituents were recovered in downgradient wells. The researchers found that, on average, 90% of NAPL constituents were removed following the injection and recovery of the alcohol. This study clearly demonstrated the importance of the cosolvency effect at high ethanol concentrations.

In another field study by de Oliviera (1997), ethanol was injected into a sand aquifer containing gasoline at residual saturation. The study was performed in order to observe the dynamics of ethanol flushing and to assess the effectiveness of ethanol flushing as a means of enhancing the removal of gasoline from the subsurface. As with the previous study, ethanol was injected below the water table via a well; and the ethanol and gasoline were recovered via a downgradient well. In this study, the ethanol migrated upwards and, thus, failed to uniformly remove the residual gasoline.

The studies cited above focused upon solubility and adsorption changes resulting from ethanol. Currently, a knowledge gap exists regarding the effects of high ethanol concentrations in the vadose zone, especially those pertaining to changes in IFT. Based on existing understanding outlined in Sections 2.2, it is expected that, as ethanol migrates downward through the vadose zone, it will dissolve primarily in the aqueous phase. The resulting reduction in the water-air and water-NAPL IFT is expected to alter moisture profiles and may mobilize residual gasoline entrapped in pores. Because of the highly preferential partitioning of ethanol into water, ethanol is not expected to dissolve in the NAPL pool.

As neat ethanol or ethanol-water mixtures migrate to the water table, the ethanol-rich solution may be entrapped within the capillary fringe. A laboratory and computer modeling study by Jawitz *et al.* (1998) looked at the displacement of water by a solution of 70% ethanol in water along a two-dimensional, cross-sectional pathway. The researchers found that the ethanol-rich solution migrated towards and became entrapped within the capillary fringe immediately above the water table because of buoyancy forces. The ethanol dissolved into the groundwater but at a rate limited by the mass transfer of ethanol away from the capillary fringe.

2.2.5.2. Oxydiesel

Oxydiesel is comprised of chemical constituents different than those comprising gasohol. Diesel and oxydiesel fuels contain much smaller quantities of the least hydrophobic BTEX compounds contained in gasoline and gasohol and instead contain greater quantities of compounds of higher molecular weight that are generally less water soluble than those in gasoline. Because the cosolvency effect generally increases with decreasing solubility (Appendix A), increases in the solubilities of oxydiesel constituents are expected to be greater on average than those in gasohol. However, the solubilities of diesel constituents increase from low baseline solubilities values relative to the BTEX compounds in gasoline; and despite higher cosolvency factors, the increased solubilities of the oxydiesel compounds would likely remain relatively low.

2.2.6. Examples of Modeling Efforts

Although there are numerous uncertainties in the specific mechanisms affecting the migration and dissolution of ethanol gasolines and the subsequent transport of ethanol and BTEX species with groundwater, a few studies have been completed to predict the effect of the ethanol on the net transport of soluble species. The study by Malcolm Pirnie, Inc. (1998) which is described below, includes a two-dimensional modeling effort to predict the transport of ethanol and benzene. Biodegradation and retardation were included in this effort, but the dissolution source term was unknown. On the other hand, Heermann and Powers (1996) had a more rigorous approach for describing the dissolution rate term, but they neglected biodegradation in the aquifer.

2.2.6.1. Effect of Biodegradation

The Malcolm Pirnie, Inc. (1998) modeling effort was aimed at quantifying changes in the length of a contaminant plume due to the addition of ethanol to gasoline. The researchers employed an analytical solution to the two-dimensional transport equation for these predictions. This approach included advection (1-D), dispersion (2-D), retardation, biodegradation, and a constant concentration of ethanol and benzene at the gasoline pool. The following assumptions were used in this analysis:

- Benzene does not biodegrade when the ethanol concentrations are greater than 3 mg/L. Below this threshold value, it degrades following a first-order rate law (λ=0.0062 day^{-1}).

- Ethanol also degrades according to a first-order rate law (λ=0.014 day^{-1}). The approach used to determine this constant was justified well.
- Adsorption of benzene can be described with a standard retardation approach; ethanol does not sorb.

The ethanol and benzene concentrations at the gasoline source are constant over time. It was assumed that ethanol concentrations near the source are 4000 mg/L, which is based on an ethanol concentration of 5% by volume in gasoline with a tenfold-dilution factor. Benzene was assumed to enter the water table at a concentration of 8 mg/L, a concentration which is representative of typical leaking underground storage tank (LUST) sites.

The aqueous-phase velocity (v = 0.004–0.4 ft/d) and fraction of organic carbon in the soil matrix (f_{oc}=0.005–0.01) were used as variables in this analysis.

As expected, based on the assumptions regarding the nature of the benzene biodegradation rates, the benzene plume traveled further when ethanol was present. With the variable velocity and retardation values, the benzene plumes were predicted to extend 17–34% further than in the absence of ethanol. For example, at v=0.4 ft/d and f_{oc}=0.005, the benzene plume traveled 220 ft without the ethanol present versus 280 ft in the presence of ethanol. Figure 2-10 illustrates the general nature of the simulation results.

This first-order analysis does provide some insight into the nature of this problem. However, no sensitivity analysis was performed relative to the high degree of uncertainty in degradation rate constants for ethanol and benzene and the critical ethanol concentration above which benzene is not degraded. Presently, ethanol biodegradation rate constants are only available for laboratory-scale microcosms (Corseuil *et al.*, 1998) at 28°C. In the Malcolm Pirnie, Inc. (1998) analysis, laboratory-measured rates on the order λ = 0.1 to 0.5 d^{-1} were extrapolated to field conditions to account for lower concentration of microorganisms and colder temperatures (15°C). Although the methods employed for this extrapolation were based on sound scientific basis, considerable uncertainties exist in the estimated ethanol decay rate (λ = 0.014 d^{-1}). With the very conservative rate of decay of ethanol in the subsurface, the distance traveled by ethanol would be overestimated; and, thus, the percentage increase in the travel distance of the benzene plume would also be overestimated.

Based on the analysis of Heermann and Powers (1996) (Section 2.2.6.2 below), the estimated concentrations of ethanol and benzene appear to be reasonable. However, the Malcolm-Pirnie, Inc. (1998) analysis did not account for eventual depletion of ethanol from the source. Once ethanol is depleted from the source, natural attenuation of the BTEX would return to the levels expected from a spill of a standard gasoline. Thus, based on the assumptions regarding dissolution, the Malcolm Pirnie, Inc. (1998) estimates could be an overestimate of the impact of the ethanol on benzene plume lengths.

The combined conservative estimates of the ethanol biodegradation rate and lack of inclusion of the depletion of ethanol from the gasohol source suggest that the Malcolm Pirnie, Inc. (1998) analysis represents a worst case scenario. Significant uncertainties in the biodegradation rate constants and concentrations of ethanol and benzene at the gasohol source prevent improved quantitative assessments of the overall impact of ethanol on the length of a benzene plume.

2.2.6.2. Effect of Cosolvency

Heermann and Powers (1996) investigated increases in the transport of BTEX species resulting purely from cosolvency. For this study, the U.S. Geological Survey's cross-sectional, flow- and solute-transport model, MOCDENSE (Sanford and Konikow, 1985), was modified to create a source term that simulated the interphase mass transfer of ethanol and a BTEX compound from a gasoline into groundwater.

The study considered an aquifer with a saturated thickness of 5 m (16.5 ft), as illustrated on Figure 2-11. Groundwater in the aquifer flowed with a uniform velocity of 0.1 m per day (0.33 ft per day). The horizontal and transverse dispersivities were 1 m (3.3 ft) and 0.1 m (0.33 ft), respectively, and the effective porosity of the aquifer was 0.25.

A gasoline pool at the water table, 10 m in length by 0.5 m thick, was comprised of three surrogate compounds that included *iso*-octane, m-xylene, and ethanol. *Iso*-octane represented the composite physiochemical properties of the alkane, alkene, and cycloalkane hydrocarbons while *m*-xylene served as a surrogate for the monoaromatic (BTEX) compounds in gasoline. To assess the impact of the ethanol on the transport of *m*-xylene, model simulations were performed considering both ethanol-bearing and ethanol-free gasolines. The ethanol-bearing gasoline was comprised of 10% ethanol by volume, 13.5% *m*-xylene, and 76.5% *iso*-octane; the ethanol-free gasoline was comprised of 15% *m*-xylene and 85% *iso*-octane.

Ethanol and *m*-xylene source rates were computed at each gasoline boundary cell using Equation (2-5). Ten boundary cells were used to add ethanol and *m*-xylene to the groundwater domain. Each boundary cell was 1 m in length and 0.1 m deep. In the gasoline domain, the *iso*-octane, *m*-xylene, and ethanol concentrations were allowed to vary over time in the gasoline. However, the gasoline was assumed to be well mixed vertically.

To address uncertainties pertaining to mass-transport processes in the gasoline and their representation using Equation (2-5), the mass-transfer coefficient was varied from 10^{-8} to 10^{-3} meters per second (m/s). The latter value was sufficiently high to maintain chemical equilibrium between the gasoline and groundwater phases at the boundary. The partition coefficient was estimated using log-linear models for *m*-xylene and ethanol with parameters determined by fitting the models to laboratory data.

Contours of simulated aqueous-phase ethanol and *m*-xylene concentrations are shown on Figure 2-12 for the elapsed period of 180 days. For the case of equilibrium between the gasoline and the groundwater table (k_i=10^{-3} m/s), the modeling analyses showed an approximate 10% increase in the distance to the leading edge of the *m*-xylene plume at 180 days due to the presence of ethanol in the gasoline. However, when smaller interphase mass-transfer coefficients were used, the size and extent of the *m*-xylene was essentially unaffected by the presence of ethanol. Ethanol was more than 90% depleted from the gasoline within several days under the local equilibrium assumption (k_i =10^{-3} m/s) and was more than 99% depleted in less than 90 days. In contrast, ethanol was only about 10% depleted from the gasoline at 180 days for $k_i = 10^{-8}$ m/s.

The above study demonstrates that the presence of ethanol in gasoline can produce a small but finite increase in the mass transfer of BTEX compounds from gasoline to groundwater and an increase in the size of a BTEX plume. Whether the impact is negligible or measurable depends upon transport mechanisms in the gasoline. Free convection may provide a sufficiently fast transport mechanism (Heermann and Powers, in preparation) to permit local chemical equilibrium between the gasoline and groundwater.

The Heermann and Powers (1996) study only provides an estimate of the increase in plume length via cosolvency mechanisms. The processes of adsorption and biodegradation would result in a decreased plume size, although this reduction would less in the presence of ethanol than for a standard gasoline. The influence of cosolvency on adsorption is dependent on the composition of the aquifer material. Adsorption will be greater for aquifer material with a high fraction of natural organic material (NOM); and so cosolvency will decrease the extent of adsorption and, thereby, enhance the length of BTEX plumes to a greater degree for systems with higher quantities of NOM.

The study did not explicitly determine the influence of the gasoline-pool size on the length of the BTEX plume. However, it could be deduced that for the case of local equilibrium between the gasoline pool and the groundwater at the phase boundary, that a thicker gasoline pool will result in a much greater concentrations of ethanol in the groundwater due to the greater mass of ethanol. Higher ethanol concentrations would produce a much greater cosolvency effect and the length of the BTEX plume would be more greatly enhanced. Any deduction regarding the effect of the lateral extent of the gasoline pool on the BTEX plume would be speculative. A much more thorough modeling study and sensitivity analysis would be required to further evaluate the range of impacts that the ethanol and cosolvency effect would have on the extent of the BTEX plumes.

2.3. Acknowledgements

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Figures

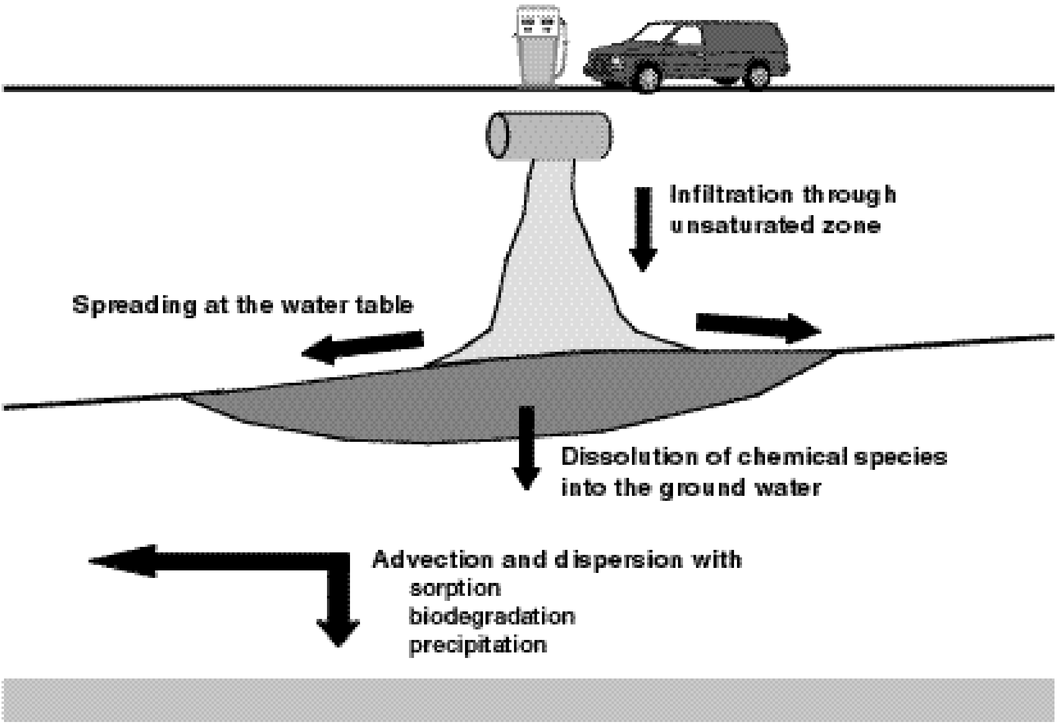


Figure 2-1. General processes governing the fate of gasolines in the subsurface.

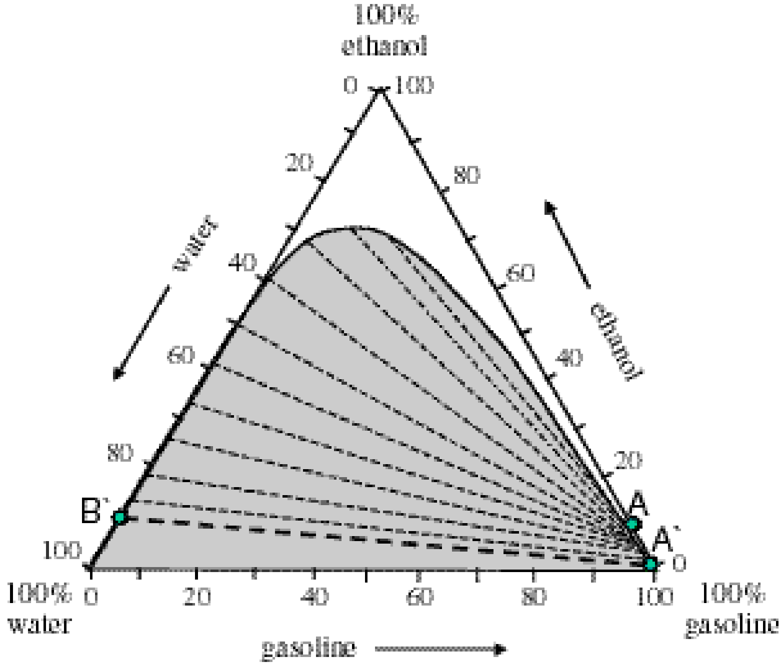


Figure 2-2. Ternary-phase diagram for gasoline-ethanol-water system at 21°C. The shaded region represents the region where the total mass fractions separate into two phases. The ends of the dashed (tie) lines indicate the composition of each phase at equilibrium. Axes represent mass percentages (adapted from de Oliveira, 1997).

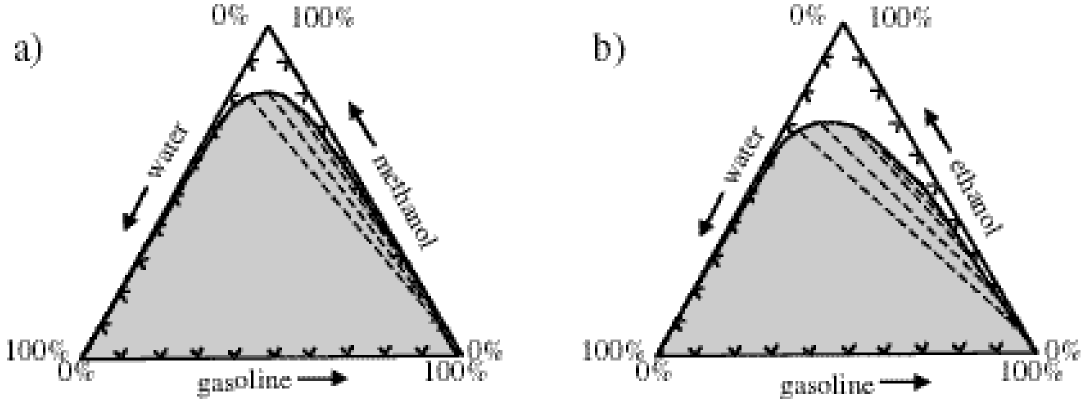


Figure 2-3. (a) Ternary-phase diagram for gasoline-methanol-water system and (b) gasoline-ethanol-water system (adapted from Letcher *et al*., 1986).

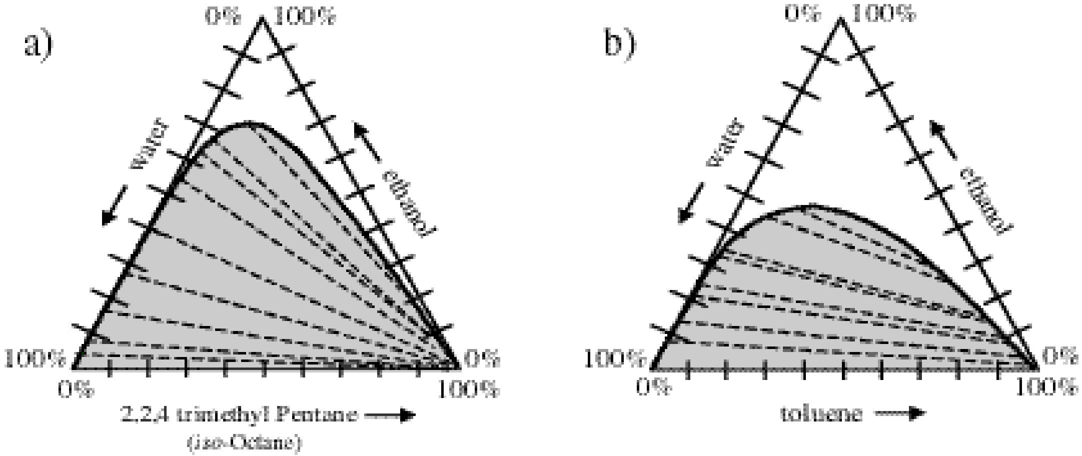


Figure 2-4. (a) Ternary-phase diagram for 2,2,4-trimethylpentane-ethanol-water system and (b) toluene-ethanol-water system at 25°C. Axes indicate mole percentages (adapted from Peschke and Sandler, 1995).

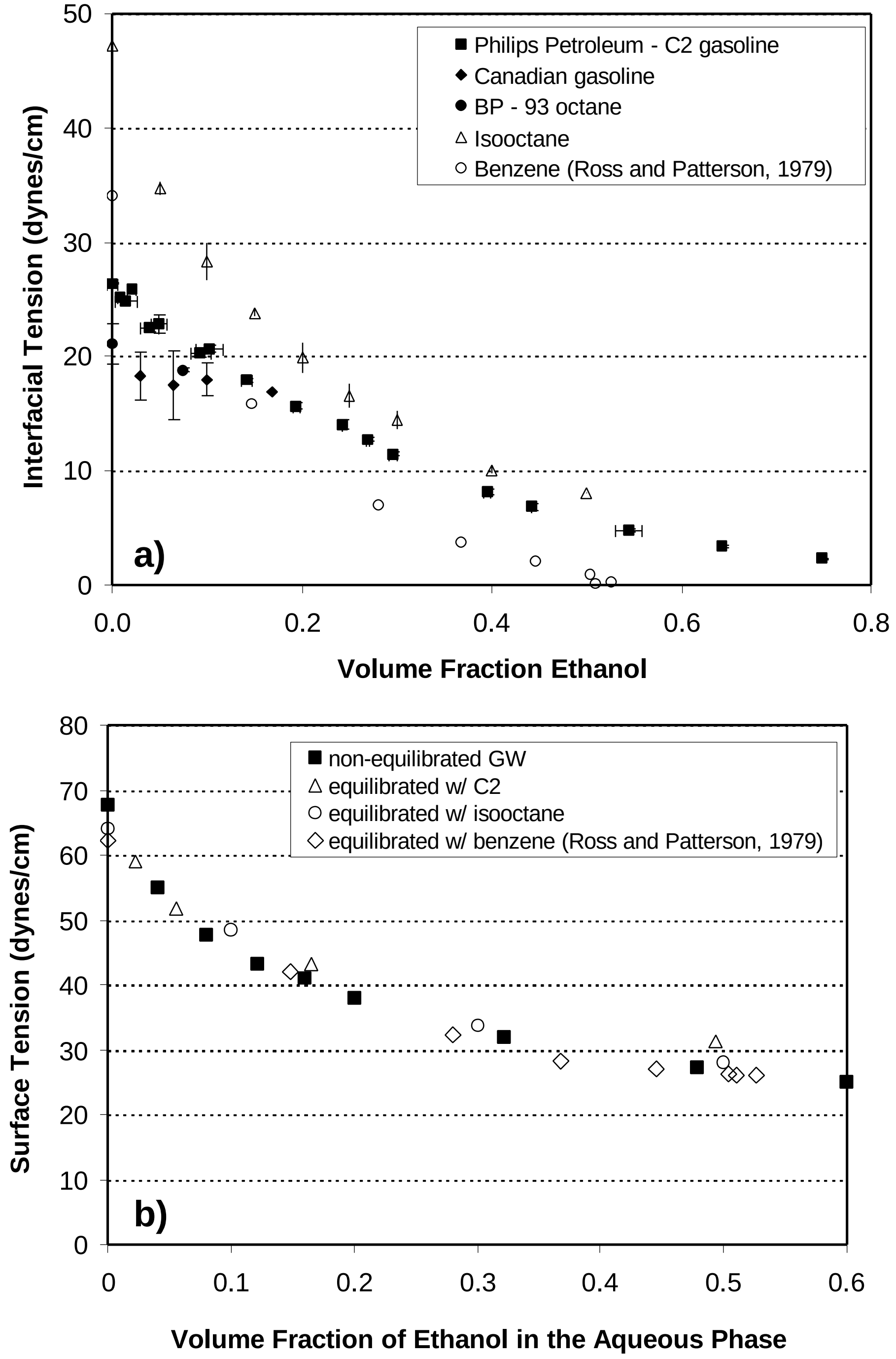


Figure 2-5. Interfacial and surface tensions of gasolines and organic chemicals in the presence of ethanol: (a) interfacial tension between organic and aqueous phases; (b) surface tension of water or water that was previously equilibrated with an organic phase. Data from Kowles and Powers (1997) except where noted.

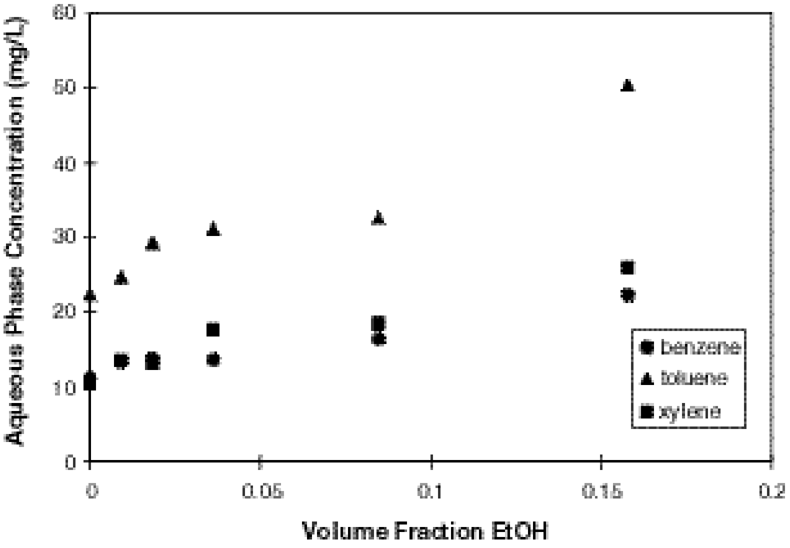


Figure 2-6. Concentration of BTX compounds in water equilibrated with a Brazilian gasoline containing 22% ethanol (data from Fernandes, 1997).

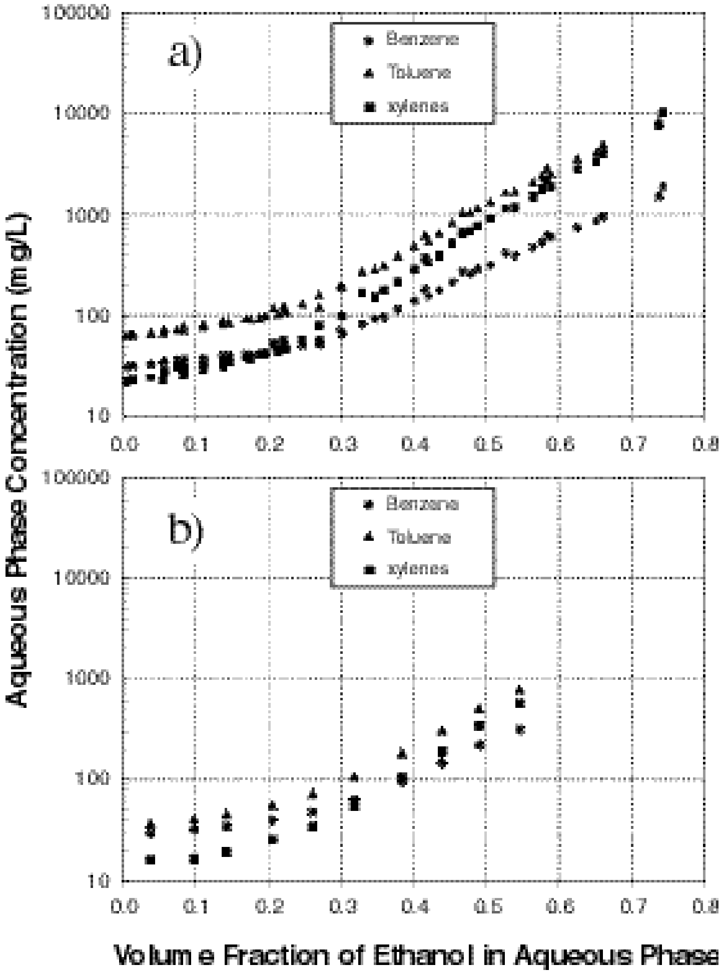


Figure 2-7. (a) Concentration of BTX compounds in water equilibrated with a certified California test gasoline from Philips Petroleum and (b) a generic ethanol-gasoline (purchased from a Gas Bar service station in Cornwall, Ontario, Canada ~3.4% ethanol by volume) (data from Heermann and Powers, 1998).

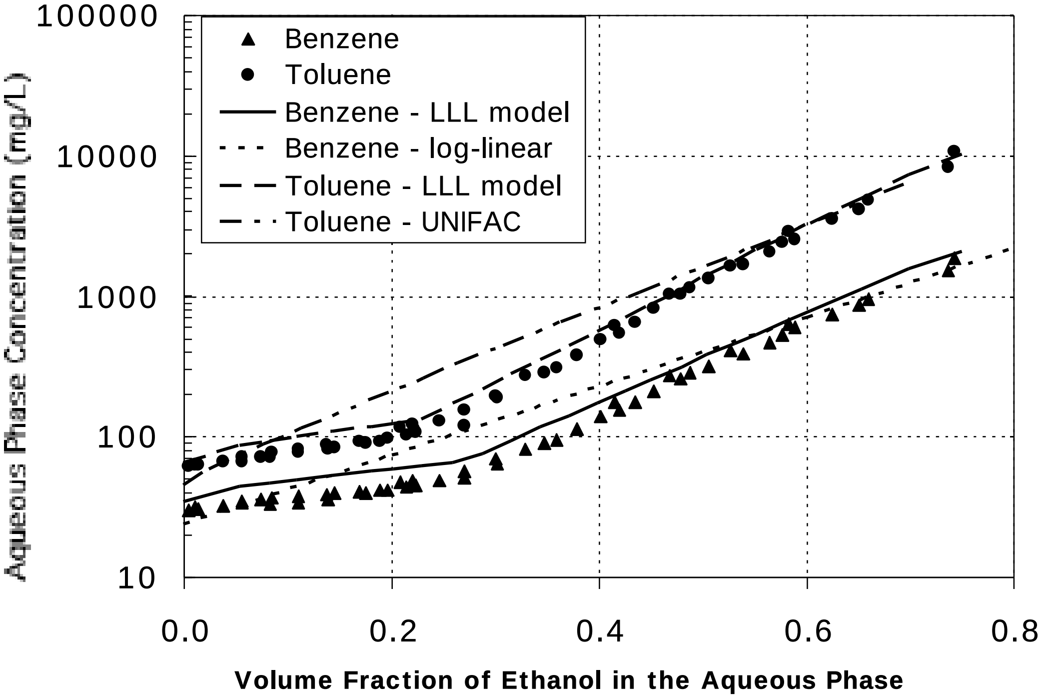
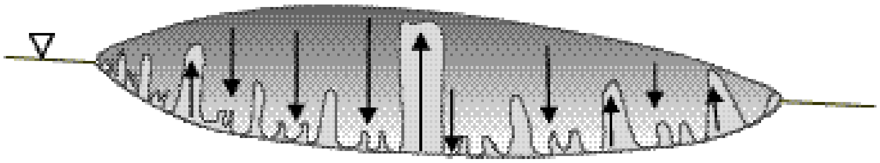
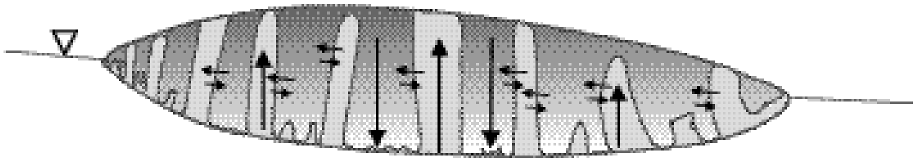


Figure 2-8. Prediction of benzene and toluene concentrations that had been equilibrated with C2 gasoline and additional ethanol. "LLL" (in legend) indicates the piecewise linear-log-linear cosolvency model (from Heermann and Powers, 1998).



(a) early development of miscible fingers as ethanol is depleted from the gasoline-water interface



(b) advanced development of miscible fingers

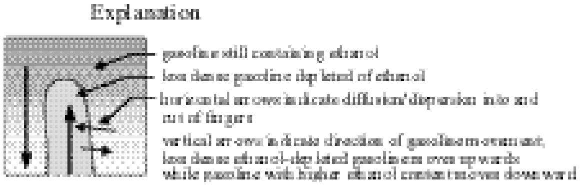


Figure 2-9. Conceptual drawing illustrating the transport of ethanol in a pool of gasoline at the water table via free convection.

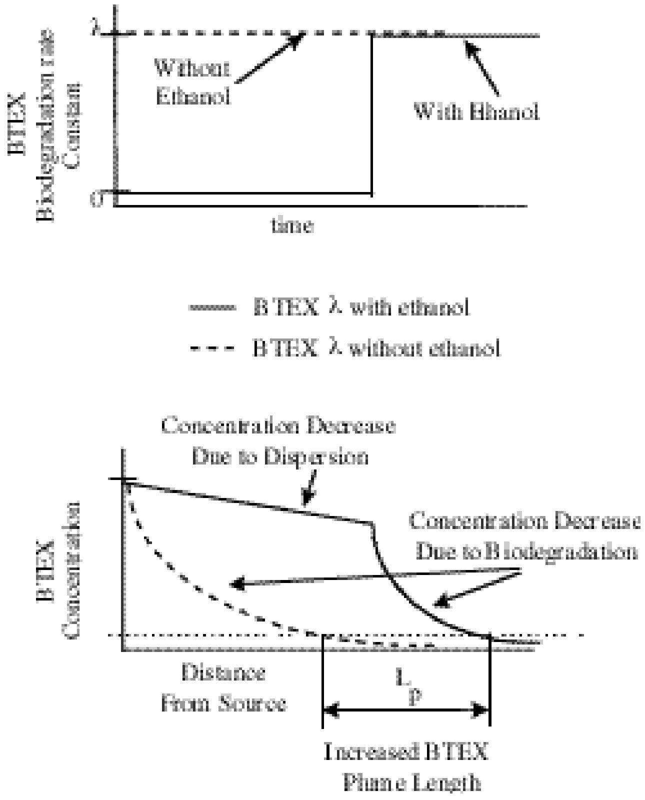


Figure 2-10. Schematic drawing of increased BTEX plume length due to the formation of a BTEX biodegradation lag time created by the presence of ethanol (from Malcolm Pirnie, Inc., 1998).

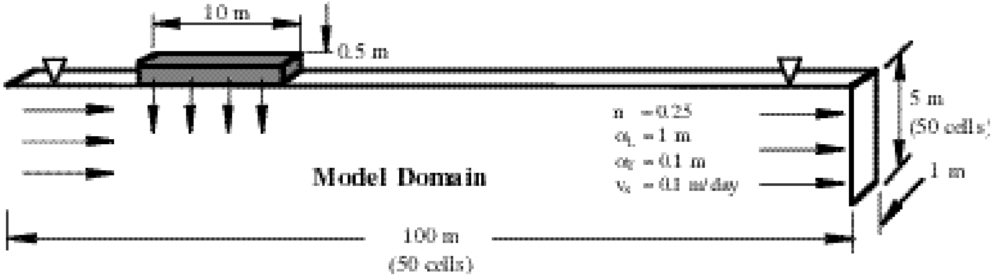
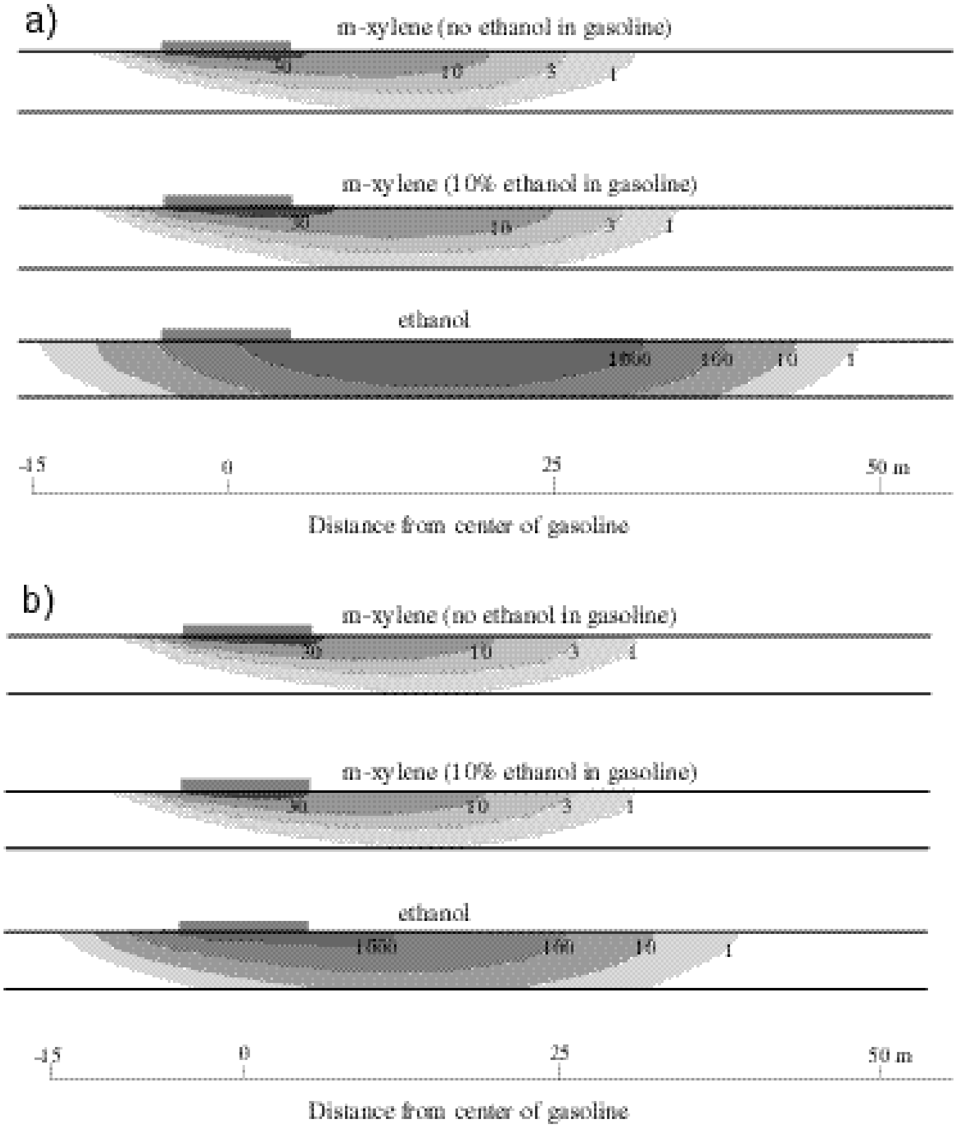


Figure 2-11. Domain used for gasoline dissolution and groundwater transport model (Heerman and Powers, 1996).



x

Figure 2-12. Predicted concentration contours for m-xylene and ethanol dissolved from oxygenated gasoline under (a) local equilibrium conditions (kin = 0^{-3} m/s) and (b) mass-transfer rate-limited conditions (kin = 10^{-8} m/s). All concentrations are in mg/L. (time = 180 days) (Heermann and Powers, 1996).

Tables

Table 2-1. Potential impacts of ethanol in gasoline on the subsurface fate and transport of gasoline and gasoline constituents.

Process	Properties/mechanisms affected	Potential impact	Variables of importance
Unsaturated Zone: • *Infiltration* • *Spreading at the capillary fringe*	• *Capillary forces—reduction in surface and interfacial tension* • *Effective permeabilities* – *Volume changes as ethanol partitions into water* – *Dehydration and cracking of clay strata*	• *Size and shape of gasoline pool* • *Distribution of gasoline residuals in the unsaturated zone and periphery of the pool*	• *Volume and duration of the spill event* • *Gasoline composition* • *Heterogeneity in mineral type, grain size, and water content*
Gasoline Source • *Leaching of chemicals into groundwater*	• *Equilibrium composition of the two phases* • *Mechanisms of transport of chemical species through the gasoline pool* • *Mass-transfer rates across the gasoline-water interface*	• *Concentrations of BTEX and ethanol at the source* • *Life span of the source*	• *Gasoline composition* • *Groundwater velocities* • *Length and depth of the gasoline pool* • *Presence of residual droplets of gasoline in the vicinity of the pool*
Aqueous Phase • *Transport of BTEX and ethanol to downgradient receptors*	• *Adsorption equilibria* • *Precipitation of gasoline droplets* • *Biodegradation rates and mechanisms*	• *Size and shape of contaminated groundwater plume*	• *All variables affecting groundwater flow* • *Concentrations of species at the source* • *Concentrations of electron acceptors* • *Organic content of mineral matrix* • *Ethanol concentration*

Table 2-2. Increased BTX concentration (%) in the aqueous phase equilibrated with C2 gasoline relative to estimated concentrations without any ethanol.[a]

Vol. fraction ethanol in aqueous phase (%)	Benzene (%)	Toluene (%)	Xylenes (%)
13.8	*7.5*	*26*	*27*
17.5	*19*	*41*	*53*

[a] *Data from Heermann and Powers, 1998.*

Appendix A
Cosolvency Mechanisms and Modeling

Appendix A
Cosolvency Mechanisms and Modeling

A-1. Thermodynamic Equilibrium Conditions

Thermodynamic equilibrium conditions for nonaqueous phase liquids (NAPL) dissolution processes are defined by equal fugacities of a species i (f_i) in the NAPL (n) and aqueous phase (w) (Stumm and Morgan, 1981). Under isothermal conditions with a consistent reference state, equilibrium conditions can be redefined by equating the activity of each species between phases:

$$a_i^n = a_i^w \tag{A-1a}$$

$$\gamma_i^n x_i^n = \gamma_i^w x_i^w \tag{A-1b}$$

where, the activity, which defines the non-ideal behavior of the solute within a given phase, is given as $a_i = \gamma_i x_i$; x_i is a mole fraction, and γ_i is the activity coefficient. Many NAPLs, including standard formulation gasolines, are comprised of mixtures of similar types of organic chemicals and can, therefore, be assumed to be chemically ideal. Under ideal conditions, NAPL-phase activity coefficients are unity while activity coefficients for dilute concentrations of solute in the aqueous phase can usually be assumed to be constant (MacKay *et al.*, 1991). Thus, a linear relationship exists between mole fractions, x_i, of a species in the two phases. This linear relationship can be reduced to Raoult's law to estimate the equilibrium aqueous-phase concentration, C^{*w}_i, in terms of the pure liquid phase solubility, C_{s_i} (MacKay *et al.*, 1991):

$$C^{*w}_i = C_{s_i} x_i^n \tag{A-2}$$

Alternatively, the linear relationship can be represented with a NAPL-water partition coefficient, K_i^{nw}, to relate the mass concentration of a constituent in the organic phase to that in the aqueous phase:

$$K_i^{nw} = \frac{C_i^n}{C^{*w}_i} \tag{A-3}$$

Under ideal conditions, the partition coefficient is constant, making it relatively straightforward to estimate concentrations in the aqueous phase that would be in equilibrium with an organic phase.

A-2. Empirical Cosolubility Models

The empirical models for the solubility of hydrophobic organic compounds (HOCs) in non-ideal systems involve the use of both linear and log-linear equations. These equations were originally used for the solubility of pharmaceuticals but have also been applied to environmental systems (Banerjee and Yalkowsky, 1988). In general, cosolvents in water generate a logarithmic increase in HOC solubility with increasing cosolvent concentration (Pinal *et al.,* 1990):

$$log(C_i^m) = log(C_{si}{}^w) + \sigma_s f^c \tag{A-4}$$

where C_i^m is the equilibrium concentration of HOC *i* in the cosolvent mixture, $C_{si}{}^w$ is the solubility of HOC *i* in pure water, f^c is the volume fraction of the cosolvent in the aqueous phase, and σ_S is termed the *cosolvency power*. Examination of the limiting case (f^c=1) enables the cosolvency power to be estimated from experimental data:

$$\sigma_s = log\frac{C_i^c}{C_{si}{}^w} \tag{A-5}$$

where C_i^c is the solubility of *i* in the pure cosolvent. Although Equation (A-4) is typically applied in an empirical manner, it has a basis in thermodynamic principles. Thus, the cosolvency power can be estimated from the physicochemical properties of the solute and solvents:

$$\sigma_s = \frac{N\left(\gamma_{i:w}^{e} - \gamma_{i:c}^{e}\right)HSA}{2.3RT} \tag{A-6}$$

where *N* is Avagadro’s number; γ^e is the interfacial energy ($J\ cm^{-2}$) between the solute (*i*) and water (*w*) or cosolvent (*c*); *HSA* is the solute’s hydrophobic surface area (cm^2/molecule); *R* is the universal gas constant ($J\ mol^{-1}\ K^{-1}$); and *T* is the absolute temperature (K) (Yalkowski *et al.,* 1976).

Deviations from the log-linear cosolubility relationship (Equation [A-4]) have been observed in studies of the solubilization of non-polar drugs in a variety of cosolvents solutions (Rubino and Yalkowsky, 1987), polychlorinated biphenyls (PCBs) in water-miscible alcohols (Li and Andren, 1994), and BTEX species in gasoline-methanol-water systems (Poulson *et al.,* 1992). For short-chained alcohols, these deviations have been attributed to changes in the interactions between water and the cosolvent molecules (Rubino and Yalkowsky, 1987). At low ethanol volume fractions, ethanol molecules are partially segregated from water via hydration spheres; whereas at higher ethanol fractions, hydration is no longer a dominant solubilization process, and the HOC has access to both water and cosolvent molecules in approximate proportion to their volume fractions.

At cosolvent volume fractions less than between 0.1 to 0.2, hydration spheres largely confine cosolvent molecules (Banerjee and Yalkowsky, 1988). Based on results of a study of aqueous-ethanol solutions, Grunwald (1984) described the volume within such spheres as being in a state of reduced hydrogen bonding as a result of disruption of the water network by the cosolvent. This would lead to a reduction in the hydrophobic effect within the spheres and an increase in HOC solubility. In contrast, outside of the hydration spheres, hydrogen bonding between water molecules is increased, and both ethanol and HOC molecules are largely excluded as a result of the hydrophobic effect.

The influence of the formation of hydration spheres was demonstrated by Banerjee and Yalkowsky (1988) using toluene as the HOC, and propylene glycol and methanol as cosolvents. At low volume fractions of the cosolvent, the solubilization of toluene was found to increase linearly with increasing cosolvent volume fraction—a direct influence of the volume of the hydration spheres. As the volumes of the hydration spheres expand, they intersect and eventually encompass the entire aqueous phase. They postulate that the intersection of the hydration spheres occurs at the breakpoint observed between linear and log-linear relationships between aqueous-phase solubilities and cosolvent volume fractions.

Because the log-linear cosolubility models (Equations [A-4]–[A-6]) do not incorporate the influence of the hydration spheres on the mechanisms of solubilization, this equation is only valid at higher cosolvent concentrations. Incorporating the observed linear relation at lower cosolvent concentrations, two equations can be written to reflect differences in solubilization mechanisms at low versus high cosolvent concentrations (Banerjee and Yalkowsky, 1988).

$$C_i^m = \left(1 - \frac{f^c}{\beta}\right) C_i^w + f^c\, C_i^\beta \qquad \text{for } f^c < \beta \tag{A-7a}$$

$$lnC_i^m = \left(1 - \frac{f^c - \beta}{1 - \beta}\right) lnC_i^\beta + \left(\frac{f^c - \beta}{1 - \beta}\right) lnC_i^c \qquad \textit{for } f^c \geq \beta \tag{A-7b}$$

where β is the volume fraction of ethanol in the aqueous phase at the breakpoint between the two segments of the model, and C_i^β is the concentration of *i* in the cosolvent mixture at this ethanol volume fraction. These model equations are referred to as the linear/log-linear model.

A-3. Models for Estimating Activity Coefficients

An alternative approach to modeling the solubilities of HOCs in a cosolvent mixture is to employ a thermodynamic model to estimate activity coefficients of each component in each phase and to equate the chemical activities in each phase (Equation [A-1b]). Most of these models (Margules, *UNI*versal *QU*Asi *C*hemical [UNIQUAC], Non-Random-Two-Liquid [NRTL]) require a substantial amount of experimental data to fit the model parameters (Smith and Van Ness, 1987). Of these, the UNIQUAC model is often used in multicomponent liquid-liquid equilibrium problems. In this model, statistical mechanics are used to include the effect of molecular structure on liquid activity coefficients, resulting in a basic equation that incorporates the influence of both the entropy effects associated with the size and shape of a molecule (the combinatorial part) and the molecular interactions of functional groups between the different molecules (the residual part) (Henley and Seader, 1981):

$$\ln\gamma_i = \ln\gamma_i^c + \ln\gamma_i^r \tag{A-8}$$

Here, superscripts *c* and *r* indicate the combinatorial and residual contributions, respectively, and subscript *i* refers to the chemical solute (Fredenslund *et al.*, 1975). The parameters γ_i^c and γ_i^r are determined from properties of the pure species, and experimental binary equilibrium data for each pair of species. These expressions are dependent on the molecular volume, molecular surface area, and binary interactions among the different molecules.

The UNIQUAC Functional-group Activity Coefficients (UNIFAC) model was developed with the same theoretical basis as UNIQUAC although the necessary parameters are estimated from the number and type of functional groups that comprise the chemical species. Because this model does not require extensive data, it is more easily implemented than UNIQUAC although additional errors are introduced by estimating rather than measuring some of the parameters. This model is based on the premise that surface volume and area properties of the individual functional groups that comprise a molecule can be summed to estimate properties of the entire molecule (Fredenslund *et al.,* 1975). The group parameters are tabulated for numerous functional groups in most standard thermodynamics textbooks (for example, Smith and Van Ness, 1987). An additional parameter, describing interactions among each of the functional groups is also required for the UNIFAC model. These group interaction parameters have been determined from a large database of experimental data and have been updated numerous times since the initial development of the UNIFAC model. The most recent corrections and additions were made in 1991 (Hansen *et al.,* 1991).

The difficulty in utilizing UNIFAC for complex systems is the need to understand the composition and structure of all components within the system. This is typically not feasible with complex petroleum hydrocarbons. Perry and Chilton (1973) suggest the use of "pseudocomponents" to lump many components into one with average properties. Peters and Luthy (1993) described a coal tar as a pseudocomponent in an assessment of phase equilibria for ternary coal tar-water-solvent systems. They found that this approach was useful for analyzing the effect of polar solvents added to increase coal tar solubilization.

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Appendix B
Modeling Interphase Mass-transfer Processes

Appendix B
Modeling Interphase Mass-transfer Processes

B-1. Interphase Mass Transfer

Interphase mass transfer describes the net movement of a substance across an interface dividing two phases in response to a chemical thermodynamic disequilibrium between those phases. If changes in concentration occur abruptly across the interface and the two phases are relatively homogeneous except near the interface, the flux, or rate of mass transfer per unit-area of the interface, can be expressed as a product of a mass-transfer coefficient and a concentration difference (Cussler, 1984)

$$N_i = k_i \cdot (C_i^{*a} - C_i^a) \tag{B-1}$$

where N_i is the flux of compound i, k_i is the mass-transfer coefficient, C_i^a and C_i^{*a} are the concentrations of compound i in phases a and the concentration of i that would be in equilibrium with the concentration in phase b, respectively. This equilibrium concentration is often defined by a partition coefficient ($K_i^{a,b}$):

$$C_i^a = K_i^{a,b} C_i^b \tag{B-2}$$

Thus, when $C_i^a = C_i^{a}*$, the net flux of compound i across the interface is 0. Within the present discussion, the two phases consist of a non-aqueous phase liquid (NAPL), designated by the superscript n and an aqueous phase, designated by the superscript w (for water). Also, for brevity, interphase mass transfer is referred to more simply as mass transfer.

B-2. Estimating the Mass-transfer Coefficient

A number of methods exist to estimate the mass-transfer coefficient. Some of these are empirical correlations derived using dimensional analysis and experimental measurements. These are typically developed for specific geometries, such as NAPL entrapped as residual blobs or ganglia within a porous medium and subject to a uniform flow field (for example, Hunt *et al.*, 1988; Powers *et al.*, 1992, 1994). Others, such as the film theory and boundary layer theory are based upon physical models of the interface (Cussler, 1984).

A pool of NAPL, as in the case of a gasoline spill, generally provides a boundary condition for modeling the transport of aqueous-phase contaminants with the groundwater flow (Figure B-1). Two approaches can be used to quantify the input of contaminants from the gasoline source to the groundwater through interphase mass-transfer processes. A first type of boundary condition can be used to stipulate the concentration, or a second type of boundary condition can be developed to specify the flux of the organic species between phases.

Several researchers have found that a first-type boundary condition equating the concentration at the boundary to the solubility of the organic species comprising the single-component NAPL is adequate (Hunt *et al.*, 1988; Johnson and Pankow, 1992; Pearce *et al.*, 1994; Voudrais and Yeh, 1994; Chrysikopoulos, 1995). This boundary condition can be written as:

$$C^{w}(x,z) = C^{w*} \text{ @ } z = 0,\ 0 < x < l, \qquad \text{(B-3)}$$

With a single-component NAPL, the composition of the LNAPL does not change significantly with time, and an analytical solution to the transport equation can be employed. The more complex case of a multicomponent NAPL has only recently been considered (Holman and Javandel, 1996). They still assumed that equilibrium is achieved at the boundary but incorporated diffusion of the hydrophobic organic compounds (HOCs) through the organic phase as a limitation of the total mass-transfer rate. In the assumed stagnant gasoline pool, diffusion would be the predominant transport mechanism.

A flux term has been utilized to describe interfacial mass-transport processes of an organic species between residual NAPL blobs and the aqueous phase. The mass-transfer flux is generally described with a linear driving force (Equation B-1). In general, it is assumed that the concentrations in each phase right at the interface are in equilibrium. A couple of different mass-transfer theories can be used to estimate the mass-transfer coefficient.

Previous models of mass transfer from NAPL lenses have assumed that mass-transfer limitations are controlled by the flux of the solute away from the interface via advection and hydrodynamic dispersion by the groundwater (Johnson and Pankow, 1992; Voudrias and Yeh, 1994; Hunt *et al.*, 1988). This physical situation most closely follows that of penetration theory (Cussler, 1984).

Penetration theory assumes that the mass transfer across an interface is controlled by the diffusive flux away from the interface. Figure B-2 illustrates changes in concentration as a result of the mass transfer from a NAPL to a flowing aqueous liquid. This is adapted from Cussler (1994) although the original figure contained a vapor phase in place of the NAPL. Using the geometry shown in Figure B-2 and assuming (1) a constant concentration in the NAPL over the length L of the interface; (2) an aqueous phase of infinite vertical extent; (3) laminar flow parallel to the interface, the steady-state mass transfer could be described by the following differential equation:

$$u_{max} \frac{\partial C_i^w}{\partial x} = D \frac{\partial^2 C_i^w}{\partial z^2} \qquad \text{(B-4)}$$

where D is the diffusion coefficient of compound i in water, u_{max} is the maximum velocity of flow, and C_i^w is the concentration of compound i in the aqueous phase. It is assumed that u_{max} occurs parallel to the interface and is constant except immediately adjacent to the interface. Solving Equation (B-4) for the following boundary conditions:

$$\begin{aligned} &C_i^w(x,z=\infty)=0 \\ &C_i^w(x,z=0)=\frac{C^n}{K_i^{n,w}} \qquad 0<x<l \qquad \text{(B-5)} \\ &C_i^w(x=0,z)=0 \end{aligned}$$

yields a solution from which the steady-state flux across the interface can be derived

$$N_i=\sqrt{\frac{D\,u_{max}}{\pi\ x}}\left(\frac{C_i^n}{K_i^{n,w}}-C_i^w\right) \qquad \text{(B-6)}$$

The mass-transfer coefficient for steady state would then be equal to (Cussler, 1984):

$$k_i=\sqrt{\frac{4\ D\,u_{max}}{\pi\ L}} \qquad \text{(B-7)}$$

Extending this to describe mass transfer in a porous medium requires several modifications. In a porous medium, spatial variations in velocity within the pores, tortuous flow around the solid phase, and divergence of flow as a result of larger-scale heterogeneities generate transverse dispersion. Considering only transverse dispersion in the vertical direction, the vertical component of the hydrodynamic dispersion tensor is equal to the sum of the molecular diffusion (divided by the tortuosity, τ_z) and the vertical component of the dispersion tensors (Bedient *et al.*, 1994). Furthermore, as a first approximation, the components of the dispersion tensor can be linearly related to the horizontal velocity by a proportionality constant, in this case α_z, the vertical dispersivity

$$D_z=\frac{D}{\tau_z}+\alpha_z v_x \qquad \text{(B-8)}$$

Finally, accounting for the volume fraction of the solid phase and not yet considering NAPL, the mass-transfer coefficient would be computed as follows:

$$k_i=\varepsilon\sqrt{\frac{4D_z\,v_x}{\pi\,L}} \qquad \text{(B-9)}$$

where ε is the porosity of the porous medium. Multiplying this by the difference in concentration between the NAPL and aqueous phases, the net steady-state flux would be then be equal

$$N_i=\varepsilon\sqrt{\frac{4D_z\,v_x}{\pi\,L}}\ \bullet\ \left(\frac{C_i^n}{K_i^{n,w}}-C_i^w\right) \qquad \text{(B-10)}$$

This approach has been applied in recent years for estimating the dissolution from pools of NAPL less dense than water (Hunt *et al.*, 1988; Voudrias and Yeh, 1994) as well as pools of NAPL with specific gravities greater than unity (Anderson *et al.*, 1992; Johnson and Pankow, 1992; Pearce *et al.*, 1994).

Holman and Javandel (1996) extended the complexity of the mass-transfer problem in a two-dimensional cross section to include time-dependent mass transfer and rate limitations caused by diffusional resistances in the NAPL. A system of two differential equations was solved. The first of these equations described the diffusive flux of HOC through the NAPL:

$$\frac{\partial C_i^n}{\partial t} = D_i^n \left[\frac{\partial^2 C_i^n}{\partial x^2} + \frac{\partial^2 C_i^n}{\partial z^2} \right] \qquad 0 \le x \le l, \;\; 0 \le z \le h_0, \;\; t > 0 \tag{B-11}$$

while the second described advective-diffusive transport of the solute through the aqueous phase:

$$\frac{\partial C_i^w}{\partial t} = D_x^w \frac{\partial^2 C_i^w}{\partial x^2} + D_z^w \frac{\partial^2 C_i^w}{\partial z^2} - u_x \frac{\partial C_i^w}{\partial x} \qquad 0 \le x \le \infty, \;\; -h \le z \le 0, \;\; t > 0 \tag{B-12}$$

Here, D_i^n is the diffusion coefficient of compound i in the NAPL, and D_x^w and D_z^w are the aqueous-phase coefficients of hydrodynamic dispersion. (It should be noted that some expressions have been altered from the original published work in order to create consistency between equations presented here.)

Boundary conditions for the NAPL consisted of zero flux at the upper and lateral boundaries and a the following conditions at the groundwater interface which served to couple Equations (B-11) and (B-12)

$$\begin{aligned} C_i^w &= K_i^{w,n} C_i^n && (0 \le x \le l, \;\; z = 0, \;\; t > 0) \\ \frac{D_z^w \rho^w}{M^w} \frac{\partial C_i^w}{\partial z} &= \frac{D_i^n \rho^n}{M^n} \frac{\partial C_i^n}{\partial z} && (0 \le x \le l, \;\; z = 0, \;\; t > 0) \end{aligned} \tag{B-13}$$

The first of these equations equates the chemical activities at the interface, and the second equates the molar flux leaving the NAPL with that entering the groundwater. The appearance of expressions for the densities, ρ^w and ρ^n, and molecular weights, M^w and M^n, of the bulk fluids in Equation (B-13) reflect the authors' use of mole fraction as a unit of concentration. Zero-flux boundary conditions are applied to the groundwater at the base of the aquifer, the upstream boundary, and at the water table where the NAPL does not exist.

The analytical solution derived from the differential equations and boundary and initial conditions is a tremendous advancement from the steady-state approach used previously (Hunt et al., 1988; Voudrias and Yeh, 1994; Anderson *et al.*, 1992; Johnson and Pankow; 1992; Pearce *et al.*, 1994). However, implementation of the solution is very difficult because the solution is presented in Laplace space and the inverse transform must be performed numerically.

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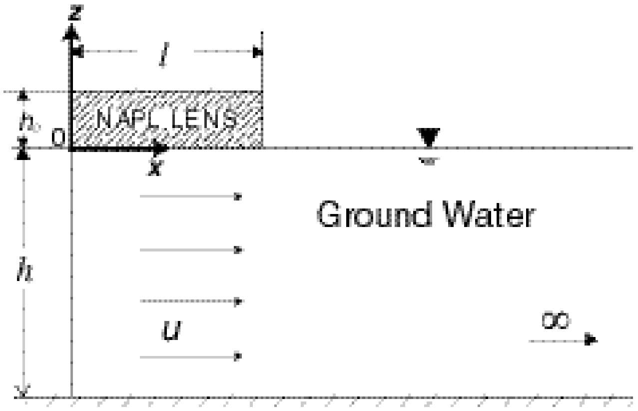

Figure B-1. Typical geometry used for modeling teaching from an LNAPL pool.

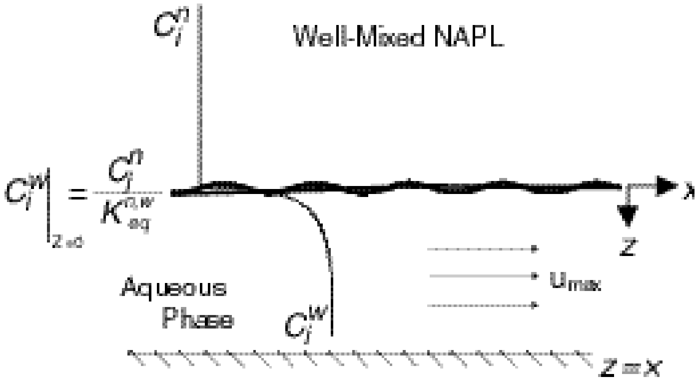

Figure B-2. Illustration for Penetration theory (adapted from Cussler, 1997).

UCRL-AR-135949 Vol. 4 Ch. 3

Volume 4: Potential Ground and Surface Water Impacts

Chapter 3: The Effect of Ethanol on BTEX Biodegradation and Natural Attenuation

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Table of Contents

List of Figures

List of Tables

3. The Effect of Ethanol on BTEX Biodegradation and Natural Attenuation

3.1. Introduction and Objectives

3.1.1. Problem Statement

The use of ethanol as a gasoline additive is increasing worldwide, both as a substitute fuel for imported oil and as an oxygenate to minimize air pollution from combustion. In Brazil, for example, approximately one-half of all automobiles run on gasoline containing 22% ethanol, with the remainder operating on hydrated ethanol (Petrobrás, 1995). In the United States, gasoline containing 10% ethanol is already available in many states. A recent effort by some members of the United States House of Representatives to repeal the 5.4-cents/gal tax subsidy for gasoline with ethanol earlier than its original (year 2000) end date was defeated. Instead, the tax subsidy was extended (*Chemical Market Reporter*, 1998). In addition, ongoing advances in biotechnology will continue to lower ethanol production costs (Lugar and Woolsey, 1999; Carver, 1996).

Given the increasing financial and political incentives for expanding its use as an automotive fuel oxygenate, ethanol appears likely to be encountered more frequently in groundwater plumes containing the fuel constituents, benzene, toluene, ethyl benzene, and xylene (BTEX). Consequently, a comprehensive understanding of the effects of ethanol on the fate and transport of BTEX compounds is needed to determine if the economic and air-quality benefits of adding ethanol to gasoline outweigh its potential detrimental effects on groundwater quality, the environment, and human health.

3.1.2. General Scope and Purpose of This Literature Review

The proposed replacement of the gasoline oxygenate, methyl tertiary butyl ether (MTBE), with ethanol represents potential economic and environmental quality benefits. However, these benefits may be offset to some extent by potential detrimental effects on groundwater quality and natural attenuation of released petroleum products. The objectives of this literature review are to bound the extent to which these impacts may occur, summarize the available information on the biodegradation of ethanol in the environment, assess the potential effect that biodegradation processes may have on the fate and transport of BTEX compounds, and provide recommendations for research to enhance related risk assessment and management decisions.

This literature review characterizes potential environmental impacts associated with a possible widespread replacement of MTBE with ethanol as a gasoline oxygenate by:

- Summarizing and critically analyzing the available information on the fate of ethanol in the environment.
- Assessing the potential environmental impacts associated with ethanol releases.
- Evaluating their potential effect on natural attenuation of BTEX compounds.

Section 3.2 provides a general review of subsurface requirements for biodegradation of organic pollutants, and Section 3.3 summarizes available information on ethanol biodegradation pathways and kinetics under aerobic and anaerobic conditions. The potential effects of ethanol on cellular and environmental processes that affect the rate and extent of BTEX biodegradation are reviewed in Section 3.4.

3.2. Requirements for Biodegradation of Organic Pollutants

Bioremediation, which involves the use of indigenous microorganisms (or the catalysts that they produce) to degrade the target pollutants within the aquifer, is receiving increasing attention due to its potential cost effectiveness. Advantages of bioremediation include potential savings in the duration and cost of cleanup operations, minimum land and environmental disturbance, and elimination of liability from transportation and disposal of hazardous wastes (Lee *et al*., 1988). In addition, bioremediation has gained considerable public acceptance because it is environmentally sound and because it ultimately transforms the target pollutants into harmless products, such as carbon dioxide and water.

The common approach to engineered *in situ* bioremediation is to provide environmental conditions that overcome limitations and foster natural degradative processes. For example, fertilizers and oxygen can be injected into gasoline-contaminated aquifers to add limiting nutrients and electron acceptors. In some cases, however, natural conditions at contaminated sites meet all the essential environmental requirements so that bioremediation can occur at high rates without human interference. This approach is called intrinsic bioremediation, and it differs from no-action alternatives in that it requires thorough documentation of the role of microorganisms in eliminating the target contaminants at a sufficiently high rate to provide adequate risk protection.

Resource-allocation problems have motivated a recent paradigm shift in the United States towards risk-based corrective action and intrinsic bioremediation. It should be emphasized, however, that this approach is not a panacea that is applicable to all situations (National Research Council, 1993). For intrinsic bioremediation to be effective, the biodegradation rate of a given pollutant in the subsurface should be fast relative to its rate of introduction and migration to ensure plume stabilization and mitigation. Otherwise, the plume will expand and potentially reach groundwater users (Corseuil and Alvarez, 1996). These relative rates depend on the type and the concentration of the contaminants, the indigenous microbial community, and the subsurface hydrogeochemical conditions. As discussed below, extensive biodegradation of gasoline pollutants requires the fulfillment of several conditions.

3.2.1. Occurrence of Microorganisms with Potential to Degrade the Target Compounds

Organic pollutants will be degraded to an appreciable extent only if microorganisms exist that can catalyze their conversion to a product that is an intermediate or a substrate to common metabolic pathways. Only a few central metabolic pathways exist; and some structural features in organic compounds called “xenophores” (for example, chlorine, nitrogen dioxide, cyanide, and sulfur trioxide [Cl, NO_2, CN, and SO_3]) can make a molecule difficult to be recognized by these pathways (Alexander, 1994). Thus, such xenobiotics tend to be recalcitrant to microbial degradation. Nevertheless, ethanol and BTEX compounds have a natural origin and have been in contact with microorganisms throughout evolutionary periods (Dagley, 1984). Thus, it is not surprising that many microorganisms have developed mechanisms to feed on these compounds and utilize them as fuel molecules to obtain energy and building blocks for the synthesis of new cell material.

The ability of microorganisms to utilize BTEX compounds as sole carbon sources has been established since 1908, when Stormer isolated the bacterium *Bacillus hexavarbovorum* by virtue of its ability to grow with toluene and xylene aerobically (Gibson and Subramanian, 1984). The ubiquitous distribution of soil bacteria capable of metabolizing aromatic compounds under aerobic conditions was demonstrated in 1928 by Gray and Thornton, who reported that 146 out of 245 uncontaminated soil samples contained bacteria capable of metabolizing naphthalene, phenol, or cresol (Gibson and Subramanian, 1984). Many bacterial pure cultures have been reported to grow aerobically on BTEX compounds as sole carbon sources, including the following genera: *Pseudomonas, Burkholderia, Arthrobacter, Alcaligenes, Corynebacterium, Flavobacterium, Norcardia, Achromobacter, Micrococcus,* and *Mycobacterium* (Atlas, 1984; Bayly and Barbour, 1984; Brown, 1989; Button and Robertson, 1986; Gibson and Subramanian, 1984; Kukor and Olsen, 1989; Oldenhuis *et al*., 1989; Schraa *et al*., 1987; Shields *et al*., 1989).

BTEX compounds can also be degraded in the absence of molecular oxygen, with toluene being the most commonly reported BTEX compound to degrade under anaerobic conditions (Alvarez and Vogel, 1995; Anderson *et al*., 1998; Beller and Spormann, 1997; Edwards and Grbic-Galic, 1992; Heider and Fuchs, 1997; Heider *et al*., 1999; Hutchins *et al*., 1991; Meckenstock, 1999; Phelps and Young, 1999; Zeyer *et al*., 1990). Benzene, which is the most toxic of the BTEX compounds, is relatively difficult to degrade under anaerobic conditions. There are reports of benzene mineralization under iron-reducing (Lovley *et al.*, 1996; Rooney-Varga *et al.*, 1999), sulfate-reducing (Edwards and Grbic-Galic, 1992; Phelps *et al.*, 1998), nitrate-reducing (Burland and Edwards, 1999), and methanogenic conditions (Grbic-Galic and Vogel, 1987; Weiner and Lovley, 1998b), with acclimation periods often exceeding one year (Kazumi *et al*., 1997). Nevertheless, research suggests that even with the appropriate environmental conditions, anaerobic benzene degradation will not occur in some contaminated aquifer sediments due the absence of microorganisms capable of performing the degradation (Anderson *et al*., 1998; Weiner and Lovley, 1998a).

The high biodegradability of ethanol is well established in the literature. Short-chain alcohols, such as ethanol, can be easily degraded under both aerobic and anaerobic conditions by microbial enzymes associated with central microbial metabolic pathways (Chapelle, 1993; Hunt *et al*., 1997a; Hunt *et al*., 1997b; Madigan *et a*l., 1997). In addition, ethanol is highly bioavailable to microorganisms in aquifer material because of its miscibility with water. Thus, a wide distribution of ethanol-degraders in the environment can be expected.

3.2.2. Bioavailability of Target Pollutants

A common limitation of natural degradative processes is the lack of adequate contact between pollutants and microorganisms. The availability of many target pollutants to microorganisms can be affected by a series of ill-defined, often uncharacterized processes (Alexander, 1994). In a physicochemical context, adsorption of a compound or complexation onto aquifer solid surfaces, sequestration in soil nanopores, and partitioning into nonaqueous phase liquids (NAPLs) are common mechanisms that reduce contaminant bioavailability. In such cases, the rate of biodegradation can be controlled by the rate desorption or dissolution (Alexander, 1994). If biodegradation is mediated by extracellular enzymes, the bonds requiring cleavage must be exposed and not occluded by sorption to solid surfaces, or sterically blocked by large atoms, such as chlorine. Most priority pollutants, however, are degraded by intracellular enzymes. Therefore, bioavailability also implies the ability of the pollutant to pass through the cellular membrane. In regards to ethanol and BTEX compounds, all of these bioavailability requirements are generally met easily because of their relatively high aqueous solubility. However, when (hydrophobic) polycyclic aromatic hydrocarbons (PAHs) are a contaminant of concern, the characteristically high sorption to soil with PAHs makes bioavailability a significant factor limiting the success of bioremediation.

3.2.3. Induction of Appropriate Degradative Enzymes

The induction of degradative enzymes involves the activation of specific regions of the bacterial genome. Some enzymes, such as those participating in central metabolic pathways, are always produced (at some level) regardless of environmental conditions. These are known as constitutive enzymes. The enzymes that initiate BTEX degradation, however, are generally inducible. Such enzymes are only produced when an inducer (for example, toluene) is present at a higher concentration than the minimum threshold for induction (Linkfield *et al.*, 1989). In general, this threshold is very low, on the order of a few micrograms per liter (Robertson and Button, 1987). Toluene is generally a good inducer of oxygenase enzymes with relaxed specificity, and its presence has been reported to enhance the degradation of other BTEX compounds (Arvin *et al.*, 1989; Alvarez and Vogel 1991, 1995; Chang *et al.*, 1993; Gülensoy and Alvarez, 1999). On the other hand, the presence of easily degradable substrates, such as ethanol, could repress the production of BTEX-degrading enzymes and result in the preferential degradation of the ethanol (Corseuil *et al.*, 1998; Duetz *et al.*, 1994).

It should be pointed out that enzyme induction could be hindered by a lack of bioavailability. Specifically, the presence of a compound in a NAPL or its sequestration in nanopores might result in subthreshold concentrations in the aqueous phase that are insufficient to trigger enzyme induction and/or sustain a viable microbial population.

3.2.4. Environmental Conditions Conducive to Microbiological Growth

Recalcitrance to biodegradation of a given compound is a consequence not only of chemical structure and physiological limitations but also of environmental properties. To function properly, microorganisms need “recognizable” substrate(s) that serve as energy and carbon source(s) (for example, the target organic pollutants) and favorable environmental conditions to sustain life functions, including nutrients, pH, temperature, and moisture.

3.2.4.1. Availability of Electron Acceptors

Ethanol and BTEX compounds are in a reduced state, and their oxidation is thermodynamically favorable. Oxidative biodegradation requires the presence of electron acceptors that microbes use during the “respiration” of the electrons removed from biodegradable contaminants. This transfer of electrons releases energy to drive microbial life functions. Under aerobic conditions, molecular oxygen is utilized for this purpose. Under anaerobic conditions, nitrate, sulfate, manganese (iv) ferric iron, sulfate, and carbon dioxide can serve as electron acceptors. Often, a sequential utilization of electron acceptors is observed in contaminated sites, in preferential order of oxidation potential (Figure 3-1).

The most energetically favored mechanism by which microorganisms oxidize organic compounds is aerobic metabolism. Therefore, oxygen is preferentially utilized over anaerobic electron acceptors because this yields more energy to the microbial community and results in faster contaminant oxidation rates. In intrinsic BTEX bioremediation, the rate-limiting attenuation mechanism is frequently the influx of oxygen, which, in turn, limits aerobic BTEX degradation kinetics (National Research Council, 1993).

The redox potential in subsurface environments is highly site-dependent. Oxygen is usually present in and around groundwater recharge areas as a result of infiltrating rainwater. Nevertheless, the available oxygen within the contaminant plume is often exceeded by the biochemical oxygen demand exerted by the contaminants, and anaerobic conditions often develop in highly contaminated areas. The depletion of oxygen results in much slower BTEX degradation rates and sometimes in the persistence of benzene, the most toxic of the BTEX compounds (Alvarez and Vogel, 1995; Anderson *et al*., 1998).

3.2.4.2. Availability of Inorganic Nutrients

Microorganisms need macronutrients to synthesize cellular components, such as nitrogen for amino acids and enzymes, phosphorus for ATP and DNA, sulfur for some coenzymes, calcium for stabilizing the cell wall, and magnesium for stabilizing ribosomes. In general, however, microbial growth in subsoils is not limited by nitrogen and phosphorus as long as the contaminant concentrations are in the sub-part-per-million (mg/L) range (Tiedje, 1993). A carbon:nitrogen:phosphorus ratio of 30:5:1 is generally sufficient to ensure unrestricted growth in aquifers (Paul and Clark, 1989). Microbes also need micronutrients to perform certain metabolic functions. For example, trace metals, such as iron, nickel, cobalt, molybdenum, and zinc, are needed for some enzymatic activities. Nevertheless, geochemical analyses and laboratory biodegradation assays should be performed to verify that the presence of inorganic nutrients is sufficient for the success of natural bioremediation.

3.2.4.3. Buffering Capacity

Most microorganisms grow best in a relatively narrow range of pH around neutrality (6 to 8). Enzymes are polymers of amino acids, and their activity requires the proper degree of amino acid protonation. This is controlled by pH. The optimum groundwater pH is usually near neutral (pH 7), but most aquifer microorganisms can perform well between pH values of 5 and 9. This range generally reflects the buffering capacity of the carbonate or silicate minerals present in aquifers (Chapelle, 1993; King *et al*., 1992). Groundwater is typically well buffered within this range, so that microbial pH requirements are generally met in aquifers (Chapelle, 1993). Nevertheless, aquifers contaminated by municipal landfill leachates may contain elevated concentrations of volatile fatty acids (VFAs) (for example, acetic acid) resulting in pH values as low as 3. In these cases, acidity may suppress microbial activity. As discussed later in this review, the potential accumulation of VFAs during anaerobic degradation of ethanol is a potential mechanism that could decrease the pH below the optimum range of common bacteria that degrade BTEX.

3.2.2.4. Temperature

Temperature is one of the most important environmental factors influencing the activity and survival of microorganisms. Microbial metabolism accelerates with increasing temperatures up to an optimum value at which growth is maximal. Most of the bacteria present in subsurface environments operate most effectively at 20° to 40°C, which is a little higher than typical groundwater temperatures in the United States (Chapelle, 1993). Low temperatures reduce the fluidity and permeability of the cellular membrane, which hinders nutrient (and contaminant) uptake. Higher temperatures are associated with higher enzymatic activity and faster biodegradation rates, up to an optimum value that is species specific. BTEX degradation rates can double or triple due to a temperature increase of 10°C (Corseuil and Weber, 1994). If the temperature rises much beyond the optimum value, proteins, enzymes, and nucleic acids become denatured and inactive. The temperature of the upper 10 m of the subsurface may vary seasonally; however, between 10 and 100 m subsurface temperatures approximate the mean annual air temperature of a particular region (Lee *et al*., 1988).

3.2.4.5. Absence of Inhibitory Substances

It is possible for aquifer microorganisms to encounter potentially toxic heavy metals, such as lead, mercury, cadmium, and chromium. While aquifer microorganisms require heavy metals in trace quantities for nutritional purposes, heavy metals can be bacteriostatic or bactericidal if they are present in soluble form at concentrations greater than about 1 mg/L. High pollutant concentrations can also have toxic effects, such as gross physical disruption (for example, membrane dissolution) or competitive binding of critical enzymes (Alexander, 1994). In addition, the presence of easily degradable substrates that are preferentially utilized commonly hinders the degradation of the target contaminants.

3.2.4.6. Other Environmental Factors

While moisture is not a limiting factor in the saturated zone, it can be an important factor in the vadose zone. A moisture content of about 80% of soil field capacity, or 15% water (H_2O) on a weight basis, is optimum for vadose zone remediation (English and Loehr, 1991). Inadequate moisture (less than 40%) can significantly reduce biodegradation rates. High salinity can also exert osmotic stress on microorganisms, which would hinder biodegradative processes.

3.3. Biodegradation of Ethanol

One of the most undesirable aspects of microbial degradation of organic pollutants is the potential formation of toxic metabolites. A large number of nontoxic chemicals can be converted to products that may be harmful to humans, animals, plants, or microorganisms. This process is a major reason to study the pathways and products of breakdown of organic molecules. This section summarizes the diversity of aerobic and anaerobic transformation pathways for ethanol. Emphasis was placed on addressing the potential accumulation of metabolites that may have adverse impacts to water quality, or that may hinder intrinsic bioremediation of BTEX compounds. The kinetics of ethanol biodegradation under aerobic and anaerobic conditions are also discussed here.

3.3.1. Ethanol Degradation Pathways

3.3.1.1. Aerobic Degradation

Most common aerobic bacteria can mineralize ethanol through Krebs cycle. In this process, ethanol is first oxidized to acetaldehyde by an alcohol dehydrogenase enzyme. Acetaldehyde is converted to acetyl-CoA either directly by an acetylating acetaldehyde dehydrogenase or through acetate by an acetaldehyde dehydrogenase and an acetate-CoA ligase. The acetyl-CoA is oxidized to carbon dioxide (CO_2,) in Krebs cycle (Figure 3-2). As shown in Figure 3-3, many bacteria are also capable of operating a modified Krebs cycle, known as the glyoxylate shunt. This shunt enables bacteria to grow on compounds with two carbon atoms (C2-compounds), such as acetate, by facilitating the synthesis of C4-building blocks, such as malate and oxaloacetate (Madigan *et al*., 1997).

None of the intermediates in these common metabolic pathways is toxic. In addition, because these intermediates are metabolized rapidly intracellularly and are rarely excreted in significant amounts, their accumulation in groundwater is highly unlikely. One exception, however, is the acetic acid bacteria which excrete acetate (Gottschalk, 1986, Xia *et al*., 1999).

Acetic acid bacteria excrete acetate because they lack the necessary enzymes to rapidly metabolize it. For example, *Gluconobacter* cannot oxidize the activated form of acetate (that is, acetyl-CoA) in Krebs cycle because it lacks a key enzyme, succinate dehydrogenase (Gottschalk, 1986). *Acetobacter* species can operate the Krebs cycle but still produce large amounts of acetic acid in the presence of ethanol (Gottschalk, 1986). These bacteria are unlikely to significantly contribute acidity to ethanol-contaminated groundwater, however, because they are obligate aerobes that typically live on the surfaces of plants and fruits (Gottschalk, 1986). Therefore, they are unlikely to thrive in aquifers contaminated with gasoline-ethanol mixtures, where the high biochemical oxygen demand often depletes available oxygen.

3.3.1.2. Anaerobic Pathways

3.3.1.2.1. Anaerobic Food Chain. Microorganisms that can ferment ethanol are ubiquitous (Eichler and Schink, 1984; Wu and Hickey, 1996). Ethanol is a common intermediate in the anaerobic food chain, where labile organic matter is degraded to nontoxic products—such as acetate, CO_2, methane (CH_4), and hydrogen gas (H_2)—by the combined action of several different types of bacteria (White, 1995). As illustrated in Figure 3-4, the anaerobic food chain consists of three stages. In the first stage, fermenters produce simple organic acids, alcohols, hydrogen gas, and carbon dioxide. Other members of the consortium, such as sulfate reducers and organisms that use water-derived protons as the major or sole electron sink, oxidize these fermentation products in the second stage to acetate, hydrogen gas, and carbon dioxide. Organisms that use water-derived protons include the obligate, proton-reducing acetogens, which oxidize butyrate, propionate, ethanol, and other compounds to acetate, hydrogen gas, and carbon dioxide. Acetate can also be produced by homoacetogens, which are bacteria that utilize carbon dioxide and hydrogen gas for this purpose (Madigan *et al*., 1997). In the third stage, mineralization occurs when acetoclastic methanogens, break down acetate into carbon dioxide and methane. Some sulfate reducers and other anaerobic microorganisms can also mineralize acetate and participate in the third and final stabilization stage (Atlas and Bartha, 1997).

Interspecies hydrogen transfer is a critical link in the anaerobic food chain. Hydrogen-producing fermentative and acetogenic bacteria are at a thermodynamic disadvantage if hydrogen accumulates (Conrad *et al*., 1985; Wolin and Miller, 1982). For example, the fermentation of ethanol to acetate and propionate by *Desulfobulbus* is strongly inhibited by high hydrogen concentrations (Schink *et al*., 1987; Wu and Hickey, 1996). Therefore, fermenters and acetogens live syntrophically with hydrogen consumers that keep the hydrogen gas levels low (Figure 3-5).

When sulfate is not limiting, sulfate reducers compete favorably for hydrogen gas and predominate over methanogens (Phelps *et al*., 1985). Incomplete oxidizers (a.k.a. Type I sulfate reducers) can oxidize ethanol, lactate, and other organic acids to acetate, while complete oxidizers (a.k.a. Type II sulfate reducers) can use either a carbon monoxide dehydrogenase pathway or a modified Krebs cycle to oxidize acetate further to carbon dioxide (Madigan *et al*., 1997; Postgate and Campbell, 1966; Thauer *et al*., 1989; Wu and Hickey, 1996).

Fermentative microorganisms can also transform ethanol by condensation reactions to form propionate (Braun *et al*., 1981; Wu and Hickey, 1996) or butyrate (Bornstein and Barker, 1948). Although these compounds are not toxic, they could adversely affect groundwater quality by impacting its taste and odor. Examples of such condensation transformations are given below.

3.3.1.2.2. *Pelobacter propionicus* Ethanol Metabolism. Propionate-forming bacteria are believed to contribute significantly to the anaerobic degradation of ethanol (Wu and Hickey, 1996). *Pelobacter propionicus* can produce propionate and acetate from its metabolism of ethanol. If sulfate is present, *P. propionicus* will oxidize ethanol to acetate, using sulfate as the terminal electron acceptor. If sulfate is not present, ethanol will be condensed with bicarbonate to form just propionate if hydrogen is available. With insufficient hydrogen, both propionate and acetate will be formed. Ethanol utilization by *P. propionicus* is diagrammed in Figure 3-6. The different stoichiometric balances for ethanol utilization are:

$$CH_3CH_2OH + HCO_3^- + H_2 \rightarrow CH_3CH_2COO^- + 2\ H_2O$$

$$3\ CH_3CH_2OH + 2\ HCO_3^- \rightarrow CH_3COO^- + 2\ CH_3CH_2COO^- + H^+ + 3\ H_2O$$

$$2\ CH_3CH_2OH + SO_4^{2-} \rightarrow 2\ CH_3COO^- + HS^- + H^+ + 2\ H_2O$$

that is,

$$\text{ethanol} + HCO_3^- + H_2 \rightarrow \text{propionate}^- + 2\ H_2O$$

$$3\ \text{ethanol} + 2\ HCO_3^- \rightarrow \text{acetate}^- + 2\ \text{propionate}^- + H^+ + 3\ H_2O$$

$$2\ \text{ethanol} + SO_4^{2-} \rightarrow 2\ \text{acetate}^- + HS^- + H^+ + 2\ H_2O$$

3.3.1.2.3. *Clostridium kluyveri* Fermentation. *Clostridium kluyveri* produces butyrate, caproate, and hydrogen from ethanol and acetate. This strain cannot ferment ethanol alone but can replace acetate with propionate as a cosubstrate for the condensation of ethanol. The ratio in which butyrate and caproate are formed can vary; an increase of the ethanol concentration of the medium favors caproate formation (Figure 3-7) (Gottschalk, 1986).

A typical fermentation balance is for this pathway is:

$$6\ CH_3CH_2OH + 3\ CH_3COO^- \rightarrow$$

$$3\ CH_3CH_2CH_2COO^- + CH_3CH_2CH_2CH_2CH_2COO^- + 2\ H_2 + 4\ H_2O + H^+$$

that is,

$$6\ \text{ethanol} + 3\ \text{acetate} \rightarrow 3\ \text{butyrate} + 1\ \text{caproate} + 2\ H_2 + 4\ H_2O + H^+$$

Thus, approximately 0.3 moles of hydrogen are evolved per mole of ethanol fermented.

3.3.2. Summary of Metabolic Intermediates of Importance in Ethanol Degradation

Microbial degradation of ethanol generates a variety of metabolic intermediates and end products (Table 3-1). Oxygen is often quickly depleted by microbial respiration in gasoline-contaminated aquifers (Lee *et al*., 1988; National Research Council, 1993). Therefore, ethanol is likely to be degraded predominantly under anaerobic conditions; and some anaerobic metabolites are likely to be encountered in contaminated groundwater. None of these metabolites is toxic although some anaerobic metabolites, such as butyrate, could adversely affect the taste and odor of groundwater supplies. In addition, acetate and other VFAs can cause a decrease in pH if they accumulate at high concentrations in poorly buffered systems. It is unknown whether the pH could decrease to a level that inhibits the further degradation of the ethanol. Such effects are likely to be system specific due to variability in buffering and dilution capacity among contaminated sites.

3.3.3. Aerobic and Anaerobic Biodegradation Kinetics

3.3.3.1. General Background

The degradation rate of BTEX and ethanol is often described by a first-order decay regime with respect to the contaminant concentration (C):

$$\frac{dC}{dt} = -\lambda C \tag{3-1}$$

For a batch, completely mixed system, Equation (3-1) can be integrated to yield:

$$\frac{C}{C_o} = e^{-\lambda t} \tag{3-2}$$

where λ is the first-order decay coefficient and C_o is the initial concentration. Equation (3-2) can be rearranged as

$$t = \frac{ln\left[\frac{C_o}{C}\right]}{\lambda} \qquad (3\text{-}3)$$

The half-life ($t_{1/2}$) of the contaminant, which is defined as the time required to reduce its concentration by one-half (that is, $C_o/C = 2$), is given by

$$t_{1/2} = \frac{ln[2]}{\lambda} \qquad (3\text{-}4)$$

It should be emphasized that these equations apply only to batch, completely mixed systems, where dilution and advection are not factors that influence contaminant concentrations. Because aquifers are open systems subject to dilution and advection, other approaches that incorporate these processes must be used to determine λ (American Society of Testing and Materials [ASTM], 1998).

The first-order kinetic assumption is often appropriate to describe the kinetics of organic pollutant biodegradation in aquifers. This is mainly due to mass-transfer limitations in porous media as the contaminants diffuse from the bulk liquid to the microorganisms, which are predominantly attached to the aquifer material (Simoni *et al*., 1999). In addition, a decrease in BTEX concentrations to levels that are below the corresponding Monod half-saturation coefficient (K_S) contributes to first-order kinetics (Alvarez *et al*., 1991). It should be pointed out that when mass transport is not rate limiting, λ can be explained in terms of Monod parameters. Specifically, when the contaminant concentration is relatively low, *C* in the denominator can be ignored, and the Monod equation reduces to a linear equation:

$$\frac{dC}{dt} = -\frac{kXC}{K_S + C} = -\left(\frac{kX}{K_S}\right)C \quad (\text{when } C << K_S) \qquad (3\text{-}5)$$

A comparison of Equations (3-1) and (3-5), therefore, reveals that

$$\lambda = \frac{kX}{K_S} \qquad (3\text{-}6)$$

This theoretical analysis indicates that the value of λ depends on:

- *k* (the maximum specific substrate utilization rate), which, in turn, depends primarily on the prevailing electron-acceptor conditions and on the type of microbe present;
- K_S (the half-saturation coefficient), which is related to enzyme affinity, bioavailability, and mass-transport limitations (Merchuk and Ansejo, 1995); and
- *X* (the active biomass concentration), which may not be constant and depends on environmental conditions and aquifer chemistry, including available substrates.

Therefore, λ is not necessarily a constant but a coefficient that can vary in time and space due to microbial population shifts resulting from changes in aquifer chemistry. This can explain the wide range of λ values that have been observed for benzene at different sites, ranging over orders of magnitude from less than 0.0001 to 0.0870 day^{-1} (Alvarez *et al*., 1991; Aronson and Howard, 1997; Howard, 1991; Rifai *et al*., 1995). Therefore, for risk-assessment purposes, λ should not be extrapolated from the literature. Rather, considerable care must be exercised in its determination to avoid overpredicting or underpredicting actual biodegradation rates and plume behavior.

3.3.3.2. Ethanol Degradation Rates in Aquifers

Ethanol can be degraded in both aerobic and anaerobic environments, faster than other gasoline constituents and oxygenates (Chapelle, 1993; Malcolm Pirnie, Inc., 1998). Ethanol (first-order) degradation rate coefficients have been measured in an aquifer microcosm study (Table 3-2) (Corseuil *et al.*, 1998). Only large concentrations (more than 100,000 mg/L) of alcohols are not biodegradable due to their toxicity to most microorganisms (Brusseau, 1993; Hunt *et al*., 1997a). Such high concentrations could be encountered near the source of neat ethanol releases. However, because the maximum allowable ethanol content in gasoline is 10% by volume in the United States, such high concentrations are unlikely to be encountered at sites contaminated with ethanol-gasoline blends (except near the fuel/water interfaces).

Ethanol concentrations should become exponentially more dilute as the distance from the source increases, but near the source they may inhibit microbial activity. Thus, indigenous microbes located a sufficient distance beyond the source should degrade alcohol plumes. The only fuel-alcohol field-scale studies performed have been with methanol, not ethanol. However, because methanol has properties similar to ethanol, these findings are relevant to biodegradation of ethanol. One field study investigated methanol biodegradation in soils from three different sites under various redox conditions. Methanol concentrations of 1000 mg/L were removed in all soils in less than one year, at pH values of 4.5 to 7.8 and at temperatures of 10° to 11°C (Butler *et al*., 1992). A similar study investigated the persistence and fate of M85 fuel (that is, fuel containing 85% methanol, 15% gasoline) in a shallow, sandy aquifer (Barker *et al*., 1998). All of the methanol (approximately 2400 L resulting in an initial concentration of 7000 mg/L) was biodegraded below 1 mg/L in 476 days, yielding a methanol half-life of about 40 days. Because of the similar properties of methanol and ethanol, the biodegradation of ethanol is also expected to be relatively fast.

While there are no known field-scale studies of the fate and transport of ethanol, a few laboratory studies have focused on ethanol biodegradation. Suflita and Mormile (1993) measured acclimation periods (periods before degradation proceeded) and zero-order biodegradation rates of ethanol and other fuel oxygenates in anaerobic aquifer slurries. For an initial ethanol concentrations of 50 mg/L, they observed an acclimation period of 25 to 30 days and an anaerobic biodegradation rate of 17.9 ± 0.6 mg/L/day. When compared to ethanol, the observed acclimation period for methanol was shorter (five days), but its biodegradation rate was slower (7.4 ± 0.7 mg/L/day). In a subsequent study, these authors determined that their initial results could be extrapolated to other redox conditions. They showed that various short-chain alcohols were easily degraded in different sediments under a range of redox conditions (Mormile *et al.*, 1994).

Corseuil *et al*. (1998) investigated biodegradation of ethanol under various redox conditions in aquifer microcosms at 20-35ºC. Table 3-2 summarizes the degradation rates of ethanol (80 to 100 mg/L) in this study. Lower microbial concentrations, colder temperatures, and mass-transfer limitations would likely result in longer degradation times *in situ* than those depicted in

Table 3-3. Nevertheless, it is expected that regardless of the available electron acceptors, ethanol will undergo rapid biodegradation in the subsurface under typical pH, temperature, and nutrient conditions.

3.3.3.3. Surface Water

In surface water bodies, the dominant process responsible for the removal of ethanol is also expected to be biodegradation (Malcolm Pirnie, Inc., 1998). Under aerobic conditions, the reported half-lives of ethanol in surface waters are short. Half-lives span 6.5 to 26 hours for ethanol (Howard, 1991). In moving water bodies, reaeration from the atmosphere generally ensures that oxygen will be available to support aerobic degradation processes; and oxygen is not expected as much of a limiting factor as in groundwater systems. Anaerobic biodegradation in oxygen-limited environments, such as the bottom layers of stratified lakes, is also expected to proceed at rapid rates. Reported half-lives for ethanol biodegradation under anaerobic conditions range from 1 to 4.3 days (Howard, 1991). The nutrient supply in rivers and lakes is generally not expected to restrict the rate of biochemical transformations because the required nutrient supplies are constantly recharged by rainfall (Alexander, 1994).

3.4. Potential Effects of Ethanol on BTEX Biodegradation

3.4.1. Direct (Intracellular) Effects

3.4.1.1. Enzyme Induction and Repression

Often, target pollutants are degraded by inducible enzymes whose expression can be repressed when easily degradable substrates are present at high concentrations (Duetz *et al.*, 1994; Monod, 1949). However, only indirect evidence has been presented in the literature about the potential effects of ethanol on the expression of enzymes involved in BTEX degradation.

Hunt *et al.* (1997a) reported that ethanol at 20 mg/L was preferentially degraded under aerobic conditions over benzene, presumably due to repression of the synthesis of enzymes needed to degrade benzene. This retarded the onset of benzene degradation. Additional microcosm studies also suggested that the preferential utilization of ethanol might increase the lag time before *in situ* BTEX biodegradation begins (Corseuil *et al*., 1998). Specifically, little or no BTEX degradation occurred in aerobic, denitrifying, iron-reducing, sulfate-reducing, and methanogenic microcosms while ethanol was present (Corseuil *et al*., 1998). Therefore, ethanol may prevent the bacteria subpopulation capable of degrading BTEX from fully expressing its catabolic potential, which would hinder BTEX degradation.

Numerous studies show that carbon-limiting conditions are conducive to simultaneous utilization of multiple substrates (for review, see Egli, 1995). This suggests that simultaneous ethanol and BTEX degradation is likely to occur when these compounds are present at low concentrations (for example, in aquifers with low levels of contamination). Interestingly, a pure culture of *Pseudomonas putida* F1 was reported to simultaneously degrade ethanol and toluene with no apparent inhibitory effect up to 500 mg/L of ethanol (Hunt *et al*., 1997a). This suggests that while high ethanol concentrations are likely to exert a diauxic effect that would inhibit *in* *situ* BTEX degradation, the metabolic diversity of microorganisms precludes generalizations about the concentration of ethanol that triggers enzyme repression. Such effects are probably species specific.

3.4.1.2. Stimulation of Microbial Growth

Ethanol represents a carbon and energy source that is likely to stimulate the growth of a variety of microbial populations, including species that can degrade BTEX compounds. A proliferation of BTEX degraders would be conducive to faster degradation rates although this positive effect is likely to be offset by the preferential degradation of ethanol and the associated depletion of electron acceptors discussed later in this chapter.

As discussed earlier, ethanol can be degraded by constitutive enzymes associated with central metabolic pathways, and microorganisms that can degrade simple alcohols are more common in nature than microorganisms that degrade BTEX compounds. Therefore, many species that cannot degrade BTEX are likely to proliferate when ethanol is present. In fact, microbial growth is generally faster on ethanol than on BTEX because of more favorable thermodynamics. Using a thermodynamic model by McCarty (1969), the predicted maximum specific growth rate on ethanol is 45% greater than the predicted maximum specific growth rate with benzene (Hunt, 1999). Nevertheless, BTEX degraders are also likely to grow faster on ethanol than on BTEX under a given set of conditions, and the effect of ethanol on the relative abundance of BTEX degraders has not been investigated.

Corseuil *et al*. (1998) pointed out that there may be some exceptions to the detrimental effect of ethanol on BTEX degradation and hypothesized that these exceptions may be related to ethanol-induced microbial population shifts. Specifically, although ethanol was preferentially degraded under all electron-acceptor conditions tested, ethanol enhanced toluene degradation in all three sulfate-reducing microcosms used in this study. The reason for this enhancement was unclear, but the possibility that this enhancement was due to an incidental growth of toluene degraders during ethanol degradation could not be ruled out. This untested hypothesis does not imply that ethanol would select for BTEX degraders, which is highly unlikely. Rather, the concentration of some BTEX degraders could increase after growth on ethanol although their fraction of the total heterotrophic consortium would likely decrease.

In summary, little is known about the effect of ethanol on microbial population shifts and the resulting catabolic diversity. Considering that the efficiency of bioremediation depends, in part, on the presence and expression of appropriate biodegradative capacities, studying the microbial ecology of aquifers contaminated with gasoline-alcohol mixtures might be a fruitful avenue of research.

3.4.1.3. Toxicity of Ethanol

The toxicity of alcohols to microorganisms has received considerable attention in the literature although only a few studies have evaluated the effect of ethanol on subsurface microbial populations. Hunt *et al*. (1997a) reported that ethanol concentrations in microcosm experiments higher than 40,000 mg/L (4% weight/weight [w/w]) were toxic to the microorganisms, as shown by complete lack of oxygen consumption. Other studies have found that some soil microbial activity can occur at 100,000-mg/L (10% w/w) ethanol, but not at 200,000 mg/L (21% w/w) (21% because at high concentrations, the conversion factor is significantly different than from 10,000 because of the density differences between ethanol and water) (Araujo *et al*., 1998).

Ingram and Buttke (1984) conducted a thorough literature review on the effects of alcohol on microorganisms. Disruption of the cellular permeability barrier is thought to be the basis of bacterial killing by high concentrations of alcohols (Brusseau, 1993; Ingram and Buttke, 1984; Harold, 1970). Ethanol concentrations above 100,000 mg/L result in the immediate inactivation of most vegetative organisms although spore-forming organisms are more resistant (Dagley *et al*., 1950; Hugo, 1967). Most bacteria exhibit a dose-dependent inhibition of growth over the range of 10,000 to 100,000 mg/L; and very few species can grow at ethanol concentrations higher than 100,000 mg/L (Ingram and Buttke, 1984).

The toxicity of alcohols is related to their chain length and hydrophobicity (Harold, 1970; Hugo, 1967). Longer-chain alcohols, such as octanol, up to a chain length of around 10 carbon atoms, are much more potent inhibitors than are the shorter-chain alcohols, such as ethanol. This is attributed to the fact that alcohols have two basic functional groups, namely, a hydroxyl function and a hydrocarbon tail. Ethanol is very polar and partitions poorly into the hydrophobic cell membrane (Figure 3-8). In contrast, the longer (hydrophobic) hydrocarbon tail of octanol favors its concentration within the membrane, which increases its toxicity. Thus, relatively high ethanol concentrations are required to cause lethal effects on biological systems (Ingram and Buttke, 1984).

Ethanol can exert a variety of biophysical effects on microorganisms. The basic actions of alcohols on prokaryotic organisms appear to be dominated by the physicochemical properties of alcohols rather than involving specific receptors. All hydrophobic and electrostatic interactions in the cytosolic and envelope components of cells can potentially be affected. These include cell membranes, conformations of enzymes and macromolecules, activity coefficients of metabolites, ionization potentials, pKa values of functional groups, and intracellular pH (Franks and Ives, 1966; Ingram and Buttke, 1984; Jukes and Schmidt, 1934; Yaacobi and Ben-Naim, 1974). High ethanol concentrations can also inhibit the synthesis of various organelles, including the cell wall (Blumberg and Strominger, 1974), RNA (Mitchell and Lucas-Leonard, 1980), DNA (Osztovics *et al*., 1981), and proteins (Haseltine *et al*., 1972). Ethanol itself is not mutagenic. However, acetaldehyde, which is a metabolite of aerobic ethanol degradation, increases cell mutation rates (Igali and Gazsó, 1980).

Ethanol has also been reported to adversely affect the activity of some critical enzymes. Addition of low ethanol at 3350 mg/L did not cause a significant inhibition of the Na^+, K^+-dependent ATPase, NADH oxidase or D-lactate oxidase (Eaton *et al*., 1982). However, 8500-mg/L ethanol inhibited these enzymes, with ATPase being the most resistant enzyme examined (Eaton *et al*., 1982). In contrast, succinate dehydrogenase, part of the Krebs cycle, is more sensitive, showing 20% inhibition with 3350-mg/L ethanol and 50% inhibition with 8500-mg/L ethanol. Transport systems are uniformly more sensitive to inhibition by ethanol. The lactose permease system exhibits a dose-dependent inhibition with increasing concentrations of ethanol (Ingram *et al*., 1980). Uptake of glutamate, proline, leucine, and the lactose permease was reduced by 10–30% with 3350-mg/L (0.335% w/w) ethanol and by 60–80% with 8500-mg/L (0.85% w/w) ethanol (Eaton *et al*., 1982). However, inhibition of both the membrane-bound enzymes and transport systems was substantially relieved after alcohol was removed by washing.

Bringmann and Kuhn (1980) developed a cell multiplication test to characterize the inhibitory effect of common water pollutants. This turbidimetric test estimates the concentration at which the inhibitory action of a pollutant starts. The toxicity threshold is taken as the pollutant concentration that yields a biomass concentration that is at least 3% below the mean value of extinction for nontoxic dilutions of the same test culture. This test was applied to the model organism *P. putida,* which is a common BTEX degrader in the subsurface environment**.** Table 3-4 compares the toxicity thresholds for several pollutants that could be a involved in a gasoline spill. Based on this study, it can be concluded that indigenous microorganisms are more resistant to high ethanol concentrations than to high BTEX and other fuel constituent concentrations.

3.4.2. Indirect (Environmental) Effects

3.4.2.1. Depletion of Nutrients and Electron Acceptors

Ethanol in groundwater constitutes a significant biochemical oxygen demand compared to that exerted by other soluble components of gasoline, and it is likely to accelerate the depletion of dissolved oxygen (Corseuil *et al*., 1998). This would decrease the extent of aerobic BTEX degradation in oxygen-limited aquifers. Such an effect is particularly important for the fate of benzene, which is the most toxic of the BTEX and degrades slowly under anaerobic conditions or not at all (Alvarez and Vogel, 1995; Anderson *et al*., 1998; Weiner and Lovley, 1998a).

Anaerobic processes are believed to play a major role in containing and removing petroleum-product releases at sites undergoing natural attenuation, where engineered oxygen addition is uncommon (Rifai *et al*., 1995; Corseuil *et al*., 1998). Because ethanol can be degraded under all common electron-acceptor conditions, it can also contribute to the consumption of dissolved electron acceptors needed for anaerobic BTEX biodegradation (for example, ferric iron and sulfate). Therefore, depending on aquifer chemistry and the rate of natural replenishment of electron acceptors, ethanol could impede natural attenuation of BTEX compounds by contributing to the depletion of the electron-acceptor pool.

The extent to which ethanol is likely to cause the depletion of nutrients and electron acceptors has not been evaluated at the field scale. Nevertheless, a relevant field study was conducted with methanol, which is likely to cause similar effects as ethanol. Barker *et al*. (1992) conducted experiments involving controlled releases of BTEX and methanol mixtures at the Borden site in Canada. At the end of the 476-day experiment, they observed that a greater mass of BTEX remained in the plume from the gasoline with methanol than in the plume from just gasoline. They attributed this effect to oxygen removal by methanol biodegradation as well as to microbial inhibition due to high methanol concentrations.

3.4.2.2. Accumulation of Volatile Fatty Acids

As discussed previously, the degradation of ethanol by mixed anaerobic cultures can result in the production of VFAs, such as acetic, propionic, and butyric acid. In the absence of adequate interspecies hydrogen gas transfer, such VFAs can accumulate and decrease the pH (Lasko *et al*., 1997; Speece, 1983). This could inhibit some microbial populations and would be particularly detrimental to methanogens, which are usually the most sensitive group of anaerobic consortia. Methanogens are generally inhibited when the pH decreases below 6 (McCarty, 1964). Because methanogens often mediate the final pollutant-stabilization step in the absence of nitrate- and sulfate-based respiration (Section 3.3.1.2.1), an inhibition of methanogens could adversely affect anaerobic BTEX mineralization.

It should be pointed out that methanogens are not significantly inhibited by VFAs in well-buffered systems. For example, methanogens are often exposed up to 2000 mg/L VFAs in anaerobic digesters (McCarty, 1964). Other bacteria, however, might be inhibited by high VFA concentrations, even if the pH does not decrease significantly. For example, protein production by *E. coli* at pH 7 is inhibited by acetate at about 2400 mg/L, especially in the case of expression of recombinant proteins, and growth is retarded at 6000 mg/L total acetate (Lasko *et al.*, 1997; Sun *et al.*, 1993).

It is unknown whether VFAs would accumulate in aquifers contaminated with alcohol-amended gasoline at sufficiently high concentrations to significantly decrease the pH and inhibit BTEX degradation. Such effects are likely to be system specific due to variability in buffering and dilution capacity among contaminated sites. It should be kept in mind, however, that VFAs are easily degraded and should not accumulate at high concentrations when alternative electron acceptors, such as nitrate, sulfate, and ferric iron, are present.

3.4.2.3. Bioavailability

BTEX bioavailability is rarely a limiting factor. However, ethanol might affect the availability of critical nutrients and co-substrates needed for BTEX bioremediation. As discussed in Section 3.4.1.3, ethanol exerts a significant biochemical demand for nutrients and electron acceptors. In addition, BTEX migration is often retarded by sorption to aquifer solids. If significant retardation is occurring, dissolved oxygen and other nutrients and electron acceptors traveling at the groundwater velocity can sweep over the contaminant plume from the upgradient margin. This can replenish nutrients and electron acceptors needed for *in situ* BTEX biodegradation. In theory, ethanol could decrease the extent to which BTEX compounds are retarded by sorption. Indeed, evidence suggests that ethanol can affect the sorptive properties of soil organic matter (Brusseau *et al.*, 1991; Kimble and Chin, 1994). A decrease in BTEX retardation would hinder the ability of essential nutrients and electron acceptors transported by bulk flow to catch up with the migrating BTEX compounds. In addition, adsorption of a contaminant to the aquifer matrix increases dilution of the dissolved contaminant plume, which is a process that might also be affected.

3.4.2.4. Impact of Microbial Processes on Aquifer Permeability

Depending on aquifer chemistry and redox conditions, ethanol could stimulate microbial processes that affect the hydrodynamic properties of the aquifer. For example, fuel-grade ethanol would stimulate microbial growth. Therefore, the formation of cell aggregates and biofilms that reduce the available pore space is a potential clogging mechanism of concern (Taylor and Jaffe, 1990; Vandevivere and Baveye, 1992). In theory, microorganisms could also affect aquifer permeability by contributing to mineral dissolution (for example, $CaCO_3$) or precipitation (for example, FeS). A combination of excessive microbial growth and mineral precipitation could result in a significant reduction in porosity and permeability over a longer period.

An important mechanism by which microorganisms could reduce the effective porosity is the production of gas bubbles that increase the pressure and restrict water flow (Soares *et al*., 1988, 1989, and 1991). Controlled experiments that address the significance and extent of such phenomena for ethanol contamination are lacking. Therefore, their potential impact is discussed below from a theoretical point of view.

The overall stoichiometry of methanogenesis from ethanol is given by:

$$CH_3CH_2OH \rightarrow 1.5\ CH_4 + 0.5\ CO_2$$

Thus,

$$\text{Potential methane production} = 1.5 \times \frac{16\text{g}-\text{CH}_4\text{/mol}}{46\text{g}-\text{ethanol/mol}} = 0.5217\,\frac{\text{g}-\text{CH}_4}{\text{g}-\text{ethanol}}$$

Based on the ideal gas law, and assuming a typical groundwater temperature of 15°C, the volume of methane produced at 1 atm from 1 gram of ethanol is

$$0.5217\,\frac{\text{g}-\text{CH}_4}{\text{g}-\text{ethanol}} \times \frac{1\text{ mol CH}_4}{16\text{ gram}} \times \frac{22.4\ \text{liters}}{\text{mole (at STP)}} \times \frac{273+15\text{K}}{273\text{K}} = 0.77\,\frac{\text{liters}\ \ \text{CH}_4}{\text{gram}-\text{ethanol}}$$

As discussed previously, a 1000-mg/L ethanol concentration is generally not toxic to methanogenic consortia. This concentration could produce up to 0.77 L of methane within a 1-L pore volume. This is likely to increase the pressure and could result in some bubble formation that could restrict groundwater flow. Such a reduction in aquifer permeability could also hinder the replenishment of nutrients and electron acceptors by natural or engineered processes into the contaminated zone. Whether sufficient methane would accumulate to create an explosion hazard is unknown.

3.5. References

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Figures

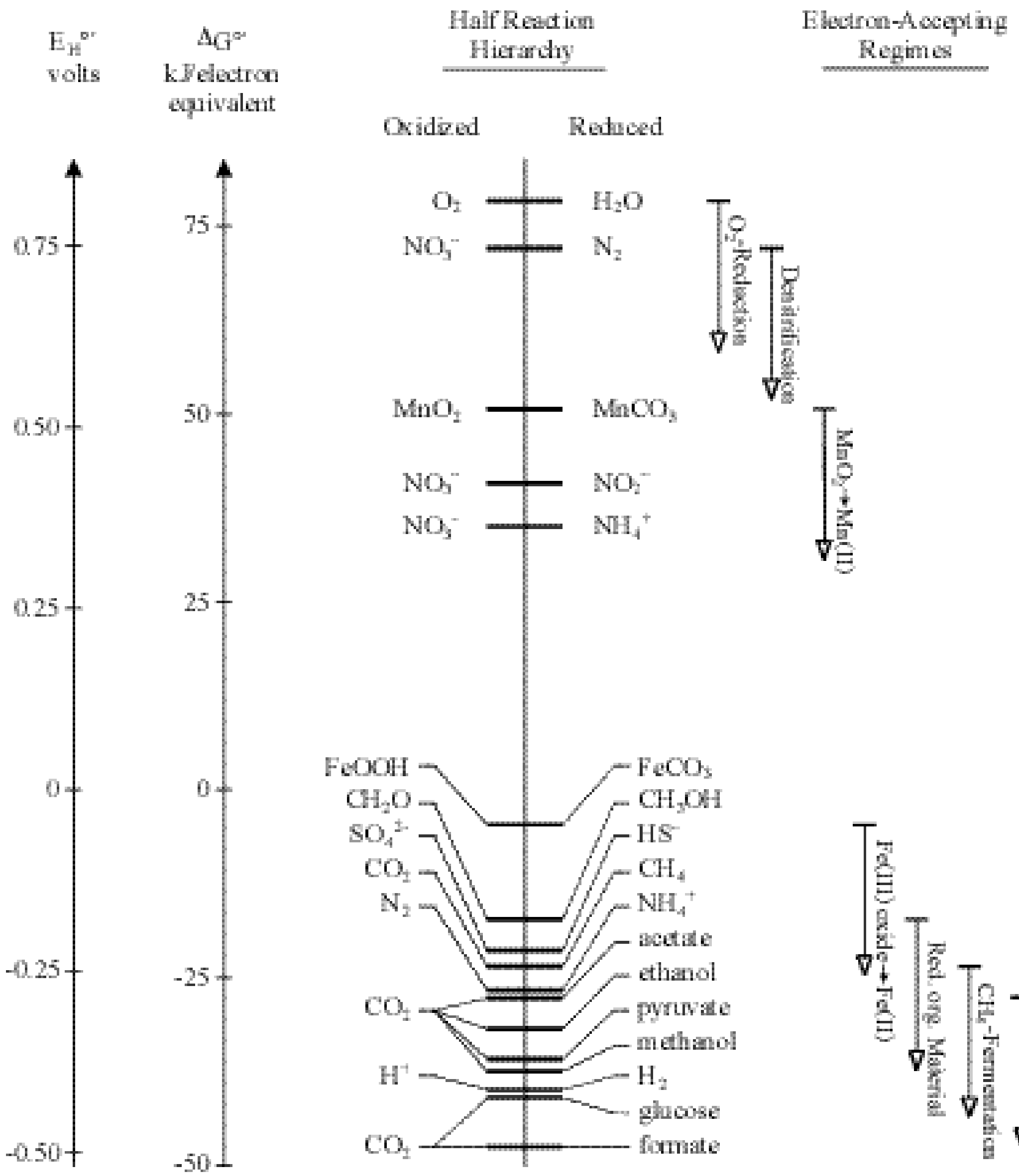

Figure 3-1. Free energy diagram for common electron acceptors and donors. The hierarchy of electron acceptors provides a simple means to integrate thermodynamics, microbiology, and physiology of oxidation-reduction reactions. $E_H^{o'}$ is the equilibrium redox potential and $\Delta G^{o'}$ is the half-reaction free energy. These values are for unit activities of oxidant and reductant in water with a pH of 7.0 (adapted from Zehnder and Stumm, 1988).

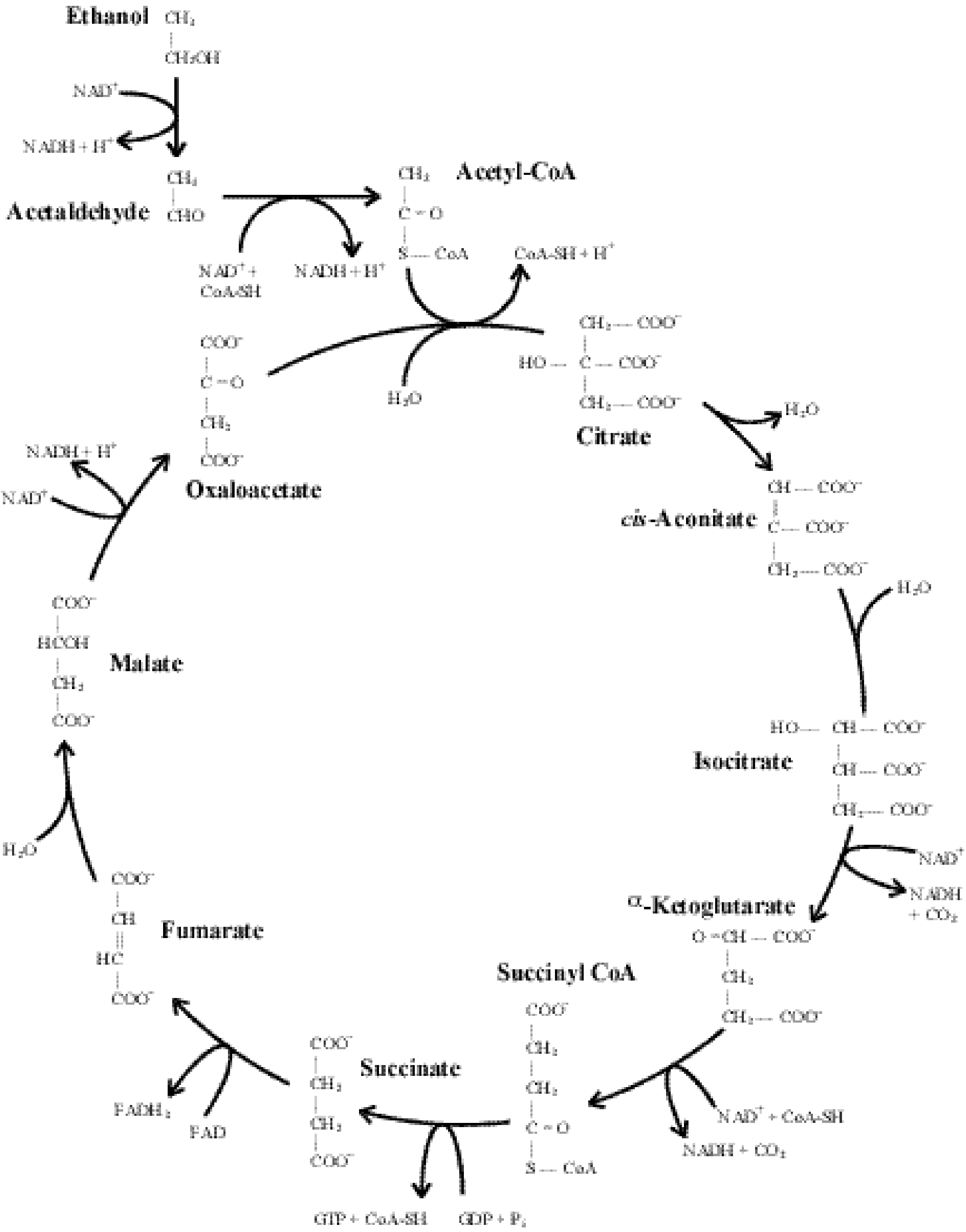

Figure 3-2. Ethanol degradation through Krebs cycle (adapted from Stryer, 1988).

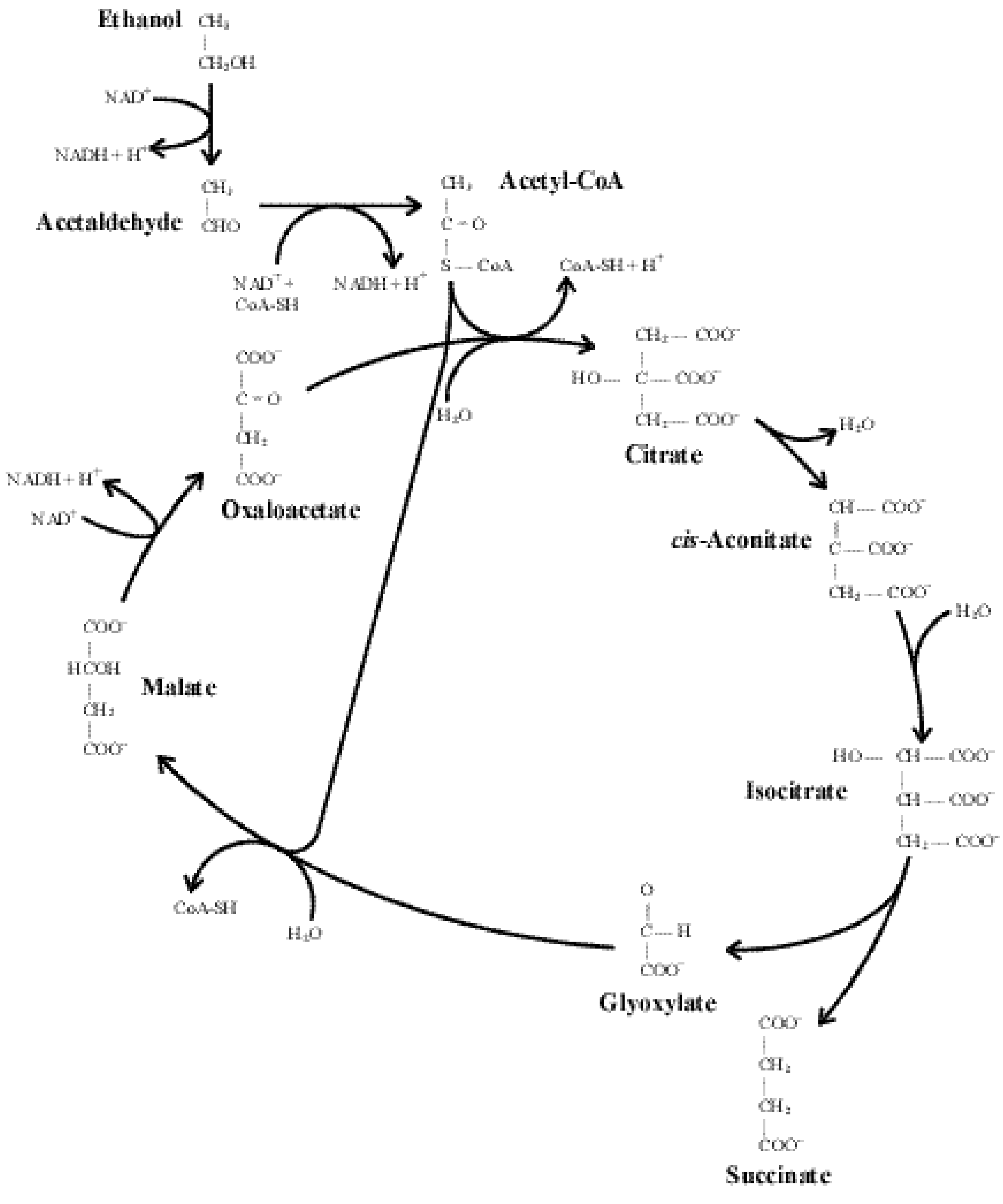

Figure 3-3. Ethanol degradation by the glyoxylate shunt (adapted from Stryer, 1988).

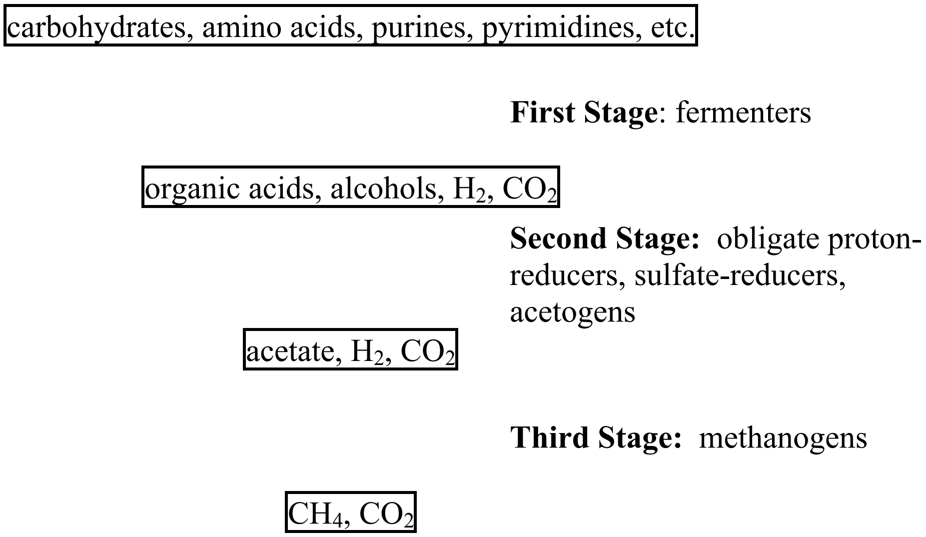

Figure 3-4. The anaerobic food chain (modified from White, 1995).

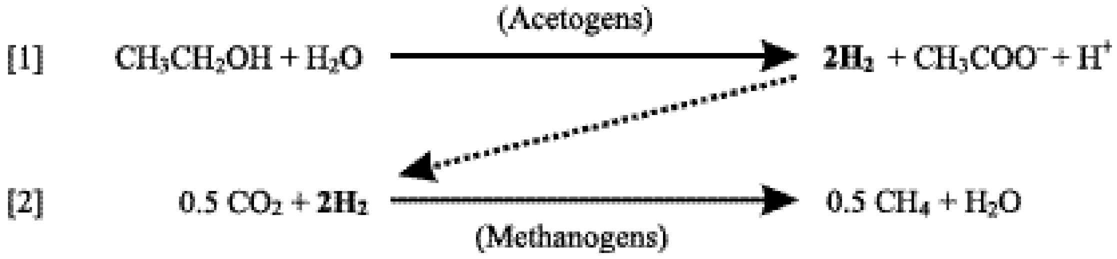

Figure 3-5. Interspecies hydrogen transfer. Anaerobic oxidation of ethanol to acetate [1] is not thermodynamically feasible under standard conditions ($\Delta G'_0 = +9.6$ kJ). This reaction can proceed only if the hydrogen (H_2) produced by acetogens and other fermenters is removed (law of mass action). The removal of H_2 by hydrogenotrophic methanogens [2] or sulfate reducers enhances the thermodynamic feasibility of acetogenesis and the subsequent mineralization of acetate by acetoclastic methanogens and (Type II) sulfate reducers. Thus, interspecies H_2 transfer prevents the accumulation of fermentation products and enhances anaerobic mineralization.

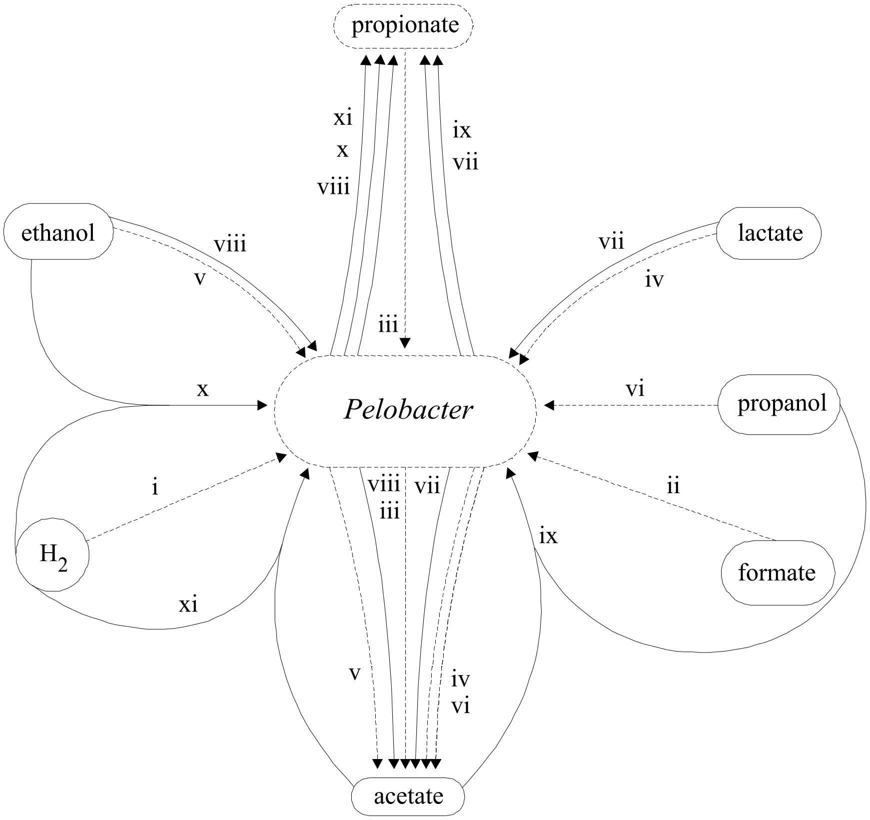

Figure 3-6. Propionate formation during ethanol fermentation by *P. propionicus* (Adapted from Laanbroek *et al.*, 1982). *Broken lines*: conversions in the presence of sulfate; *solid lines*: conversions in the absence of sulfate. The numbers correspond with the following reactions:

i. $H_2 + \frac{1}{4}H^+ + \frac{1}{4}SO_4^{2-} \rightarrow \frac{1}{4}HS^- + H_2O$

ii. $\text{formate}^- + \frac{1}{4}H^+ + \frac{1}{4}SO_4^{2-} \rightarrow HCO_3^- + \frac{1}{4}HS^-$

iii. $\text{proprionate}^- + \frac{3}{4}SO_4^{2-} \rightarrow \text{acetate}^- + HCO_3^- + \frac{3}{4}HS^- + \frac{1}{4}H^+$

iv. $\text{lactate}^- + \frac{1}{2}SO_4^{2-} \rightarrow \text{acetate}^- + HCO_3^- + \frac{1}{2}HS^- + \frac{1}{2}H^+$

v. $\text{ethanol} + \frac{1}{2}SO_4^{2-} \rightarrow \text{acetate}^- + \frac{1}{2}HS^- + \frac{1}{2}H^+ + H_2O$

vi. $\text{1-propanol} + \frac{5}{4}SO_4^{2-} \rightarrow \text{acetate}^- + HCO_3^- + \frac{5}{4}HS^- + \frac{3}{4}H^+ + H_2O$

vii. $\text{lactate}^- \rightarrow \frac{1}{3}\text{acetate}^- + \frac{2}{3}\text{proprionate}^- + \frac{1}{3}HCO_3^- + \frac{1}{3}H^+$

viii. $\text{ethanol} + \frac{2}{3}HCO_3^- \rightarrow \frac{1}{3}\text{acetate}^- + \frac{2}{3}\text{proprionate}^- + \frac{1}{3}H^+ + H_2O$

ix. $\text{1-propanol} + \frac{2}{3}\text{acetate}^- + \frac{2}{3}HCO_3^- \rightarrow \frac{5}{3}\text{proprionate}^- + \frac{1}{3}H^+ + H_2O$

x. $\text{ethanol} + HCO_3^- + H_2 \rightarrow \text{proprionate}^- + 2H_2O$

xi. $\text{acetate}^- + HCO_3^- + H^+ + 3H_2 \rightarrow \text{proprionate}^- + 3H_2O$

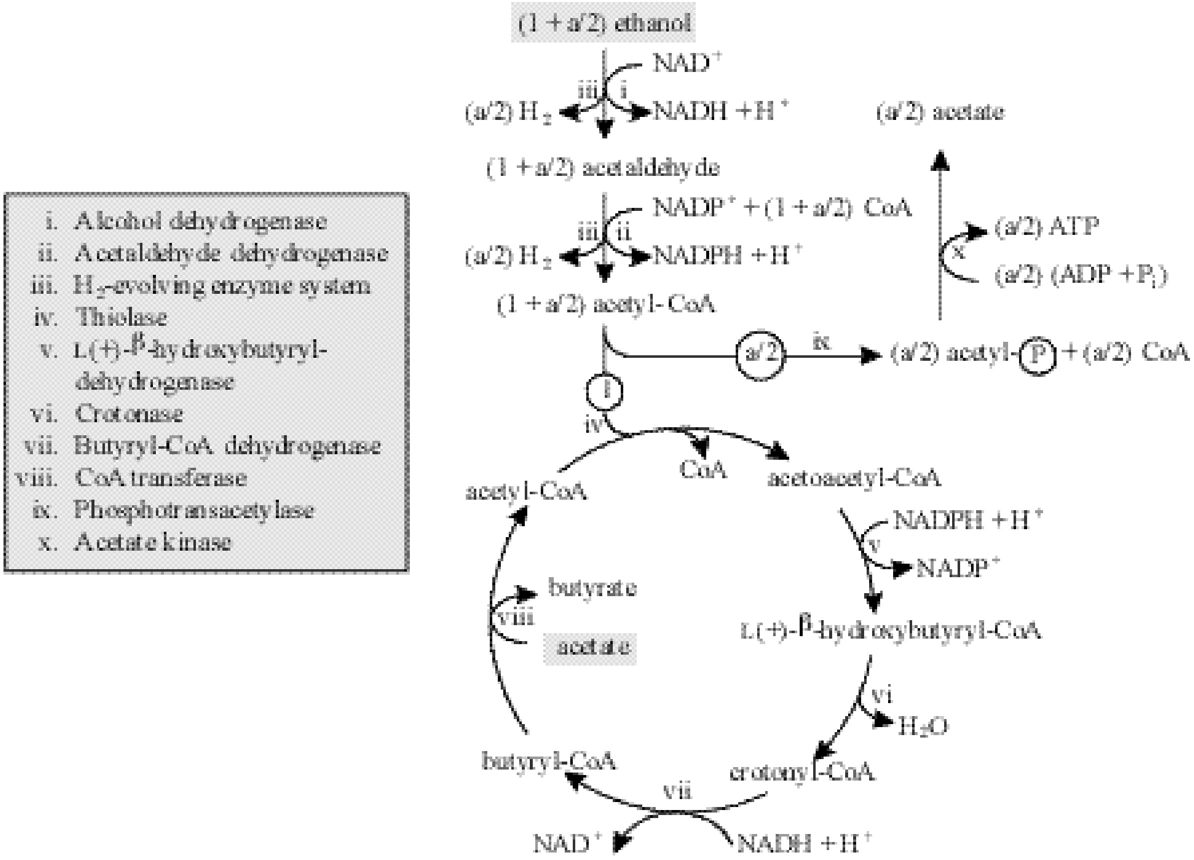

Figure 3-7. The ethanol-acetate fermentation of *C. kluyveri* (from Gottschalk, 1986).

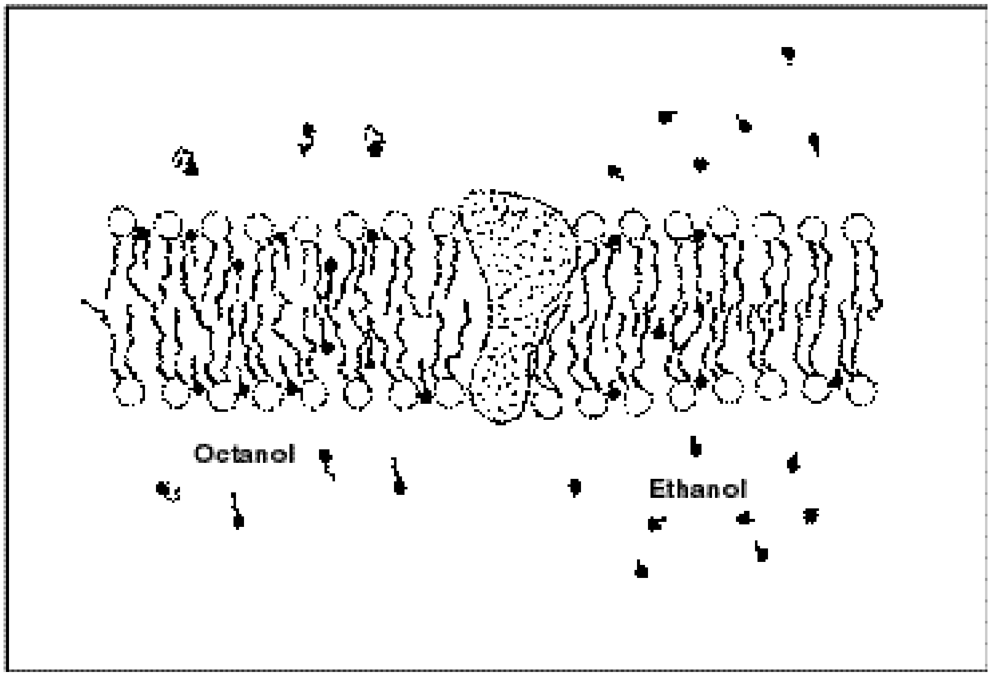

Figure 3-8. Model showing interactions of octanol and ethanol with a cell membrane (adapted from Widdel, 1986). Octanol is much more hydrophobic than ethanol and will partition into the membrane more favorably.

Tables

Table 3-1. Metabolites and end products of ethanol biodegradation.

Aerobic	Anaerobic
acetaldehyde	*acetaldehyde*
acetate	*acetate*
acetyl-CoA	*butyric acid*
carbon dioxide (CO_2)	*propionic acid*
	hydrogen gas
	n-propanol
	acetone
	carbon dioxide (CO_2)
	methane

Table 3-2. First-order rate coefficients (λ) for anaerobic and aerobic degradation of ethanol by aquifer microorganisms.[a]

Electron acceptor	λ (day^{-1})	Half-life (days)
O_2	0.23–0.35	2-3
NO_3^-	0.53	1.3
Fe^{3+}	0.17	4
SO_4^{-2}	0.1	7
CO_2	0.12	6

[a] *Estimated from laboratory experiments by Corseuil et al., 1998).*

Table 3-3. Toxicity thresholds for a *Pseudomonas putida*.[a]

Compound	Concentration (mg/L)
ethanol	6,500
methanol	6,600
1-propanol	2,700
2-propanol	1,050
1-butanol	650
2-butanol	500
tertiary amyl alcohol	410
methyl ethyl ketone	1,150
acetic acid	2,850
n-butyric acid	875
benzene	92
toluene	29
ethylbenzene	12

[a] *Source: Bringmann and Kuhn, 1980.*

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Volume 4: Potential Ground and Surface Water Impacts

Chapter 4: Screening Model Evaluation of the Effects of Ethanol on Benzene Plume Lengths

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Table of Contents

List of Figures

List of Tables

Appendices

4. Screening Model Evaluation of the Effects of Ethanol on Benzene Plume Lengths

4.1. Introduction

The possibility of subsurface releases of gasoline from leaking underground fuel tanks (LUFTs) and piping, along with potential surface spills during tank filling and other activities, creates scenarios for hydrocarbon plume formation in groundwater downgradient from the source (See Rice *et al*., 1999, Vol 4, Chapter 1 of this report). Fuel hydrocarbon plumes that are *not* characterized by the presence of ethanol have been studied extensively (for example, Rice *et al.*, 1995; Mace *et al*., 1997). However, the potential role of ethanol in influencing the behavior of benzene, toluene, ethyl benzene, and xylene (BTEX) component plumes needs to be addressed because:

- A binary water-ethanol mixture can produce a cosolvency effect that serves to enhance the solubility of nonpolar organic compounds, such as BTEX constituents (see Powers and Heermann, 1999, Vol 4, Chapter 2 of this report), and
- The rapid biotransformation of ethanol can reduce the biotransformation rates of BTEX constituents, most notably benzene, by reducing the availability of electron-acceptor species (for example, dissolved oxygen and nitrate) that participate in biogeochemical oxidation reactions (see Alvarez and Hunt, 1999, Vol 4, Chapter 3 of this report).

The result of both effects, in theory, may be longer BTEX plume lengths, principally those of benzene, the constituent of greatest environmental concern.

The most direct means of measuring the effects of ethanol on benzene plume lengths is to measure benzene concentrations at LUFT sites where ethanol has been used as a gasoline additive and compare those, using appropriate statistical methods, to benzene concentrations from LUFT sites where ethanol was not in use. Unfortunately, aside from anecdotal accounts from experimental studies (for example, Hubbard *et al.,* 1994), a sufficient database of plumes from gasohol release sites does not yet exist for such an analysis.

In the absence of field data, we can employ screening-level mathematical modeling to explore plausible plume behavior scenarios. In this present evaluation, we have chosen to generate synthetic populations of benzene plumes, both with and without ethanol as a cosolute, using a physically-based, semi-analytical model with distributions of model input parameters that represent the ranges of conditions encountered in shallow aquifer settings. Model output consisted of concentrations of benzene, ethanol, and the implied biochemical oxygen demand (BOD) induced by biotransformation of ethanol for random combinations of input variables.

4.2. Methodology

4.2.1. Overview

The plume model is based upon the solution presented by Baetsle (1969) for an instantaneous, solute point-source in an infinite, homogeneous, three-dimensional (3-D) domain with uniform groundwater flow, dispersivity tensor, and biotransformation rate (modeled by first-order kinetics). Numerical integration of the source term in both space and time allows for the simulation of a finite-sized source (for example, a lens of light nonaqueous phase liquid (LNAPL) floating on the water table) and a finite release with respect to time (that is, a continuous source as opposed to an instantaneous one). Although such a semi-analytical solution is highly idealized (neglecting, for example, heterogeneities in the flow domain), it does provide a useful average model of plume behavior that can be used, in conjunction with a Monte Carlo simulation strategy, to produce probability distributions of concentrations as well as a means for assessing model sensitivity to input parameters.

One reason for utilizing probabilistic approaches in evaluating the mathematical transport model stems from the lack of sufficient field data on site-specific features of plume behavior. Probabilistic modeling of contaminant transport involves employing user-specified probability distributions of physical and chemical model variables, based on available data, to produce forecasts through multiple Monte Carlo realizations. Monte Carlo analyses are routinely used in engineering probability forecasting applications (for example, Ang and Tang [1984]). Woodbury *et al.* (1995) applied Monte Carlo analyses to practical groundwater engineering problems. In this report, the Monte Carlo approach permits uncertainties in hydrogeological data (the groundwater velocity, for example), the nature of the source, and chemical data (biotransformation rates, for example) to be translated into uncertainties regarding contaminant concentrations as a function of time and space. Parameter sensitivities can be evaluated by performing regression analyses of model output values against those of input variables.

The conceptual model for the gasohol release is a source, such as a LUFT, continually discharging a small flux of LNAPL (less than 3 gal/day), which spreads along the water table, maintaining a square footprint and a fixed thickness-to-length ratio (Figure 4-1). This corresponds to a “slow drip” scenario representative of a chronic, undetected LUFT condition and is the most likely release scenario to be encountered. The “slow drip” release scenario is in contrast to a catastrophic release scenario, which would include different source dynamics but which would, presumably, be subject to an immediate detection and remediation response.

Ethanol is assumed to be present at either a 10% volume fraction in the gasohol (for half of the realizations) or else is absent. Because of its high affinity for water, the ethanol, when present, is assumed to leach completely and instantaneously across a specified portion of the LNAPL/groundwater interface into the water (that is, all of the ethanol contained within the source flux is assumed to be injected into the aquifer along a specified portion of the interface). The ethanol migrates through the aquifer, carried along by advection as well as longitudinal, transverse, and vertical dispersion. Benzene enters the aquifer by diffusion and vertical dispersion across the LNAPL/groundwater interface, with its limited solubility, in principle, a function of the ethanol concentration at the interface.

In theory, biotransformation of the ethanol produces an anaerobic zone that, in turn, will presumably affect the biotransformation rate of benzene on a local scale (Alvarez and Hunt, 1999, Vol. 4, Chapter 3 of this report). However, there is a paucity of biotransformation rates for benzene under the most anaerobic conditions (that is, sulfate-reducing and methanogenic). Moreover, although the presence of ethanol may pose significant issues, such as competitive substrate utilization and shifts in the nature of the local microbial population, there is an absence of biotransformation rate data that can be readily adapted for modeling purposes. Given the current state of knowledge, it is problematic to justify or construct a mathematical model (analytical or numerical) that specifically addresses spatial dependencies of the benzene biotransformation rate on the extent of the anaerobic shadow. At the screening level addressed by our model, therefore, we have chosen to use a global average biotransformation rate for benzene—a rate that is inversely correlated with the BOD signature in the vicinity of the source area. In other words, we assumed that, in the lognormal distribution of biotransformation rates, the slowest globally averaged rates are associated with a high BOD near the source area; whereas the highest rates occur in realizations where the ethanol-induced BOD values are comparatively low. This is a very conservative assumption because it neglects the replenishment of electron acceptors from other sources, such as diffusion of atmospheric oxygen from the vadose zone across the water table and from dissolution of ferrous and manganese-bearing oxyhydroxide minerals in the sediments. The assumption is also additionally conservative in that ethanol biotransformation effects are the *only* presumed influence on benzene biotransformation rates, thus leading to a very high inverse correlation between benzene plume lengths and BOD in the source area.

The present study uses a conservative assumption and neglects retardation as a result of adsorption. This is because (1) the Baetsle (1969) model does not directly address retardation, and (2) the superposition calculations used to quantify BOD are not valid when retardation of the substrate (ethanol) is significant. Because the organic carbon partitioning coefficients of benzene and ethanol are low, retardation resulting from adsorption would not be expected to play a large role in influencing the fate of the plumes in comparison to the influence of biotransformations. Furthermore, because the purpose of our screening model exercise is to compare benzene plume lengths between ethanol and no-ethanol scenarios, and because ethanol is not likely to exert significant effects on benzene adsorption away from the source area, the omission of retardation is not likely to exert a significant effect on the findings.

As an additional analysis, prior to calculating the Monte Carlo realizations, a sensitivity analysis was performed to assess whether the mass transfer of ethanol into groundwater would best be modeled as a point source or be distributed over all or some finite fraction of the gasoline lens. Because of its hydrophyllic nature, ethanol may not spread laterally to the same extent as the gasoline but may instead partition into the groundwater over some smaller area near the source of the leak. These analyses considered only ethanol and assumed that ethanol would biotransform based on a conservative first-order constant of 0.01 day^{-1}. It was expected that the point-source approach would lead to a localized increase in the cosolvency effect because concentrations will be greater. However, the increased cosolvency effect presumably would occur over a much smaller area, and the differences between the two modeling approaches may be insignificant.

4.2.2. Model Construction

MathCad (Mathsoft, Inc.) was used as the computational engine for the model. Parameter definitions, the complete set of governing equations, and internal model documentation are shown in Appendix A. We conducted a total of 50 Monte Carlo realizations[1] for each of two different benzene biotransformation scenarios that are described below. The probability distributions and modeling constants associated with the variable input parameters are presented in Tables 4-1a and 4-1b, respectively. For each realization, the model steps may summarized as follows:

1. The footprint of the LNAPL is calculated as a function of time based on the LNAPL flux, the porosity, the fixed LNAPL thickness-to-length ratio, and the ethanol content.
2. The ethanol plume is modeled via a prescribed flux boundary condition, where the injection of ethanol (the product of the LNAPL flux rate and the ethanol volume fraction in the LNAPL) is divided across the full spatial extent of the LNAPL.
3. BOD is calculated by superposition where, at any location and time, the BOD is indicated by the difference between the hypothetical ethanol degradation if ethanol was a conservative species (that is, a biotransformation rate of zero) minus the concentration predicted with a finite biotransformation rate, adjusted for mineralization reaction stoichiometry.
4. The source term for the benzene plume is modeled by a prescribed boundary condition, with the benzene boundary concentration (that is, its effective solubility) determined by the average ethanol concentration under the LNAPL, according to a relationship developed by Heermann and Powers (1998). The benzene flux across the prescribed concentration boundary is modeled using a relationship suggested by Johnson and Pankow (1992). The Johnson and Pankow (1992) model is for a steady-state plume; we assumed, therefore, that the benzene plume in the vicinity of the source jumps from steady-state to new steady-state as time advances. In practice, this simplifying assumption is reasonable, given that simulated plumes stabilize fairly quickly, particularly near the source, when a finite transformation rate is employed.

It is important to note that all concentrations are measured with respect to a specific depth (for example, 5 ft below the water table), owing to the three-dimensional nature of the model. In reality, groundwater samples always reflect an average across a finite depth interval because of the finite length of wells screens and sampling techniques that require some form of purging. In comparison to real water samples collected from wells with large screened intervals, model results are likely to be conservative because they do not account for sample dilution resulting from the inevitable mixing with nearby less contaminated water.

An initial set of realizations was simulated assuming no relationship between the benzene biotransformation rates and any other modeled variables (that is, the “uncorrelated” scenario). However, because the BOD values were recorded for each realization, we developed a second set of simulations, which employed the identical input parameter set except that the benzene

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[1] The complexity of the calculations involved in the semi-analytic model, as shown in Appendix A, resulted in relatively slow computational execution times, so that only a small number of realizations could be run easily.

biotransformation rates were now inversely correlated with the BOD values 50 ft from the center of the LNAPL footprint (that is, the "correlated" scenario).

4.3. Results and Discussion

4.3.1. Uncorrelated Biotransformation Rates

A comparison of probability distributions of benzene concentration at 50 ft downgradient of the source location (that is, the center of the LNAPL footprint) between the scenarios with and without ethanol suggests that the cosolvency effect of ethanol is negligible, at least according to the model used in this study (Figure 4-2). This finding arises because the aqueous ethanol concentrations remain well below the volume percent-level concentrations needed to produce a cosolvency effect as a result of dilution by flowing groundwater and dispersion along the LNAPL/groundwater interface.

Additional sensitivity analyses pertaining to the ethanol source-term distribution showed that cosolvency effects are negligible whether the ethanol is added at a point source or distributed over the entire footprint of the gasoline pool. For example, it was found that when ethanol solubilized into the groundwater at 0.3 gal/day at a point, the maximum ethanol concentrations would be expected to range between 10,000 mg/L and 50,000 mg/L. In this range of aqueous ethanol concentrations, benzene solubilities would be expected to increase between 5% and 30% as a result of cosolvency (Heermann and Powers, 1998). However these increases occur over an area less than 2 m^2 and comprise a small fraction of the gasoline pool. When the 0.3 gal/day of ethanol was distributed over a finite area of 25 m^2 or greater, ethanol concentrations in groundwater were found to be less than 5000 mg/L. Below this ethanol concentration, increases in benzene solubilities are less than 3%.

The absence of any significant cosolvency effect is attributed to the slow rate of ethanol mass transfer from the gasoline into the groundwater system. Cosolvency effects are more likely to be encountered following a catastrophic release of gasoline where large volumes of ethanol may move rapidly into the groundwater. However, even under this scenario, cosolvency effects are expected to be small. For example, model simulations by Heermann and Powers (1998) showed that the length of a BTEX plume would increase by only about 10% due to presence of ethanol in the gasoline. Despite the absence of cosolvency, the net volume of ethanol and BTEX solubilizing in groundwater may be much greater for the slow-leak scenario considered in this analysis than with a catastrophic scenario. The slow leak may go undetected for long periods of time whereby a catastrophic release would probably be detected much more rapidly.

4.3.2. Correlated Biotransformation Rates

Unlike the uncorrelated scenario, which neglects the effects of ethanol on benzene biotransformation rates, the correlated scenario indicates an observable difference in benzene concentration distributions near the source area between the ethanol and no-ethanol realizations (Figure 4-3). The significance of the biotransformation effect is also evident in comparing the influence of the LNAPL flux terms (Figure 4-4). When biotransformation rates are uncorrelated with the BOD, there is little forecast dependence of benzene concentrations on the flux term because of the limited solubility of benzene in water. Any relationship at all would be a result of the expanded size of the LNAPL/groundwater interface. On the other hand, in the correlated scenario, benzene concentrations are significantly influenced by the LNAPL flux, primarily because larger quantities of ethanol in the source term imply larger BOD values and, hence, lower benzene biotransformation rates.

This biotransformation effect on benzene concentrations appears to diminish with distance downgradient from the source because of changes in parameter sensitivity. For example, near the source area (for example, 50 ft downgradient from the LNAPL center), benzene concentrations exhibit a relatively weak dependence on groundwater velocity, but they are instead somewhat differentiated, based on whether or not ethanol is present as a cosolute (Figure 4-5). Nevertheless, the linear regression analyses we performed on the relationships between concentration and input variable (by rank) as a function of distance suggest that variability in groundwater velocity becomes the dominant influence on variability in concentration forecast downgradient from the source (Figure 4-6). This is at the expense of the biotransformation rate influence, which, in turn, declines significantly away from the source area.

Interpreted median plume lengths, defined by the distance from the LNAPL center to the 1- and 10-parts-per-billion (ppb) concentration contours, are provided in Table 4-2 for the results of this study as well as two other recent studies (Malcolm Pirnie, Inc., 1998; Ulrich, 1999). The agreement between the models is good, suggesting a modest potential for an extension of benzene plume lengths, less than a factor of two, in the presence of ethanol over cases where ethanol is not used. It is important to stress, however, that this finding is very preliminary in the absence of the data needed for more refined estimates. Moreover, its is particularly important to stress the conservative nature of the model assumptions, notably the global reduction in benzene biotransformation rates associated with the ethanol-induced BOD, and the non-depth-averaged benzene concentration predictions. Thus, the model results should be viewed as representing an expected upper bound to the effects under consideration.

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Figures

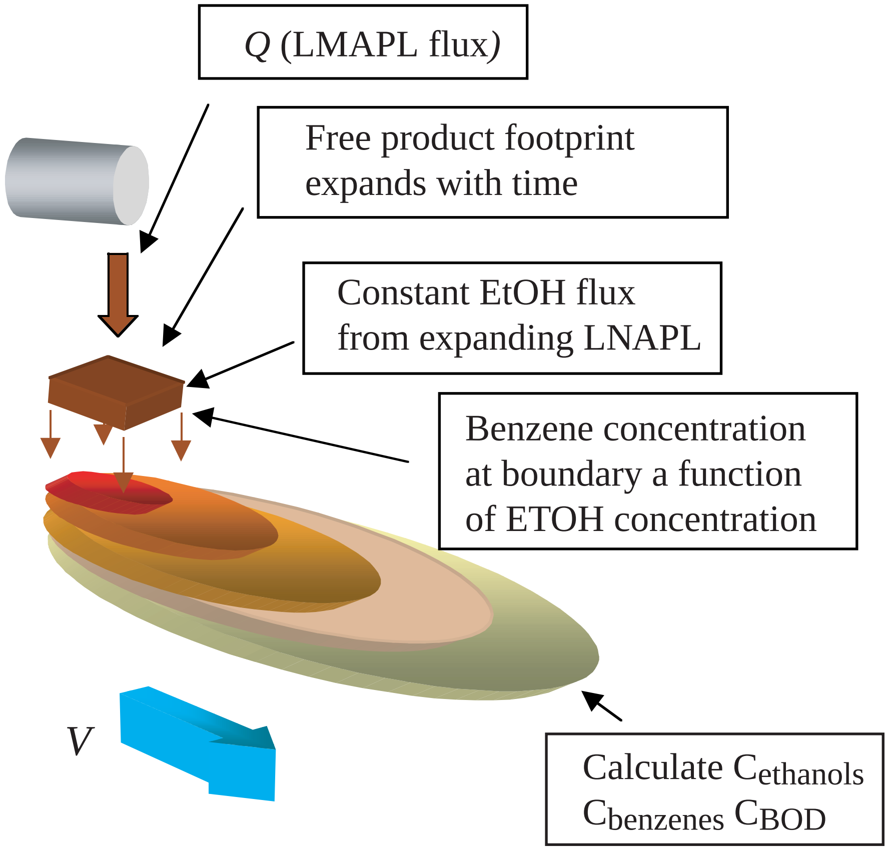

Figure 4-1. Idealized model of LNAPL gasohol release to the subsurface.

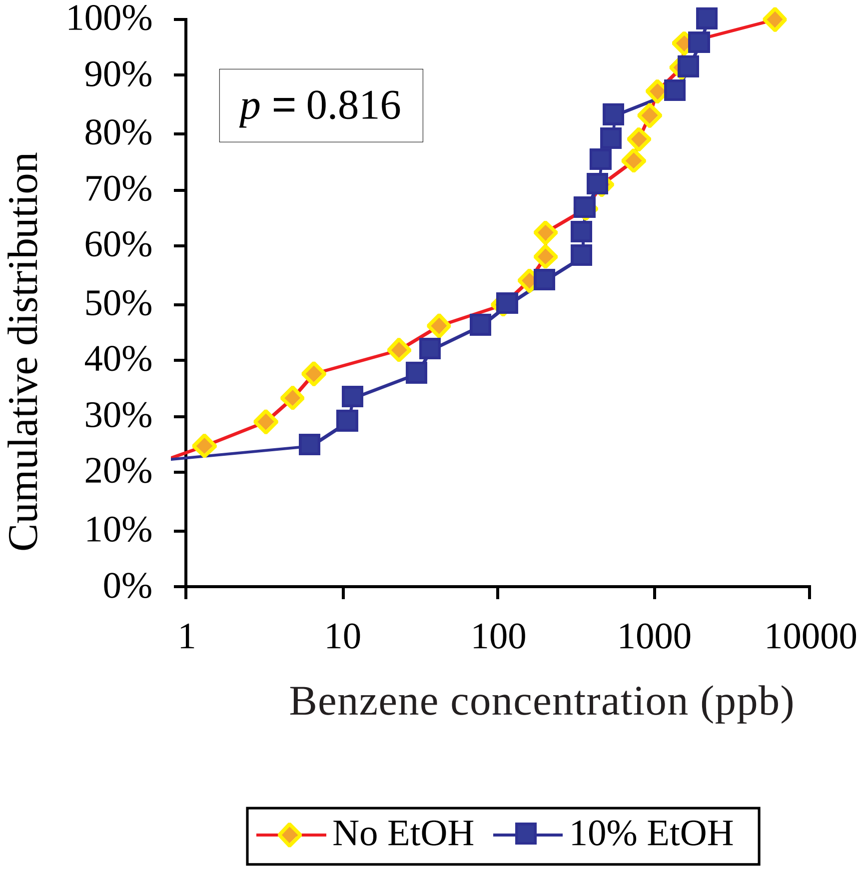

Figure 4-2. Forecast probability distributions of benzene concentrations 50 ft downgradient from the center of the LNAPL footprint. A comparison between gasolines with and without ethanol when benzene biotransformation rates are uncorrelated with biochemical oxygen demand.

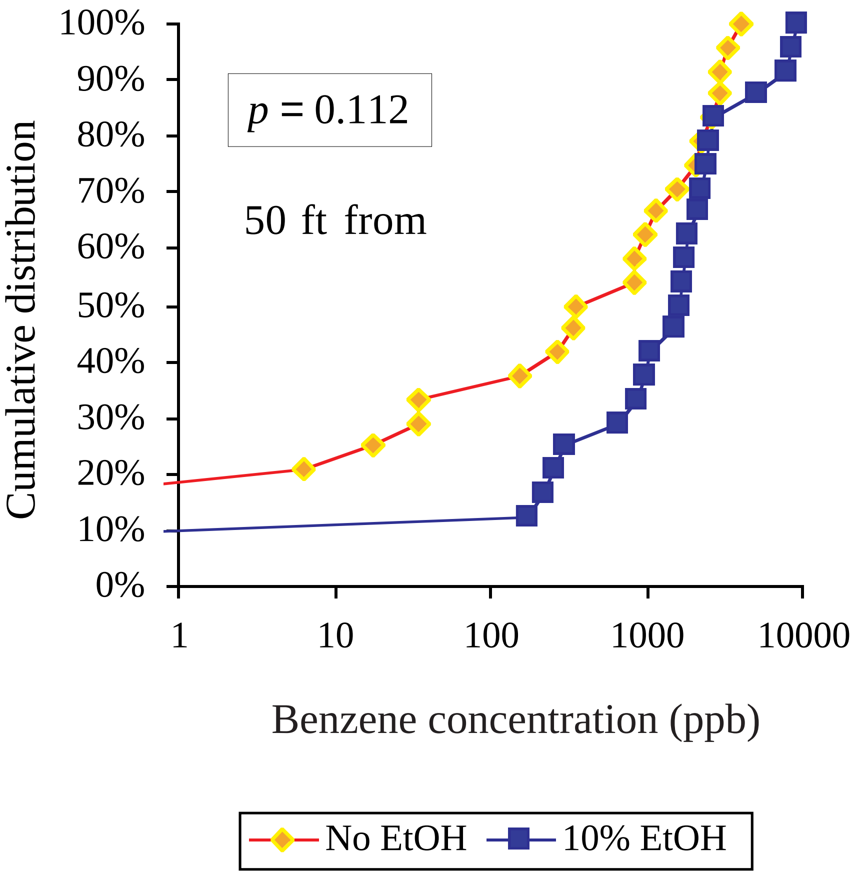

Figure 4-3. Forecast probability distributions of benzene concentrations 50 ft downgradient from the center of the LNAPL footprint. A comparison between gasolines with and without ethanol when benzene biotransformation rates are correlated with biochemical oxygen demand.

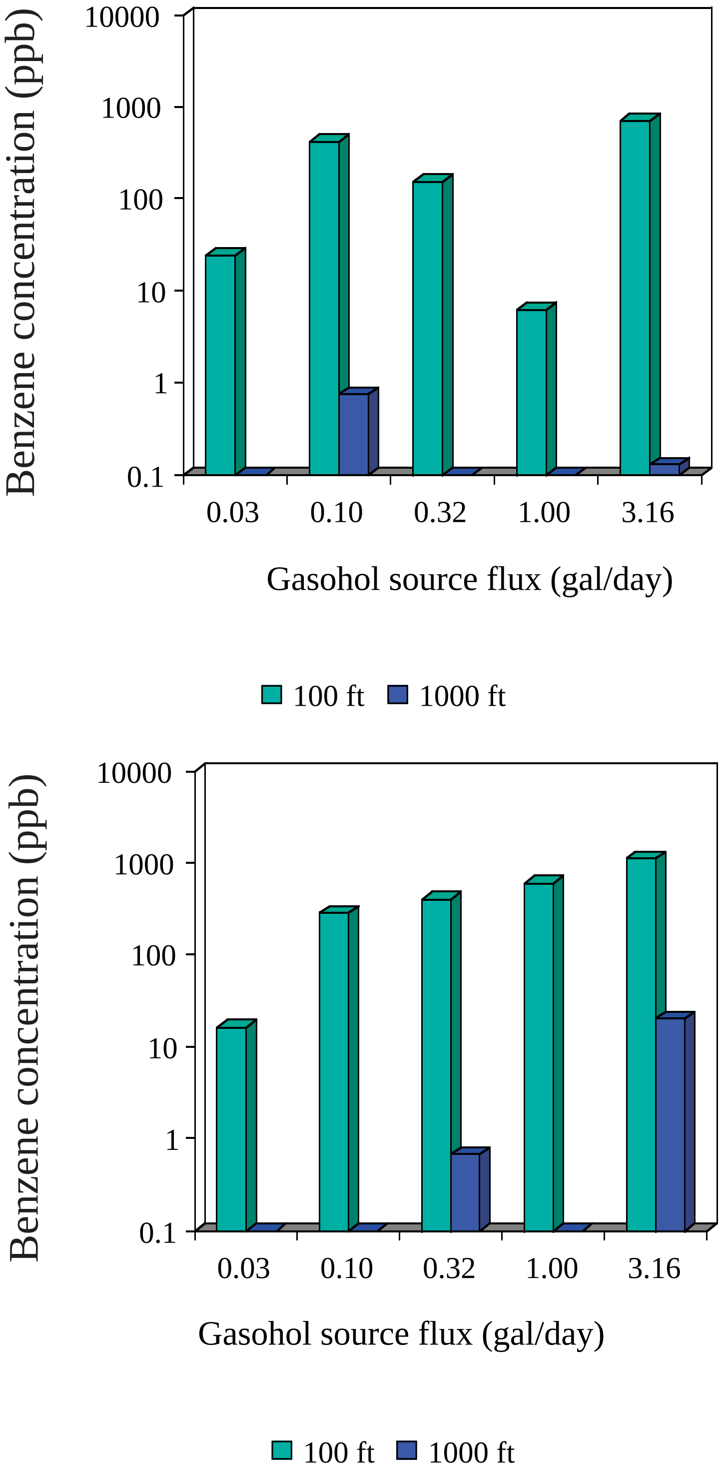

Figure 4-4. Forecast influences of LNAPL flux source term on benzene concentrations; (a) uncorrelated and (b) correlated benzine biotransformation rates.

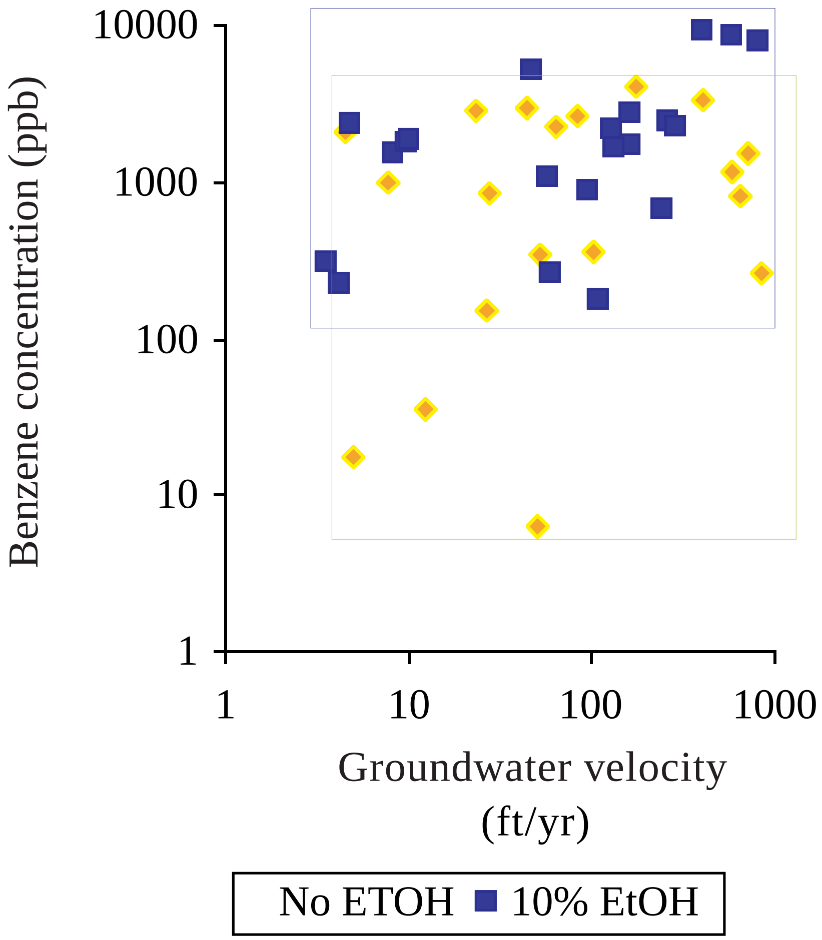

Figure 4-5. Forecast relationship between benzene concentrations 50 ft downgradient from the center of the LNAPL footprint and groundwater velocity, with and without ethanol, when benzene biotransformation rates are correlated with biochemical oxygen demand.

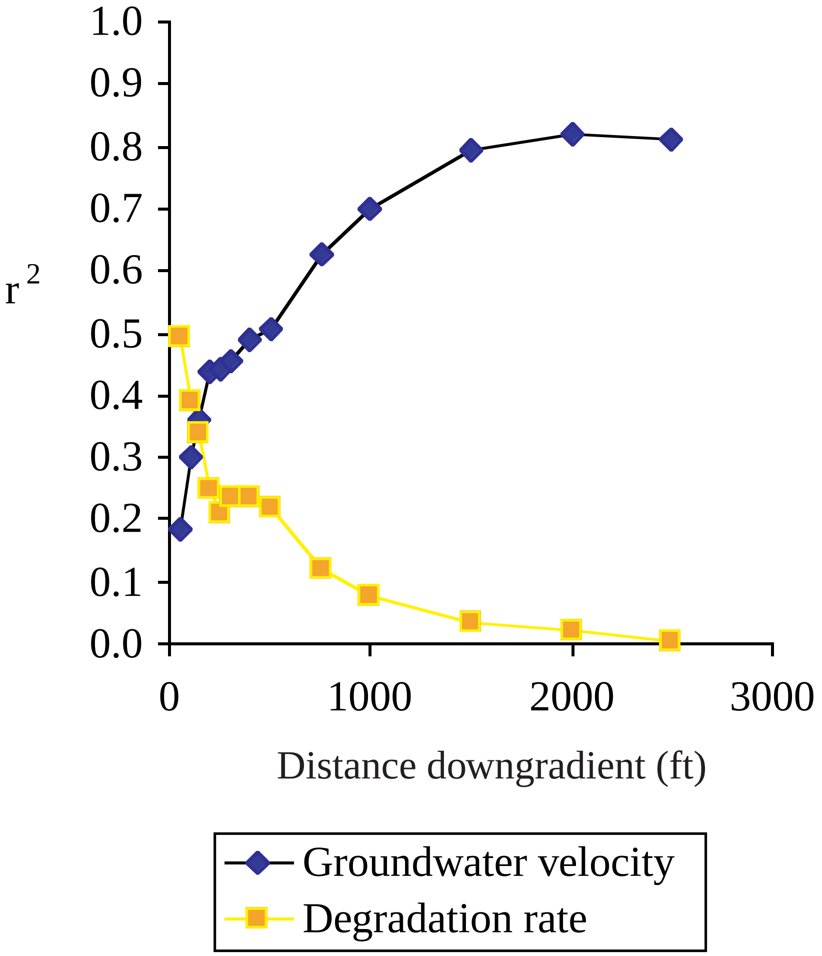

Figure 4-6. Influence of input variables on forecast benzene concentrations as a function of distance, as indicated by rank correlation (for correlated benzene biotransformation rates).

Tables

Table 4-1a. Probability distribution input parameters for modeled Monte Carlo forecasts.

Parameter	**Description**	**Remarks**	**Prescribed distribution**
X_{EtOH}	Ethanol fraction in gasohol	Represents maximum expected in California reformulated gasoline	1% and 10%, by mass or mole fraction
Q	Rate of NAPL replenishment	Based on current uncertainty of tank release monitoring	Loguniform distribution 3.16–0.0316 [log(uniform range of 0.5 to–1.5)]
T	NAPL lens thickness-to-length ratio	Based on estimates from Dooher, 1998	Loguniform distribution 0.1–0.01 [log(uniform range of -1 to -2)]
λ_{EtOH}	Ethanol first-order degradation rate	Estimated from laboratory experiments of Corseuil *et al.*, 1998; Alvarez and Hunt, 1999. Howard *et al.* (1991) reports a range of half-lives 1/3 to 2/5 faster.	Lognormal distribution. 5th percentile = 1.28×10^{-1} day^{-1} ($t_{1/2}$ = 5.43 days) mean = 2.46×10^{-1} day^{-1} ($t_{1/2}$ = 2.82 days) 95th percentile = 4.51×10^{-2} day^{-1} ($t_{1/2}$ = 1.67 days)
$\lambda_{Benzene}$	Benzene first-order degradation rate	Rice *et al.*, 1998. Median value may be fairly typical as a macroscopic average for many sites (e.g., Ulrich, 1999; Dooher, 1998).	Lognormal distribution. 5th percentile = 9.75×10^{-5} day^{-1} ($t_{1/2}$ = 7110 days or 19.5 years) mean = 3.65×10^{-2} day^{-1} ($t_{1/2}$ = 19 days) 95th percentile = 1.23×10^{-1} day^{-1} ($t_{1/2}$ = 5.6 days)
p	Fraction of NAPL footprint over which ethanol partitions in water.	Postulation based (Powers and Heermann, 1999).	Loguniform distribution 0.1– 0.01 [log(uniform range of -1 to -2)]
K	Hydraulic conductivity	Values typifying California hydrogeology (Dooher, 1998). Values supported by Mackay *et al.*, 1985, and Guven *et al.*, 1984.	Lognormal distribution. 5th percentile = 3.82×10^{-6} m/s (0.33 m/day) mean = 1.25×10^{-4} m/s (10.8 m/day) 95th percentile = 4.75×10^{-4} m/s (41 m/day)
∇h	Hydraulic gradient	Values typifying California hydrogeology (Dooher, 1998). Values supported by Mackay *et al.*, 1985, and Guven *et al.*, 1984.	Lognormal distribution. 5th percentile = 1.42×10^{-3} mean = 1.66×10^{-2} 9th percentile = 5.58×10^{-2}
ϕ	Porosity	Based on 252 samples taken at the Lawrence Livermore National Laboratory Superfund Site (Dooher, 1998) and Jury (1985).	Normal distribution. mean = 0.42 standard deviation = 0.07

Table 4-1b. Model constants for input parameters.

Parameter	Description	Remarks	Prescribed distribution
$X_{Benzene}$	Benzene fraction in gasahol	Represents maximum expected in California reformulated gasoline	1.5%, by mass or mole fraction
α_x	Longitudinal dispersivity.	Based on results presented in Gelhar *et al.* (1992).	20 ft
α_y	Horizontal transverse dispersivity.	Based on results presented in Gelhar *et al.* (1992).	2 ft
α_z	Vertical transverse dispersivity.	Based on results presented in Gelhar *et al.* (1992).	0.5 ft
C_w	Benzene solubility in pure water		1780 ppm
β	Volume fraction of EtOH at the break point between the linear and the log-linear model	Powers and Heermann (1999).	0.27
C_β	Benzene solubility at β.	Powers and Heermann (1999).	4420 ppm
D_e	Effective molecular diffusion coefficient	Taken to be identical for ethanol and benzene.	$5x10^{-10}$ m^2/s

Table 4-2. Summary of simulation results indicative blended gasoline plume length effects.

Study	Plume lengths: regular gasoline	Plume lengths: blended gasoline
LLNL screening model	200-250 ft at 10 ppb	250-300 ft at 10 ppb (~20% longer)
	200-250 ft at 1 ppb	400-500 ft at 1 ppb (~100% longer)
Malcolm Pirnie, Inc. (1998)	145-330 ft at 1 ppb	195-420 ft at 1 (ppb)
	Median: 240 ft	Median: 310 ft (~30% longer)
Governor's Ethanol Coalition (Ulrich, 1999) model of Borden aquifer site	200 ft	365 ft (~80% longer)
Waterloo blended methanol-gasoline field study[a] (Hubbard *et al.*, 1994)	~75 ft	~115 ft (50% longer)

[a] Gasoline with 15% MeOH, introduced as a slug source in a controlled field experiment.

Appendix A

Semi-analytical Gasohol Solute Transport Model in 3-D with a Finite, Time-dependent LNAPL Source

Semi-Analytical Gasohol Solute Transport Model in 3-D with a Finite, Time-Dependent LNAPL Source

This worksheet contains a full 3-D semi-analytical model for the development of ethanol, benzene, and biochemical oxygen demand plumes emanating from a light non-aqueous phase liquid (LNAPL) source as a function of time and space. The LNAPL source itself grows over time, depending on the input of fresh gasohol. The transport model is based on spatial and temporal integration of the Baetsle (1969) instantaneous point source solution in 3-D. The ethanol source term consists of a prescribed flux boundary condition across the LNAPL/groundwater interface which changes as a function of time as the LNAPL pool grows. The benzene source term is handled by a prescribed boundary condition, with the prescribed benzene boundary concentration (that is, its effective solubility) determined by the average ethanol concentration under the LNAPL (again, a function of time). The coupling between the source terms is handled by equations provided by Johnson and Pankow (1992) and Heerman and Powers (1998). The biochemical oxygen demand is calculated by superposition with respect to the ethanol plume.

Unit definitions and MathCad parameters ...

$\mathrm{ppb} := 10^{-6}\,\frac{\mathrm{gm}}{\mathrm{L}}$ $\mathrm{ppm} := 10^{-3}\,\frac{\mathrm{gm}}{\mathrm{L}}$ $\mathrm{TOL} \equiv 1 \cdot 10^{-4}$ $\mathrm{ORIGIN} \equiv 1$

Aquifer properties (for downgradient plume simulation)

Hydraulic conductivity: $K := 10\,\frac{\mathrm{ft}}{\mathrm{day}}$

Hydraulic gradient: $I := 0.002$

Porosity: $\phi := 0.25$

Pore velocity by Darcy's law: $v := \frac{K \cdot I}{\phi}$ $v = 29.219\,\frac{\mathrm{ft}}{\mathrm{yr}}$

Dispersion tensor:

Longitudinal: $\alpha_x := 20\ \mathrm{ft}$ $D_x := \alpha_x \cdot v$

Transverse: $\alpha_y := 2\ \mathrm{ft}$ $D_y := \alpha_y \cdot v$

Vertical: $\alpha_z := 0.5\ \mathrm{ft}$ $D_z := \alpha_z \cdot v$

Gasohol source properties

NAPL replenishment rate: $Q := 0.5 \, \frac{\text{gal}}{\text{day}}$

Ethanol mass/mole/volume fraction in gasohol: $X_{\text{EtOH}} := 10\,\%$

Benzene mass/mole/volume fraction in gasohol: $X_{\text{B}} := 1.5\,\%$

NAPL thickness-to-length ratio: $T_{\text{ratio}} := 0.1$

Solute properties

First-order decay coefficient for ethanol: $\lambda_{\text{EtOH}} := 0.01\,\text{day}^{-1}$

First-order decay coefficient for benzene: $\lambda_{\text{B}} := 0.003\,\text{day}^{-1}$

Effective molecular diffusion coefficient (assume the same for both ethanol and benzene): $D_{\text{e}} := 5 \cdot 10^{-10} \, \frac{\text{m}^2}{\text{sec}}$

Governing equations for ethanol plume model

Size of square-footprint NAPL/groundwater interface

$\varepsilon := 1\ \mathrm{cm}$

(Used to prevent divide-by-zero error)

$$L_p(t) := \sqrt[3]{\frac{Q \cdot t \cdot \left(1 - X_{EtOH}\right)}{T_{ratio} \cdot \phi}} + \varepsilon$$

(Length of one side of the LNAPL lens as a function of time, corrected for product loss due to ethanol dissolution. LNAPL lens is assumed to have a square footprint, with a thickness to length ratio of T_{ratio}.)

Ethanol source function, assuming a specified flux across the NAPL/groundwater interface

Density of ethanol: $\rho_{EtOH} := 0.7 \frac{\mathrm{gm}}{\mathrm{cm}^3}$

Implied constant ethanol mass injection rate: $M_{EtOH} := Q \cdot X_{EtOH} \cdot \rho_{EtOH}$

Fraction of NAPL footprint over within which ethanol partitions into water: $p := 25\ \%$

$$M_{fEtOH}(t) := \frac{M_{EtOH}}{p \cdot L_p(t)^2}$$

(The implied ethanol flux, based on assumption of complete, instantaneous partitioning into the water phase, is divided over the some portion, *p*, of the growing NAPL footprint.)

Plume model for ethanol, based on the solution of Baetsle (1969). The solute transport model used for ethanol is based upon an instantaneous point source (that is, mass slug) solution into a 3-D domain. To modify the mathematical solution for the conditions of interest, the point source is integrated over finite distances in the *x*- and *y*-directions to simulate leaching from the LNAPL lens and is integrated in time to emulate a finite source (the changing size of the LNAPL lens over time is accounted for). The source functions are multiplied by 2 for superposition of the source to account for the boundary condition imposed by the water table.

$$C_1(x,y,z,t,\lambda) := \int_0^t \int_{\frac{-p\cdot L_p(t-\tau)}{2}}^{\frac{p\cdot L_p(t-\tau)}{2}} \int_{\frac{-p\cdot L_p(t-\tau)}{2}}^{\frac{p\cdot L_p(t-\tau)}{2}} \frac{2\cdot M_{fEtOH}(t-\tau)}{8\cdot(\pi\cdot\tau)^{\frac{3}{2}}\cdot\sqrt{D_x\cdot D_y\cdot D_z}}\cdot\exp\left[\frac{-\left[\left(x-x_s\right)-v\cdot\tau\right]^2}{4\cdot D_x\cdot\tau}-\frac{\left(y-y_s\right)^2}{4\cdot D_y\cdot\tau}-\frac{z^2}{4\cdot D_z\cdot\tau}-\lambda\cdot\tau\right] dx_s\, dy_s\, d\tau$$

Biochemical oxygen demand (BOD) for mineralized of ethanol to CO $_2$

Reaction stoichiometry: $EtOH + 3O_2 \text{-->} 2CO_2 + 3H_2O$

Molecular weights: $MW_{EtOH} := 46.07 \frac{gm}{mol}$ (Ethanol)

$MW_{O2} := 32 \frac{gm}{mol}$ (O_2)

Biochemical oxygen demand weighting factor: $w_{BOD} := 3\cdot\frac{MW_{O2}}{MW_{EtOH}}$

Ethanol biotransformation shadow $\delta e(x,y,z,t,\lambda) := C_1\left(x,y,z,t,0\ day^{-1}\right) - C_1(x,y,z,t,\lambda)$

Analysis: Ethanol plume and anaerobic shadow

Elapsed time since release began $t := 30\ \mathrm{yr}$

Cumulative ethanol mass introduction over release period

$\Sigma_{EtOH} := M_{EtOH} \cdot t$ $\Sigma_{EtOH} = 1.452 \cdot 10^{3} \cdot \mathrm{kg}$

Concentrations versus position for example parameter set

$x := 40\ \mathrm{ft}$ $y := 0\ \mathrm{ft}$ $z := -5\ \mathrm{ft}$

Ethanol $C_1(x, y, z, t, \lambda_{EtOH}) = 3.227 \cdot \mathrm{ppm}$

BOD $\delta e(x, y, z, t, \lambda_{EtOH}) \cdot w_{BOD} = 41.847 \cdot \mathrm{ppm}$

$x := 100\ \mathrm{ft}$ $y := 0\ \mathrm{ft}$ $z := -15\ \mathrm{ft}$

Ethanol $C_1(x, y, z, t, \lambda_{EtOH}) = 0.674 \cdot \mathrm{ppb}$

BOD $\delta e(x, y, z, t, \lambda_{EtOH}) \cdot w_{BOD} = 13.165 \cdot \mathrm{ppm}$

Governing equations for benzene plume model

Average ethanol concentration vs. time at LNAPL/water boundary. The specified concentration boundary condition for benzene (see below) requires that the ethanol concentration at the LNAPL/groundwater interface be known. Because the ethanol source function is a specified flux at the interface, this value cannot be defined precisely at the interface. As an alternative, a finite-thickness boundary layer may be delineated underneath the LNAPL where an ethanol boundary concentration may be defined. For computational simplicity, and to meet as much as possible mathematical constraints required for the Johnson and Pankow (1992) solution to hold (see below), an average ethanol concentration across the entire LNAPL/groundwater interface is calculated as a function of time. This value is then used to calculated an average benzene boundary concentration. To simplify computations, the averaged ethanol concentrations are stored in an array to avoid having to recalculate the integrals in the equation for C_1 as a function of time. This necessitates time-discretizing the continuous benzene source term, rather than assuming a continuous integral.

Assumed boundary layer thickness: $b := 1\ \mathrm{mm}$

Ethanol density: $\rho_{\mathrm{EtOH}} := 0.7\,\frac{\mathrm{gm}}{\mathrm{cm}^3}$

Time discretization: $N_t := 20$ $\Delta t := \frac{t}{N_t}$ $i := 1..N_t$ $t_{d_i} := (i - 0.5)\cdot\Delta t$

Discretization of NAPL pool length as a function of time: $L_{d_i} := L_p\left(t_{d_i}\right)$

Spatial discretization of NAPL/groundwater interface over time for estimating average ethanol concentration:

$N_s := 5$ $\Delta x_i := \frac{L_{d_i}}{N_s}$ $j := 1..N_s$ $x_{d_{i,j}} := \frac{-L_{d_i}}{2} + (j - 0.5)\cdot\Delta x_i$

$\Delta y_i := \frac{L_{d_i}}{N_s}$ $k := 1..N_s$ $y_{d_{i,k}} := \frac{-L_{d_i}}{2} + (k - 0.5)\cdot\Delta y_i$

Temporal discretization of average ethanol concentration:

$$f_i := \frac{\sum_j \sum_k C1\left(x_{d_{i,j}}, y_{d_{i,k}}, \frac{-b}{2}, t_{d_i}, \lambda_{EtOH}\right)}{N_s^{2} \cdot \rho_{EtOH}}$$

(Average volume fraction of ethanol under the LNAPL pool in ethanol-water mixture over each discrete time interval.)

Average benzene concentration and benzene mass flux/area vs. time at the LNAPL/groundwater boundary. Because of the limited solubility of benzene in water, the benzene source term is one of a prescribed concentration boundary, as opposed to the presribed flux boundary condition used for ethanol. Because the cosolvency effect of ethanol can increase the solubility of benzene, the boundary condition solubility of benzene is calculated from the mean ethanol concentration under the LNAPL pool as a function of time and the method proposed by Heerman and Powers (1998). The mass flux of benzene per unit area is calculated using the solution of Johnson and Pankow (1992). Their solution is one for a steady-state plume that has developed beneath a LNAPL pool. In this model, it is assumed that the system jumps from steady-state to steady-state over each discrete time interval. The mass flux is then updated accordingly.

Pure benzene solubility in pure water: $C_w := 1780\,\text{ppm}$

Volume fraction of ethanol in the aqueous phase at the break point between the linear and log-linear models: $\beta := 0.27$

Solubility of benzene at β: $C_\beta := 4420\,\text{ppm}$

Equilibrium concentration of benzene in the binary mixture (for f < β) after Heerman and Powers (1998):

$$C_{B_i} := \left(1 - \frac{f_i}{\beta}\right) \cdot C_w \cdot X_B + \frac{f_i}{\beta} \cdot C_\beta \cdot X_B$$

Benzene mass flux/area over discrete time intervals, after Johnson and Pankow (1992):

$$M_{fB_i} := C_{B_i} \cdot \phi \cdot \sqrt{\frac{4 \cdot \left(D_z + D_e\right) \cdot v}{\pi \cdot L_{d_i}}}$$

Plume model for benzene, based on the solution of Baetsle (1969). The form of this mathematical solution for the benzene plume is similar to that for ethanol, except that the source term has been discretized over a specified finite number of time intervals. The equation has been split into two terms here simply for clarity.

$$\psi(x,y,z,t,\lambda) := \frac{2}{8\cdot(\pi\cdot t)^{\frac{3}{2}}\cdot\sqrt{D_x\cdot D_y\cdot D_z}}\cdot\exp\left[\frac{-(x-v\cdot t)^2}{4\cdot D_x\cdot t}-\frac{y^2}{4\cdot D_y\cdot t}-\frac{z^2}{4\cdot D_z\cdot t}-\lambda\cdot t\right]$$

$$C_2(x,y,z,t,\lambda) := \sum_i \int_{t_{d_i}-\frac{\Delta t}{2}}^{t_{d_i}+\frac{\Delta t}{2}} \int_{\frac{-L_{d_i}}{2}}^{\frac{L_{d_i}}{2}} \int_{-\frac{L_{d_i}}{2}}^{\frac{L_{d_i}}{2}} M_{fB_i}\cdot\psi\left(x-x_s,y-y_s,z,t-\tau,\lambda\right)\,dx_s\,dy_s\,d\tau$$

Concentrations versus position for example parameter set

$x := 40\ \text{ft}$ $y := 0\ \text{ft}$ $z := -5\ \text{ft}$

Benzene $C_2\left(x,y,z,t,\lambda_B\right) = 399.296\ \text{ppb}$

$x := 100\ \text{ft}$ $y := 0\ \text{ft}$ $z := -15\ \text{ft}$

Benzene $C_2\left(x,y,z,t,\lambda_B\right) = 10.457\ \text{ppb}$

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Chapter 5: Potential Impact of Ethanol-containing Gasoline on Surface Water Resources

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Table of Contents

List of Figures

List of Tables

Appendices

5. Potential Impact of Ethanol-containing Gasoline on Surface-water Resources

5.1. Introduction

The phaseout of methyl tertiary butyl ether (MTBE) from gasoline in California will result in changes in the composition of gasoline in order to meet air-quality requirements. For example, unless a Clean Air Act requirement for oxygen content is waived for California, ethanol will have to be added to gasoline sold in areas that have not attained compliance with air-quality standards for ozone. The importation, distribution, and use of large quantities of ethanol in the state raises potential concerns regarding impacts to surface-water supplies from accidental releases, discharges from recreational boats, and washout of ethanol from the atmosphere. In this assessment, we review information on the environmental chemistry of ethanol and conduct a series of screening-level simulations of various releases in order to understand the nature and magnitude of potential impacts to surface waters. To put the results in perspective, we compare the environmental behavior of ethanol with that of MTBE.

5.2. Background

Ethanol (EtOH) and MTBE are fuel compounds that have been added to gasoline for many years. These compounds contain elevated amounts of oxygen (that is, 18 and 35 wt% for MTBE and ethanol, respectively), and they have octane numbers over 100. In Table 5-1 we summarize some of their key physicochemical properties affecting their behavior in the environment. Both EtOH and MTBE are hydrophilic substances, with low octanol-water partition coefficients and elevated solubilities in water (ethanol is miscible in water, and MTBE has a solubility of 488 mol/m^3, or 43 g/L). Ethanol is subject to fairly rapid biodegradation in the hydrosphere, but MTBE is recalcitrant biologically. Reviews of the environmental chemistry of these oxygenated fuel compounds are contained in the *Interagency Assessment of Oxygenated Fuels* (National Science and Technology Council [NSTC], 1997), and in reports by Malcolm Pirnie, Inc. (1998a,b).

5.3. Washout of Ethanol and MTBE from the Atmosphere

Both ethanol and MTBE can enter the atmosphere directly as a consequence of volatilization during different stages of their life cycles, such as fugitive or accidental emissions from manufacturing, distribution, and use, and from incomplete combustion. Although these volatilized compounds may undergo some degree of degradation in the atmosphere, that fraction that is not degraded by chemical processes will be subject to washout by precipitation. Accordingly, any significant rainout (i.e., wet deposition) can potentially impact surface waters. To determine the significance of rainout, we estimated the concentrations of MTBE and ethanol in rainwater during a precipitation event based on atmospheric concentrations of 1 part per billion by volume (ppb[v]) or for any other concentration of a substance (s) in units of ppb(v), (that is, 10^{-9} L_s/L_{air}) using Equation (5-1)

$$C_{rain} = \frac{C_{air}\ M_s\ cf\, P}{H'R\ T}, \tag{5-1}$$

where

C_{rain} = concentration of substance in rain, μg/L;

C_{air} = concentration of substance (s) in air, ppb(v);

M_s = molar mass (molecular weight) of substance (s), g/mol;

P = pressure, 1 atm;

R = gas constant, 0.0821 atm-L/mol-K;

T = temperature, K;

cf = conversion factor, 10^6 μg/g; and

H' = dimensionless Henry's law constant (that is, C_{air}/C_{water}).

An important property with respect to rainout is the dimensionless Henry's law constant, which essentially describes the propensity for a compound to volatilize to air from water, or conversely, to enter water and remain in the water phase. The dimensionless Henry's law constant (H') is expressed mathematically as the ratio of the air-to-water concentrations of a compound at equilibrium (Zogorski *et al.*, 1997). Ideally, when an ambient air concentration for a substance is multiplied by 1/H´, the result is the concentration in the rainwater phase. The ratio of the dimensionless Henry's law constants for a temperature of 298 K for MTBE and ethanol, respectively, exceeds a factor of 80 (H´ for MTBE = 2.16×10^{-2}, and H´ for ethanol = 2.57×10^{-4}). Therefore, based on H´ alone, more ethanol than MTBE will be present in rainwater during a precipitation event, especially if both are present at equal concentrations (expressed as mass per unit-volume [for example, $\mu g/L_{air}$]).

As expected, applying Equation (5-1) reveals that the estimated concentration of ethanol in rainwater for a 1-ppb(v) concentration of ethanol in air (that is, 1.9×10^{-3} μg/L or 41 n mol/ m^3) could be as high as 7.3 μg/L (160 n mol/L) during a precipitation event; whereas, a 1-ppb(v) concentration of MTBE in air (that is, 3.6×10^{-3} μg/L or 41 n mol/ m^3) would yield only about 0.17 μg/L (1.9 n mol/L) in rainwater during a precipitation event. This difference of more than a factor of 40 in mass per unit-volume rainwater concentration (almost two orders of magnitude in moles per unit volume) is due to the large difference between the dimensionless Henry's law constants for the two compounds because the mass per unit-volume atmospheric concentration for MTBE is only about a factor of two greater than that for ethanol.

Equation (5-1) is particularly useful when considering the atmospheric levels of MTBE and ethanol in a specific air basin, such as the greater Los Angeles region of California. For example, Allen *et al.* (1999a) have estimated emissions and annual-average air concentrations for MTBE and ethanol for 1997 and 2003 in the greater Los Angeles air basin. According to that data, the emissions of MTBE could decline by 32% between 1997 and 2003. Corresponding maximum, annual-average atmospheric concentrations in the greater Los Angeles air basin[1] are 3.9 and 2.6 ppb(v) (160 and 100 n mol/ m^3, respectively). From Equation (5–1), it is estimated these concentrations could yield maximum, average concentrations of MTBE in rainwater during a precipitation event of 0.65 and 0.43 µg/L (7.4 and 4.9 n mol/L, respectively). Similarly, the assessment performed by Allen *et al.* (1999a,b) suggests vehicular emissions of ethanol in the air basin could increase ambient levels of ethanol by as much as 50% (from a value of 5.1 ppb[v] [210 n mol/m^3]) to a value of 7.6 ppb[v] [300 n mol/m^3]) if ethanol is added to gasoline in 2003 to achieve 2 wt% oxygen; or ambient concentrations of ethanol could rise more than 72% (from 5.1 ppb[v] [210 n mol/m^3] to 8.8 ppb[v] [370 n mol/m^3]) if ethanol is added to gasoline in 2003 to achieve 3.5 wt% oxygen. According to Equation (5–1), the corresponding concentrations of ethanol in rainwater for ambient levels of 5.1, 7.6, and 8.8 ppb(v) (210, 300, and 370 n mol/m^3) would be 37, 56, and 64 µg/L (about 800, 1200, and 1400 n mol/L, respectively).

5.4. Releases to Rivers and Streams

We employed a two-tiered approach for evaluating the potential water-quality impacts on rivers and streams caused by releases of ethanol. First, we examined the relative effectiveness of volatilization and biodegradation as removal mechanisms, using a modified version of a methodology presented by Pankow *et al.* (1996). We then analyzed the consequences of a major release to a river using a surface-water transport model. Based on the results of these analyses, we identified uncertainties and data gaps that need to be addressed to improve our ability to predict the behavior of ethanol in aquatic environments.

5.4.1. Volatilization and Biodegradation of Ethanol in Rivers and Streams

Pankow *et al.* (1996) presented a methodology for calculating the volatilization rates of fuel-oxygenate compounds in rivers and streams. In their methodology, the half-life of a compound is calculated using a rate constant for volatilization calculated from its mass-transfer velocity (from the water column to air) and the depth of the river. Losses due to transformation processes, such as biodegradation, were not considered. However, if such transformation processes are rapid, they can be as effective as volatilization losses in reducing the concentrations of the fuel compounds dissolved in water. We, therefore, calculated the half-life of a fuel oxygenate due to the combined processes of volatilization and biotransformation as

$$t_{half} = \frac{0.693}{\left(\mathrm{k_v} + \mathrm{k_b}\right)}, \tag{5-2}$$

where

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[1] As indicated by either the “best” or “upper” baseline, population-weighted annual exposure for summer, which is probably a lower value than that for winter, according to Allen *et al.* (1999b).

t_{half} = half-life of oxygenate in surface water, d;

k_v = rate constant for volatilization, 1/d; and

k_b = rate constant for biodegradation, 1/d.

Pankow *et al.* (1996) also introduced another measure of the persistence of a compound, termed the “half-life distance,” which is simply the distance traveled during the half-life of a compound,

$$d_{half} = u_w t_{half}, \tag{5-3}$$

where u_w is the velocity of the water (m/d).

As a means of evaluating the various parameters that control the persistence of ethanol released to a river, we examined two transport cases (after Pankow *et al.* [1996]), one for conditions supporting reduced volatilization (that is, calm winds at 0.25 m/s, a river-flow velocity of 2732 m/d, and a river depth of 3 m) and enhanced volatilization (that is, high winds at 5.5 m/s, a river-flow velocity of 27,320 m/d, and a river depth of 1 m). With a water temperature of 25°C, the volatilization-rate constants (that is, k_v) for ethanol are 0.017/d for the conditions associated with reduced transfer to atmosphere and 0.21/d for enhanced conditions (equivalent half-lives of 40 and 3.3 days with half-life distances over 90 km). In contrast, the rate constants for MTBE determined using the same conditions are significantly higher—0.083/d and 1.3/d (with correspondingly lower half-lives of 8.4 and 0.52 days and associated distances of 23 and 14 km) for reduced and enhanced volatilization, respectively. Ethanol has a much lower Henry’s law constant than MTBE; and consequently, the relative importance of the air-side mass-transfer velocity in controlling the overall mass transfer to air is more important (see Appendix A).

The persistence of ethanol in surface water, however, is also a function of its biodegradation rate. As already explained (see Alvarez and Hunt, 1999, Vol. 4, Chapter 3 of this report), ethanol represents a carbon and energy source for microorganisms[2]. Howard *et al.* (1991) comment that, according to best scientific judgment, the aerobic-biodegradation half-life of ethanol in surface water is estimated to range from 6.5 h to 26 h. This judgment is consistent with results from an experiment performed by Apoteker and Thévenot (1983) to study the biodegradation of ethanol in samples of Seine river water that were incubated at 20°C. This experiment produced an exponential-growth-phase rate constant of 0.22 per hour, from which the aerobic-biodegradation half-life can be estimated to be about 3.2 h (that is, 3.2 h = 0.693/[0.22 per h]). However, this exponential growth-phase was preceded by a 10-h lag phase, and so the effective half-life for ethanol is closer to 13 h, rather than 3 h. This biphasic behavior was interpreted by Apoteker and Thévenot (1983) to occur as a result of microorganism adaptation to a change in environment, which involved the sudden introduction of the new substrate compound (that is, ethanol). Both the lag time and subsequent degradation rate are expected to vary by receiving-water body properties as discussed by Alvarez and Hunt (1999, Vol. 4, Chapter 3 of this report). With a biodegradation half-life of 13 h, the rate constant for EtOH becomes 1.3/d, which is comparable to the volatilization rate constant for MTBE under enhanced transport conditions.

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[2] In comparison to ethanol and most other gasoline components, MTBE is considered resistant to aerobic microbial degradation (Suflita and Mormile, 1993).

Biodegradation is particularly sensitive to temperature, decreasing with decreasing temperature. This low-temperature effect occurs because low temperatures reduce cellular membrane fluidity and permeability, which thereby reduces the uptake of both nutrients and contaminants. Thomann and Mueller (1987) suggest that the biodegradation rate for temperatures other than 20°C can be adjusted using the following relationship:

$$k_{b(T)} = k_{b(20)} 1.06^{(T-20)}, \tag{5-4}$$

where T is in degrees centigrade. Thus, if the water temperature were 5°C, the resulting biodegradation rate would only be about 40% of the rate at 20°C. Temperatures warmer than 20°C increase the rate of biodegradation by improving enzymatic activity up to an optimum value that is specific to the microbial species (see Alvarez and Hunt, 1999, Vol. 4, Chapter 3 of this report). At temperatures above the species-specific optimum, proteins and nucleic acids become denatured and inactive; and the biodegradation process will cease. Given the variable effects of temperature and the microbial characteristics of different receiving waters, a nominal half-life for ethanol of 24 h can be assumed.

5.4.2. Accidental Releases of Ethanol to Rivers and Streams

The transport of ethanol to various locations in California where it would be blended with gasoline raises the possibility that transportation accidents could occur that impact rivers and streams. There are potentially many different scenarios that could be constructed to assess the consequences of such accidents. We note, however, that the transport of ethanol is not inherently any different than the transport of other bulk liquids; hence, the likelihood of releases should not differ either. For the purposes of this screening-level assessment, therefore, we simply postulated an accidental release in which a rail tank car carrying 30,000 gal of ethanol derails and discharges its entire inventory to a river. To estimate the concentrations of ethanol in water resulting from such a hypothetical release, we have adopted an empirically-based methodology developed by Jobson (1996) that is especially suited for cases where there are limited amounts of hydrologic information on an impacted river.

The basic equation for determining the peak downstream concentration of a substance spilled into a river is:

$$C_{pc}\left(T_{pc}\right) = \frac{k_{pc}\left(T_{pc}\right) M_s e^{-k_{tot} T_{pc}}}{\mathrm{nf}\, Q} \tag{5-5}$$

where,

$$T_{pc} = \frac{x}{V_{pc}} \tag{5-6}$$

and

$C_{pc}(T_{pc})$ = peak concentration (pc) of spilled contaminant at a given downriver location at time T_{pc}, mg/L;

k_{pc} = dissipation-rate constant of the peak concentration (pc) due to longitudinal dispersion, 1/s;

T_{pc} = arrival time of the peak concentration (pc) at a location downstream of the release point, h;

x = distance to receptor location downstream of spill site, m;

v_{pc} = velocity of the peak concentration (pc) of the plume, m/s;

M_s = initial mass of the substance (s) discharged, mg;

k_{tot} = loss-rate constant for volatilization and degradation, 1/d (note: for ethanol there is minimal degradation);

nf = normalization factor introduced by Jobson[3] (1996), 1×10^6 (dimensionless); and

Q = volumetric-discharge rate for the river at time of release, L/s.

The time-concentration profile of a contaminant at a fixed location downstream from a spill site is a complex function of channel properties, flow rate, drainage, slope, etc. As a water-borne plume of spilled material is transported downstream, the plume will spread longitudinally in the direction of river flow, creating a gaussian-type pattern of contaminant concentrations in the river at any given point measured downstream (Hemond and Fechner, 1994). Longitudinal dispersion increases with the travel time of the plume, causing the peak concentration to decrease as the plume-width spreads. Jobson (1996) developed an empirical relationship that estimates the value of the rate constant describing the reduction of the peak concentration (that is, k_{pc}) in terms of plume travel time, and the ratio of the volumetric-discharge rate at the time of the release to the mean-annual volumetric-discharge rate of the stream (see Appendix B).

As described in Equation 5-6, the travel time of the plume's peak concentration is equal to the distance from the release point to the downstream receptor location divided by the velocity of the plume's peak concentration in the river. Jobson (1996) developed a set of empirical relationships to determine the velocity of the peak concentration in the dispersing plume, as well as its maximum probable velocity (see Appendix B). Input parameters include the drainage area of the watershed, the slope of the river channel that the plume is transiting, the volumetric-discharge rate at the time of release, and the mean annual volumetric-discharge rate of the river at a receptor location. To assess the consequences of the postulated spill, we used the hydrological parameters of the Sacramento River (in California), south of Dunsmuir and north of Lake Shasta. This particular section of the river has a railroad line adjacent to it and was impacted by a tank car spill in 1991 (California Central Valley Regional Water Quality Control Board [CalCVRWQCB], 1991). The associated watershed has a drainage area of 1100 km^2 (425 mi^2), a slope of 0.015, an average annual-average volumetric-discharge rate of 32.1 m^3/s

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[3] The factor 10^6 arises from the fact that Jobson (1996) defines a "unit concentration" (identified as k_{pc} in Equation [5-5]) as 10^6 times the concentration produced in a unit discharge due to the injection of a unit mass of substance. Jobson (1996) relates the "unit concentration" to a mass flux of solute (mass/time) per unit of mass injected.

(1133 ft^3/s) (see U.S. Geological Survey [USGS], 1999). The assumed volumetric-discharge rate at the time of the hypothetical release is 5.6 m^3/s (200 ft^3/s).

The best estimate for the velocity of the peak concentration of the dispersing plume is 1.2 km/h, while the maximum probable velocity is 2.1 km/h, or almost double the best estimate (see Appendix B). A biodegradation half-life of 24 h was used to simulate the *total* loss rate of ethanol (volatilization loss is minimal for ethanol). Figures 5-1 and 5-2 depict the decreases in the peak concentrations as a function of distance downriver from an assumed release point. The predicted concentrations are highest for the maximum probable velocity of the peak concentration for the dispersing plume, because at high velocity less longitudinal dispersion occurs within the plume during transit over a given distance. Under the spill scenario considered here, the concentrations in river water could affect aquatic species. In a review of the aquatic toxicity of ethanol, for example, Malcolm Pirnie, Inc., (1998a) reported that the LC_{50} (lethal concentration for 50% of a population) for different aquatic species ranged from 454 to 14,740 mg/L. The toxic levels of ethanol would, therefore, be expected to occur at variable distances downstream from the hypothesized spill, with the extent of such toxic concentrations depending on volumetric-discharge conditions. As shown in Figures 5–1 and 5–2, toxic effects could occur many kilometers downstream for a catastrophic release, such as the one that was simulated. For example, if the average volumetric-discharge rate (that is, 32.1 m^3/s) were selected at the time of release, instead of the low volumetric-discharge rate we chose to use, the predicted concentrations would be nearly a factor of six lower—reducing the extent of any possible toxic effects to aquatic species. In addition, if only a portion of the tank-car inventory were released, the resulting concentrations would also be reduced proportionately. Aside from the acute toxicity for aquatic species that might be associated with a spill and their associated recovery, it is unlikely that there would be any long-term toxic effects, as the ethanol will not persist in water because of its rapid biodegradation.

5.5 Releases to Reservoirs and Lakes

One of the unexpected surface-water impacts resulting from the use of MTBE in reformulated gasoline is the occurrence of MTBE in reservoirs and lakes in California (see McCord and Schladow, 1998; Malcolm Pirnie, Inc., 1998b). The principal source of this contamination is recreational boating (Reuter *et al.*, 1998), particularly carbureted two-stroke engines (see Appendix C). Consequently, such recreational watercraft could also represent a potential source of ethanol in surface waters used for boating. In order to assess the significance of ethanol discharges from watercraft to surface waters, we have conducted a screening-level analysis in which we compare the water-quality impacts of MTBE discharges into a lake with those associated with ethanol.

5.5.1. Background: Watercraft Releases of Fuel Compounds

Concerns over the impacts of motorized watercraft on the quality of Lake Tahoe prompted the Tahoe Regional Planning Agency to invoke a ban on two-stroke marine engines. The ban was effective on June 1, 1999; and consequently, this provided a unique opportunity to investigate the differences in the concentrations of MTBE and other fuel compounds in lake water before and after the ban. Appendix C contains the results of a study recently completed by

Allen and Reuter of the Tahoe Research Group at the University of California at Davis, California. This study tracks the changes in fuel compounds in Lake Tahoe from 1997–1998 to 1999. They found that there were significant decreases in the concentrations of MTBE and benzene, toluene, ethyl benzene, and xylene (BTEX) compounds after the ban. For example, for 1999 the mean concentrations of MTBE and toluene were 95.8 and 88.3% lower, respectively, than the levels reported in 1997–1998. The only exception in 1999 was that isolated activities associated boat launch areas, marinas, etc., produced elevated levels in certain locations or “hot spots.”

5.5.2. Water Quality Impacts of MTBE and Ethanol Due to Recreational Boating

The concentrations of fuel hydrocarbons in recreational lakes or reservoirs are a function of the types of watercraft operated (that is, the mix of two-stroke versus four-stroke engines), the temporal pattern of recreational boating (particularly during the summer months and peak vacation periods), and the limnology of the surface water. Important limnologic parameters determining the magnitude and persistence of fuel compounds discharged into water are the mixing or dilution volume of surface water, wind velocity, water temperature, and rate of water flowing through the mixing volume. The primary determinant of the mixing volume is the depth of the epilimnion, or the relatively warm layer of water that sits atop the colder, denser waters of the hypolimnion. Volatilization of fuel compounds increases as the wind velocity rises, thereby decreasing the depth of the surface-boundary layer (which, in turn, increases the mass-transfer velocity of dissolved fuel compounds). Water temperature influences the rates of volatilization and biodegradation. The flow of water through the epilimnion is another mechanism for reducing residual levels of dissolved fuel compounds.

During the summer boating season, the peak discharges of fuel compounds and their related concentrations in water coincide with the holidays (namely, Memorial Day, Fourth of July, and Labor Day), when boating activity increases (Reuter *et al.*, 1998). Needless to say, it is not possible to simulate the levels of fuel compounds in water at a given lake unless watercraft usage is known along with fuel-discharge rates to water. However, as a screening-level analysis, we have chosen to simulate a discrete period of watercraft discharges at Donner Lake in northern California, using data presented in studies by McCord and Schladow (1998) and Reuter *et al.* (1998).

The total mass and concentration of a fuel compound in the epilimnion after a continuous watercraft discharge of a fixed duration can be estimated from

$$M_{s,ep}\left(T_d, t\right) = \frac{E_r \,\mathrm{cf}}{k_{tot}}\left[1 - e^{-k_{tot}T_d}\right]e^{-k_{tot}t} \tag{5-7}$$

and

$$C_{s,ep} = \frac{M_{s,ep}(T_d, t)}{V_{ep}}, \tag{5-8}$$

where

$M_{s,ep}(T_d,t)$ = mass of substance (i.e., fuel compound, *s*) in the epilimnion (*ep*) at time *t* (days) after a continuous discharge of duration T_d (days), μg;

$C_{s,ep}$ = concentration of the substance (i.e., fuel compound, *s*) in the epilimnion (*ep*), μg/L;

E_r = constant discharge rate of substance (i.e., fuel compound, *s*) from boating activity, *kg/d*;

cf = conversion factor, 10^9 μg/kg;

k_{tot} = first-order loss rate for volatilization and biodegradation, 1/d; and

V_{ep} = volume of the epilimnion (*ep*), L

Reuter *et al.* (1998) reported that during a seven-day period lasting from July 1–7, 1997, the total mass of MTBE in Donner Lake rose by 250 kg, resulting in an increase of 10 μg/L in the epilimnion of the lake. The depth of the epilimnion by July was between 9 and 11 m, and the average daily wind velocities from March to November 1997, ranged from 1.7 to 2.1 m/s. After the last major boating activity associated with Labor Day, the mass of MTBE dropped at a rate of 8.1 kg/d, which, according to Reuter *et al.* (1998), reflects a half-life of 14 days (equivalent to a first-order loss rate of 0.05/d). The MTBE loss rate was smaller after the July 7th peak (that is, 6.7 kg/day); however, inputs of MTBE from watercraft still occurred, so that this loss rate is not an accurate indicator of volatilization losses.

We can estimate the average discharge of MTBE into the lake during this seven-day period by solving for E_r in Equation (5-7) and setting $M_{ep}(T_s,t)$ = 250 kg, k_{tot} = 0.05/d, T_s = 7 days, and *t* = 0 day. The resulting discharge rate is 42 kg/d. As an alternative, we also calculated the value of k_v ($\cong k_{tot}$, because MTBE's biodegradation is assumed to be negligible) for MTBE using the mass-transfer velocities estimated from the physicochemical properties of MTBE, wind speed, and mixing depth (as presented in the Appendix A). We used the temperature-dependent equation for estimating H_L given in Robbins *et al.* (1993) to estimate a value of 43 Pa-m^3/mol for MTBE at 20°C. Loss-rate constants were computed for alternative values of the depth of the epilimnion and wind velocities for the seven-day period in July and are shown in Table 5-2. McCord and Schladow (1998) indicate that the average wind speed was approximately 3 m/s and the surface area of the lake was 3.6 km^2. While the depth of the epilimnion across the lake was about 10 m, the effective transport depth for MTBE was probably smaller, based on the portions of lake-surface area overlying regions with water depths under 10 m. Accordingly, we have provided in Table 5-2 estimates of the loss-rate constants for varying depths of the epilimnion and also two different wind speeds. We also show the corresponding mass loadings and concentrations of MTBE in the epilimnion at the end of a seven-day period during which time total MTBE discharged to the lake was considered to be at a constant rate of 40 kg/d from watercraft.

The predicted concentrations decrease with increasing depth of the epilimnion because the mixing volume increases, reducing the concentration of MTBE. The predicted mass loadings increase due to the reduction in loss rates caused by smaller mass-transfer rates as the depth of the epilimnion increases. The best agreement with the observed MTBE loadings and concentrations is for an epilimnion layer of 7 m and a wind speed of 2 m/s. However, all of the predicted values are in general agreement with the values reported by Reuter *et al.* (1998)—given the uncertainties in both the measurements (for example, sampling biases) and the mass-transfer models.

We used the MTBE-release case for Donner Lake as the basis for assessing the nature and magnitude of surface-water quality impacts of ethanol discharged from watercraft. The reference epilimnetic depth of the lake was set at 8 m and the wind speed is 3 m/s. We used the Henry's law constant given at 25˚C (see Table 5–1) to estimate volatilization losses (which are negligible for ethanol). To bracket the range of potential biodegradation losses, we estimated concentrations for biodegradation half-lives of 12, 24, and 48 h. In Figure 5-3, we show the predicted concentrations of ethanol in the lake's epilimnion after a continuous discharge of 40 kg/day of ethanol lasting seven days. With a nominal biodegradation half-life of 24 h, the peak concentration is 2 µg/L, compared with 8.3 µg/L for MTBE with the same source term (Table 5-2).

5.6. Summary

A quantitative risk assessment designed to compare the results of MTBE and ethanol releases to surface waters was not performed and was not the objective of this chapter. Instead, we performed a series of screening-level simulations of various releases to better understand the nature and magnitude of the impacts of ethanol and MTBE on surface waters both temporally and spatially. However, based on the health-protective concentrations for drinking water alone, (which are summarized by the State of California Environmental Protection Agency, Office of Environmental Health Hazard Assessment in Volume 5 of this report [CalEPA/OEHHA, 1999]), it is clear that any catastrophic or even major release of MTBE to surface water is far more likely to represent a potential public-health problem than a similar release of ethanol. This is because the draft health-protective concentration for oral exposures to drinking water for ethanol is 1,100,000 µg/L, whereas the public-health goal for drinking water for MTBE is only 13 µg/L—a difference of almost 5 orders of magnitude (that is, 10^5 or 100,000). The problem of MTBE release to surface water is further exacerbated because it appears to be recalcitrant to aerobic biodegradation (Suflita and Mormile, 1993).

Our analyses indicate that ethanol is considerably less volatile than MTBE in surface waters because of its low Henry's law constant. Although its volatilization-loss rate from water will be much less than that of MTBE, it will not persist in water because it undergoes fairly rapid biodegradation.

The primary uncertainties associated with ethanol in surface water are associated with the determination of biodegradation rates for specific surface waters, including lakes and streams, as a function of water temperature, oxygen content, etc. Also, temperature-dependent values for the Henry's law constant would improve estimates of air/water partitioning for different ambient conditions.

A key data gap involves the potential impact that rainout will have on surface waters situated in urban areas where the ambient concentrations of ethanol are predicted to be the highest.

Ethanol in urban runoff will undergo biodegradation in surface waters; however, there will be a balance between the inputs from rainfall and losses due to degradation—with the sequencing between storms an important variable in determining the average concentrations in surface-water supplies.

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Figures

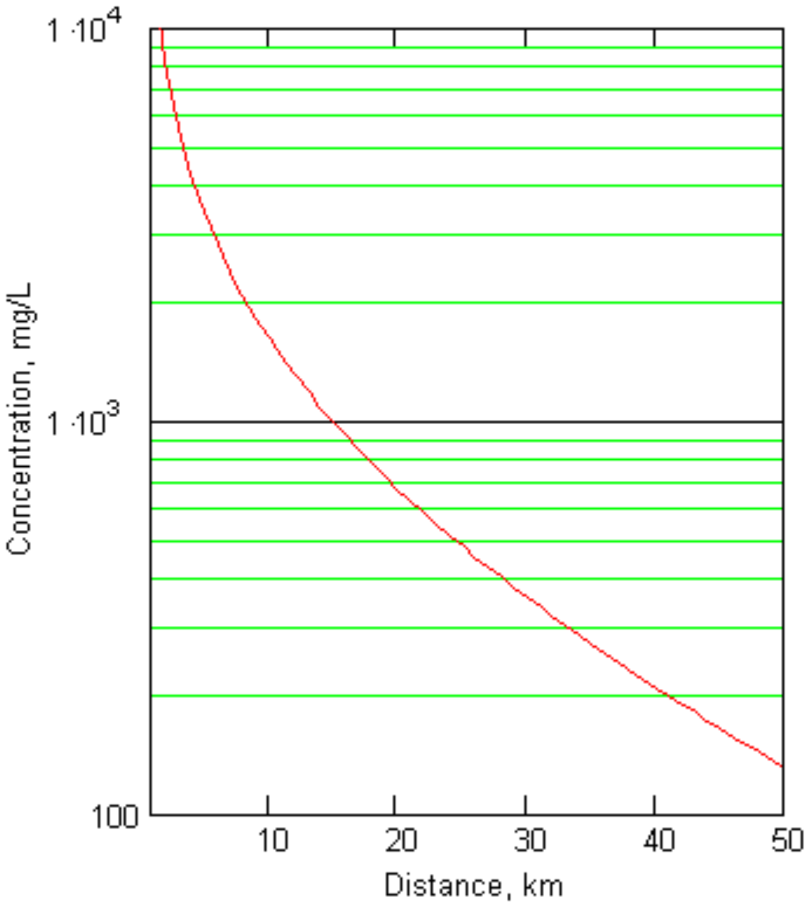

Figure 5-1. Peak concentrations of ethanol in a channel of the Sacramento River above Lake Shasta after a hypothetical tank-car release. Concentrations are based on an estimate of the most likely river-flow velocity for peak concentration (see Appendix B) and a biodegradation half-life of 24 h for ethanol (representing k_{tot} in Equation [5-5]).

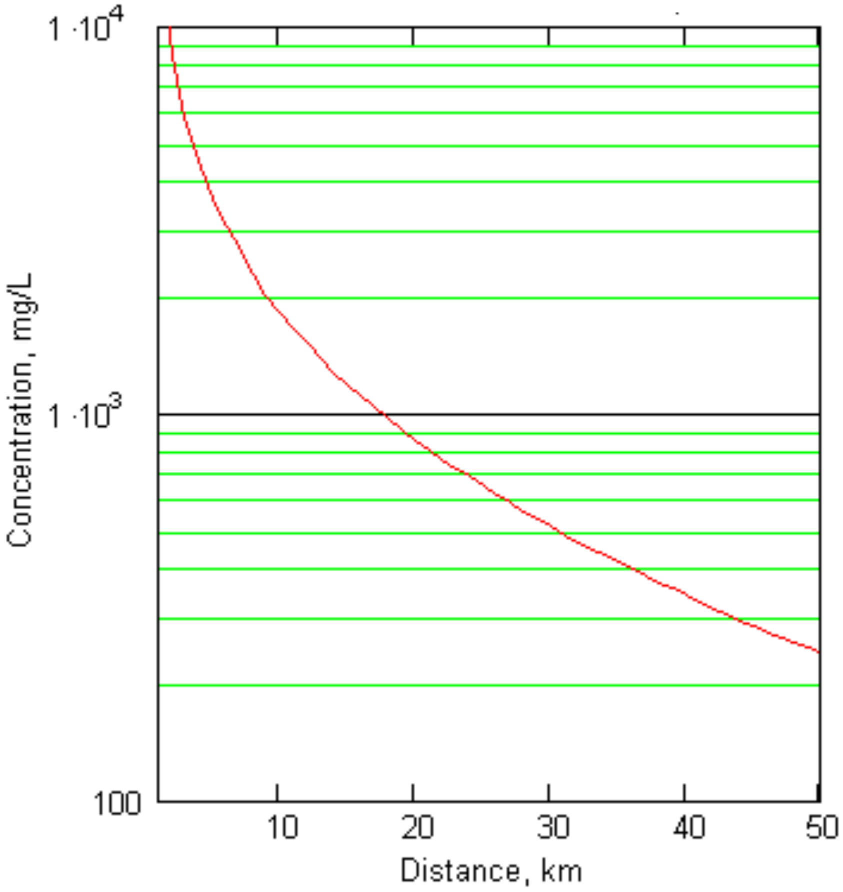

Figure 5-2. Peak concentrations of ethanol in a channel of the Sacramento River above Lake Shasta after a hypothetical tank-car release. Concentrations are based on an estimate of the maximum probable river-flow velocity for peak concentration (see Appendix B) and a biodegradation half-life of 24 h for ethanol (representing k_{tot} in Equation [5-5]).

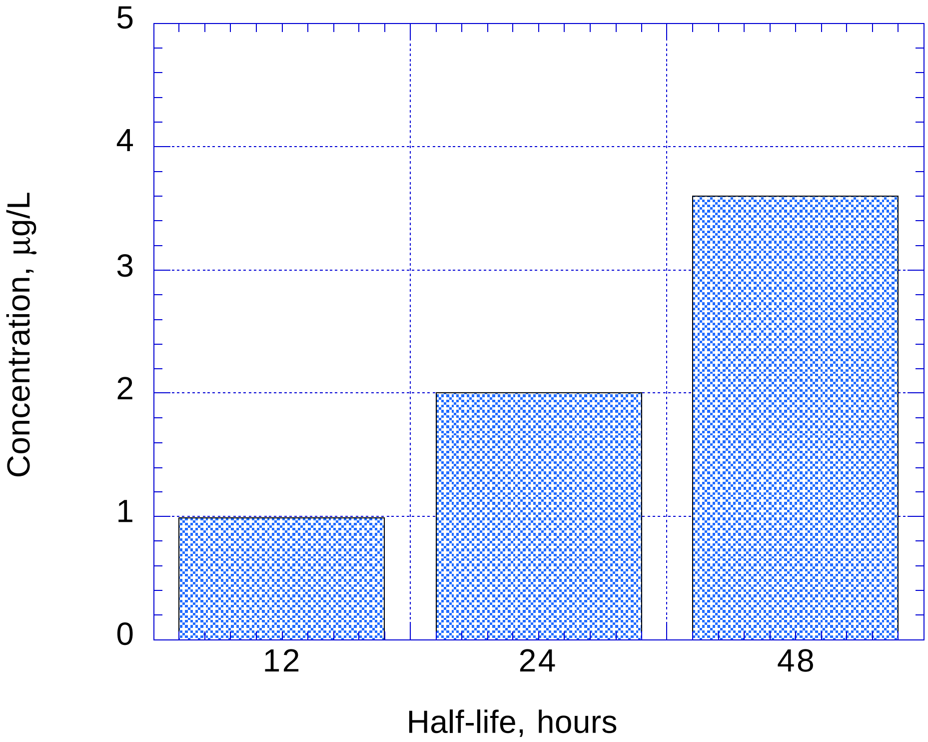

Figure 5-3. Predicted peak concentrations of ethanol in epilimnion waters of Donner Lake after a seven-day period based on alternative biodegradation half-lives and a constant discharge of 40 kg/d from watercraft. Effective depth of the epilimnion for mass transport is 8 m, and the wind velocity is 3 m/s.

Tables

Table 5-1. Physicochemical properties for MTBE and ethanol.

	Chemical	
Property	**MTBE**	**Ethanol**
Molecular weight (g/mol)	88.15	46.07
Density as liquid (g/mL) at 20°C	0.740[a]	0.789[b]
K_{OW} (dimensionless)	8.71[c]	0.50[c]
Vapor pressure (Pa) at 25°C	32,664[d]	7869[e]
Solubility (mol/m^3)	476 (at ≅ 20˚C)[f]	Miscible in water[g]
Henry's law (Pa-m^3/mol) at 25°C	53.5[h]	0.64[i]
Henry's law (dimensionless = H/RT)	0.0216	0.00026

[a] Reported by MacKay *et al.* (1993) and based on three cited, closely agreeing recent values.

[b] Reported by MacKay *et al.* (1995) and based on four cited, closely agreeing recent values.

[c] Reported by Syracuse Research Corporation (SRC) (1999 WebSite) and based on one cited, recent value, for each substance.

[d] Reported by Budavari *et al.* (1989).

[e] Reported by Boublík *et al.* (1984) and based on one cited value.

[f] Measured value reported by Stephenson (1992).

[g] Reported by Riddick *et al.* (1986).

[h] Reported by Robbins *et al.* (1993) as a measured value obtained using static headspace method.

[i] Reported by Hine and Mookerjee (1975) and based on two cited sources.

Table 5-2. Comparison of the predicted mass loadings, peak concentrations, and loss-rate constants for a MTBE release into Donner Lake[a].

Depth of epilimnion h_{ep}, m	Wind velocity u_a, m/s	Loss-rate constant k_v, 1/d	MTBE mass in epilimnion $M_{s,ep}$, kg	MTBE-peak concentration[b] $C_{s,ep}$, μg/L
7	2	0.041	244	9.7
7	3	0.054	233	9.2
8	2	0.036	248	8.6
8	3	0.048	238	8.3
9	2	0.032	251	7.7
9	3	0.043	242	7.5
10	2	0.029	253	7.0
10	3	0.039	245	6.8

[a] Release rate from watercraft is 40 kg / day for seven days.

[b] The dilution volume is calculated as the product of the depth of the epilimnion and the estimated surface area of the lake (that is, 3.6×10^6 m^2, from McCord and Schladow [1998]). Mass loadings and peak concentrations are for the end of the seven-day period and are calculated from Equations (5-7) and (5-8), respectively.

Appendix A
Estimation of Mass-transfer Parameters

Appendix A
Estimation of Mass-transfer Parameters

The key parameter in determining the rate constant for volatilization is the mass-transfer velocity, or the rate with which a compound moves from water to air as a function of its physicochemical properties and environmental conditions, such as the water velocity of a stream, water temperature, and wind velocity. The mass-transfer velocity is estimated using a two-layer transfer model in which there are two thin, stagnant films at the air-water exchange boundary—one is a water film and the other a gas film (see Liss and Slater, 1974; Schwarzenbach *et al.*, 1993). Contaminant movement in these layers is via diffusion, whereas turbulent flow in air and water adjacent to these regions is the dominant method of contaminant transport and mixing. The total transport velocity across these layers is calculated as the reciprocal of the sum of the resistances to transport in the water and air phases, or

$$\upsilon_{tot} = [r_w + r_a]^{-1}, \tag{A–1}$$

where the water and air-phase resistances are computed from

$$r_w = \frac{1}{\upsilon_w} \tag{A–2}$$

$$r_a = \frac{1}{\upsilon_a H_L} \tag{A–3}$$

and the transfer velocities for water and air are estimated from

$$\upsilon_w = \phi\left(D_{O_2}\frac{u_w}{h_{riv}}\right)^{0.5} 1.0241^{(t-20)} \quad \text{(for rivers, from Pankow \textit{et al.}, 1996),} \tag{A–4}$$

$$\upsilon_w = \phi\left(4\times10^{-4} + 4\times10^{-5}u_a^2\right)\times cf \quad \text{(for lakes, from Schwarzenbach \textit{et al.}, 1993),} \tag{A–5}$$

$$\upsilon_a = \alpha\left(0.2u_a + 0.3\right)\times cf \quad \text{(from Schwarzenbach \textit{et al.}, 1993),} \tag{A–6}$$

given

υ_{tot} = total mass-transfer velocity through the air and water layers, m/d;
r_w = resistance to mass transport in air, d/m;
r_a = resistance to mass transport in water, d/m;
υ_a = air-side mass-transfer velocity, m/d;

H_L = dimensionless Henry’s law constant;
υ_w = water-side mass-transfer velocity, m/d;
D_{O_2} = diffusivity of oxygen in water, 1.8×10^{-4} in m^2/d at 20 ^oC;
u_w = water-current velocity in river or stream, m/d;
ϕ = compound-specific adjustment factor for the water-side transfer velocity (unitless);
u_a = wind velocity at a height of 10 m, m/s;
h_{riv} = depth of river or stream (or h_{ep} for depth of epilimnion of lake), m;
t = temperature of water, ^oC;
cf = conversion factor of 864 m/d per cm/s;
and
α = compound-specific adjustment factor for the air-side transfer velocity (unitless).

The rate constant for volatilization (k_V) from a river or stream is equal to υ_{tot}/h_{riv} (from Pankow *et al.*, 1996), while for lakes it is equal to υ_{tot}/h_{ep}, where h_{ep} is the depth of the lake’s epilimnion (Ulrich *et al.*, 1994). The values of ϕ and α for ethanol and MTBE given in Pankow *et al.* (1996) are 0.738 and 0.753, and 0.586 and 0.558, respectively.

The relative importance of the air- and water-side boundary layers in controlling mass transport can be evaluated by comparing the air and water resistances. According to Schwarzenbach *et al.*, (1993), values of $r_a/r_w > 10$ indicate that mass transfer is controlled by the air film, whereas values below 0.1 indicate that mass transfer is controlled by the water film. Values of r_a/r_w between 0.1 and 10 demarcate a region where both boundary layers influence mass transport. For ethanol, both layers are important, although the air-side resistance is greater than the water-side resistance. The mass transfer for MTBE, in contrast, is controlled primarily by the water-side boundary layer.

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Appendix B
Transport Parameters for Riverine Releases

Appendix B

Transport Parameters for Riverine Releases

A spill of a soluble substance into a river creates a dispersing plume that gradually spreads out in a longitudinal direction as a function of time. Dispersion occurs as the plume moves in a meandering stream channel, encountering various forms of current-induced turbulence. For a conservative contaminant, the mass within the plume remains constant with time, and as the plume spreads out along the direction of transport, the peak concentration decreases with time. Consequently, to estimate the amount of dispersion that has occurred during transport, estimates of the plume's travel time are needed. Travel time is estimated by determining the distance traveled from the release point to the measurement (or receptor) location and the velocity of the peak concentration within the plume.

Jobson (1996) developed a series of empirical formulas for estimating the average velocity of the plume's peak concentration and its maximum probable velocity. Using tracer data from a number of watersheds, the plume velocities are computed from

$$V_{pc} = 0.094 + 0.014\, D_{area}^{0.919}\, Q_{adj}^{-0.469}\, R_{slp}^{0.159}\, \frac{Q}{D_{area}} \tag{B-1}$$

$$V_{mpc} = 0.25 + 0.02\, D_{area}^{0.919}\, Q_{adj}^{-0.469}\, R_{slp}^{0.158}\, \frac{Q}{D_{area}} \tag{B-2}$$

where

$$D_{area} = W_{area}{}^{1.25}\, \frac{\sqrt{g}}{Q_{ave}}, \tag{B-3}$$

$$Q_{adj} = \frac{Q}{Q_{ave}}, \tag{B-4}$$

and

V_{pc} = velocity of the peak concentration in a dispersing plume, m/s;

V_{mpc} = maximum probable velocity of the peak concentration in a dispersing plume, m/s;

W_{area} = watershed-drainage area, m^2;

g = acceleration due to gravity, 9.8 m/s^2;

Q_{ave} = annual-average volumetric-discharge rate of the river at receptor location, m^3/s;

Q = volumetric-discharge rate of the river at the time of the release, m^3/s;

R_{slp} = slope of the river channel, m/m;

D_{area} = dimensionless drainage area; and

Q_{adj} = dimensionless relative discharge.

The dissipation rate constant for the peak concentration in a plume is estimated from

$$k_{pc} = 857 T_{pc}^{-0.760} \left(\frac{Q}{Q_{ave}} \right)^{-0.079} \tag{B-5}$$

where T_{pc} (in hours) is the arrival time of the peak-concentration (pc) at a receptor location downstream from the release point, which is equal to the downstream distance from the source to receptor divided by the peak-concentration (pc) velocity or maximum probable peak-concentration (mpc) velocity (that is, V_{pc} or V_{mpc}).

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Appendix C
Changes in MTBW and BTEX Concentrations in Lake Tahoe, CA-NV, Following Implementation of a Ban on Selected Two-stroke Marine Engines

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Changes in MTBE and BTEX Concentrations in Lake Tahoe, CA-NV, Following Implementation of a Ban on Selected Two-stroke Marine Engines

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ABSTRACT

Effective June 1, 1999, the Tahoe Regional Planning Agency imposed a ban on certain types of two-stroke marine-engine technologies. Previous studies had shown that these types of two-stroke carbureted engines accounted for only 11–12% of the total fuel used by watercraft on Lake Tahoe, but they were responsible for approximately 90% of the methyl tertiary butyl ether (MTBE) emissions to the lake. In 1999, Lake Tahoe was monitored in late August and over the Labor Day weekend when peak boating activity traditionally occurs. The purpose of the monitoring was to determine if concentrations of MTBE and gasoline constituents (benzene, toulene, ethyl benzene, and xylene[BTEX]) were affected by implementation of the new marine-engine policy. Samples were taken on three dates: (1) mid-week, (2) after a weekend, and (3) after Labor Day. They were taken from mid-lake (open-water locations), at ten stations located around the perimeter of the lake, and at ten “hot spots” along the south shore where boating and boating-related activities are high. The 1999 results showed a significant decline in both MTBE and BTEX compounds when compared to 1997–1998 levels. Many of the 1999 concentrations of MTBE were below the 0.06-µg/L limit of analytical detection, in contrast to previous monitoring that had many fewer samples this low. High levels of MTBE were still found at certain “hot spots,” but these levels were attributed to isolated boating actions not related to overall boating intensity. Combined, the data strongly suggest that the ban on certain types of two-stroke carbureted engines at Lake Tahoe has been very successful in reducing concentrations of both MTBE and BTEX.

INTRODUCTION

Discovery of the fuel oxygenate, methyl tertiary butyl ether (MTBE), in groundwater, lakes, and reservoirs used for drinking water raised considerable concern among health officials and water suppliers. The U.S. Environmental Protection Agency (US EPA) has classified MTBE as a possible human carcinogen. Recent California legislation has established primary and secondary drinking-water standards at 13 μg/L and 5 μg/L, respectively. In March 1999, the Governor of California called for a statewide phaseout of MTBE as a fuel additive to be completed by the end of 2002.

Since 1997, the Lake Tahoe basin has received considerable state and national attention with regards to MTBE contamination of both groundwater drinking supplies and the lake itself. Contamination of groundwater wells serving the City of South Lake Tahoe is considered to pose more of a potential threat to public health than MTBE concentrations that have been found in the waters of Lake Tahoe. However, because Lake Tahoe has been designated as an Outstanding National Water Resource (ONWR) under the federal Clean Water Act, protection of the lake from controllable sources of pollution is paramount. Samples collected by the Tahoe Research Group (TRG) at the University of California at Davis, the University of Nevada at Reno (UNR), and the U.S. Geological Survey (USGS) during the summers of 1997 and 1998 showed detectable levels of MTBE and the fuel constituents (benzene, toluene, ethyl benzene, and xylenes [BTEX]) lake-wide (Allen *et al.,* 1998). Concentrations were shown to vary with the level of motorized watercraft traffic. However, at specific locations, levels exceeded not only the California drinking-water standards but also the higher US EPA advisory value of 35 μg/L. Samples from open water in the middle of the lake, where little summer boating occurs, revealed the presence of fuel constituents to a depth of 10 m, but at concentrations near or below the analytical levels of detection (mean value for MTBE and BTEX of 0.3 μg/L) (Allen *et al.*, 1998).

Along the shoreline of the lake where motorized watercraft activity is more common, fuel-constituent concentrations were found to be about an order of magnitude higher (for example, 2.6-μg/L mean value for MTBE). However, these shoreline concentrations were still below the established drinking-water standards. In areas where motorized watercraft traffic is considered to be exceptionally high (such as marinas and fueling facilities), mean concentrations for both MTBE and benzene during certain times of the summer boating season exceeded primary drinking-water standards. Further investigation by the California Air Resources Board (CARB) and UNR into the direct contribution of fuel constituents from various engine technologies revealed that carbureted two-stroke engines were contributing a disproportionate share of the fuel-component load to Lake Tahoe (Miller, no date). In fact, Allen *et al.* (1998) calculated that while using only 11 to 12% of the total fuel used for Lake Tahoe boating, these engines contributed 90% of the MTBE to the water. In contrast, four-stroke engines consumed 87% of the fuel but were responsible for only 8% of the estimated MTBE loading to the lake from all marine engines.

Based on the results of these cumulative studies, the Tahoe Regional Planning Agency (TRPA) banned certain types of two-stroke marine-engine technologies (that is, carbureted two-stroke engines). This ban took effect on June 1, 1999. The City of South Lake Tahoe took additional steps to rid the Tahoe basin of MTBE by selling MBTE-free gasoline. Under pressure from the Governor of California, several large oil companies had begun producing gasoline without MTBE and delivering it to the south end of the lake. While this program was intended to reduce the risk of further contamination of groundwater aquifers, it may also have had an effect on concentration of MTBE in the lake. Because fuel costs at marine facilities are significantly higher than at roadside gas stations, conceivably many boaters would choose to refuel while their vessel was still on the trailer.

With both programs to abate MTBE loading to the lake and groundwater in place by late spring 1999, the summer boating season was expected to produce lower levels of in-lake fuel constituents. We began sampling in August to evaluate the effectiveness of these changes; that is, we compared lake concentrations of MTBE and BTEX in the summer of 1999 to those in the summers of 1997 and 1998.

METHODS

We focused our sampling on locations which had had positive results (that is, those sites where these constituents had been found during the 1997 and 1998 monitoring). We selected sampling locations in Lake Tahoe that would best reflect any changes in MTBE and BTEX concentrations that may have resulted from policy decisions within the basin. Therefore, we separated site selections into three categories: 1) open-water, offshore areas above a depth of 10 m, 2) near shore, at locations around the perimeter of the lake, where the majority of boat traffic transits the lake, and 3) locations where boat traffic is concentrated ("hot spots"), often associated with launch ramps, refueling facilities, marinas, or a combination of the above (Figure C-1). Within each category, we chose specific sites, whenever possible, to replicate those sampled in previous years.

The timing of our sampling, in late August and after the Labor Day weekend in September, coincided with the peak of the summer boating season. To avoid potential biases resulting from increased boating on weekends and holidays, we chose three sampling dates. For mid-week days, we chose Wednesday, August 25, and Thursday, August 26, 1999. For weekends, we collected samples from the following Monday (August 30); and for the Labor Day weekend we took samples on the Tuesday after the holiday (September 7).

At all locations, with the exception of mid-lake, water samples were taken by hand at a depth of 0.5 m. (Our previous sampling at Lake Tahoe showed this to be a representative depth for the near-shore stations.) At each location, we submerged a closed volatile organic analysis (VOA) vial to the sampling depth and then opened it and allowed it to fill completely. We replaced the cap while the vial was still submerged. We checked the samples to ensure no air space remained within the VOA vials before placing them on ice in a cooler. The mid-lake samples were collected using a 1.2-L, stainless-steel Kemmerer well sampler with Teflon end-caps. The sampler was lowered to depth and closed with a messenger. We then transferred the water to a VOA vial and filled it until no air spaces remained. All samples were kept on ice from collection through transport to Lawrence Livermore National Laboratories (LLNL) in Livermore, CA. All analytical determinations were made by LLNL staff at their facilities (Koester, 1999). Analyses were performed using a gas chromatograph/mass spectrometer (GC/MS) operated in the selected-ion monitoring mode and in accordance with US EPA Method 8260. An internal standard of deuterated-MTBE was used to quantify MTBE and also to monitor instrument performance. The limit of quantification obtained by this procedure for MTBE is 0.06 parts per billion (ppb).

RESULTS

The raw data, as supplied by the LLNL laboratory, are presented in Table C-3. Open lake and near-shore samples showed a significant decrease in MTBE concentration when compared to data collected in 1997 and 1998 (Table C-1). In general, ambient concentrations decreased by an order of magnitude (a factor of ten). Samples around the north end of the lake (Glenbrook to Homewood) were at or below the 0.06-µg/L level of detection. The samples we collected in the vicinity of the south end of the lake (Zephyr Cove to Emerald Bay) showed a similar drop in concentration from previous years but remained above the level of detection at a few tenths of a part per billion (µg/L).

Ambient concentrations of the BTEX compounds at the near-shore locations were also found to be lower than levels recorded during the past two years of monitoring (Table C-2). However, we were unable to determine changes in ambient concentrations when data from all three years (1997, 1998, and 1999) were below the analytical level of detection, as was the case for BTEX at all samples taken from open water and at the near-shore sites of Glenbrook and Homewood.

To further characterize fuel-constituent concentrations, we collected samples from isolated areas where motorized watercraft traffic is heavy and above the levels observed at the shoreline locations. These "hot spots" are typically associated with marinas, launch ramps, and refueling facilities. While all ten of the selected sites had greater mean fuel-constituent concentrations than the open-shoreline and open-water areas, only four locations approached or exceeded drinking-water standards. The remaining six "hot spots" had fuel-constituent concentrations similar to near-shore areas sampled during the 1997 and 1998 monitoring. At the four "hot spots" where fuel-constituent concentrations neared or exceeded drinking-water standards, MTBE and BTEX concentrations were highly variable. MTBE concentrations ranged from 0.46 µg/L up to 56.5 µg/L. This highend value is over four times the primary drinking-water standard of 13 µg/L. There was no statistically significant difference in concentration for MTBE or any of the BTEX compounds between any of the three years of data at the "hot-spot" locations (Tables C-1, C-2a, and C-2b). The dramatic difference in results between these "hot spots" and the remainder of the lake suggests that source contamination has not been completely eliminated by the regulatory actions taken to date, but that contaminants entering the lake were significantly reduced in the summer of 1999.

DISCUSSION

The sampling dates selected during this study were at the end of the summer boating season during August and after the Labor Day weekend in September. Fuel-constituent concentrations in surface waters can peak following the Fourth of July weekend with changes in concentration being attributed to the dramatic increase in recreational boating (Reuter *et al.*, 1998). However, for a sampling program which more accurately characterizes the summer fuel-constituent load to a waterbody, rather than a worst-case, single-day event, the month of August has proven to be appropriate. Allen *et al.* (1998) showed that mean concentrations of MTBE and BTEX compounds were the highest at Lake Tahoe during August.

With the exception of a few of the "hot spots," the data we collected during this study showed little variation between sampling dates. Both the open-water (mid-lake) and near-shore samples (with the exception of the Edgewood site) remained within a few hundredths of a µg/L at each site over the course of the three days, allowing us to pool the data for comparisons to the monitoring data collected in previous years.

The "hot spots" around the south end of the lake showed greater variation over the three sampling dates. However, concentrations at individual sites did not change consistently between the three sampling dates. Half of the sites recorded their highest concentrations during the mid-week sampling, which was expected to represent the lowest concentrations due to suspected lower boat traffic. The remainder of the sites recorded their highest values following the Labor Day weekend, which is to be expected due to higher boating activity. The lowest values at each of the “hot spots” occurred on the sampling date following the regular summer weekend. It is assumed that this was a result of a high-wind event on both Sunday and Monday, keeping many boaters on shore and possibly allowing increased volatilization rates of fuel constituents from the water. We also suspect that at the “hot spots,” variation in MTBE concentration within a given day was high. For example, if there had been a minor spillage during fueling, or if a boat’s bilge water had drained while it was being removed from the lake, concentrations would be expected to be temporarily higher in the vicinity of these activities. It was beyond the scope of this study to determine if the higher concentrations persisted throughout the day or if they were simply associated with a single action as described above.

Comparisons of data collected during this study with that of previous years shows a dramatic decrease in MTBE concentration at both offshore and near-shore locations (86.7% and 95.8%, respectively). This demonstrates that programs to eliminate MTBE from Lake Tahoe are having an effect. The offshore and most of the near-shore locations around the lake had MTBE concentrations at or near the analytical limit of detection (LOD) throughout the sampling period. In fact, if we had used the LOD of 0.1 μg/L from the 1997 and 1998 monitoring, instead of the very low LOD of 0.06 μg/L, samples from all but Emerald Bay, Kiva Beach, and Edgewood would have been below detection. These remaining three locations also had dramatic decreases in 1999, but the level of motorized watercraft traffic in these areas is greater than in other portions of the lake (Nevada Division of Wildlife, 1988) resulting in higher fuel-constituent concentrations. It is important to recognize that none of the recorded concentrations around the near-shore or offshore during 1999 ever approached California or Nevada drinking-water standards.

The sampling of “hot spots” around the south end of Lake Tahoe resulted in highly variable results (that is, an MTBE range <0.06 to 56.5 μg/L). MTBE samples collected at Ski Run Marina exceeded the California primary drinking-water standard of 13 μg/L by four-fold on two separate sampling dates. Additionally, the California drinking-water standard for benzene (0.1 μg/L) was surpassed on the post-Labor Day sampling (September 1999). These samples stand out from the rest as being extremely high even for the “hot spot” locations. The reasons may be due to above-average concentration of boats per unit-area or some problem with operations at the facilities. The two other locations where measured concentrations of MTBE approached or exceeded California drinking-water standards were associated with boat-launch ramps. However, because neither boat-ramp location is in the immediate proximity of fueling facilities, the fuel constituents may have come from the boats themselves.

While it is unclear how the fuel entered the water, any number of human errors and boat malfunctions could have contributed. One distinct possibility associated with launch ramps is the draining of the bilge while removing the boat from the water. Either the intentional removal of boat plugs to allow draining while the boat was on the incline ramp or the automatic operation of electrical bilge pumps when water rushed to the back of the boat causes fuel-laden water to flow directly into the lake in the vicinity of the ramp.

CONCLUSION

Overall, fuel-constituent concentrations in Lake Tahoe in 1999 were down dramatically from previous monitoring years (1997 and 1998), possibly as a result of the TRPA regulation that banned certain types of two-cycle marine-engine technologies, or as a byproduct of some service stations within the Tahoe basin selling MTBE-free fuel.

We compared the decreases in ambient MTBE and toluene concentrations to determine which of the corrective actions was having the greatest impact on Tahoe water quality. If the MTBE-free fuel was having the greatest impact, we expected the ambient MTBE concentrations to decrease while toluene concentrations in the lake would remain near the levels recorded in 1997 and 1998. If the new boating regulations were having the greatest impact, we expected both MTBE and toluene concentrations to drop. Indeed, both mean MTBE and mean toluene concentrations did drop significantly (95.8% and 88.3%, respectively), indicating that the elimination of the highly polluting, carbureted two-stoke engines is having an impact on water quality.

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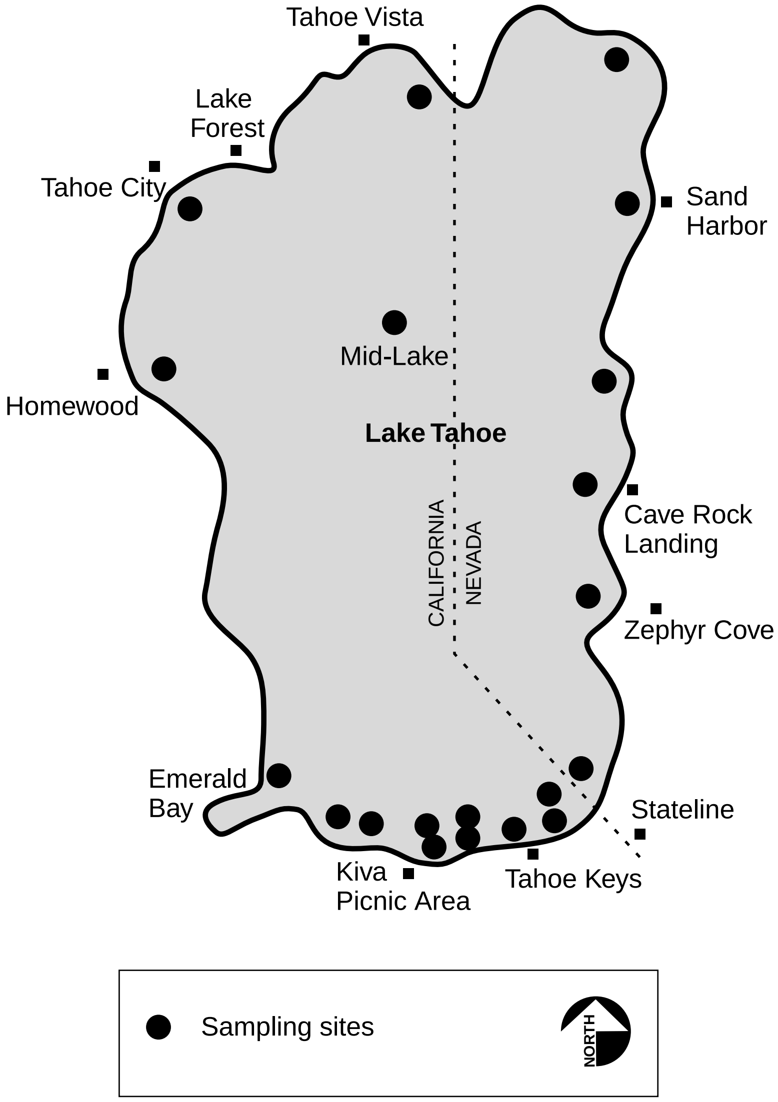

Figure 5-1. 1999 sampling locations at Lake Tahoe.

Table C-1. Comparative Lake Tahoe MTBE concentrations, 1997, 1998, 1999[a].

	MTBE Concentration (μg/L)		
Site	**1997[b]**	**1998[c]**	**1999[d]**
Mid-lake	0.54	0.28	0.04
Incline Village	0.45	0.84	0.05
Kings Beach	1.7		0.08
Tahoe City	2.85	1.1	0.04
Homewood	0.45	0.78	0.06
Emerald Bay		4	0.33
Kiva Beach		1.8	0.1
Edgewood		2.4	0.2
Zephyr Cove	1	1.3	0.08
Glenbrook	0.3	0.47	0.03
Sand Harbor			0.06
Cave Rock			0.18
Zephyr Pier			0.15
Ski Run Inside			26.96
Ski Run Outside	20.8		19.77
El Dorado Ramp			2.68
Tahoe Keys Ramp			7.06
Tahoe Keys Channel	0.68	2	1.8
Camp Rich Pier	1.79		0.16
Camp Rich Pumps			0.11
Ski Boat Beach			0.1

[a] When more than one data point exists at a single site within a given year, a mean value is presented (<0.1 = 0.05 for calculation of mean).

[b] 1997 data was collected by the University of Nevada at Reno (UNR), and the United States Geological Survey (USGS) during July, August, and September.

[c] 1998 data was collected by USGS and Tahoe Research Group (TRG) in August and September.

[d] 1999 data was collected by TRG during August and September.

Table C-2a. Comparative fuel-constituent data (BTEX), 1997, 1998, and 1999[a].

Site	Benzene concentration, (μg/L)			Toluene concentration (μg/L)		
	1997[b]	1998[c]	1999[d]	1997[b]	1998[c]	1999[d]
Mid-Lake	0.03	0.05	0.05	0.05	0.06	0.04
Incline Village	0.05	0.17	0.16	0.13	1	0.14
Kings Beach	0.13		0.1	0.68		0.18
Tahoe City	0.24	0.28	0.05	1.24	0.64	0.14
Homewood	0.05	0.05	0.05	0.15	0.27	0.06
Emerald Bay		0.44	0.18		1.5	0.24
Kiva Beach		0.17	0.07		0.78	0.16
Edgewood		0.21	0.07		1	0.17
Zephyr Cove	0.15	0.61	0.07	0.7	4.4	0.12
Glenbrook	0.04	0.05	0.05	0.1	0.27	0.08
Sand Harbor			0.05			0.11
Cave Rock			0.12			0.32
Zephyr Pier			0.13			0.14
Ski Run Inside			0.14			0.22
Ski Run Outside	0.88		0.43	7.3		1.75
El Dorado Ramp			0.45			0.92
Tahoe Keys Ramp			0.15			0.28
Tahoe Keys Channel	0.07	0.18	0.31	0.26	0.91	1.53
Camp Rich Pier	0.29		0.17	1.53		0.5
Camp Rich Pumps			0.14			0.38
Ski Boat Beach			0.12			0.33

[a] When more than one data point exists at a single site within a given year, a mean value is presented (<0.1 = 0.05 for calculation of mean).

[b] 1997 data was collected by the University of Nevada at Reno (UNR), and the United States Geological Survey (USGS) during July, August, and September.

[c] 1998 data was collected by USGS and Tahoe Research Group (TRG) in August and September.

[d] 1999 data was collected by TRG during August and September·

Table C-2b. Comparative fuel-constituent data (BTEX), 1997, 1998, and 1999.

	Ethylbenzene (μg/L)			m,p, and o Xylene expressed as total xylene (μg/L)		
Site	**1997**[b]	**1998** [c]	**1999**[d]	**1997**[b]	**1998** [c]	**1999**[d]
Mid-lake	0.02	0.04	0.04	0.04	0.05	0.09
Incline Village	0.02	0.24	0.04	0.1	1.4	0.14
Kings Beach	0.12		0.04	0.72		0.16
Tahoe City	0.24	0.11	0.04	1.39	0.58	0.12
Homewood	0.02	0.04	0.04	0.1	0.26	0.09
Emerald Bay		0.2	0.04		2.1	0.34
Kiva Beach		0.12	0.04		0.81	0.16
Edgewood		0.18	0.04		1.3	0.11
Zephyr Cove	0.12	1.1	0.04	0.75	6.7	0.14
Glenbrook	0.01	0.06	0.04	0.06	0.36	0.13
Sand Harbor			0.04			0.14
Cave Rock			0.09			0.47
Zephyr Pier			0.14			0.83
Ski Run Inside			0.04			0.55
Ski Run Outside	1.1		0.3	6.3		2.34
El Dorado Ramp			1.1			1.29
Tahoe Keys Ramp			0.08			0.47
Tahoe Keys Channel	0.04	0.17	0.12	0.3	1	0.95
Camp Rich Pier	0.4		0.12	1.45		0.84
Camp Rich Pumps			0.19			0.46
Ski Boat Beach			0.08			0.53

[a] When more than one data point exists at a single site within a given year, a mean value is presented (<0.1 = 0.05 for calculation of mean).

[b] 1997 data was collected by the University of Nevada at Reno (UNR), and the United States Geological Survey (USGS) during July, August, and September.

[c] 1998 data was collected by USGS and Tahoe Research Group (TRG) in August and September.

[d] 1999 data was collected by TRG during August and September·

Table C-3. Fuel-constituent concentrations in Lake Tahoe 1999.

MTBE

Offshore	8/25/99	8/30/99	9/7/99
0m	<.06	<.06	<.06
3m	<.06	<.06	<.06
10m	0.08	<.06	<.06

Near shore	8/25/99	8/30/99	9/7/99
Incline Village	0.07		<.06
Kings Beach	0.08		0.07
Tahoe City	0.07	<.06	<.06
Homewood	0.06	0.09	<.06
Emerald Bay	0.35	0.36	0.29
Kiva Beach	0.14	<.06	0.13
Edgewood	0.14	0.35	0.11
Zephyr Cove	0.09	0.06	0.08
Glenbrook	<.06		<.06
Sand Harbor	0.08		<.06

Hot Spots	8/25/99	8/30/99	9/7/99
Cave Rock	0.08	<.06	0.42
Zepher Pier	0.09	0.06	0.31
Ski Run In	1.39	23	56.5
Ski Run Out	55.6	1.58	2.14
El Dorado Ramp	4.92	0.46	2.66
Tahoe Keys Ramp	7.28	6.93	6.98
Tahoe Keys Channel	2.14	0.53	2.72
Camp Rich Pier	0.19	0.08	0.2
Camp Rich Pumps	0.19	<.06	0.1
Ski Boat Beach	0.11	<.06	0.16

Blanks	8/25/99	8/30/99	9/7/99
Field	<.06		<.06
mid-lake	<.06		

BENZENE

Offshore	8/25/99	8/30/99	9/7/99
0m	<0.1	<0.1	<0.1
3m	<0.1	<0.1	<0.1
10m	<0.1	<0.1	<0.1

Near shore	8/25/99	8/30/99	9/7/99
Incline Village	0.27		<.1
Kings Beach	0.15		<.1
Tahoe City	<.1	<.1	<.1
Homewood	<.1		<.1
Emerald Bay	0.1	0.19	0.24
Kiva Beach	<.1	<.1	0.12
Edgewood	<.1	<.1	0.12
Zephyr Cove	0.1	<.1	<.1
Glenbrook	<.1		<.1
Sand Harbor	<.1		<.1

Hot Spots	8/25/99	8/30/99	9/7/99
Cave Rock	<.1	<.1	0.26
Zepher Pier	<.1	<.1	0.28
Ski Run In	<.1	<.1	0.33
Ski Run Out	<.1	<.1	1.18
El Dorado Ramp	0.79	<.1	0.51
Tahoe Keys Ramp	<.1	<.1	0.36
Tahoe Keys Channel	<.1	<.1	0.84
Camp Rich Pier	0.11	<.1	0.34
Camp Rich Pumps	0.26	<.1	0.11
Ski Boat Beach	<.1	<.1	0.26

Blanks	8/25/99	8/30/99	9/7/99
Field	<0.1		<0.1
mid-lake	0.12		

TOLUENE

Offshore	8/25/99	8/30/99	9/7/99
0m	<.09	<.09	<.09
3m	<.09	<.09	<.09
10m	<.09	<.09	<.09

Near shore	8/25/99	8/30/99	9/7/99
Incline Village	0.11		0.18
Kings Beach	<.09		0.32
Tahoe City	0.18	<.09	0.2
Homewood	<.09	<.09	0.1
Emerald Bay	<.09	0.11	0.57
Kiva Beach	<.09	<.09	0.4
Edgewood	<.09	<.09	0.43
Zephyr Cove	<.09	<.09	0.26
Glenbrook	<.09		0.11
Sand Harbor	<.09		0.18

Hot Spots	8/25/99	8/30/99	9/7/99
Cave Rock	0.13	<.09	0.77
Zepher Pier	<.09	<.09	0.34
Ski Run In	<.09	<.09	
Ski Run Out	<.09	<.09	5.17
El Dorado Ramp	0.24	<.09	2.47
Tahoe Keys Ramp	<.09	<.09	0.76
Tahoe Keys Channel	<.09	<.09	4.5
Camp Rich Pier	<.09	<.09	1.42
Camp Rich Pumps	0.6	0.15	0.4
Ski Boat Beach	<.09	<.09	0.89

Blanks	8/25/99	8/30/99	9/7/99
Field	0.18		<.09
mid-lake	0.27		

ETHYLBENZENE

Offshore	8/25/99	8/30/99	9/7/99
0m	<.09	<.09	<.09
3m	<.09	<.09	<.09
10m	<.09	<.09	<.09

Near shore	8/25/99	8/30/99	9/7/99
Incline Village	<.09		<.09
Kings Beach	<.09		<.09
Tahoe City	<.09	<.09	<.09
Homewood	<.09	<.09	<.09
Emerald Bay	<.09	<.09	<.09
Kiva Beach	<.09	<.09	<.09
Edgewood	<.09	<.09	<.09
Zephyr Cove	<.09	<.09	<.09
Glenbrook	<.09		<.09
Sand Harbor	<.09		<.09

Hot Spots	8/25/99	8/30/99	9/7/99
Cave Rock	<.09	<.09	0.17
Zepher Pier	<.09	<.09	0.34
Ski Run In	<.09	<.09	<.09
Ski Run Out	<.09	<.09	0.82
El Dorado Ramp	2.77	<.09	0.48
Tahoe Keys Ramp	<.09	<.09	0.14
Tahoe Keys Channel	<.09	<.09	0.27
Camp Rich Pier	<.09	<.09	0.27
Camp Rich Pumps	0.47	<.09	<.09
Ski Boat Beach	<.09	<.09	0.15

Blanks	8/25/99	8/30/99	9/7/99
Field	<.09		<.09
mid-lake	<.09		

m,p and o Xylene, expressed as total*

Offshore	8/25/99	8/30/99	9/7/99
0m	<.18	<.18	<.18
3m	<.18	<.18	<.18
10m	<.18	<.18	<.18

Near shore	8/25/99	8/30/99	9/7/99
Incline Village	<.24		<.30
Kings Beach	<.19		<.46
Tahoe City	<.18	<.18	<.33
Homewood	<.18	<.18	<.18
Emerald Bay	<.18	<.26	0.79
Kiva Beach	<.18	<.18	<.60
Edgewood	<.18	<.18	<.30
Zephyr Cove	<.18	<.18	<.46
Glenbrook	<.18		<.33
Sand Harbor	<.18		<.36

Hot Spots	8/25/99	8/30/99	9/7/99
Cave Rock	<.18	<.18	1.23
Zepher Pier	<.18	<.18	2.31
Ski Run In	<.18	<.18	1.48
Ski Run Out	<.18	<.18	6.83
El Dorado Ramp	<.83	<.18	3.36
Tahoe Keys Ramp	<.18	<.18	1.23
Tahoe Keys Channel	<.18	<.18	2.67
Camp Rich Pier	<.18	<.18	2.33
Camp Rich Pumps	0.57	<.32	0.64
Ski Boat Beach	<.18	<.18	1.4

Blanks	8/25/99	8/30/99	9/7/99
Field	<.18		<.18
mid-lake	<.18		

*m,p and o xylenes were added for total xylenes.
When either m,p or o xylenes were reported as '<' the total xylenes were also expressed as '<'

m,p-Xylene

Offshore	8/25/99	8/30/99	9/7/99
0m	<.1	<.1	<.1
3m	<.1	<.1	<.1
10m	<.1	<.1	<.1

Near shore	8/25/99	8/30/99	9/7/99
Incline Village	<.1		0.22
Kings Beach	<.1		0.38
Tahoe City	<.1	<.1	0.25
Homewood	<.1	<.1	0.1
Emerald Bay	<.1	0.18	0.69
Kiva Beach	<.1	<.1	0.52
Edgewood	<.1	<.1	0.22
Zephyr Cove	<.1	<.1	0.38
Glenbrook	<.1		0.25
Sand Harbor	<.1		0.28

Hot Spots	8/25/99	8/30/99	9/7/99
Cave Rock	<.1	<.1	1.05
Zepher Pier	<.1	<.1	2
Ski Run In	<.1	<.1	1.22
Ski Run Out	<.1	<.1	5.89
El Dorado Ramp	<.1	<.1	2.83
Tahoe Keys Ramp	<.1	<.1	1.04
Tahoe Keys Channel	<.1	<.1	2.13
Camp Rich Pier	<.1	<.1	2.03
Camp Rich Pumps	0.42	0.24	0.56
Ski Boat Beach	<.1	<.1	1.21

Blanks	8/25/99	8/30/99	9/7/99
Field	<.1		<.1
mid-lake	<.1		

o-Xylene

Offshore	8/25/99	8/30/99	9/7/99
0m	<.08	<.08	<.08
3m	<.08	<.08	<.08
10m	<.08	<.08	<.08

Near shore	8/25/99	8/30/99	9/7/99
Incline Village	0.14		<.08
Kings Beach	0.09		<.08
Tahoe City	<.08	<.08	<.08
Homewood	<.08	<.08	<.08
Emerald Bay	<.08	<.08	0.1
Kiva Beach	<.08	<.08	<.08
Edgewood	<.08	<.08	<.08
Zephyr Cove	<.08	<.08	<.08
Glenbrook	<.08		<.08
Sand Harbor	<.08		<.08

Hot Spots	8/25/99	8/30/99	9/7/99
Cave Rock	<.08	<.08	0.18
Zepher Pier	<.08	<.08	0.31
Ski Run In	<.08	<.08	0.26
Ski Run Out	<.08	<.08	0.94
El Dorado Ramp	0.73	<.08	0.53
Tahoe Keys Ramp	<.08	<.08	0.19
Tahoe Keys Channel	<.08	<.08	0.54
Camp Rich Pier	<.08	<.08	0.3
Camp Rich Pumps	0.15	<.08	0.08
Ski Boat Beach	<.08	<.08	0.19

Blanks	8/25/99	8/30/99	9/7/99
Field	<.08		<.08
mid-lake	<.08		

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Chapter 6: Environmental Transport and Fate of Fuel Hydrocarbon Alkylates

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Table of Contents

List of Figures

List of Tables

6. Environmental Transport and Fate of Alkylates

6.1. Introduction

Alkylates—high-octane solutions of branched alkanes—are already components in gasoline, but gasoline distributed in California after a phase-out of methyl tertiary butyl ether (MTBE) will likely include an increased amount of alkylates. MTBE is a high-octane, anti-knock additive; and to maintain octane levels in gasoline after MBTE is removed, additional amounts of alkylates will be required. For example, although ethanol also has a high-octane level, its oxygen content is about twice that of MTBE; consequently, less ethanol is required to meet a specified oxygen content (e.g., 2.5 wt% oxygen). To compensate for the resulting octane deficit that would be produced, petroleum companies could add more alkylates as the high-octane blending components. If an oxygen requirement is eliminated altogether, even greater amounts of high-octane components, such as alkylates, must be added to gasoline.

Assuming that California gasoline contains on average approximately 10 wt% MTBE and approximately 14 wt% alkylate, and that the oxygen requirement is to remain fixed at about 2 wt%, ethanol would have to be added at the 5 wt% level. The octane rating of ethanol is close to that of MTBE (approximately 110), and the octane rating of an alkylate solution is about 92. To achieve an overall gasoline octane rating of 88 in the ethanol fuel, a linear calculation indicates the need to increase the percentage of alkylate component from approximately 14 to approximately 34 wt%. This is a rough estimation because there are other requirements that gasoline formulations must meet besides octane rating, and many of the specification parameters (including octane rating and vapor pressure) are not linear functions of the mass. However, it illustrates that the percentage of alkylate in gasoline could increase significantly (approximately 20%) after a phaseout of MTBE.

The goal of this chapter of the report is to characterize the environmental transport and fate of representative alkylate components, based on available information about their physicochemical properties as well as on relevant studies conducted on their environmental chemistry in soil, air, and water. Unlike ethanol or MTBE, the physicochemical properties of alkylate components resemble those of other hydrocarbons present in gasoline, that is, very low solubility in water, high octanol-water partition coefficient, high Henry's law constant, etc. Therefore, an increase in the alkylate percentage of gasoline may not effect significantly the way gasoline behaves in environmental releases.

6.2. Background

Alkylation is an industrial synthetic process used to produce a high-octane solution of branched alkanes (called isoalkanes). This solution is called alkylate and is used as a blending component for gasoline. During World War II, alkylate production was increased to meet the demand for high-octane gasoline used by fighter planes. After the war, the demand for high-octane components for aviation fuels diminished, and the use of alkylate shifted towards the automotive market (Owen, 1995; Kinnear, 1998). The production capacity remained more or less constant during the 1950s and 1960s because of the competitive cost of other high-octane blending components for automotive fuel, such as tetraethyl lead. In 1985, the United States Environmental Protection Agency (US EPA) imposed a drastic reduction of lead in gasoline formulations lowering it, from 1.1 to 0.5 g/gal, which increased the demand for alkylates. Today, approximately 14% of the gasoline in the United States consists of alkylates (Miller, 1999). However, as noted above, this percentage may be increased significantly in the future to compensate for the loss in octane number, resulting from either the removal of MTBE and use of ethanol (EtOH) or no oxygenates in fuel.

Compared to products of other refining processes, alkylates have relatively low Reid vapor pressure[1] as well as relatively low concentrations of aromatics, olefins, and sulfur. From an environmental standpoint, these are some of the more desirable properties for a blending component for gasoline. Therefore, as environmental regulations move toward cleaner burning fuels, it is likely that the use of alkylates as blending stock for gasoline could rise. However, alkylates have not been examined critically and systematically in terms of their potential environmental, health, and safety impacts. This examination becomes particularly important before they are used in greater quantities. Here we briefly examine some of the relevant transport and fate issues related to alkylates.

6.3. Production of Alkylates

In the alkylation process, isobutane is combined with light olefins (double-bonded compounds of 3 to 5 carbon atoms: C_3 to C_5) in the presence of a strong acid catalyst. The only catalysts presently used for industrial production of alkylates are sulfuric and hydrofluoric acids (H_2SO_4 and HF, respectively), with sulfuric acid accounting for about 46% of the world's production capacity (Peterson, 1999). Currently, research on alternative, solid catalysts is taking place. In addition, there is some effort to convert alkylation units from hydrofluoric- to sulfuric-acid catalysis because of the more serious health hazards associated with using hydrofluoric acid.

Studies on alkylation catalyzed by sulfuric acid have shown that there are at least four basic reaction mechanisms. The first mechanism results in the direct alkylation of isobutane with C_3 to C_5 olefins to produce C_7 to C_9 isoalkanes, including isooctane (2, 2, 4-trimethylpentane). The following equation shows a typical alkylation reaction by this process (that is, isobutene and isobutane are combined in the presence of HF or H_2SO_4 at a temperature greater than 10°C):

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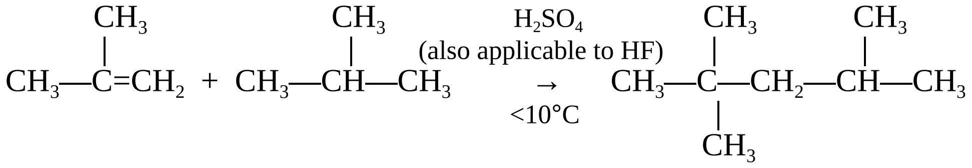
[1] Vapor pressure of a liquid measured by the American Society for Testing and Materials (ASTM) D323 procedure and generally applied to gasoline and gasoline components (Owen and Coley, 1995).



$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 + CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_3 \xrightarrow[<10^\circ C]{H_2SO_4\ \text{(also applicable to HF)}} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_3 \qquad (6\text{-}1)$$

Isobutene	Isobutane	Isooctane
(2-Methyl propene)	(2-Methyl propane)	(2,2,4-Trimethylpentane)

The second mechanism consists of polymerization-fragmentation reactions that produce less branched paraffins, typically C_5 to C_{10}. The third mechanism is a polymerization reaction that results in C_{10} and heavier isoalkanes. Finally, the fourth mechanism is a hydride transfer that accounts for the production of isopentane and trimethylpentane (Kinnear, 1998; Peterson, 1999).

Kinnear (1998) indicates that a typical alkylate product can be composed of 100 to 200 paraffins ranging from C_5 to C_{16}. Calculations based on the analysis of an alkylate indicate that more than 86 moles per 100 moles of alkylate correspond to the C_8 family of isoalkanes (see Table II in Albright *et al.*, 1993). In addition, the average number of carbon atoms in an alkylate molecule is shown to be between 7 and 8 under various alkylation conditions (Albright *et al.*, 1993). It is important to keep in mind that any current gasoline blend already does contain alkylate hydrocarbons. Therefore, the concentration of any given hydrocarbon in gasoline will be the result of its weighted contribution to the entire blended mixture. Only the alkylate component is discussed in this chapter.

6.4. Chemical Composition and Properties of Alkylates

In 1963, Durrett *et al*. (1963) presented a detailed component analysis of alkylates, including five commercial ones produced by either sulfuric- or hydrofluoric-acid catalysis. Based on the yields (see Table V in Durrett *et al*., 1963), 13 compounds were chosen to represent, in principle, more than 90% by mass of a typical alkylate; and these are listed in Table 6-1. (Note that Table 6-1 is intended as a generic list; it is not a complete list and component yields of alkylates vary depending on process parameters.) In the same reference, 2,2,4-trimethylpenatane (isooctane) accounts for approximately 30–49% of the yield, and the isomers 2,3,4 and 2,3,3 account for approximately 18–32%. Miller (1999) indicated that a typical alkylate produced in a refinery contains approximately 26% isooctane and approximately 25% of other alkylated octanes, which agrees favorably with Durrett *et al*. (1963).

Table 6-1 summarizes some physical properties along with the Chemical Abstracts registry numbers. Other physicochemical properties are presented in Table 6-2.

6.5. Environmental Behavior and Fate of Alkylates

Alkylates are produced in refineries and used as a high-octane blending stock for gasoline. Therefore, typical scenarios for gasoline releases in the environment apply to alkylates as well. Refueling, evaporative emissions, and incomplete combustion introduce alkylate compounds to the atmosphere. In addition, accidental spills on land or water, or leaking underground fuel tanks

(LUFTs) discharge alkylate compounds to the environment. Unlike MTBE or ethanol, however, alkylate components behave very much like other gasoline hydrocarbons. The average molar mass of an alkylate solution is close to that of gasoline (approximately 100 g/mol), and these compounds have high Henry's law constants, very low solubilities in water, and high octanol-water partition coefficients. If they are spilled into surface waters, they will float because of the density contrast and form surface pools or films from which the hydrocarbons will evaporate into the atmosphere. A small fraction will also dissolve in the water. These compounds will be retained in the organic fraction of soils and sediments after release from LUFTs because of their high octanol-water partition coefficients.

6.5.1. Air

The principal release mechanisms to the atmosphere include incomplete combustion, and evaporative emissions from automotive-fuel systems and from direct spills on land and/or water. For hydrocarbon solutions, such as light-crude oils and refined products, evaporation can account for up to 75% of volume loss a few days after a spill occurs **(**Fingas, 1995). A similar behavior should be expected for alkylates. The evaporation process of an alkylate (or any other hydrocarbon solution) is difficult to describe because the vapor pressure is a function of the changing composition of the solution. Qualitatively, as the solution evaporates, the vapor composition becomes richer in the more volatile components, and the liquid composition becomes richer in the less volatile components. As a result, the vapor pressure of the remaining solution decreases as the evaporation progresses.

Fingas (1995) reviewed models used to predict evaporation from oil spills. One of the most frequently used models is that of Stiver and MacKay (1984). In this model, it is assumed that a liquid evaporates at a rate given by

$$N = k\,A\,P\,/\,(RT), \qquad (6\text{-}2)$$

where N (mol s^{-1}) is the evaporative molar flux, A (m^2) is the area, k (m s^{-1})is the mass-transfer coefficient under the prevailing wind, P (Pa) is the vapor pressure of the bulk liquid, R (8.314 Pa m^3 mol^{-1} K^{-1}) is the gas constant, and $T(K)$ is the ambient temperature. Stiver and MacKay (1984) rearranged this equation to give

$$dF_v = H\,d\theta \qquad (6\text{-}3)$$

where F_v is the volume fraction evaporated, H is a dimensionless Henry's law constant, and θ is defined as a dimensionless "evaporative exposure." If the liquid is not pure, H is a function of F_v, and Equation (6-3) can only be integrated if the vapor pressure is expressed as a function of composition. In those cases, the evaporation rate slows, as expected, as the evaporation proceeds.

In a recent study (Kirchstetter *et al.*, 1999), vehicle emissions were measured in a heavily used roadway tunnel (Caldecott tunnel) located in the San Francisco Bay Area. The researchers also measured the composition of liquid gasoline in samples from local service stations. In 1996, the average local gasoline formulation contained, in weight percent, 3.64% isooctane (2,2,4-trimethylpentane), 0.58% benzene, and 10.91% MTBE. (For purpose of comparison, only the results for isooctane, benzene, and MTBE are discussed here.) From these values, Kirchstetter *et al.* (1999) calculated a headspace-vapor composition of 1.21% isooctane, 0.36% benzene, and 16.83% MTBE. Their measurements of the non-methane, organic-carbon emissions in the tunnel during the summer of 1996 were 2.67±0.20% isooctane, 3.34±0.29% benzene, and 5.47±0.74% MTBE. From this study, it is clear that isooctane, a typical alkylate component, is already measurable in automotive emissions; and its concentration should be expected to rise if the percentage of alkylate in gasoline increases. In addition, it is important to note that the relative fractions measured in the tunnel show more isooctane and benzene, and less MTBE than the values corresponding to the equilibrium vapor composition. One possible explanation is that MTBE burns more efficiently than isooctane or benzene.

Once in the atmosphere, the isoalkanes representing the alkylate mixture can be destroyed by chemical degradation and, to a lesser degree, removed by precipitation. The oxidation reactions normally used to estimate the residence time of a chemical in the atmosphere are those involving hydroxyl radicals (OH) and ozone. Alkanes react primarily with hydroxyl radicals to form alkyl radicals:

$$R\text{—}H + OH \rightarrow R\cdot + H_2O. \qquad (6\text{-}4)$$

The alkyl radicals (R·) formed react subsequently with oxygen to form peroxyls. The reaction of alkanes with ozone is relatively slow; thus, the reaction with OH is considered the main initiation path for the oxidation of hydrocarbons in the atmosphere. The oxidized species eventually undergo deposition and biodegradation. The rate of reaction ($-d[RH]/dt$) (see Equation 6-4) is given by the product of a temperature-dependant rate constant ($k(T)$) and the reactant concentrations:

$$\frac{-d[RH]}{dt} = k(T)\,[OH]\,[RH]. \qquad (6\text{-}5)$$

For alkanes having between 2 to 8 carbons, the rate constant range is about $(0.3\text{–}9) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Finlayson-Pitts and Pitts, 1986). Note that methane has a very low hydroxyl-rate constant (0.0084×10^{-12} cm^3 molecule^{-1} s^{-1}) compared to other alkanes and is, by far, the most abundant alkane in the atmosphere. For a typical akylate component, such as isooctane, the rate constant is 3.66×10^{-12} cm^3 molecule^{-1} s^{-1}. For a mean global concentration of OH of 1×10^6 molecules cm^{-3} (Prinn *et al.*, 1995), the half-life ($t_{1/2}^{OH} = \ln(2)/k(T)[OH]$) for 2,2,4-trimethylpentane would be 2.2 days. Similar estimations of half-life for benzene, ethanol, and MTBE are 5.8, 2.7, and 2.7 days, respectively, based on OH-reaction rates from Lyman (1990a) for benzene and ethanol, and from Jenkin and Hayman (1999) for MTBE. It should be noted that the average concentration of hydroxyl radical may be 10^7 molecules cm^{-3} or higher in polluted atmospheres (Lyman, 1990a). Therefore, under such conditions, the half lives may be reduced by an order of magnitude or more.

The formation of ground-level ozone is a serious pollution concern. Photochemical interactions of volatile organic compounds in combination with oxides of nitrogen generate ozone at ground level. The rate of reaction and mechanism will depend, among other parameters, on the organic compound in question. Carter (1994) discusses the various ways of quantifying the reactivity (the potential to form ozone) of a volatile organic compound. One of them is the Maximum Incremental Reactivity or MIR scenario. Isooctane, benzene, and MTBE have reactivities in the MIR scale of 0.93, 0.42, and 0.62 g of ozone per gram of organic compound (gO_3/g_{oc}), respectively (Carter, 1994). Other isoalkanes present in alkylates have reactivities in the range 0.3–1.5 gO_3/g_{oc}. Even though the ozone-forming capacity of some alkylate components is higher than MTBE or benzene, it is much lower than those corresponding to olefins that are already present in gasoline at a level between 2 and 3%, and they have reactivities reaching as much as 10 $gO_{3/}g_{oc}$.

6.5.2. Water

The solubility data in Table 6-2 consists of only three measured values, but it can be inferred from the general solubility trends of hydrocarbons that these isoalkanes are sparingly soluble in water, that is, in the range 10^{-4}–10^{-5} M. The vapor pressures are in the range 10^3–10^4 Pa at 25°C (water-vapor pressure is 3.17×10^3 Pa at 25°C). In addition, the contrast in density will cause the insoluble fraction of these compounds to float on water. Because of their low solubility in water, they have relatively large Henry's law constants (approximately 10^5 Pa m^3 mol^{-1}). This translates into a tendency for the compound to evaporate easily from aqueous solutions. As a rule, compounds in aqueous solution with Henry's law constants larger than approximately 10^2 Pa m^3 mol^{-1} are considered highly volatile (Thomas, 1990). In this case, as long as the concentration in the gas phase remains negligible, the evaporation is controlled by the liquid-phase transfer rate.

The concentration of alkylate in water from a precipitation event is expected to be negligible. For example, a calculation based on an initial concentration in the atmosphere of 1 part per billion (ppb[v])) predicted rainwater to contain 3.6×10^{-5} μg/L for isooctane, 0.17 μg/L for MTBE, and 7.33 μg/L for ethanol (see Chapter 5, Equation [5-1] in this report). The other isoalkanes will also have very low concentrations in rainwater.

6.5.3. Soil and Groundwater

As seen in Table 6-2, the components of an akylate have very high K_{ow}; therefore, they will tend to be retained by organic matter in the environment. Using a soil-partitioning model (Jury *et al.*, 1983), predictions can be made on the distribution of an organic compound in soil phases. The model considers soil to have three phases (solid, water, and air), and the properties of the soil are considered uniform. Some of these properties are water content θ_w, bulk density ρ_b, porosity ϕ, air content θ_A, and organic carbon fraction f_{oc}. The total concentration of a given compound in the soil is given by the sum of the contributions from each phase, as shown in the following equation:

$$C_T = \rho_b C_S + \theta_w C_L + \theta_A C_G, \tag{6-6}$$

where C_T, C_S, C_L, and C_G, are the total, solid, water, and air concentrations, respectively. Using linear-equilibrium approximations, Equation (6-6) may be written as

$$C_T = R_S C_S = R_L C_L = R_G C_G \tag{6-7}$$

where

$$R_S = \rho_b + \theta_w / K_D + \theta_A H / K_D \tag{6-8}$$

$$R_L = \rho_b K_D + \theta_w + \theta_A H \tag{6-9}$$

$$R_G = \rho_b K_D / H + \theta_w / H + \theta_A \tag{6-10}$$

H is Henry's law constant, and K_D is the solid-liquid partition coefficient. The K_D of isooctane was calculated from

$$K_D = f_{oc} K_{oc} \tag{6-11}$$

where K_{oc} was calculated using the regression equation from Kenaga and Goring (1980), as cited by Lyman (1990b).

$$\log (K_{oc}) = 0.544 \log(K_{ow}) + 1.377. \tag{6-12}$$

Using this model and assuming an initial total concentration of 1 mg/L of the organic compound in soil (isooctane, ethanol, MTBE, and benzene), we performed calculations for two types of soil as defined by Jury *et al.* (1990):

a) Sandy soil (ρ_b = 1590 kg/m^3, f_{oc} = 0.0075, ϕ = 0.4, and θ_w = 0.18) and

b) Clayey soil (ρ_b = 1320 kg/m^3, f_{oc} = 0.025, ϕ = 0.5, and θ_w = 0.375).

The purpose was to see how isooctane, a typical alkylate component, compares to other gasoline components. The results of the calculations are plotted in Figure 6-1 for the sandy soil and in Figure 6-2 for the clayey soil. A distinctive feature of isooctane is its relatively high preference for the air phase in both soils, even when compared to benzene. One-year evaporation losses calculated for benzene in 1-m-deep soil are 34.3% for sandy soil and 0.01% for clayey soil

(Jury *et al.*, 1990). The rate of volatilization is somewhat proportional to the concentration in the air phase; hence, isooctane would volatilize more rapidly than benzene. Therefore, volatilization into the atmosphere could be the main mechanism determining the half-life of an alkylate component in soil for surface contamination.

The limited distribution of the alkylate compounds in soil water and their high retention in soils (see Figures 6-1 and 6-2) indicates that their mobility in infiltrating water will be quite limited—particularly when compared to ethanol or MTBE. Alkylate compounds that are not volatilized to air will probably undergo slow biodegradation based on the study by Solano-Serena *et al.* (1998), discussed in the next section.

6.5.4. Biodegradation

The biodegradability of a compound can be affected by many variables (pH, temperature, substrate composition, oxygen availability, microorganisms present and their interaction, etc.). Consequently, it is quite difficult to predict the actual biodegradation rates for individual isoalkanes. A simple approach would be to consider the solution as a single compound; for example, gasoline has been considered as a single compound that is moderately biodegradable (Scow, 1990). However, an alkylate (and gasoline) is a complex solution, and the rate of biodegradation of each component may be significantly different. Unfortunately, there have not been many specific studies on the biodegradation of alkylate components. In general, n-alkanes are degraded rapidly in the environment, but highly branched alkanes tend to be more resistant to biodegradation because of their molecular structure. Under aerobic conditions, the oxidation of alkanes normally proceeds by the oxidation of a terminal methyl group to form a carboxylic acid, followed by β-oxidation of the acid. The presence of a quaternary carbon near the end of the chain interferes with the β-oxidation step and the degradation stops. It is possible that later these compounds are degraded by other, slower mechanisms (Alexander, 1994; Chapelle, 1993).

A recent laboratory study using unpolluted spruce-forest soil as substrate (Solano-Serena, 1998) has shown that all components of a model-gasoline solution were biodegraded below detection limit after 28 days with the exception of 2,2,4-trimethylpentane (isooctane), 2,3,4-trimethylpentane, and cyclohexane. From Table 2 of Solano-Serena *et al.* (1998), the percentages of degradation after 28 days of incubation at 30°C are 18% for 2,2,4-trimethylpentane, 9% for 2,3,4-trimethylpentane, and 100% for benzene. In addition, mineralization yields (fraction of compound converted to CO_2) for 23 individual components of this gasoline solution were determined (see Table 1 in Solano-Serena, 1998) by measuring the CO_2 produced after 34 days of incubation at 30°C. The mineralization yield was 2% for 2,2,4-trimethylpentane and 0% for 2,3,4-trimethylpentane. On the other hand, the mineralization yield for benzene was 56%. Note, it appears that the resistance to degradation is not due to the inhibitory capacity of isoalkanes or cycloalkanes but rather to a population deficiency of the naturally occurring microorganisms degrading these hydrocarbons.

Based on the previous values for 2,2,4-trimethylpentane, we can estimate a first-order degradation constant of approximately 0.007 day^{-1} and a half-life of about 98 days. In the case of 2,3,4-trimethylpentane, the first-order degradation constant is approximately 0.003 day^{-1} and the half-life is approximately 206 days. Because benzene degraded completely, the same constant cannot be determined for benzene from this data. In another experiment, the first-order degradation constant of benzene in an aerobic aquifer was measured to be between 0.07 and

0.5 day^{-1} (Nielsen *et al.*, 1996). These values would predict over 85% degradation of benzene in 28 days, which generally agrees with the results of Solano-Serena *et al.*, (1998) for this compound. The half-life for mineralization of 2,2,4-trimethylpentane would be around three years (compared to 25 days for the case of benzene).

A detailed laboratory study was conducted on gasoline biodegradation using microflora from an urban-waste activated sludge (Solano-Serena, 1999). Based on the kinetics of oxygen consumption, the authors concluded that there are two main degradation phases: a fast phase and a slow phase. The rate of oxygen consumption is about 40 times lower during the slow phase. Aromatic hydrocarbons were degraded mostly during the fast phase while linear, branched, and cyclic alkanes were degraded mostly during the slow phase. After 25 days of incubation, the undegraded compounds (6% of gasoline) were essentially branched alkanes with a quaternary carbon and/or alkyl chains in consecutive carbons. For example, the undegraded fractions of 2,2,4-trimethylpentane, 2,3,3-trimethylpentane, and 2,3,4-trimethylpentane were 49.7%, 72.1%, and 30.5%, respectively, after 25 days of incubation. One reason given for the relatively slow biodegradation rate of some linear alkanes and isoalkanes is their low solubilities in water and high Henry’s constants. The alkane in the gas phase of the culture flask is not readily available to the microflora, and the rate-limiting step could be the transfer of the alkane from the gas to aqueous phase. However, the incomplete biodegradation of some branched alkanes seems to indicate that there is also a metabolic limit in this case.

6.6. Summary

Alkylates are solutions of highly branched alkanes produced in refineries by the reaction of isobutane with light olefins, using either sulfuric or hydrofluoric acid as a catalyst. For many years, alkylates have been used as gasoline-blend stock because of their high-octane number. In the near future, the percentage of alkylate in gasoline may increase significantly to compensate for the phase out of high-octane MTBE. The purpose of this chapter was to characterize the transport and fate of alkylates in the environment. For simplicity, we concentrated on the properties of isooctane as a typical alkylate component. Clearly, alkylates are complex solutions of isoalkanes, and some properties like biodegradability may not be easily extrapolated to all components. The low water solubility and high volatility of alkylate components indicate that they would not exacerbate problems of ground or surface water contamination by gasoline in the manner MTBE has done. Overall, it appears that alkylates would not effect dramatic changes in the way gasoline behaves in the environment and, thus, in the treatment of accidental releases.

Unfortunately, there is no toxicity data on the chronic effects of isooctane in humans; however, liver and kidney effects have been observed in rats that have been exposed chronically (US EPA, 1991). Additionally, cancer risk and reproductive and developmental effects have not been addressed. It should be noted that toxicity related to alkylate addition to gasoline is a complex problem because any percentage increase of alkylate in gasoline composition must be accompanied by a percentage decrease of other blending components (e.g., BTEX) in the final formulation. Therefore, the toxicity of the final product should be evaluated in an integral manner.

The physicochemical properties of alkylate components are typical of many hydrocarbons and determine their behavior in the environment. They have very low solubility in water and very high octanol-water partition coefficient. They are less dense than water and have relatively high Henry’s law constants. Surface releases of alkylate either on water or land will probably result in the evaporation of most of the alkylate into the atmosphere. In the atmosphere, their oxidation will be initiated mostly by the presence of atmospheric OH, with half-lives of about 2–3 days. Their potential to form ground-level ozone is about double that of MTBE in the MIR scale. Alkylates will be strongly absorbed by the organic fraction of soils and sediments. Their biodegradation rate is relatively slow compared to other organic compounds, and some components may not biodegrade in reasonable time frames.

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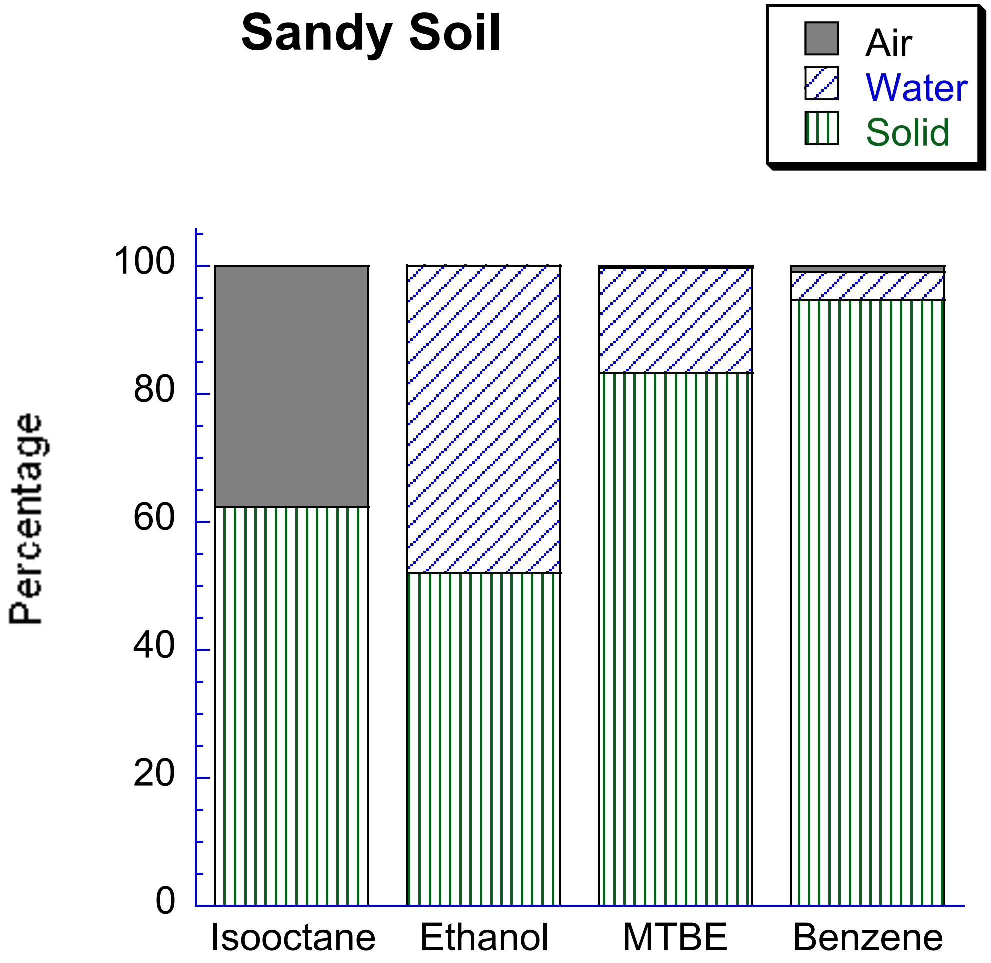

Figure 6-1. Model of equilibrium distribution for isooctane between the phases of a sandy soil (air, water, solid). This partitioning model was developed by Jury *et al.* (1983); soil characteristics were taken from Jury *et al.* (1990).

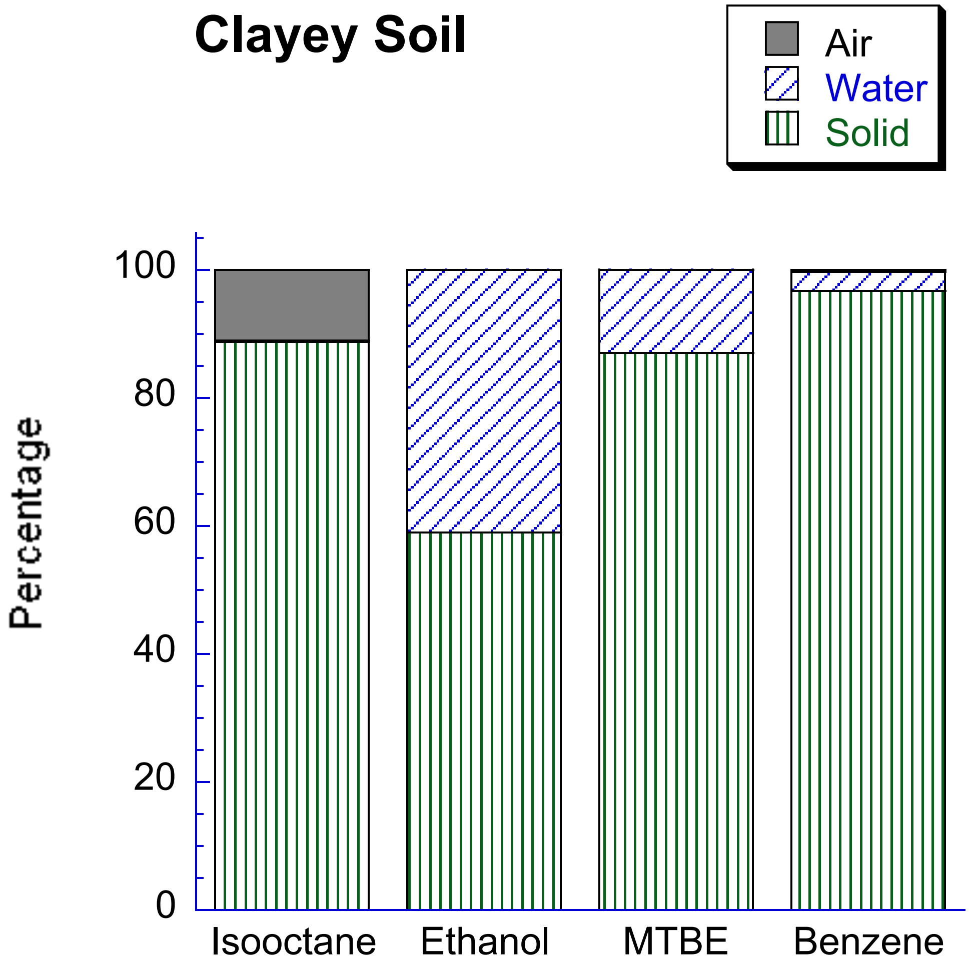

Figure 6-2. Model of equilibrium distribution for isooctane between the phases of a clayey soil (air, water, solid). This partitioning model was developed by Jury *et al.* (1983); soil characteristics were taken from Jury *et al.* (1990).

Tables

Table 6-1. Representative components of a typical alkylate[a].

Alkylate compound	Formula	CAS number[b]	Molar mass (g/mol)[b]	Melting point (°C)[b]	Boiling point (°C)[b]	Density (g/cm^3)[b]
2,2,4-Trimethylpentane	C_8H_{18}	540-84-1	114.23	-107	99.2	0.692
2,3,3-Trimethylpentane	C_8H_{18}	560-21-4	114.23	-101	115	0.726
2,3,4-Trimethylpentane	C_8H_{18}	565-75-3	114.23	-109	113	0.719
2,2,3-Trimethylpentane	C_8H_{18}	564-02-3	114.23	-112	110	0.716
2,2,5-Trimethylhexane	C_9H_{20}	3522-94-9	128.25	-106	124	0.707
2,3-Dimethylbutane	C_6H_{14}	79-29-8	86.17	-128	58	0.661
2,3-Dimethylpentane	C_7H_{16}	565-59-3	100.2	N/A	90	0.695
2,4-Dimethylpentane	C_7H_{16}	108-08-7	100.2	-119	81	0.673
2,5-Dimethylhexane	C_8H_{18}	592-13-2	114.23	-91	109	0.694
2,3-Dimethylhexane	C_8H_{18}	584-94-1	114.23	N/A	116	0.712
2,4-Dimethylhexane	C_8H_{18}	589-43-5	114.23	N/A	109	0.700
2,3,5-Trimethylhexane	C_9H_{20}	1069-53-0	128.25	-128	131	0.722
2-Methylpentane	C_6H_{14}	107-83-5	86.17	-154	62	0.653

[a] From Durett *et al*. (1963).

[b] Values estimated using ChemFinder® Software (CambridgeSoft Corporation, 1998a).

Table 6-2. Physical-chemical properties of representative alkylate components.

Alkylate compound[a]	Vapor pressure[b] (Pa at 298K)	Solubility[c] (mg/L)	Henry's law constant[d] (Pa m^3 mol^{-1})	K_{ow}[e]	LeBas molar volume[f] (cm^3 mol^{-1})	D_{air}[f] (m^2 d^{-1}; at 298 K)	D_{water}[f] (m^2 d^{-1}; at 298 K)
2,2,4-Trimethylpentane	6.49×10^{3}	2.44	3.23×10^{5}	1.22×10^{4}	185	0.575	7.03×10^{-5}
2,3,3-Trimethylpentane	NA	NA	4.17×10^{5}	1.22×10^{4}	185	0.575	7.03×10^{-5}
2,3,4-Trimethylpentane	3.57×10^{3}	NA	1.83×10^{5}	1.12×10^{4}	185	0.575	7.03×10^{-5}
2,2,3-Trimethylpentane	NA	NA	3.85×10^{5}	1.22×10^{4}	185	0.575	7.03×10^{-5}
2,2,5-Trimethylhexane	2.22×10^{3}	NA	5.26×10^{5} 3.44×10^{5}	3.77×10^{4}	207.2	0.541	6.57×10^{-5}
2,3-Dimethylbutane	3.13×10^{4}	NA	1.30×10^{5}	1.38×10^{3}	140.6	0.670	8.29×10^{-5}
2,3-Dimethylpentane	9.18×10^{3}	NA	1.74×10^{5}	4.29×10^{3}	162.8	0.618	7.59×10^{-5}
2,4-Dimethylpentane	1.31×10^{4}	4.06	3.00×10^{5}	4.29×10^{3}	162.8	0.618	7.59×10^{-5}
2,5-Dimethylhexane	4.05×10^{3}	NA	3.33×10^{5}	1.33×10^{4}	185	0.575	7.03×10^{-5}
2,3-Dimethylhexane	3.12×10^{3}	NA	3.85×10^{5}	1.33×10^{4}	185	0.575	7.03×10^{-5}
2,4-Dimethylhexane	3.64×10^{3}	NA	3.57×10^{5}	1.33×10^{4}	185	0.575	7.03×10^{-5}
2,3,5-Trimethylhexane	NA	NA	5.00×10^{5}	3.47×10^{4}	207.2	0.541	6.57×10^{-5}
2-Methylpentane	2.82×10^{4}	13.8	1.71×10^{5}	1.64×10^{3}	140.6	0.670	8.29×10^{-5}

[a] Representative components of a typical alkylate (Durett *et al.*, 1963).

[b] Vapor pressure calculated using Antoine equation from National Institute of Standards and Technology (NIST) (1999).

[c] Values were obtained using Chem3D® Software (CambridgeSoft Corporation, 1998b).

[d] Henry's law constant obtained from NIST (1999). Note: 2,2,5-trimethylhexane has two values.

[e] Octanol-water partition coefficients obtained using LogKow (KowWin) Demo software (SRC, 1999).

[f] Calculated according to methods described by Tucker and Nelken (1990).

UCRL-AR-135949 Vol. 4 Ch. 7

Volume 4: Potential Ground and Surface Water Impacts

Chapter 7: Evaluation of Analytical Methods for the Detection of Ethanol in Ground and Surface Water

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Table of Contents

Table

7. Evaluation of Analytical Methods for the Detection of Ethanol in Ground and Surface Water

7.1. Analytical Requirements

7.1.1. Routine Detection of Trace Amounts of Ethanol in Environmental Waters

Ethanol in the environment might be present in air, soil, and water. Ethanol in air partitions to water[1]. In an organic soil/water system, ethanol partitions almost exclusively into the water[2]. Thus, water is an important environmental reservoir for ethanol. The primary objective of this chapter is to review methods applicable to the routine analysis of ethanol in environmental waters. (The analysis of ethanol in air and soil is outside the scope of this document and will not be addressed.)

The analysis of ethanol in environmental waters is difficult. In order to analyze ethanol, or any other contaminant of interest, one must first extract (or remove) it from water. Once it is removed from water, the contaminant must then be separated from hundreds or thousands of other contaminants so that it can be specifically identified or detected. Once it has been identified, the quantity of that contaminant in the water can be determined. Of these steps, the extraction of ethanol from water is the most challenging.

Ethanol is a small, polar molecule. Ethanol associates (or hydrogen bonds) with water, making it difficult to extract from water and difficult to measure low concentrations in the environment. However, if ethanol can be extracted from water, sufficient methods exist to separate, identify, and measure it.

The appropriate analytical methods to analyze (that is, extract, separate, identify, and measure) ethanol, or any other environmental contaminant, are dictated by the intended use of data. This review considers three uses of collected data:

- Assessment of ethanol concentrations at a spill site.
- Documentation to meet regulatory requirements.
- Understanding of the environmental fate and transport of ethanol.

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[1] Based on accepted values of Henry's law constant for ethanol that range from 0.5 to 0.6 Pa•m^3/mol (MacKay, *et al.*, 1995).

[2] Ethanol's low octanol-water partition coefficient (K_{OW}), log K_{OW} values of –0.3 to –0.2 (MacKay *et al.*, 1995) indicate that ethanol partitions into water rather than remaining in soil.

Several issues influence the selection of an analytical method that will provide the data needed for these three uses. In all cases, the selected analytical methods must possess the following characteristics:

- Appropriate DLs.[3]
- Good precision.[4]
- Good accuracy.[5]
- Easily performed and reproducible by different analysts in different laboratories.
- No false positive (interferences) or negative detections.
- Adherence to quality assurance/quality control (QA/QC) protocols.[6]

For any type of chemical analysis, adherence to stringent QA/QC protocols is the criterion most critical to providing data that can be compared by different investigators. It is for this reason that the United States Environmental Protection Agency (US EPA) has promulgated specific analytical methods (and strict QA/QC protocols) for the monitoring of contaminants in the environment. For example, all laboratories performing regulatory analyses must strictly adhere to the US EPA protocols to prove regulatory compliance.

Another issue of concern is practicality. The chosen analytical methods need to be cost effective and easily performed (with minimal manual labor). Costs of current analyses for organic compounds range from approximately $100–$400. Thus, in order to be cost effective, analyses of environmental samples for the presence of ethanol should fit into this price range.

7.1.2. Regulatory Requirements Versus Detection Limits for Fate and Transport Studies

We previously stated that there are several reasons that one might wish to monitor ethanol contamination in the environment, including (1) to assess ethanol contamination at a spill site, (2) to document that regulatory requirements are being met or exceeded, and (3) to understand the environmental fate and transport of ethanol. In each case, it is important to establish what concentration of ethanol needs to be detected in order to meet the objective of the study.

For example, a regulatory concentration limit for a specific contaminant might be based on predicted health effects and risk-assessment models. Let's assume that the regulated limit of Analyte X is 30 parts-per-billion (ppb) in drinking water. In order to prove that the regulatory concentration of Analyte X is not exceeded, the method selected to analyze drinking water must be capable of accurately and reproducibly measuring 30 ppb of ethanol. Thus, the DL (or the minimum concentration of Analyte X that can be detected by an analytical method) required for this analysis is 30 ppb or lower. In practice, the desired detection limit (DL) should be three to

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[3] The analyte must be detected at a sufficiently low concentration to meet the study/regulatory requirements.

[4] Multiple measurements of an analyte in the same sample will give identical results.

[5] Measured concentration of analyte reflects its true concentration in a sample.

[6] A QA/QC program encompasses procedures used to ensure that analyses are consistently performed, meet user requirements, and that data generated by a laboratory are accurate, precise, reproducible, and defensible in a court of law.

five times lower (6–10 ppb) than the set regulatory limit desired in order to ensure that Analyte X is easily detected at its regulated limit of 30 ppb.

Currently, ethanol is not considered by the federal government or by the state of California to be a regulated compound. No guidance is available to dictate needed DLs. However, based on the potential uses of ethanol data, we can make some good assumptions about what DLs are needed to provide data for specific studies:

- **Case 1: Assessing Ethanol Contamination at a Spill Site.** The expected concentration of ethanol in contaminated groundwater near a spill site is likely to range between 400 to 4000 parts per million (ppm) (Malcolm Pirnie, Inc., 1998). Thus, the monitoring of ethanol-contaminated water associated with fuel spills would require methods with DLs of 400 ppm in order to document significant ethanol contamination at a site. In addition, the selected analytical method must detect ethanol in the presence of high concentrations of hydrocarbons found in gasoline.
- **Case 2: Documenting That Regulatory Requirements Are Met.** The taste and odor thresholds of ethanol in drinking water are 50 ppm and greater than 100 ppm, respectively (Malcolm Pirnie, Inc., 1998). If we assume that no adverse health effects are associated with consuming trace quantities of ethanol, we would predict that a drinking-water standard would be set at the taste threshold of ethanol (50 ppm). Thus, a method at least 50 ppm would be sufficient to ensure water quality. This DL is approximately a factor of ten lower than that required to characterize ethanol contamination at a spill site.
- **Case 3: Understanding Environmental Fate and Transport.** In order to determine the movement of ethanol through the environment, the environmental background levels of ethanol at uncontaminated sites need to be assessed. Parts-per-billion concentrations of ethanol, possibly produced by “natural” chemical and biological processes, might be present in environmental surface and groundwaters. It is also possible that surface and groundwaters will be indirectly impacted by the use of blended fuels. In order to understand the native background of ethanol in the environment and to understand the impact of ethanol from blended fuels, the lowest DLs achievable (parts per billion, or better) would be needed.

7.2. Evaluation of Current Analytical Methods for Ethanol Detection

Few papers have been published describing the analysis of ethanol in environmental samples. This pretermission is, in part, because ethanol has not been considered to be a contaminant of environmental concern. Ethanol is not included in several comprehensive references of groundwater contaminants (Prager, 1995; Montgomery, 1996). In addition, because the human body tolerates percent quantities of ethanol that are present in alcoholic beverages, human consumption of trace quantities of ethanol, which might contaminate food and drinking water, have not been of great concern.

7.2.1. Ethanol Analysis Methods Used by Food and Biomedical Industries

Table 7-1 summarizes the methods that have been used for ethanol analyses. It also contains information about the analytical technique applied, the type of sample analyzed, and the limit of detection obtained. It also indicates if the method might be useful in the analysis of environmental waters.

The alcoholic beverage industry performs many ethanol analyses to insure the quality of its products. Ethanol DLs for the analyses of beer and wine cited in Table 7-1 range from 1 to 50,000 ppm. However, many of these methods do not have sufficient DLs to be applied to the analysis of ethanol in environmental samples. The method using an oxygen-electrode sensor (5–10 ppm DLs) lacks a large dynamic range and would not be applicable to environmental analyses. The gas-diffusion membrane coupled with amperometric detection (1-ppm DL) might prove useful for the analysis of environmental samples; however, studies need to be performed to determine if this method is applicable to environmental samples.

DLs for ethanol in biological fluids reported within the last five years are 10 ppm or better (see Table 7-1). Note that these DLs are below the taste and odor thresholds for ethanol in water. The recent methods cited used either headspace gas injection or direct injection of the biological fluid coupled with gas chromatography combined with flame-ionization detection (GC/FID). GC/FID is more analyte specific than many of the electrochemical methods used in the alcoholic beverage industry. Because of their good DLs, GC/FID methods are potentially applicable to the analysis of ethanol in environmental samples.

7.2.2. Ethanol Analysis Methods Used by the Environmental Community

In 1986, the United States Environmental Protection Agency (US EPA) suggested that ethanol analysis might be performed by purge-and-trap gas chromatography coupled with a flame-ionization detector (that is, Method 8015 [US EPA, 1986]). Method 8015 listed no method DL, linear range, precision, or accuracy data. By 1996, both US EPA Methods 8015B and 8260B stated that purge-and-trap extraction was inappropriate for ethanol analysis (US EPA, 1996c and 1996d). Instead, these methods suggested that azeotropic distillation (that is, Method 5031 [US EPA, 1996a]) and vacuum distillation (Method 5032 [US EPA, 1996b]), were appropriate techniques to extract and concentrate ethanol from water samples. In addition, these methods suggested that direct aqueous injection of water into a GC/FID, or the use of a gas chromatograph coupled with a mass spectrometer (GC/MS) was appropriate for ethanol analysis. Again, because ethanol is not a regulated compound, the US EPA methods contained no information regarding DL, linear range, precision, or accuracy.

While the US EPA does not endorse the use of the purge-and-trap technique for ethanol analysis, several methods have successfully used this extraction technique. *Geo*Chemistry of Canoga Park, CA (recently purchased by and soon to relocate to ZymaX Envirotechnology, Inc., of San Luis Obispo, CA) is one of the few California laboratories known to perform ethanol analyses for environmental samples. Global *Geo*Chemistry (1999) uses a modified version of Method D4815 of the American Society of Testing and Materials (ASTM, 1997) to determine ethanol in aqueous samples. ASTM Method D4815 was developed to measure

0.1% concentrations of ethanol in gasoline and uses two-dimensional gas chromatography (2D-GC) to remove interferences. The sample is injected directly into the gas chromatograph and first eluted through a polar, capillary gas-chromatograph column that retains all oxygenates, including ethanol. The oxygenates are then backflushed into a nonpolar, capillary gas-chromatograph column for final separation and detection by a flame-ionization or thermal-conductivity detector.

The Global *Geo*Chemistry method combines purge-and-trap extraction with two-dimensional chromatography coupled with a flame-ionization detector. DLs for ethanol in clean water and in water contaminated with 5% nonaqueous phase liquid (NAPL) are 200 ppb and 100 ppm, respectively.[7]

Zymax Envirotechnology, Inc. (McMurphy, 1999) has modified US EPA Method 8260B to obtain 50-ppb DLs for ethanol in water. Its method uses purge-and-trap extraction at ambient temperature and cryofocussing prior to final analysis by GC/MS[8].

Researchers at the University of Nebraska have developed a solid-phase microextraction (SPME) method coupled with GC/MS for the determination of ethanol in water. The SPME method uses a small fiber (~1 cm in length by ~0.3 mm in diameter), which is coated with 85 μm of a carboxen/polydimethylsiloxane polymer, to extract ethanol from water. After it has soaked in the sample for about 30 minutes, the fiber, now containing ethanol, is removed from the sample and directly injected into a GC/MS so that the amount of ethanol that has been collected can be measured. This method yields DLs for ethanol of 15 ppb (Cassada *et al.*, 1999). This represents the best DL that has been reported to date for the determination of ethanol in water. Although SPME can be automated easily, this technique requires a greater level of expertise to perform than purge-and-trap methods.

7.3. Handling and Preservation of Ethanol Samples

In addition to the instrumentation used for ethanol analysis, researchers must consider sample collection, preservation, and storage. If a sample is not properly collected, preserved, and stored, then the data provided by sample analyses will be of questionable quality and will not be scientifically (or legally) defensible.

Little has been reported regarding the collection and preservation of samples containing ethanol. The conventional US EPA methods for sample collection and storage are often applied, even though the storage methods endorsed have not always been rigorously tested. The US EPA recommends collecting water samples in 40-milliliter (mL), glass vials with Teflon®-lined

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[7] Sample matrix affects DLs. In general, DLs will increase, or worsen, as the complexity of the sample matrix increases. In a complex matrix, many compounds are present at much higher concentrations than the compound of interest, and these other compounds can interfere with the analytical signal produced by the compound of interest. To obtain the best DLs possible, analysts must separate ethanol from other unknowns that might interfere with its detection.

[8] For optimal gas chromatographic (GC) analysis, it is necessary to introduce the analytes as a narrow band on the head of the GC column. In practice, very volatile compounds, such as ethanol, often “smear” at the head of the GC column. One method to reduce this band broadening is to cool the GC column to sub-ambient temperatures (or, to temperatures that are below the boiling points of the analytes). This, in effect, traps (or focuses) volatile compounds as a narrow band of liquid at the head of the GC column and affords optimal GC analysis.

septum caps. No headspace should be visible in the vials after sample collection. The samples should then be stored at 4°C for a maximum of 14 days prior to analysis. To help preserve water samples and to minimize bacterial growth that might degrade analytes in the sample, four drops of concentrated hydrochloric acid may be added prior to cooling (Keith, 1996). In accordance with US EPA-recommended procedures, Global *Geo*chemistry (1999) refrigerates water samples but does not preserve them with acid.

Researchers working on samples of biological fluids have also refrigerated samples prior to analysis. McCarver-May and Durisin (1997) stored blood at 4°C prior to analysis. According to Macchai *et al.* (1995), ethanol was stable for seven days in urine, serum, plasma, and saliva when stored at 4°C; and ethanol in these matrices was also stable for up to two years when stored at -20°C. Tangerman (1997) observed that ethanol in blood was stable for two weeks when stored at room temperature, refrigerated, or frozen. Water, blood, serum, and urine samples containing ethanol could be stored for three months at -20°C without ethanol loss (Tangerman, 1997).

7.4. Recommendations to Improve Sampling and Analysis of Ethanol in Ground and Surface Water

7.4.1. Rigorous Study of Sample Preservation

The best conditions for the preservation and storage of samples containing ethanol need to be determined. The commonly used protocol of collecting water samples in 40-mL vials with Teflon®-lined septum caps and with no headspace should be continued. Data from the biomedical community appears to validate the commonly used practice of storing aqueous samples at 4°C for up to 14 days prior to analysis. Because the biomedical community suggests that frozen samples containing ethanol can be stored for periods as long as two years, it is possible that, under certain conditions, samples collected for ethanol analysis can be stored longer than 14 days prior to analysis. It will be important to determine if environmental samples can be stored for long periods without loss of ethanol.

7.4.2. Improved Extraction of Ethanol from Aqueous Samples

The analysis of ethanol in environmental waters is difficult. As previously discussed, ethanol is a small, polar molecule and is difficult to remove from water. The poor extraction efficiency of ethanol from water is the main contributor to its poor analytical DLs. Thus, any improvements in methods to remove ethanol from water will result in better DLs. The literature reviewed for this study indicates that either direct injection of an aqueous solution or injection of the headspace above an aqueous liquid can be used to obtain DLs of 10 ppm or less. Thus, these sample introduction techniques are sufficient to detect ethanol at its taste or odor threshold. Both of these techniques are easy and inexpensive to perform.

Other sample introduction techniques, such as purge and trap, azeotropic distillation, or vacuum distillation, could be investigated in the search for lower ethanol DLs. Of these techniques, azeotropic distillation and vacuum distillation are more expensive and labor-intensive (and not often performed) than purge and trap, which is performed easily, cost-effectively, and routinely by contract laboratories. The newer technique of solid-phase microextraction (Zhang, 1994), in which ethanol might be removed from water using a small fiber coated with special material, might also merit investigation. However, solid-phase microextraction is not currently performed routinely by contract laboratories.

7.4.3. Improved Strategies for Ethanol Detection

In order to eliminate problems with potential interferences, we recommend that gas-chromatographic (GC) separation be used in all future ethanol analyses. There are two practical strategies that can be used for the sensitive detection of ethanol in the presence of interfering compounds. The first is to use the best possible gas-chromatography procedure to separate ethanol from any interferences and, then, to detect ethanol with a nonspecific detector, such as a flame-ionization detector. The second strategy is to perform a less rigorous gas-chromatographic separation coupled with a detector that would respond specifically to ethanol but would not respond to potentially interfering compounds. Both of these strategies merit consideration.

7.4.3.1. Use of Gas Chromatography and Nonselective Detector

In the literature reviewed, flame-ionization detectors (FIDs) were the detectors of choice for ethanol analysis. A FID is frequently used because it responds well to a variety of organic compounds. Because of the nonselective nature of the FID (that is, the FID provides a signal whenever an organic compound is detected and provides no information about the nature of that analyte), two-dimensional chromatography is recommended for use with this detector to minimize interferences.

7.4.3.2. Use of Gas Chromatography with an Analyte-specific Detector

To improve detection specificity, we recommend investigating the coupling of a gas chromatograph with an analyte-specific detector, such as either an atomic-emission detector (AED) or a mass spectrometer (MS). The AED, operated in the oxygen-specific mode, can be "blinded" to potentially interfering hydrocarbons. The MS is capable of providing a mass-spectral "fingerprint" unique to each organic compound. Neither the AED nor the GC/MS would be cost prohibitive for an environmental laboratory to purchase, staff, or maintain. It might be possible that use of the AED or MS would simplify the chromatographic requirements such that only one GC column would be required to separate ethanol from potential interferences.

7.4.4. Minor Modifications to Improve Existing Methods

In addition to the choice of experimental approach and instrumentation used for ethanol analysis, there are several other analytical aspects to consider. Minor modifications to existing methods might improve the detection of ethanol in water. For example, if conventional purge-and-trap extraction is to be used, the sample could be heated to improve ethanol extraction efficiency. The choice of GC column dictates how efficiently ethanol can be separated from interferences. Many different types of GC columns are available and could be tested for their applicability to ethanol analysis. The use of cryofocussing in combination with gas chromatography might be beneficial.

7.5. Summary

The literature reviewed indicates that the technology currently exists to enable researchers to detect ethanol at spill sites. Sufficient methods exist to determine ethanol at its taste threshold of 50 ppm in water. The implementation of these methods would require some study of extraction and detection conditions and the establishment of strict QA/QC protocols. These are of great importance in the development of a method that would be used to demonstrate regulatory compliance. No methods reported are currently able to detect ethanol below 15 ppb in water. Thus, much time and effort must be invested to enable the detection of trace concentrations of ethanol. Until this is accomplished, we will be unable to completely understand the fate and transport of ethanol in the environment. Regardless of the analytical methods selected for use, it is recommended that a proposed method be evaluated using a variety of sample matrices—a strategy that has been used previously to evaluate detection methods for methyl tertiary butyl ether (MBTE) and other gasoline oxygenates (Happel *et al.,* 1998).

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Table

Table 7-1. Summary of ethanol methods. Data are ordered by publication date and subgrouped by decreasing limit of detection.

Technique	Sample	Limit of detection (ppm)	Useful in environmental analysis?	Reference
Headspace GC/FID	plasma	1000	no	Watts and McDonald, 1990
Derivatization to ethyl dithiocarbonate; differential-pulse polarography	beer	200	no	Chan *et al.*, 1992
Oxygen electrode based on NADH oxidase from *Bacillus licheniformis* and alcohol dehydrogenases	wine	5–10	no	Ukeda *et al.*, 1993
Online, membrane inlet ion mobility spectrometry	beer	500	no	Kotiaho *et al.*, 1995
Heated (75°C) headspace GC/FID	biol. fluids	10	maybe	Macchia *et al.*, 1995
Flow injection analysis coupled with gas-diffusion membrane and immobilized alcohol oxidase; amperometric detection	beer, wine	1	maybe	Mohns and Künnecke, 1995
Micellar electrokinetic capillary chromatography; diode-array detection	wine	50,000	no	Collins *et al.*, 1997
Solid-phase extraction cleanup; flow-injection analysis; amperometric detection	wine	500	no	Chen *et al.*, 1997
Heated (75°C) headspace GC/FID	blood	0.3	yes	McCarver-May and Durisin, 1997
10-microliters (-µL) direct injection, GC/FID	biol. fluids	0.1	yes	Tangerman, 1997
5-µL direct injection, GC/FID	water	3	yes	Corseuil *et al.*, 1998
5-µL direct injection, GC/FID	water	1	yes	Alvarez, 1999
Modified ASTM Method D4815 (purge & trap, 2D GC/FID)	soil, water	0.2	yes	Global *Geo*Chemistry, 1999
Modified US EPA Method 8260B with cryofocussing	water	0.05	yes	McMurphy, 1999
Solid-phase microextraction coupled with GC/MS	water	0.015	yes	Cassada, *et al.*, 1999

Key:

2D-GC = two-dimensional gas chromatography

ASTM = American Society of Testing and Materials

US EPA = United States Environmental Protection Agency.

GC/FID = gas chromatography with flame-ionization detection

GC/MS = Gas chromatograph with a mass spectrometer.

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Volume 4: Potential Ground and Surface Water Impacts

Chapter 8: Screening Analysis of Potential Groundwater Resource Impacts from Gasoline Containing Ethanol or MTBE

Using an Empirically based, Probabilistic Screening Model

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Table of Contents

List of Figures

List of Tables

Appendix

8. Screening Analysis of Potential Groundwater Resource Impacts from Gasoline Containing Ethanol or MTBE

Using an Empirically based, Probabilistic Screening Model

8.1. Introduction

Although California has implemented an Underground Storage Tank (UST) upgrade program, releases from leaking underground fuel tanks (LUFTs) will continue to be an issue (Giannopoulos, 1999). Moreover, various authors (Chapter 4, Vol. 4 of this report; Malcolm Pirnie, Inc., 1998; Molson *et al.*, 1999; Schirmer *et al.*, 1999; Ulrich, 1999) report that ethanol may lengthen benzene plume lengths due to preferential biodegradation of ethanol. Longer plumes suggest that potentially more public and private drinking water wells in California may be impacted by benzene released from LUFTs.

In this study, we utilized a systems-based approach to estimate the differences in groundwater resource impacts from LUFT releases of benzene, benzene under the influence of ethanol, and methyl tertiary butyl ether (MTBE). Benzene in association with ethanol is the primary focus of this study, because it is a known human carcinogen, and because increased benzene groundwater plumes are predicted. This report examines the potential for benzene to contaminate drinking water sources from future releases of gasoline containing ethanol in contrast to the potential for MTBE to contaminate drinking water sources. MTBE is a possible carcinogen, can affect water quality, has a disagreeable taste and odor at low parts-per-billion (ppb) concentrations, and has been shown as generally recalcitrant in groundwater under *in situ* conditions. This study does not examine the potential for ethanol-only plumes to impact drinking water supplies because ethanol degrades rapidly in groundwater and is expected to have very localized and minor impacts relative to benzene or MTBE.

To estimate the potential future impact of gasoline containing either ethanol or MTBE, we considered some important characteristics of drinking water wells and LUFT sites. These characteristics include:

- The current distribution of the distance to the nearest well from a LUFT site.
- Densities of LUFTs and drinking water wells.
- Past impacts of benzene, toluene, ethyl benzene, and xylenes (BTEX) and MTBE on drinking water wells.

The estimation makes use of probabilistic analytical screening models, using empirically based compliance data collected throughout the state of California. Details of this collection are found in Rempel *et al*. (1996), and the data are described in Dooher (1998).

For chemistry data, locations of wells, LUFT sites, and well yield and construction, we relied on data collected from state and local agencies[1] that has been reviewed and standardized for

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[1] The state agencies include information from the State Water Resources Control Board (SWRCB) Leaking Underground Storage Tank Information System (LUSTIS) database (SWRCB, 1999); the California Department of

import into the SWRCB Internet-accessible database, the Geographic Environmental Information Management System (GEIMS)[2].

8.1.1. Methodology

Our estimate of future impacts to public drinking water wells is based on a series of assumptions regarding the spatial distribution of LUFTs that may act as release points, and their proximity to drinking water wells. To compare the potential future impacts to drinking water wells, we developed a baseline impact estimate for benzene without the presence of ethanol (or MTBE). This baseline impact estimate provided a basis for comparing estimated future impacts with MTBE and those associated with benzene under the influence of ethanol.

To estimate the baseline percentage of benzene LUFT-related releases that may impact public drinking water wells over time, we developed a methodology to estimate benzene plume behavior using a Monte Carlo simulation of a one-dimensional advection, three-dimensional (3-D) dispersion equation developed by Cleary and Ungs (1978). The first step in this methodology is to model expected populations of benzene plume lengths without ethanol. Next, we compared the benzene-only plume-length results against measured, historical-case benzene plume lengths to validate the model. Finally, we used the model to develop a population of MTBE plume lengths to be compared against the baseline benzene impacts. Section 8.2. details this methodology and the resulting benzene and MTBE plume length population distributions that we used in this comparative analysis. The samples of benzene plume lengths with ethanol present used for comparison to the baseline were derived from modeling results (McNab *et al.*, 1999b; Vol. 4, Chapter 4 of this report). Figure 8-1 is an example of how this was applied to two sample populations of plume length distributions. We used the difference between benzene plume lengths with and without ethanol as developed in McNab *et al.* (1999b; Vol. 4, Chapter 4 of this report) as a multiplier for the benzene plume lengths used in this study (Section 8.3.).

We used the three population distributions (benzene without ethanol, benzene with ethanol, and MTBE) to estimate the absolute probability of threat to drinking water wells near LUFT sites. The difference between the probabilities of impact was then used to develop the relative impact threat between benzene with ethanol and MTBE compared against the baseline benzene realizations. Finally, these results are discussed in context to known well BTEX and MTBE detections as found in the CAL-DHS Water Quality Monitoring (WQM) database. Additionally, we examined confounding factors and discussed their potential influences on public- and private-well impacts.

Health Services (CAL-DHS) Water Quality Monitoring (WQM) and the Permitting, Inspection, Compliance, Monitoring, and Evaluation (PICME) databases (CAL-DHS, 1999a,b); and the California Department of Water Resources (CAL-DWR) EXTERRA database (CAL-DWR, 1997). Yield and well construction data was obtained from local agencies including the Santa Clara Valley Water District (SCVWD, 1999) and Orange County Water District (OCWD, 1999).

[2] GEIMS is a water resources and contaminant database created for the SWRCB to manage LUFT sites. It is accessible through an Internet Geographic Information System (GIS) interface, GeoTracker, at <http://geotracker.llnl.gov>.

8.2. Forecasting Benzene (Degrading) and MTBE (Nondegrading) Fuel Hydrocarbon Plume Behavior

8.2.1. Introduction

Dooher (1998) discussed the importance of developing models appropriate to the available data when assessing situations of high uncertainty. Because the goal of any model is to predict the future or to fill in the gaps where not enough information is available, a modeling approach should attempt to develop confidence intervals for future predictions or fill in these gaps. These predictions forecast at some point in space what may occur now, five, ten, or 100 years in the future. In this screening model, these forecasts are used for developing "probability domains" to describe the likely area of movement of fuel hydrocarbon (FHC) plumes in the subsurface. The analysis of McNab *et al.* (1999b; Vol. 4, Chapter 4 of this report) applies a similar approach to the assessment of benzene plumes affected by ethanol.

This section provides the details for three major methodologies used in forecasting resource impacts associated with the use of ethanol as a fuel oxygenate:

- A comparison of forecast benzene plume lengths to plume lengths derived through various methodologies (Dooher, 1998), in order to validate the general model.
- An examination of the time history of degrading chemicals (such as benzene), its plume lengths, growth rates, and recedence rates.
- An examination of the time history of nondegrading chemicals, (such as MBTE), their plume lengths, growth rates, and recedence rates.

These plume lengths derived here for a large population of sites are then used as the basis to develop the probability of well impacts in California from benzene with and without ethanol and from MTBE.

The following discussion addresses two important elements of the evaluation of plume impacts to groundwater resources. The first examines the development of an underlying conceptual model of a plume, and the second applies Monte Carlo analysis to the conceptual model.

8.2.2. Conceptual Model of a Plume

A plume in its most abstract form moves downgradient, dispersing normally to the primary gradient direction in two directions. Figure 8-2 shows the conceptualization of the three-dimensional case. The greatest spread takes place horizontally in the primary direction of groundwater flow, with a lesser lateral and vertical transverse spread due to dispersion and smearing through zones of relatively higher conductivity (Gelhar *et al*., 1985).

For advection-dispersion and degradation in the subsurface, due to the heterogeneities present, an "exact" solution for the transport of a contaminant is possible only when these heterogeneities are accounted for—typically in some form of numerical modeling. This section examines a probabilistic approach, wherein a mathematically exact or approximate analytical solution is derived for three dimensions and used to produce a series of probabilistic realizations by applying a Monte Carlo methodology. Although analytical solutions to the advective-dispersion solute transport equation lack the general flexibility offered by numerical methods, they may serve as probability distribution models for contaminant concentrations as a function of space and time in many situations. Analytical approaches are particularly well suited for application of Monte Carlo techniques because of the speed of solution.

Monte Carlo analyses allow uncertainties in governing parameters (for example, groundwater velocity, contaminant degradation rate, source attenuation rate) to be addressed as assumed probability distributions for input to the model. The analytical solutions typically assume a homogeneous environment in which the groundwater flow is uniform in one direction. Probability distribution functions for the various parameters are placed into the models, and upper and lower confidence intervals are developed. When compared to actual environmental measurements, this method leads to a greater understanding of the uncertainty of the contaminant-plume movement relative to the variability of the subsurface.

The descriptive equation of transport for a uni-directional flow, three-dimensional plume with sorption and decay is the advection-dispersion equation

$$R\frac{\partial C}{\partial t} = D_x\frac{\partial^2 C}{\partial x^2} + D_y\frac{\partial^2 C}{\partial y^2} + D_z\frac{\partial^2 C}{\partial z^2} - v_x\frac{\partial C}{\partial x} - \lambda RC \qquad (8\text{-}1)$$

There are multiple analytical solutions that can be used with Equation (8-1), both for transient and nontransient situations. Many of these are discussed by Bear (1972, 1979), Wilson and Miller (1978), Cleary and Ungs (1978), van Genuchten and Alves (1982), and Wexler (1992). The 3-D solution to the Cleary and Ungs (1978) model of the form:

$$C = f\left(x, y, z, t, v, D_x, D_y, D_z, R, \lambda, \gamma\right) \qquad (8\text{-}2)$$

is used to as the plume probability domain. The specifics of the solution are found in Appendix A. Table 8-1 shows the variables used in the solution.

8.2.3. Monte Carlo Analysis

When used in conjunction with analytical models, Monte Carlo analyses of contaminant transport involves running multiple simulations (realizations) in which input parameters are allowed to vary in accordance with assumed probability distributions. The output of the Monte Carlo analyses is forecast frequency distributions of variables of interest (that is, plume length, plume growth, and recedence rate). Thus, the probability of a plume reaching a certain length or achieving a certain growth rate may be quantified (along with associated uncertainties).

For the first analyses, we conducted 4000 Monte Carlo realizations on two different source populations using the analytical solution (Equation A-4a) of Cleary and Ungs (1978). These realizations were used to forecast the 1 part-per-billion (ppb) contour-interval hydrocarbon-plume lengths and associated growth rates. Probability distributions of governing parameters were generated using literature sources, best professional judgment (BPJ), and data developed in Dooher (1998) (shown in Table 8-2). Plume-length distributions developed are then compared to the resultant Monte Carlo forecasts.

8.2.4. Results of Plume Length Forecasts

8.2.4.1. Degrading Plumes

8.2.4.1.1. Plume Lengths. Forecast cumulative distribution functions of benzene plume lengths are generated, as defined by the distance from the source (x = 0) to the 1-ppb contour interval along the plume longitudinal axis. These were created using the three-dimensional model described earlier, applying two different input distributions to simulate free product (FP) and non-free-product (NFP) sources. The only change in variables between them is the concentration distribution. FP concentrations are based on observed distributions on sites that have recorded free product, while the dissolved-concentration distribution is representative of sites with no observed free product.

Staff of the State Water Resources Control Board (SWRCB) drew over 500 plumes (some are plumes drawn at several periods on the same site) using BPJ. (BPJ is defined as manually viewing the spatial distribution of concentrations and the groundwater gradient direction.) Concentration contours are then drawn on a site map, and the plume length measured. The measure of the plume length across its long axis is C to C, “contour to contour.” Max to C is the measurement of the plume length across its long axis from the point of maximally found concentration. Typically measured were the 10-ppb and 1-ppb contours for benzene. Contours were drawn to be as conservative as possible, using historical data to fill in gaps of missing groundwater chemistry concentrations. The length was estimated using the highest historical groundwater concentrations. We used these lengths as a comparison in the following analyses. Figure 8-3 shows BPJ plume lengths[3] correlated against maximum site concentration.

It is immediately apparent that there is an effective “exclusion zone” in which, for a given concentration, there are no plumes greater than a certain length, implying the existence of natural constraints imposed by the physics of the subsurface transport phenomena. These constraints are likely to be the maximum velocity and the minimum degradation rate. For higher maximum benzene concentrations above 5000 ppb[4], the plume lengths begin to fall out of the exclusion zone. Figure 8-4 shows the same figure with log-transformed plume lengths, where the “exclusion zone” still holds for larger plume lengths. McNab *et al.* (1999a) found a very similar trend for chlorinated volatile organic compounds but with much exaggerated plume lengths.

Figure 8-5 compares this distribution with the distributions developed using BPJ and through the nonparametric approach found in Dooher (1998). To create uniformity, all plume lengths less than 25 ft were deleted because these small plumes would not be typically detected at the sampling distances characterized by monitoring well spacing. Though there is a definite scatter of the cumulative distributions, the same trends and ranges are very apparent. The Monte Carlo-generated plumes fall nicely into the center of the range and, more importantly, characterize what would be the 95th-percentile confidence level associated with a plume forecast.

8.2.4.1.2. Plume-growth Rates. For the population evaluated, plumes were forecast over time, starting at Year 1, and then at 5-year intervals starting at Year 5 after the release. Figure 8-6 shows the cumulative distributions of plume lengths for Years 1, 5, 20, 30, 40, 50, 60,

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[3] As developed by Rick Rempel of the SWRCB (Dooher, 1998).

[4] Dooher (1998) found that concentrations at these levels are highly correlated with “free product” or floating nonaqueous phase liquid (NAPL) product.

70, 80, 90, and 100. Some plumes literally explode into existence and can then rapidly decline, whereas others grow gradually and degrade gradually. Because a large percentage of the plumes expires over time, at Year 100 almost 70% of all plumes have decayed. Figure 8-7 shows the percentile plume lengths over time. The 95th percentile results show a peak at ten years at approximately 1600 ft, declining to 250 ft by Year 100. Figure 8-8 shows the same results with the plume length on a log scale. Figure 8-9 shows a sampling of various generated degrading plumes, from which the populations shown in Figures 8-6, 8-7, and 8-8 were developed.

Figure 8-10 shows the year interval at which the plume population reaches a peak. After 50 years, almost all plumes will have reached a maximum peak length. Figure 8-11 shows a box distribution of the plume lengths at the time of maximum extent for the populations in Figure 8-10. Median plume length ranges from 100 to 1000 ft with a slight trend upwards as time progresses as expected. Plumes that are still growing after 50 years must have very small degradation rates.

Figure 8-12 shows the cumulative distributions of plume-growth rates for various intervals of time. The maximum growth rate typically takes place in the first year, diminishing over time to a maximum of 0.1 ft/day for the 40- to 100-year range. For the plume-length decay rate, the initial decay is almost at its peak, peaking in the five- to ten-year range and then dropping off. The differences in the distributions are no more than a few tenths of a foot per day.

Figures 8-13 and 8-14 show the time required for plumes to extinguish. Initial surges of plumes vanish entirely within one year (approximately 10%). These would be associated with small releases. After this initial surge, there is an upward trend of time necessary to reach zero length, peaking for both FP and NFP populations at around 50 years. Figure 8-14 shows the maximum plume length associated with the time necessary to reach zero. The median for those plumes taking less than 20 years to reach zero length is generally small—no more than 20 ft. The median plume length tends to stabilize around 80 ft as longer times are necessary to reach zero-plume length.

8.2.4.2. Nondegrading Plumes

8.2.4.2.1. Plume Lengths. Nondegrading plumes behave very differently from those where source depletion and overall degradation occur. Figure 8-15 shows the cumulative distributions of plume lengths for (nondegrading) plumes with a constant source. A small percentage of simulations result in zero-length plumes; all are associated with low initial concentrations and rapid velocities. As time progresses, however, the plume distribution approaches an asymptote with the 95th percentile approaching approximately 15,000 ft (3 mi) in length. In contrast to the degrading plume sites where, on a year-by-year basis, an increasing number of sites reach a zero-plume length, no such effect occurs here. It is likely that sites exist where groundwater has been impacted but due to local conditions (such as a low relative flux rate from the vadose zone in combination with a high advective groundwater flow rate), the effect is minimal.

8.2.4.2.2. Plume-growth Rates. Figures 8-16, 8-17, and 8-18 show the plume length trends over time for various percentile intervals. Figures 8-16 and 8-17 show a close-up of the lower percentile ranges as well as the total range. Very few of the percentiles have reached steady state. Figure 8-18 shows this more explicitly. Most of the percentiles show a slowly declining rate of growth trend on a log-log scale, with only the lowest percentiles showing any deviation downward. These lengths are overly conservative because there is no source attenuation, which would occur in reality. Figure 8-19 shows a sampling of the various plume lengths from which the cumulative distributions are developed. Further work is being performed to assess the general source attenuation rate for MTBE sites.

Figure 8-20 shows the year at which the simulated plumes reach steady state for nondegrading plumes. By Year 100, 46% of the simulations have not reached steady state. Figure 8-21 shows the growth rates for FP and NFP plumes after 100 years. The 95th percentile is still approximately 60 ft/y. Figures 8-22 and 8-23 show growth rates at various time intervals for FP and NFP. Initial growth rates are much higher than those found in degrading plumes and stay high. This is in contrast to the growth rates of degrading sites that at Year 100 are an order of magnitude less in size than nondegrading plumes.

8.3. Comparison of Potential Future Impacts Associated with Benzene Either in the Presence of Ethanol or in the Presence of MTBE

8.3.1. Location Relationship between LUFT Sites and Public Drinking Water Wells

The potential threat from a LUFT site release to a well depends on the relative locations of nearby drinking water wells and the density (or count) of LUFT sites near the well. Figure 8-24 shows the minimum separation distance of LUFT sites from public drinking water wells and vice-versa[5]. Because there are many more LUFT sites than drinking water wells (approximately 35,000 LUFTs versus approximately 15,000 wells), 32% of LUFT sites are estimated to be within 2000 ft of a drinking water well, while 38% of well locations are estimated to be within 2000 ft of a LUFT site.

Figures 8-25 and 8-26 show density distributions as a percentage of LUFT sites and public drinking water wells within a range of distances. These graphs show the percentage of wells (or LUFT sites) and a count of the number of LUFT sites (or wells) within a given distance. For example, in Figure 8-25, approximately 45% of wells have at least one LUFT site within 2500 ft, and 31% of wells have at least two LUFT sites within 2500 ft.

8.3.2. Screening Model Estimate of the Probability of Future Impacts to Public Drinking Water Wells from LUFT Sites

8.3.2.1. Probability of a LUFT Site Impacting the Closest Well

To assess the potential impact of LUFT releases of gasoline containing either ethanol or MTBE, we considered the distribution of the separation distances between known LUFT sites and drinking water wells (Figure 8-24). The probability distributions of plume lengths for MTBE and benzene (Figures 8-6 and 8-15) and for the increased lengths for benzene with ethanol may be compared against distances between LUFT sites and drinking water wells as a function of time since plume release. The distance between the LUFT site (the plume source)

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[5] The determination of the locations of LUFT sites and public drinking water wells are discussed in Dooher and Happel (1999) and were originally found in SWRCB (1999) and CAL-DHS (1999b).

and the nearest drinking water well is related to the probability that a plume may migrate that distance. The probability of impact from benzene, benzene under the influence of ethanol, or MTBE for each LUFT/well distance may then be determined. It is then possible to compare the absolute and relative probabilities[6] of increased threat to the closest well adjacent to a given LUFT.

In developing these probabilities of impact, we assumed that the plume is heading downgradient toward the drinking water well. This conservative assumption is made because the direction of groundwater flow for these sites are unknown. Typically, LUFT sites are randomly situated in relation to drinking water wells; it is likely that the actual impacts may be much less. These impact probabilities for MTBE are conservative in that they assume no source or dissolved plume attenuation; however, they do allow the determination of relative changes in the probability over time. Section 8.5. discusses further how various uncertainties can affect these estimates.

Figures 8-27 and 8-28 show absolute probability of threat for benzene, with and without ethanol. Intervals as shown are for 1-, 5-, 10-, 15-, 50-, and 100-year cumulative probabilities of threat. The absolute probability of threat for benzene under the influence of ethanol, as seen in Figure 8-28, increases substantially. For the one-year interval for at least 10% of sites, the absolute probability of threat more than doubles. Similarly, the five-year interval, which shows the maximal predicted threat probability, also increase by a factor of two, to approximately 28%.

Figure 8-29 and 8-30 show the absolute probabilities of threat in detail. Twenty-five years after the benzene release, in both cases, the plume has returned to approximately the same probability distribution as Year 1. Maximal probabilities of threat occur in the five- to ten-year range. The decline of benzene over this timeframe (as seen in Section 8.2.) is due primarily to the attenuation of benzene sources and the degradation of the plume. This attenuation and degradation cause the benzene plume to slowly recede over time. Source attenuation rates are based on the results of field compliance data as stated in Dooher (1998). Degradation rates are based on results obtained from the same source as well as published data. In the case of MTBE, Figure 8-31 shows the total range of the LUFT-site populations and probabilities, as do Figures 8-27 and 8-28. In contrast, MTBE continues to have an increasing absolute probability of impacting wells for as long as 100 years although at this point it is reaching an asymptotic limit.

Of greater interest is Figure 8-32, which shows the relative change in probability between the absolute probabilities of Figures 8-27 and 8-28. The differences in these two distributions were used. We assumed that the benzene probabilities are the baseline case because benzene has been a ubiquitous contaminant at LUFT sites for many years. The important factor, therefore, is the *change* in the probability of impact to a drinking water well. The results show an initial increase in impact probability of 18% by the fifth year for a small percentage of sites (less than 3%). The average impact is an increase of approximately 10%. Examining the temporal change in relative probability (Figure 8-33), the greatest increase is in the first five years, dropping to a negative

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[6] The meaning of “absolute probability” is different from a statement that this is the actual probability that the well will be impacted, as there are many additional confounding factors that are not taken into account in this simple two-dimensional exercise. It is the relative probability that is of the greatest importance here. See Section 8.4. for a discussion of these.

rate change thereafter (as can be seen from the overall trends). The average change is approximately 2.5% in the first five years.

Figure 8-34 shows the temporal trend of the change in absolute probability for MTBE. The first five years show the greatest growth patterns, reaching a maximum of approximately 24%. This growth continues in the five- to ten-year range, where the relative change is still 10%, dropping to 5% for the five- to ten-year range, and to 2.5% for the 20- to 25-year range. This indicates that unmanaged MTBE sources can continue to act as a hazard for long periods into the future. Current work is attempting to ascertain rates of source attenuation that can be applied to MTBE; earlier work (reported in Happel *et al.,* 1999) shows a marked difference when a source-attenuation rate similar to benzene is used.

8.3.2.2. Probability of a LUFT Site Impacting Many Surrounding Wells

Basic probability calculus (de Morgan's rule) (Ang and Tang, 1975) can be used to estimate an absolute and relative probability of threat to drinking water wells. This approach assumes independence of the well locations. For multiple wells in a given LUFT-site area, the probability of impacting any well in the area is given by de Morgan's rule:

$$\begin{aligned} P\left\{E_1 \cup E_2 \cup \ldots \cup E_n\right\} &= 1 - P\left\{\overline{E_1 \cup E_2 \cup \ldots \cup E_n}\right\} \\ &= 1 - P\left\{\overline{E}_1 \overline{E}_2 \ldots \overline{E}_n\right\} \end{aligned} \qquad (8\text{-}3)$$

where E_i is the event probability, and $\overline{E}_i$ is the complementary form of the event probability, or $\overline{E}_i = 1 - E_i$. An assumption of independence for the surrounding wells is not exactly correct, as their spatial position is approximately known. Known locations turns the problem into one where there is dependence (that is, if the plume moves in a direction where three wells are located, the probability of impact of a further well necessitates the impact of the closer well). A sensitivity study of this dependence is under development.

As an example, we assumed that the probability of a plume reaching a well 1000 ft distant would be 0.25, and for a well 2000 ft distant, it would be 0.10. Assuming a well at 1000 ft and one at 2000 ft, the total probability of impact threat to either well is

$$\begin{aligned} P\left\{E_1 \cup E_2\right\} &= 1 - (1 - 0.25)(1 - 0.10) \\ &= 0.325 \end{aligned} \qquad (8\text{-}4)$$

Taking the example further, using this screening approach the probability of threat to any of six wells, all at a distance of 1000 ft, would be 82.2%.

Using information in the GEIMS database, the above approach to estimating the probability of impact from a single LUFT was applied to all known open LUFT sites and active drinking water wells in California. Drinking water wells that exceeded a distance of 30,000 ft from a given LUFT were excluded in this analysis[7]. In all, we evaluated 15,525 open-case LUFT sites with geocodable addresses.

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[7] This is due to the almost nonexistent probability of a plume reaching this distance (based on the modeling).

Figure 8-35 shows the modeled absolute probability over a 100-year time span for the 30% of LUFT sites in California where benzene may threaten to impact a well. Potential impacts for benzene with and without ethanol are shown. For example, the addition of ethanol increases the initial impact threat difference by over 20% for up to 10% of LUFT sites. Thereafter, this change in total probability decreases. For at least 20% of LUFT sites, the increased difference in probability is at least approximately 14%. For 30% or more of sites, the change in total threat probability is at least 7%. All these maxima occur in the five- to ten-year timeframe, much as we saw with the LUFT site and the single well. The decrease is due to benzene-source attenuation and overall degradation.

The relative change, as stated above, is of primary import. Given the addition of ethanol, a majority of LUFT sites will show relatively little additional chance of impacting nearby wells. Those sites that are already at a high absolute probability of threat will increase dramatically up to 20%, or approximately 1550 wells.

Figure 8-36 shows the estimated absolute probability of a given percentage of LUFT sites in California where MTBE may threaten to impact a well across a 100-year time span. For example, 10% of the sites have a 30% probability of threat in the first five years, increasing again by an additional 15% during Years 5 to 10. Because the modeled MTBE plumes are assumed to be nondegrading, they continue to expand and represent increasing threats with time. This expansion and increasing threat are in contrast to the benzene sites that have peak potential impact threat approximately seven years after release, after which point they begin to decrease in threat (Figure 8-35).

Figure 8-37 shows the relative probability increase between sites impacted by benzene alone and those sites where benzene is under the influence of ethanol, for approximately 5% of sites (the 95th percentile as shown on the figure). Benzene is again stated to be the baseline for comparison. The result of this comparative estimate is that there is an approximately 20% maximum predicted increase in public drinking water well impacts for benzene with ethanol in the five- to ten-year frame. This relative rate of impact begins to decrease thereafter.

An examination of the relative change in probability of MTBE impact reveals a significantly increased chance of impacting a well. At about seven years, the probability of impact for MTBE and benzene under the influence of ethanol is about the same. The major difference between MTBE and benzene under the influence of ethanol is that the probability of MTBE impact continues to increase with time as MTBE plumes continue to grow. Figure 8-37 shows the maximum expected change in well impacts, using benzene without ethanol as a baseline. By Year 10, an MTBE release has an increased probability of impact of 45% over the baseline benzene impacts, or more than twice the threat that benzene in the presence of ethanol represents.

It is important to note that all quantitative findings, such as the estimated relative probability of impacts, reflect probabilistic modeling results and are highly sensitive to the underlying probability distributions and simplifying assumptions for the various modeling inputs. This comparative analysis is intended as a screening tool and is not intended to provide formal quantitative predictive values that could be used for detailed resource planning purposes. Further work is being performed to assess the absolute and relative probabilities with known maximum concentrations of benzene and MTBE. These results should be significantly less than those shown here and will be of significantly greater use.

8.4. Important Uncertainty Considerations

To estimate the impact to public drinking water wells, we assumed that the modeled increase in probability due to a change in gasoline composition could be based on what is current knowledge of benzene impacts. However, some important uncertainties are inherent in the use of the known benzene impacts:

- Many wells had not been tested as of January 1995 (approximately 50% of those wells had been sampled more than once). That five-year period may have resulted in a low concentration impact that, upon mixing with other water sources, would not be noticed. The same holds true for MTBE.
- The statistical population used as a baseline for MTBE impacts is those wells that are required by CAL-DHS[8] to sample for nonregulated chemicals or secondary maximum contaminant levels (MCLs) (such as MTBE). This decrease in sampling frequency may increase the possibility that benzene or MTBE could reach a drinking water well undetected.
- Although most LUFT data collected are two-dimensional in nature, the problem is in reality three-dimensional. Wells are screened at different depth intervals across the state, depending on the type of water usage and the local groundwater depth. Factors that introduce uncertainty include vertical flows that occur from well use (which could increase the vertical transport downward), artesian aquifers (that cause upward gradients), and confining layers of low hydraulic conductivity that act to prevent downward flow, upwards or downwards. Although hydrocarbons, which are light nonaqueous phase liquids (LNAPLs), are referred to as “neutrally buoyant” in the dissolved phase, rainfall can also act to drive the plume downward.

8.4.1. Location Accuracy of Drinking Water Wells and LUFT Sites

An important uncertainty in this analysis and in any future assessment of potential impacts is the accuracy of locations of public drinking water wells in the CAL-DHS (1999b) PICME database. Dooher and Happel (1999) demonstrated a technique to improve significantly the location accuracy of public drinking water wells. The improved location data are used in this analysis. CAL-DHS, in cooperation with the SWRCB, plans to expedite finding accurate locations of wells in close proximity to LUFTs by November 2000 in order to comply with Senate Bill 989 (1999).

Ascertaining the locations of LUFT sites and operating UST sites within the pilot areas and within the state is much simpler than locating wells accurately. Because LUFTs and USTs are specific, large facilities, their locations can be determined with moderate to high accuracy based on addresses of commercial sites. LUFT sites used in this study are based on ETAK[9] geocoding, which returns an approximate location and associated accuracy based on street addresses. Geocoding finds latitude and longitude of street addresses using an electronic database of streets

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[8] Excluded from this population are 3859 public water systems that are considered to be transient noncommunity (TNC) systems (e.g., restaurants, campgrounds). These TNC systems are not required to monitor for unregulated chemicals or chemicals with secondary MCLs.

[9] Available at <http://www.etak.com/>.

and returns a qualifier stating the source of the position. Dooher and Happel (1999) examine the accuracy of geocoding.

Potential problems in geocoding are based more on poor LUFT site and UST facility address data. The SWRCB, in cooperation with Regional Water Quality Control Boards and local permitting agencies, is currently addressing this problem by reconciling local and state databases within the GEIMS database.

8.4.2. Sampling Frequency and Impact Rates of Public Drinking Water Wells and LUFT Sites

Because our estimate indicates that the use of ethanol as a fuel oxygenate may be expected to increase drinking water well impacts as much as 20%, routine monitoring of public and private drinking water wells would be an important step to identifying actual impacts. Figure 8-38 shows the first and most recent sampling-date distributions for 10,972 drinking water sources that have been tested for benzene[10] (CAL-DHS, 1999b). Only those wells that have had multiple sampling are included in this graph. The reported, first-time sampling rate of approximately 1800 sources/year decreased substantially in 1987 to a reported rate of approximately 450 sources/year. This rate is likely due to new wells annually created around the state and reflects initial sampling. In 1999, the sampling-event rate for many of these wells substantially increased. However, a large percentage (40%) of wells has not been sampled or reported as sampled in eight years. It is, thus, not known if there have been any well impacts for this percentage of the population. For MTBE, most sampling has taken place since January 1996, approximately the same time as the first reported impact to Santa Monica's well fields.

In estimating the impact to public drinking water wells, we assumed that the modeled increase in probability due to a change in gasoline composition can be based on the current detection rate. Variations in that detection rate may have a direct impact on the estimate of future impacts.

Figure 8-39 shows the cumulative distribution of time between samples and the average time between samples. The average time between samples is conservative, because "two samples over 10 days" would result in an artificially high sampling rate. In the past year, 10% more wells—a large increase—have been sampled for BTEX. Only 50% of the wells sampled have been sampled more than once. The above results point to an uncertainty in the baseline "detection rate" of BTEX and MTBE in wells around California; therefore, there is inherent uncertainty in the exact estimate of impacted wells.

Appendix B summarizes the results of the routine testing of public water sources throughout California. Tables 8-3 to 8-5 show the yearly count of tested public water sources throughout California. Tables 8-6 to 8-8 show the same counts for sources reporting BTEX and MTBE detections. Overall, the average yearly benzene source detection rate is under 0.35%, as seen in Table 8-9 (also seen as Figure 8-40). Both toluene and total xylenes have a higher rate, 0.53%

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[10] It should be noted that these are the numbers reported to CAL-DHS and may not accurately reflect the true sampling frequencies. Almost half (2285) of the 4681 public water systems are small systems and nontransient noncommunity systems regulated by local primary agencies (LPAs), designations given to 34 of California's 58 counties. Data from LPA-regulated systems are not required to be submitted to CAL-DHS. In July 1998, CAL-DHS requested LPAs to provide their MTBE detection data. These data are included as they are received from the LPAs.

and 0.36% respectively. MTBE shows a 1.17% yearly detection rate, much higher than any of the BTEX constituents alone, although similar to the combined BTEX detection rate (1.15%). BTEX and MTBE have a combined water source detection rate of 1.75%. The total detection rate for BTEX and MTBE, as of 1999 (Table 8-10) shows a 0.68% detection for benzene alone, 1.64% for toluene, 1.0% for the xylenes, and 0.62 for ethylbenzene. MTBE, which has not had as many sources tested (approximately 42.3%) and which has only been tested for (and used) recently, has already almost equaled the cumulative yearly detections of toluene, at 1.55%. The combined cumulative detection rate of BTEX is 2.85% and BTEX with MTBE is 3.35%. Finally, the change in detections are seen in Table 8-11. Figure 8-41 shows these trends in a better format, but it can be seen that the average change in detection for MTBE is higher, by 25%, then the change in benzene detections. The overall change in detection trends for BTEX is 6.6%, and with MTBE included, 8.3%.

8.4.3. Comparisons of Well BTEX/MTBE Detection Levels, Well Construction, Well Yield, and Groundwater Levels

Figure 8-42 shows a cumulative distribution of maximum concentrations as found in public drinking water wells. These concentrations are orders of magnitudes less than what is observed typically at LUFT sites. If ethanol is added to gasoline, it will likely have a similar effect on the entire range of BTEX components. The levels observed may rise as a result of ethanol's addition to unknown but higher levels.

Figure 8-43 shows the depth to the top of the screen interval for various well types found throughout California. Municipal (public) wells are generally deeper than domestic wells. The median depth for domestic wells, based on selected CAL-DWR records and a more complete database obtained (Dooher and Happel, 1999) from the Santa Clara Valley Water District (SCVWD, 1999) shows a range of 75 to 100 ft. The median for SCVWD and from data collected from the public wells of the Orange County Water District (OCWD, 1999) shows a median that is more wide ranging—from 175 to 350 ft. This range is probably characteristic of depth to top of screen interval for California groundwater, the depth of which is in general deeper in southern California. The CAL-DWR and SCVWD data are from northern California.

Figure 8-43 also shows the cumulative distribution of the top of the screen depth for MTBE-impacted wells across California. It is similar to the SCVWD public wells and deeper than the private well distribution, implying that the depth of private wells may not be sufficient protection against impact.

Of importance in determining concentration levels in wells are both the well yield and the plume concentration that the well takes in. As an example, the Santa Monica Arcadia wells were found to have maximum MTBE levels of 19.6 ppb and 86.5 ppb for average monthly well yields of 7.1 and 13 million gal, respectively (CAL-DHS, 1999a). These levels represent the 85th and 95th percentiles of the distribution of known MTBE impacts to public wells. The result of performing a simple mass balance gives the actual MTBE levels (on a monthly basis) of 0.14 and 1.13 gal, respectively. Figure 8-44 shows the well yields as collected from SCVWD (1999). The Arcadia wells represent the 84rd and 89th percentiles of the well yields as found in that database. Private well yields are much less; these are also shown in Figure 8-44.

Figure 8-45 shows the correlation of the depth to top of well screen and the maximum depth to groundwater, based on CAL-DWR records, for the set of private wells found in Figure 8-43.

Where the points lie above the line, the groundwater level is below the top of the well screen, leaving the well more vulnerable to contaminants that come from the surface. Twenty percent of the wells have top of screen intervals that are greater than the groundwater depth. An additional 20% of the maximum groundwater level in the wells are within 20 ft of the top of the screened interval. Various studies have shown the intrinsic vulnerability of domestic wells to surface contamination (specific vulnerability). Details of these studies are found in Dooher (1999).

It is apparent that in public wells, any combination of concentration and yield is possible (that is, low concentrations, low yields; high concentrations, high yields). The Santa Monica Arcadia wells represent the near maximum yield and impacted concentrations seen in California and are, therefore, near the upper limit of what is known to be possible. Little is known concerning the levels of concentrations as seen in private wells. It is known that a private well in Glennville, California, reported MTBE concentrations at the 20,000-ppb level in a fractured rock environment. There were other concerns with this, however, including impacts of coliform and nitrates, as well as *E. coli* in other nearby private wells. Little is known concerning actual impacts to private wells, and more work must be performed to assess that population.

8.4.4. Vulnerability of Private Drinking Water Wells

What is not reflected in the screening analysis of potential impacts to public wells are the approximately 1.3 million individuals in California who rely on private drinking water wells as their primary source of water. According to 1990 United State census data, 464,621 California households use some kind of private well US Census, 1992a). Although the locations of these are not exactly known, U.S. census data do provide the information to determine the densities of private wells (see Figure 8-46) from which the relative specific vulnerability of these private wells may be determined[11], as seen in Figure 8-47. Some local agencies possess databases or listings of private wells; due to privacy considerations, this information is not generally available.

Few compendiums have been issued that look in detail at LUFT sites that have impacted wells, nor the reason for those impacts. In 1995, 55 water-supply wells in the jurisdiction of the Central Valley Regional Water Quality Control Board (CVRWQCB) were reportedly affected by BTEX. The SWRCB reviewed 36 LUFT case files (Rempel, 1995) on those wells and found that unreasonable impairment of actual beneficial uses by benzene from LUFT sites is rare. Of the 55 wells reviewed, only 25 could be reasonably attributed to 19 LUFT sites out of the 5871 sites then reported in the LUSTIS database. Seven of these sites were located in fractured rock and impacted nine water wells, with six of these being onsite wells. The remaining 12 LUFT sites were located in alluvial soils and affected 16 supply wells, five of which were onsite wells. In all cases, the affected wells were less than 200 ft away from the LUFT. Twenty-four of the 25 affected wells were private, domestic wells. The review also found that 11 of the 24 affected private, domestic water-supply wells were shallow, onsite wells at the LUFT site itself. Many of them were described as “hand-dug” and probably had not been completed to current drinking water well specifications. The review concluded that the LUFT potential impacts to groundwater resources should be evaluated based on the proximity and the construction of water-supply wells within a few hundred feet of a LUFT site.

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[11] The methodology used to determine this is described in Dooher (1998).

This evaluation was performed prior to the use of MTBE in gasoline, and there are now several hundred well-affected LUFT sites reported in LUSTIS. These sites should be re-examined for detection of MTBE. Additionally, examination of MTBE-impacted public wells may uncover trends or weaknesses in current regulatory oversight that require correction.

8.5. Conclusions

In conclusion, we used a distance approach combined with known impact probabilities and estimated plume lengths to compare the probabilities of threat from LUFT benzene releases (with or without ethanol), or MTBE, impacting drinking water wells in California. This method provides an important advantage because it provides comparative estimates of potential future impacts between MTBE and benzene in the presence of ethanol. The methodology described herein can act as a screening-level approach to identify highly vulnerable areas. The identification of such areas would then be based not only on a single site, but also on multiple sites. The methodology also provides a probability factor for assessing the degradation of the resource in a specific area using a summation of sites.

This method is based on the assumption that only one major variable, plume length, will change as a result of the addition of ethanol to gasoline. All other variables, such as well depth, yield, and locations will stay the same. Therefore, we can use the benzene without ethanol as a baseline on which to assess the changes in detections.

Based on the results of our analysis, an approximate 20% peak relative difference in public drinking water wells impacted by benzene was estimated if MTBE is replaced by ethanol, when compared to benzene alone. This relative increase in public drinking water well impacts is estimated to decline from this peak by ten years after the initial release. However, the estimated potential future increase in public wells impacted by MTBE is significantly higher if MTBE remains the primary fuel oxygenate. By the conclusion of the first ten-year period, estimated MTBE well impacts increase by as much as a 45% difference form the baseline, and continue to increase thereafter. This analysis is very conservative, especially with MTBE. Known concentration levels at LUFT sites were not used in the analysis because only a limited number of LUST sites have a known concentration associated with them. A comparative analysis is underway to evaluate the difference between the above analysis and that of the more limited population.

This approach may be subject to misinterpretations. Because we are examining first an absolute probability, there is a concern that the absolute probability can be taken out of context. It is important that the relative probabilities be used, using the benzene-alone distributions as the baseline.

The evaluation of known detection levels in public water sources as discussed in Section 8.4.2, is to provided some perspective to the magnitude of benzene or MTBE impacts in the past. Overall, the average yearly public drinking water source benzene detection rate is under 0.35%. Both toluene and total xylenes have a higher rate, 0.53% and 0.36%, respectively. MTBE shows a 1.17% yearly detection rate—much higher than any of the BTEX constituents alone—although similar to the combined BTEX detection rate (1.15%). Currently, benzene shows a fairly constant detection rate over time, with a slight downward trend when yearly rates are compared. The use of ethanol as a fuel oxygenate would likely increase this detection rate which may stabilize at some higher level. MTBE shows definite upward detection trends; its continued use could, based on the trend results, result in more detections in water sources than benzene within the foreseeable future.

Based on the results of this preliminary evaluation, the following are recommended:

- Modeling based on detailed site-specific information is needed. Because the results of these estimates are largely dependent on the input parameter probability distributions, historical-case data that better constrain the uncertainty in these probability distributions will improve the predictive capability of any future modeling. The uncertainty inherent in using the complete distribution of benzene concentrations and velocities increases substantially the increase in expected probability for well impacts. Site-specific, maximum concentrations should be used, as opposed to a generic distribution that assumes no knowledge of the LUFT site.
- Groundwater capture zones should be included in the analysis. This model approach assumes that all plumes move towards a nearby well but with no influence from the well itself. Further probabilistic modeling should be performed to ascertain the sensitivity of this approach to well-capture zones and known groundwater-flow directions.
- More knowledge is required concerning the subsurface environment in California. One of the major unknowns in any hydrogeological investigation is the lack of knowledge of subsurface geology. A great deal can be learned even from the moderate to poor quality of data available in CAL-DWR well logs. This data should be transcribed into electronic format for use by researchers attempting to draw conclusions on the subsurface.
- A drinking water well sampling frequency policy that is based on proximity to LUFT sites may be more protective of public water supplies. Public water agencies should consider higher sampling rates for wells that are situated near known LUFT releases, or any other known release, in order to protect public health[12].
- Further comparative analysis of impacted public drinking water wells to gasoline continuing ethanol or MTBE and well-impacted LUFT sites is needed. Rempel’s 1995 report should be updated to help to understand what factors result in well impacts throughout California.
- A voluntary sampling program for private wells should be established by the state of California. In order to protect a portion of the public that currently has no regulatory oversight to protect against well contamination, California should institute a program designed to identify areas where sampling of private wells may be required and offer screening samples to that population.
- Data already collected by various state organizations should be systematically organized for use in decision analysis.

8.6 Acknowledgments

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[12] This was a recommendation of the MTBE Blue Ribbon Panel (BRP, 1999) as well.

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Figures

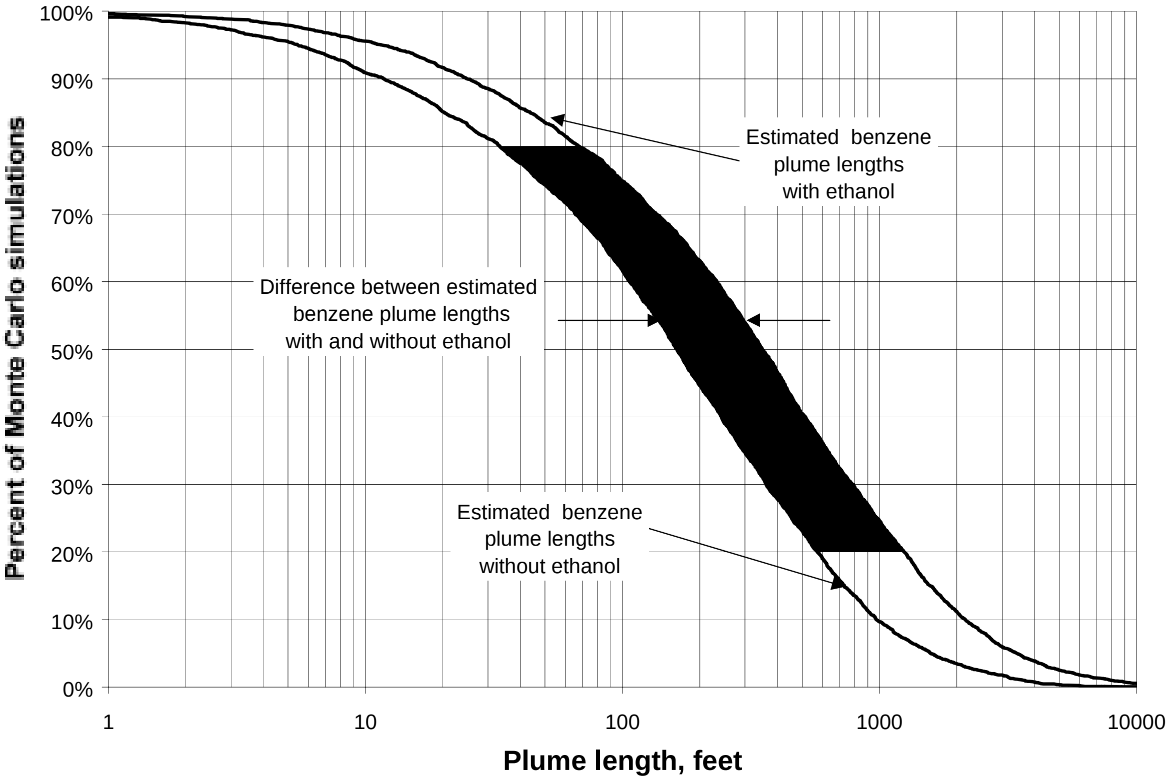

Figure 8-1. Example of the derivation of the multiplier used in this analysis.

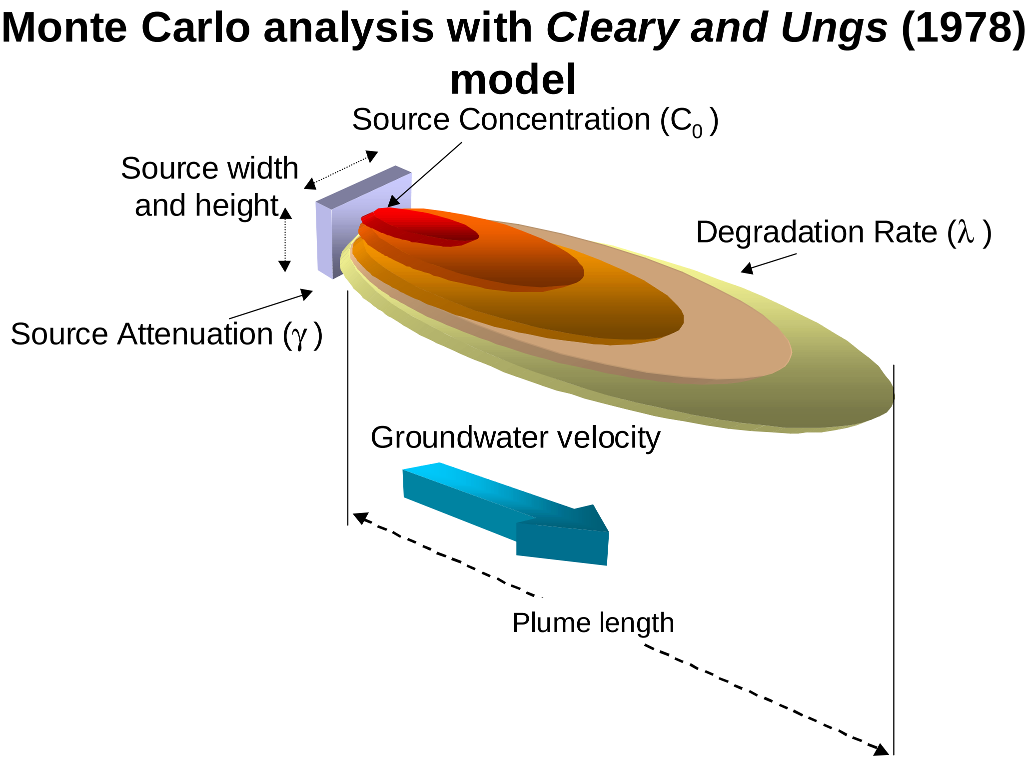

Figure 8-2. Conceptualization of the three-dimensional plume.

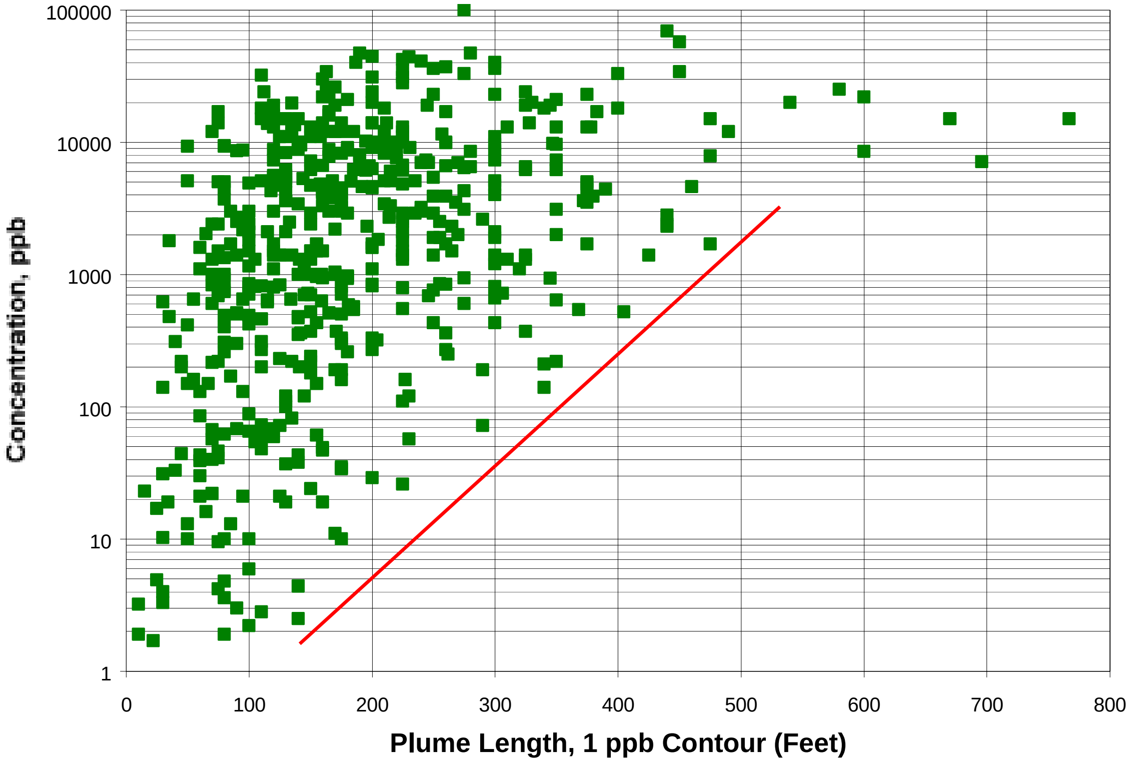

Figure 8-3. **Best Professional Judgement benzene plume length vs. maximum benzene concentration.**

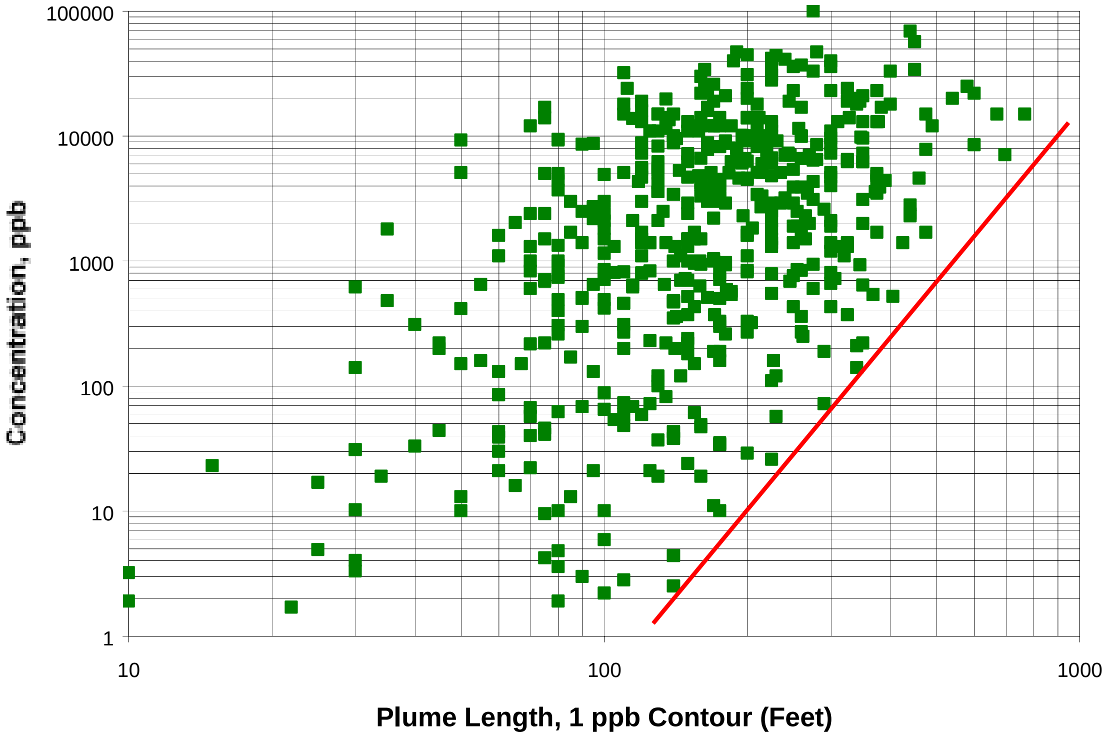

Figure 8-4. **Best Professional Judgement plume length vs. maximum concentrations (log-log scale).**

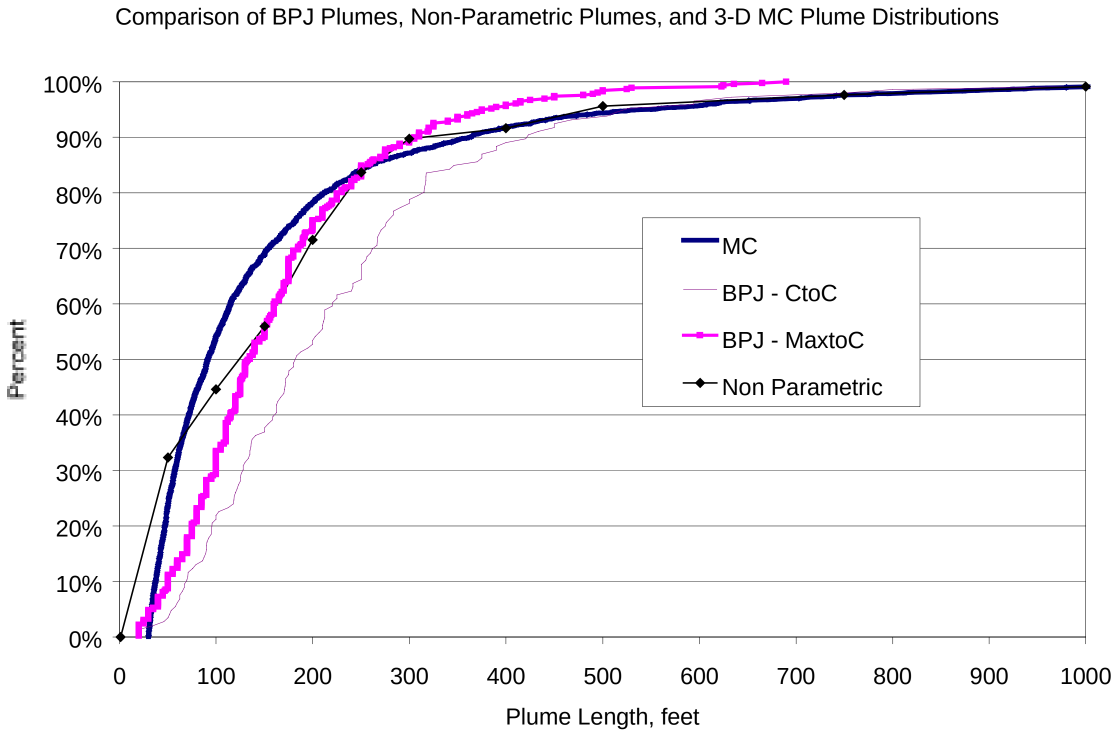

Figure 8-5. Comparison of 3-D Monte Carlo simulated plumes with nonparametric and Best Professional Judgement derived plumes.

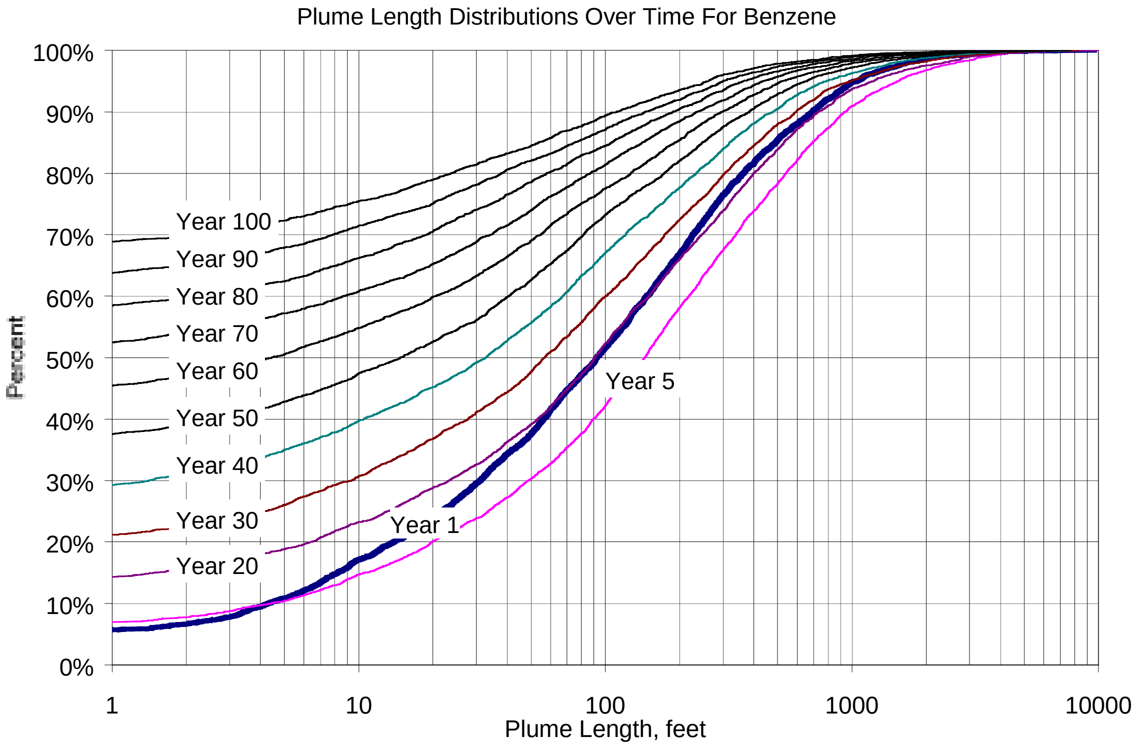

Figure 8-6. Cumulative distributions of benzene plume length over time.

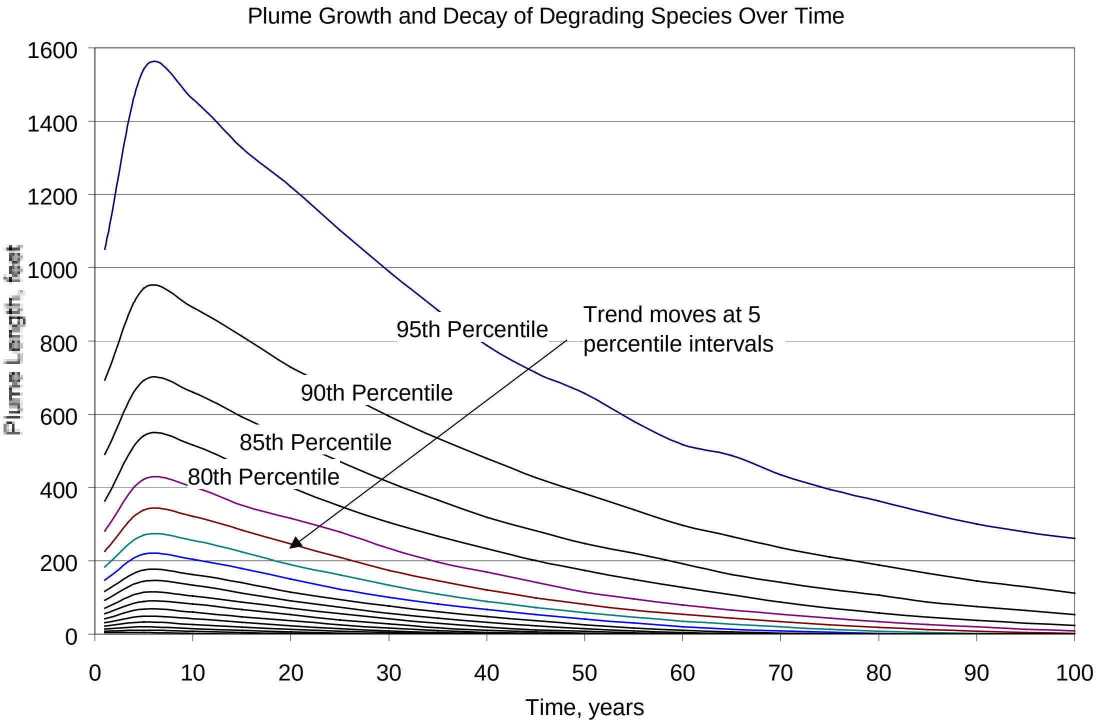

Figure 8-7. Plume length vs. time elapsed for various percentile intervals.

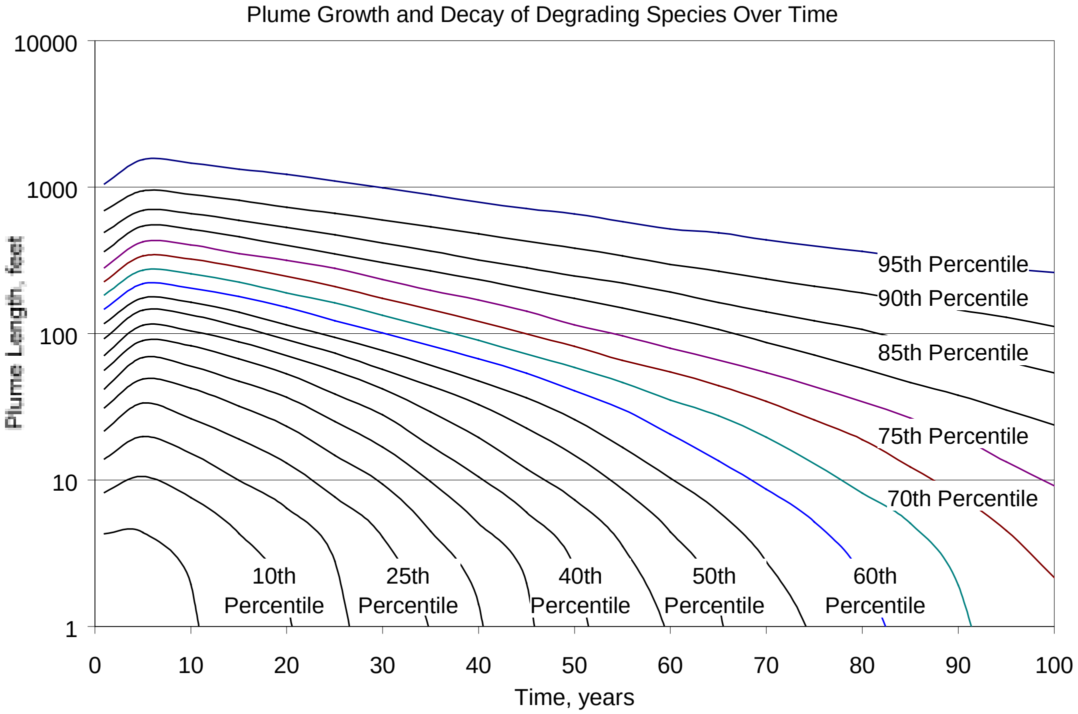

Figure 8-8. Log scale plume length vs. time elapsed for various percentile intervals.

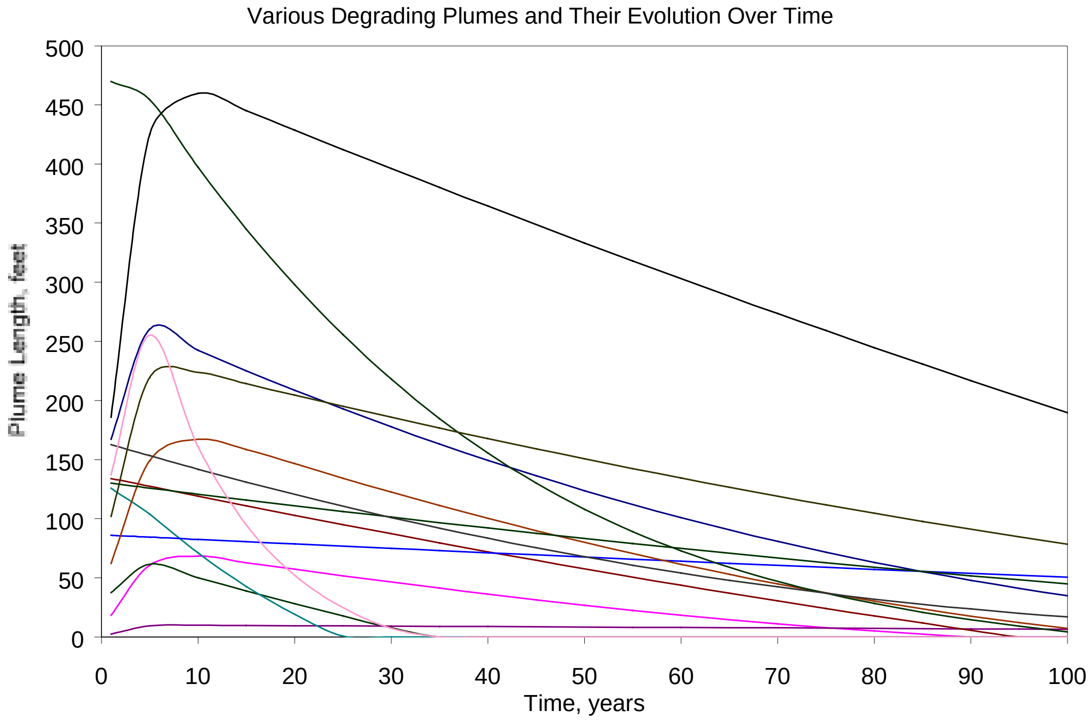

Figure 8-9. Plume length vs. time elapsed for randomly generated plumes.

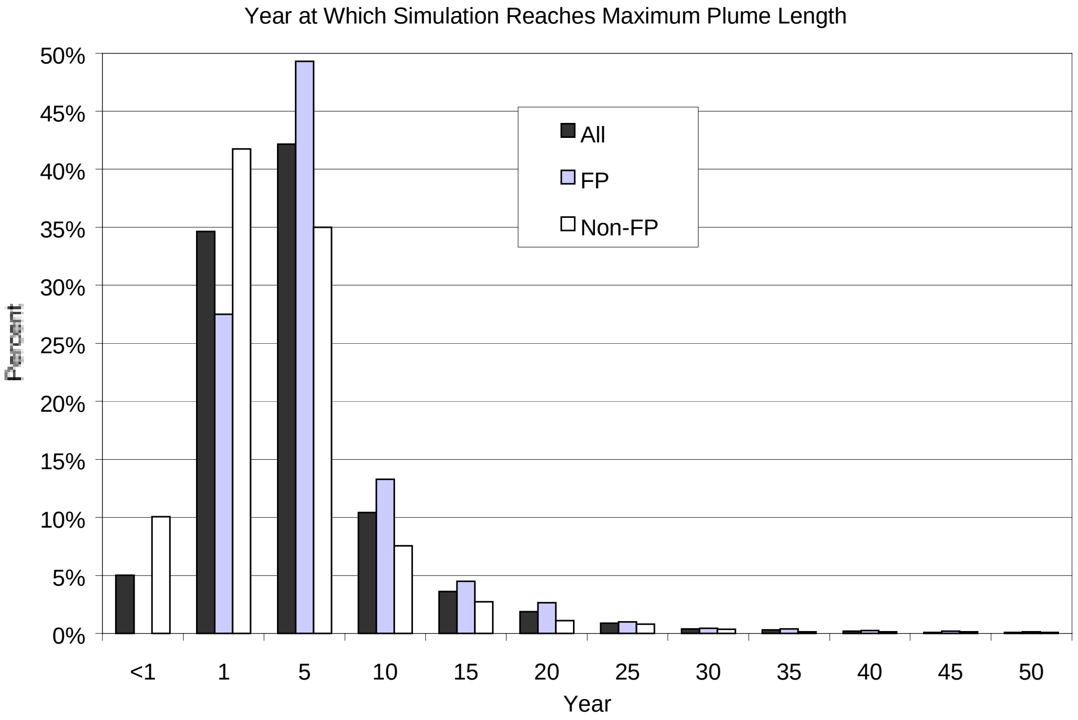

Figure 8-10. Time at which degrading plume reaches its maximum length.

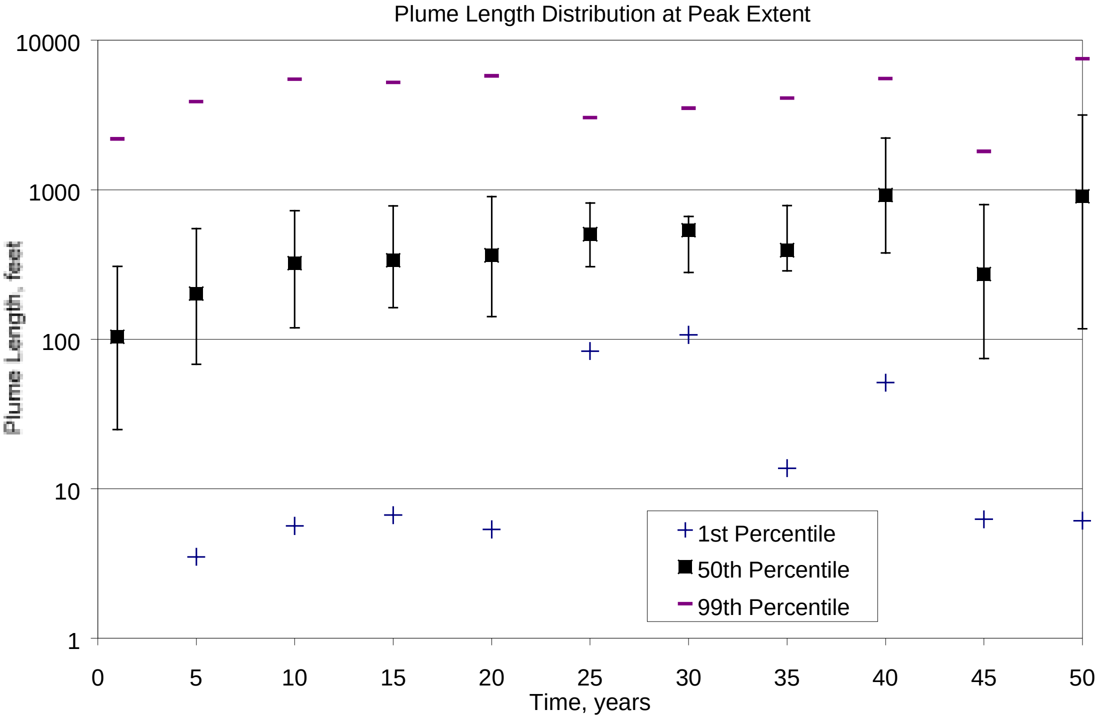

Figure 8-11. Plume length distributions for time interval at which degrading plume reaches its maximum length.

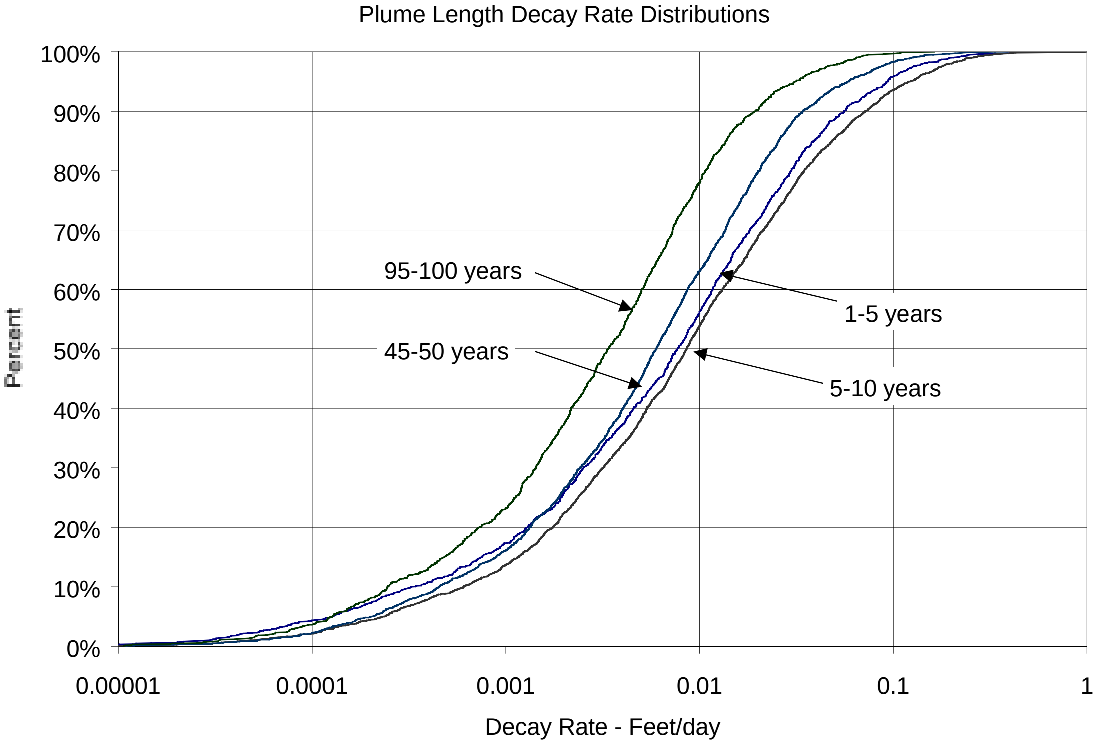

Figure 8-12. Distribution of plume decay rate at various time intervals.

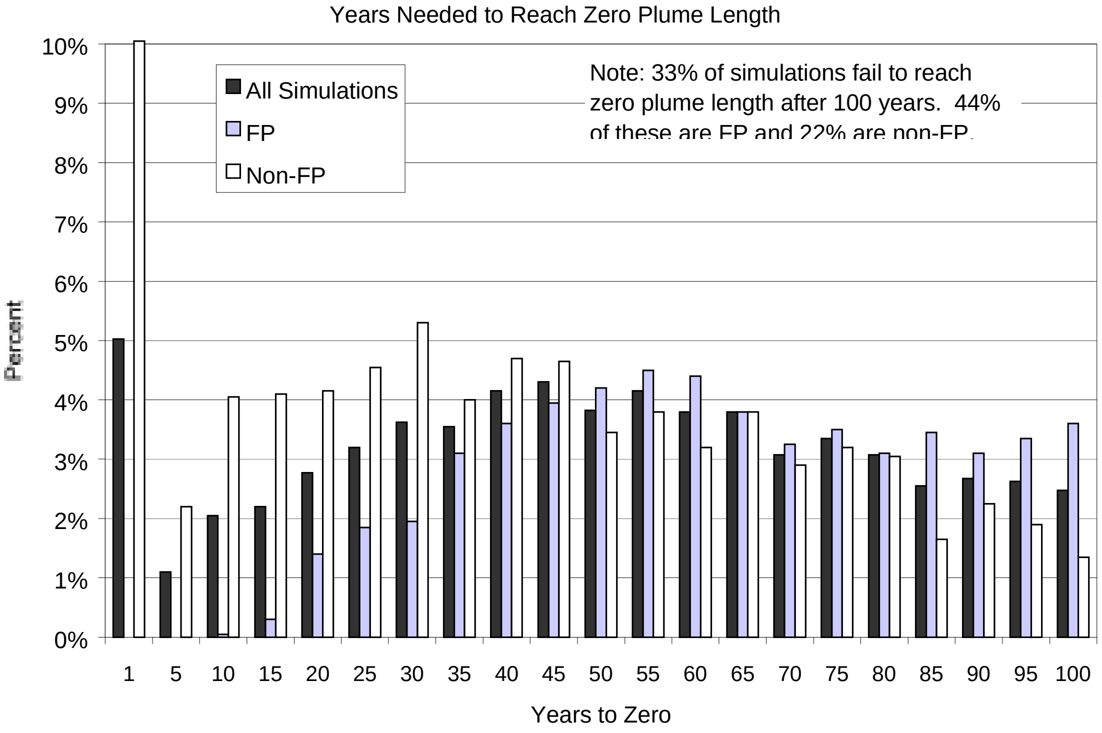

Figure 8-13. Years required for plumes to reach zero plume length.

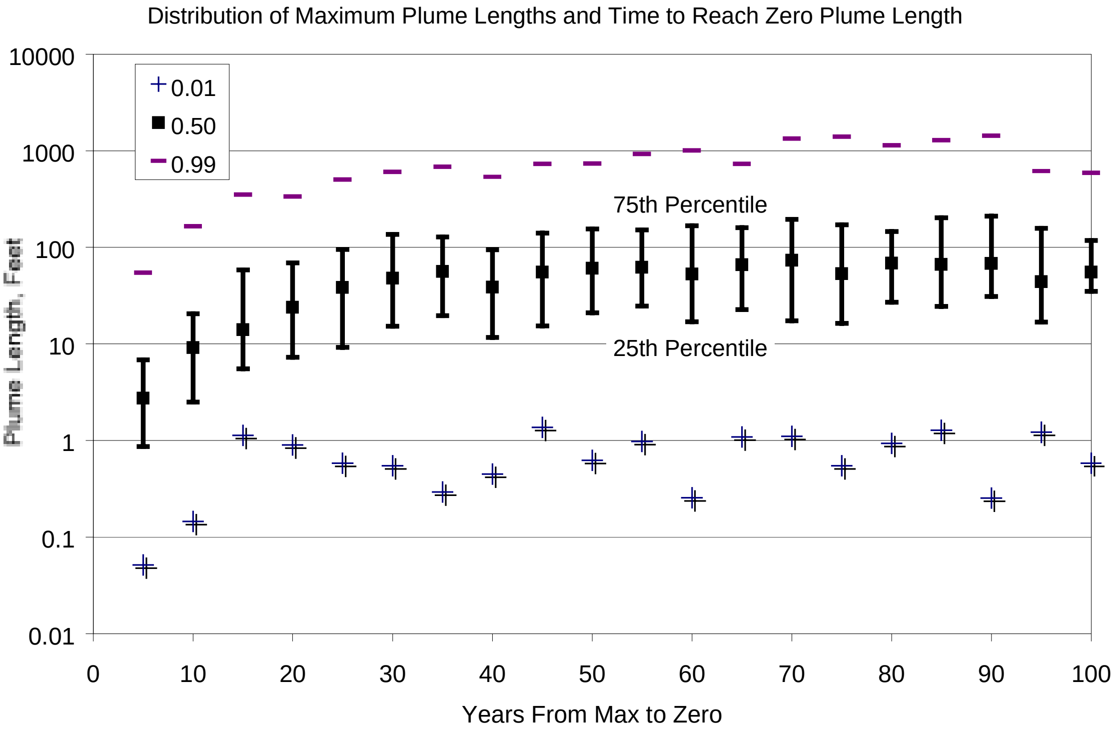

Figure 8-14. Maximum plume length distributions for time interval necessary for plume length to reach zero.

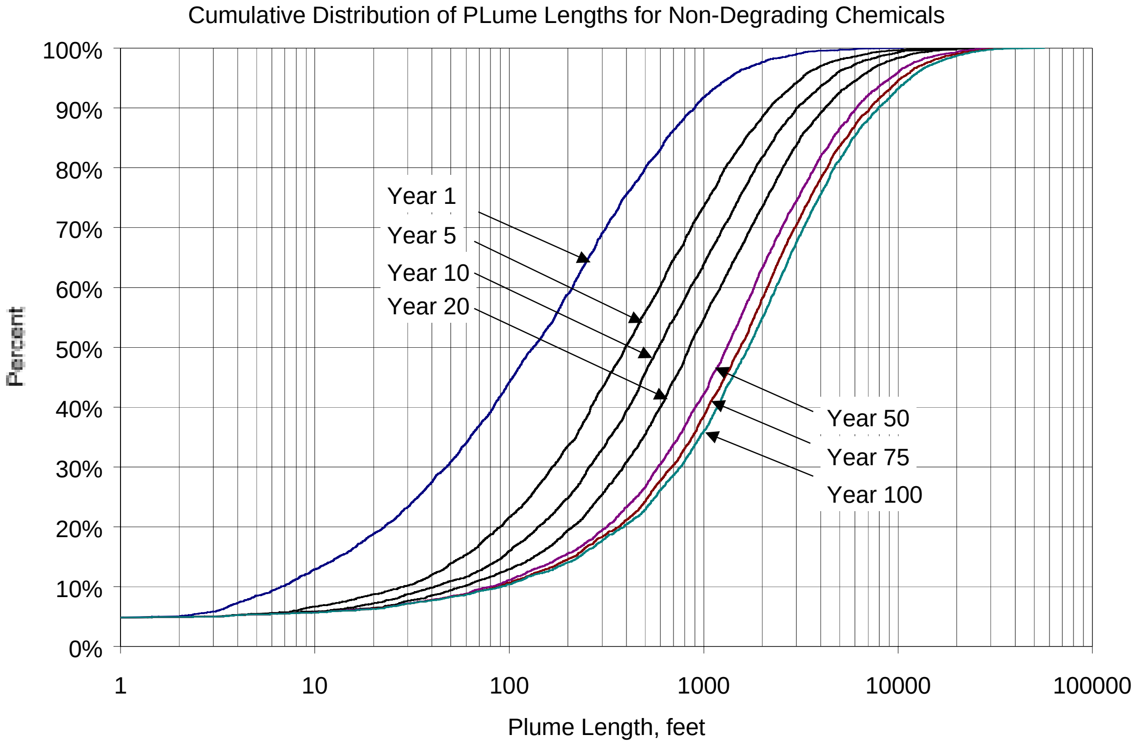

Figure 8-15. Plume length distributions for nondegrading plumes.

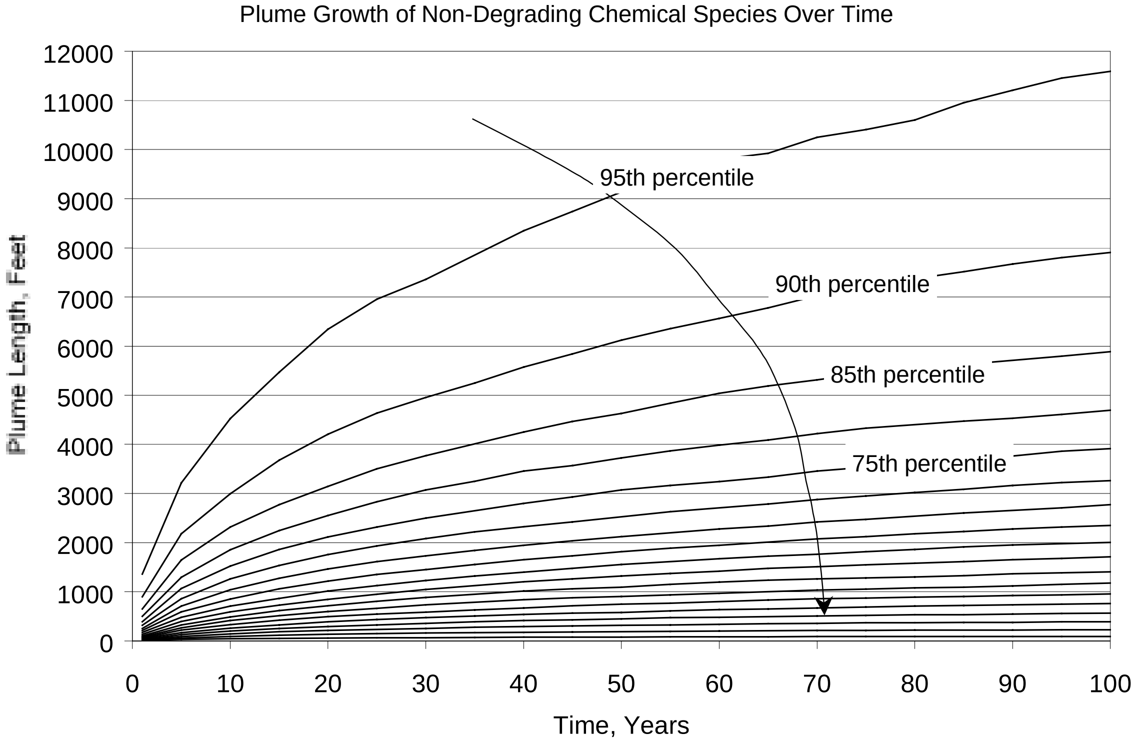

Figure 8-16. Plume length vs. time elapsed for various percentile intervals.

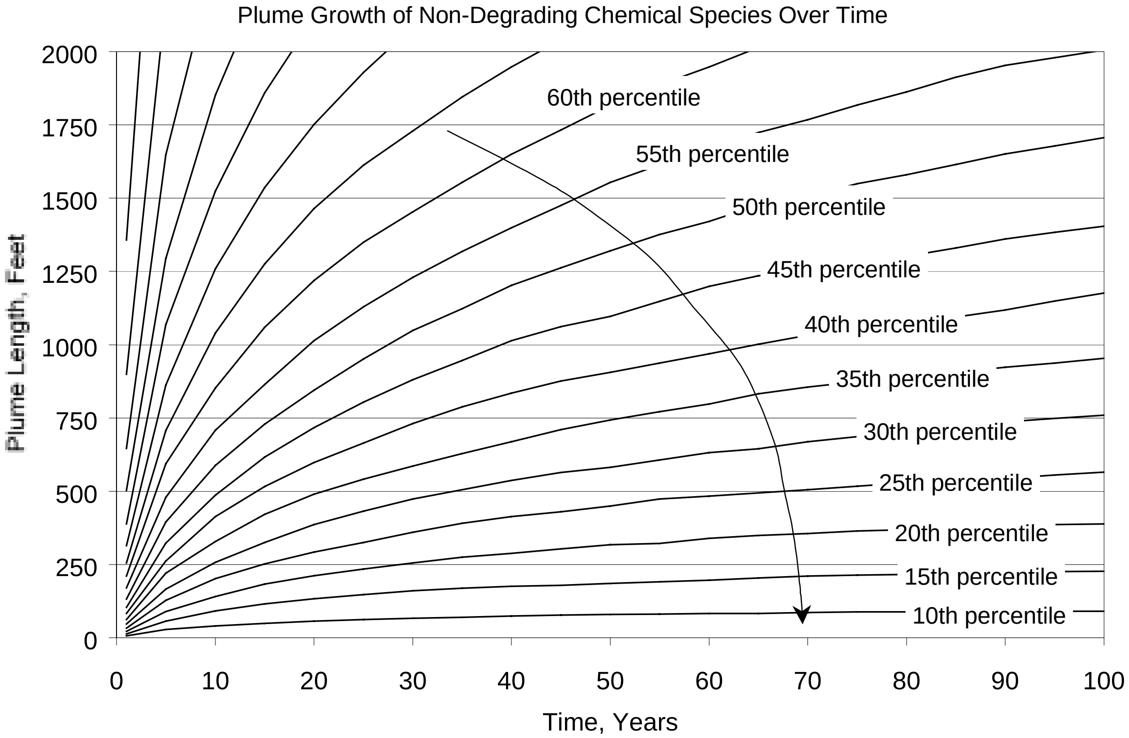

Figure 8-17. Plume length vs. time elapsed for various percentile intervals.

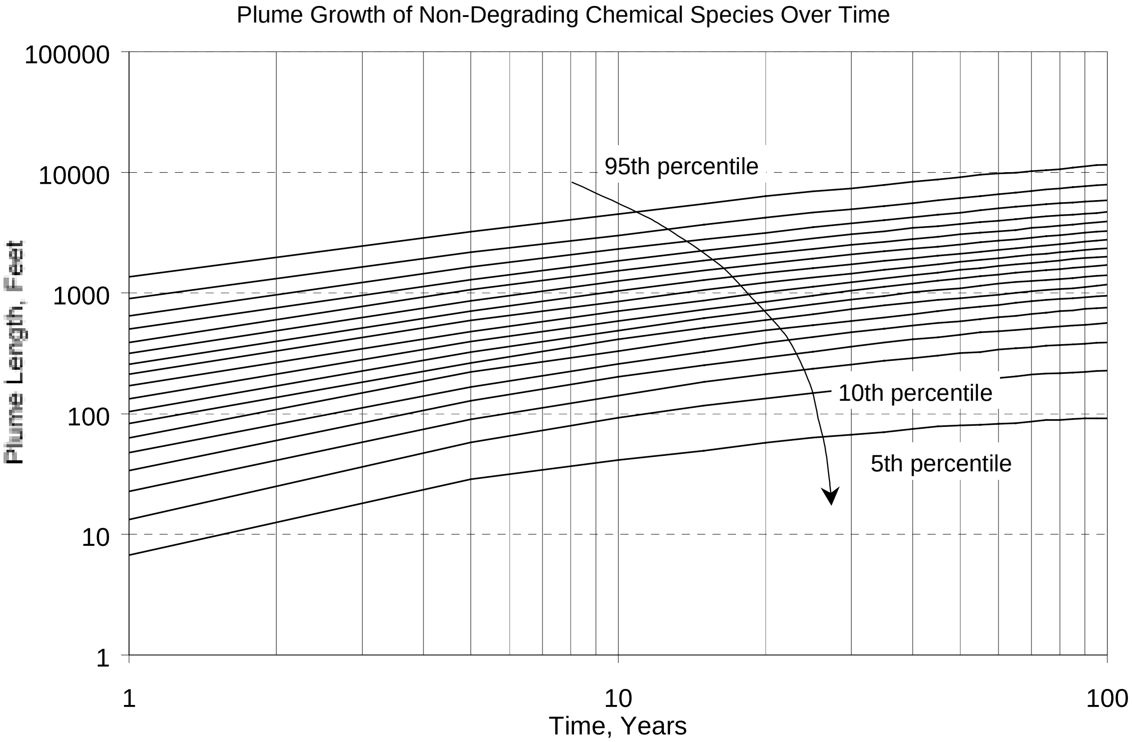

Figure 8-18. Log plume length vs. log time elapsed for various percentile intervals.

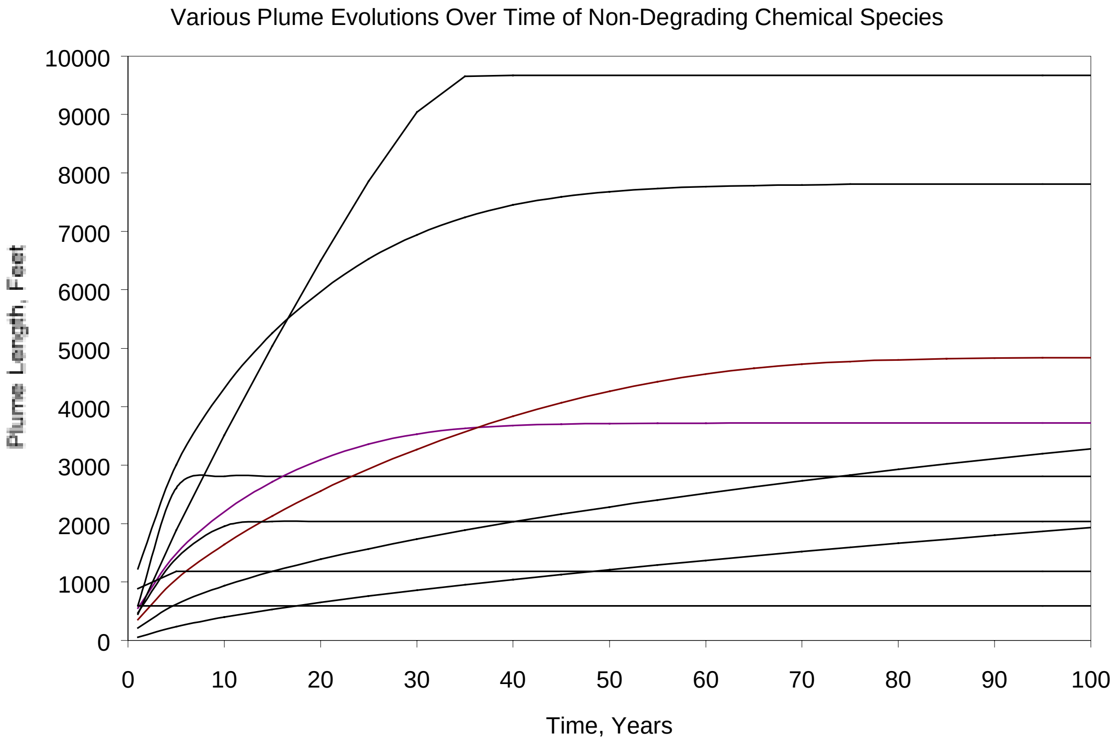

Figure 8-19. Plume length vs. time elapsed for randomly generated plumes.

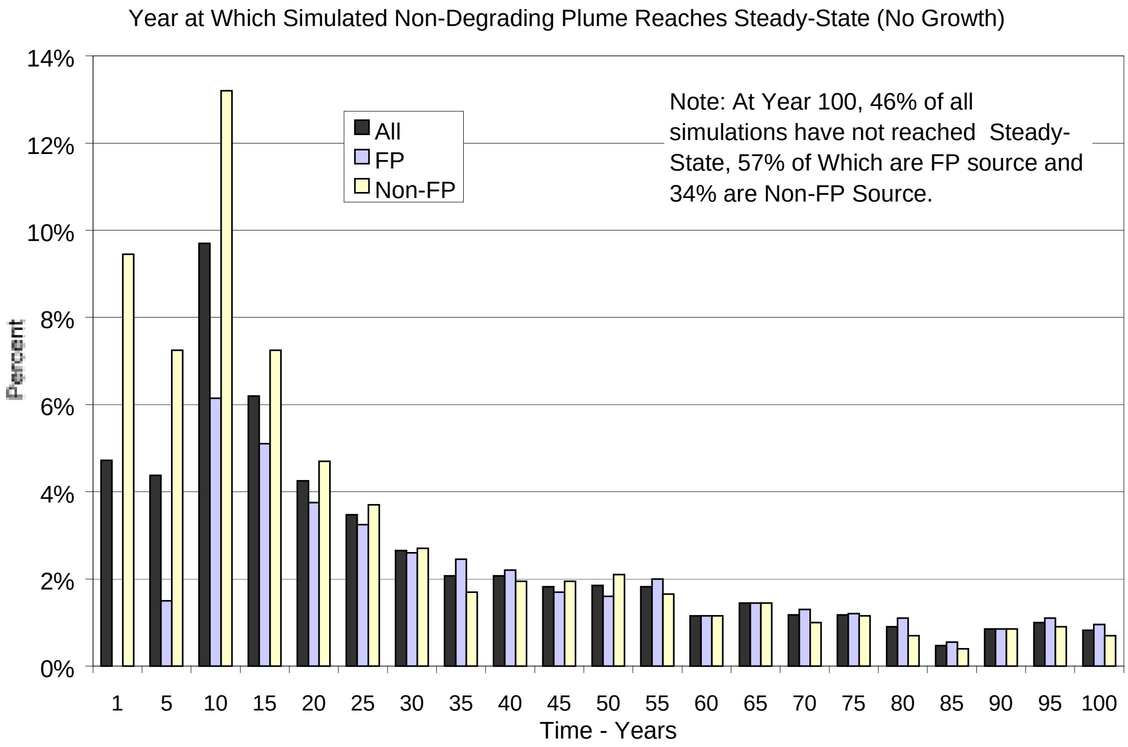

Figure 8-20. Year at which simulated nondegrading plumes reach steady-state.

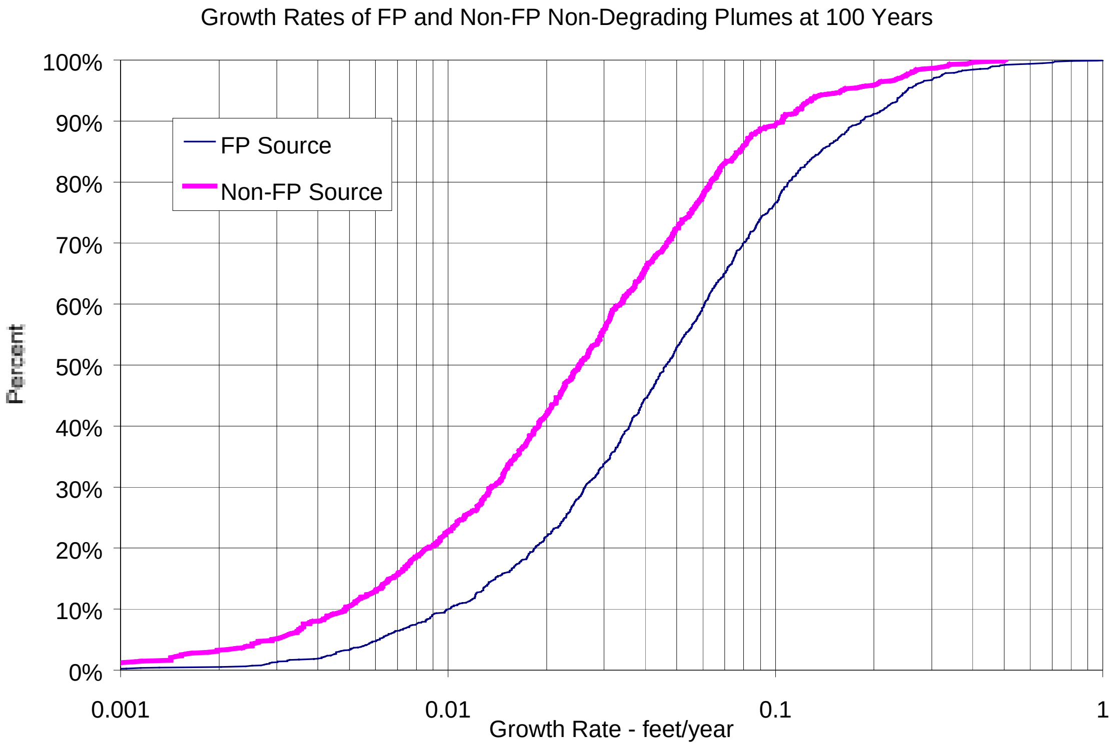

Figure 8-21. Growth rates of free-product and non-free-product plumes at 100 years.

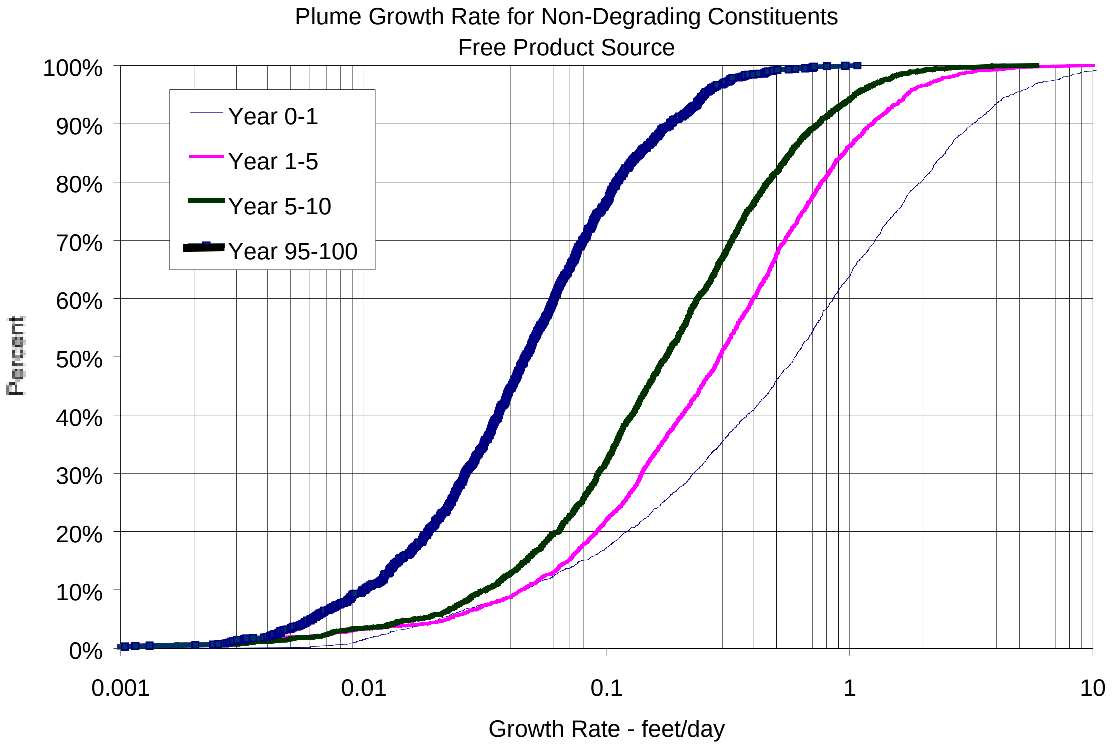

Figure 8-22. Growth rates of free-product plumes over time.

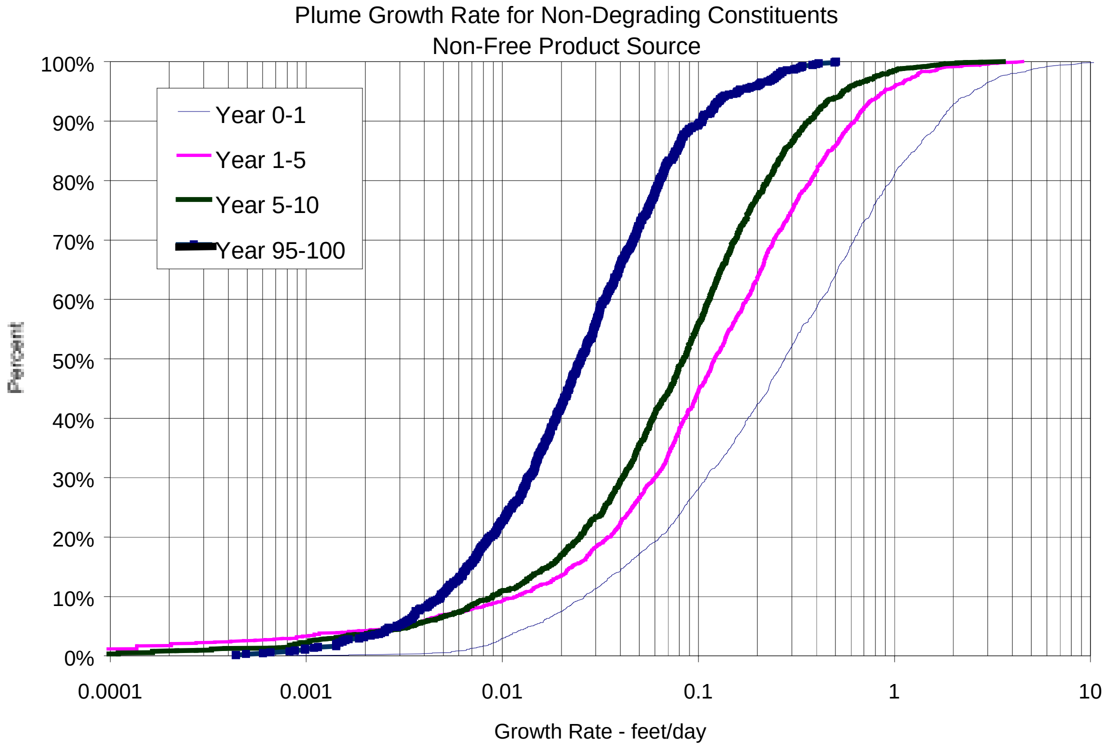

Figure 8-23. Growth rates of non-free-product pumes over time.

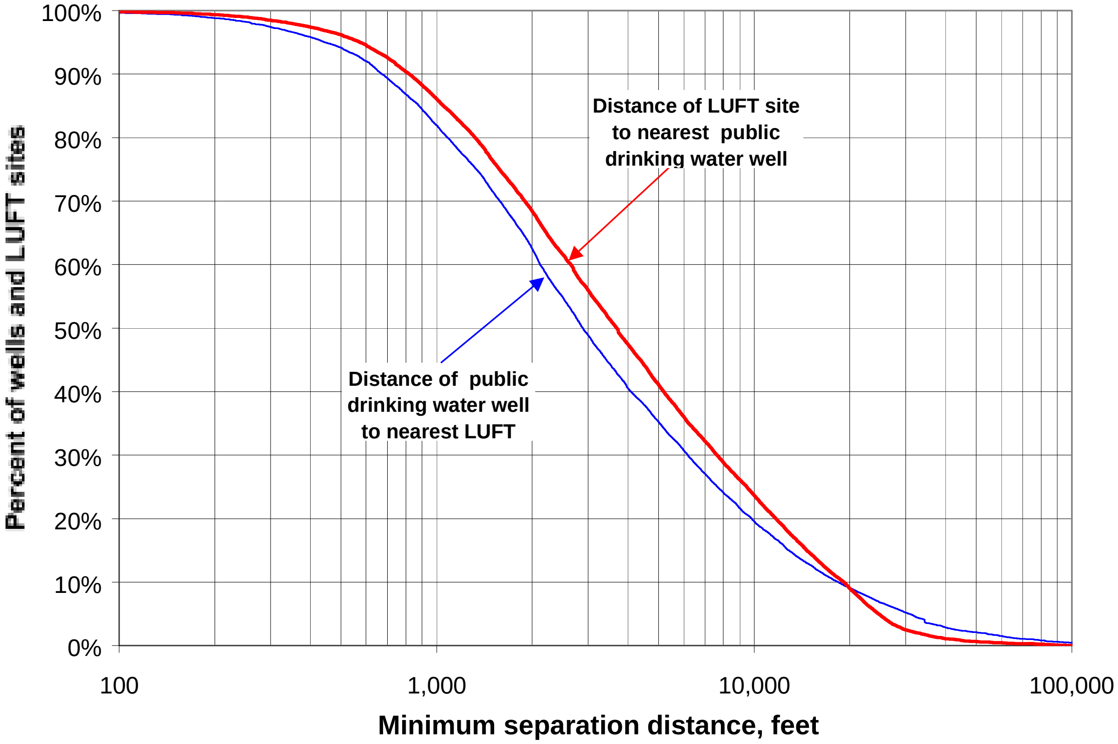

Figure 8-24. Distance of drinking water wells and LUFT sites from each other.

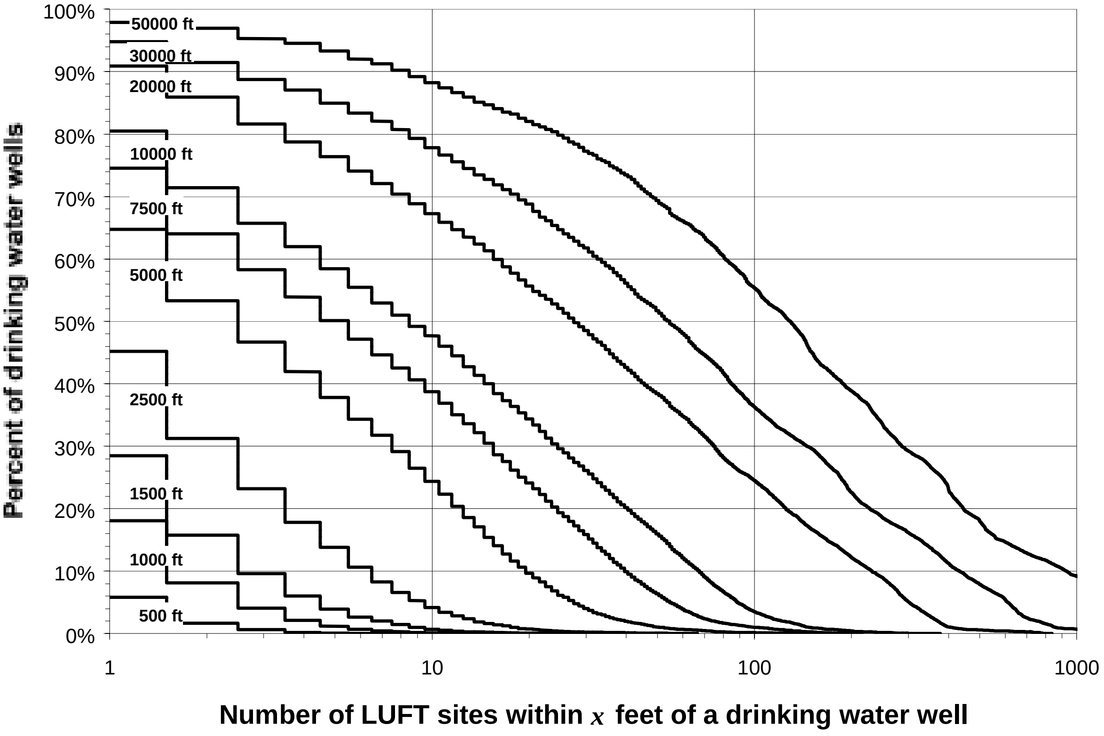

Figure 8-25. Distribution of the number of LUFT sites within *x* feet of a drinking water well.

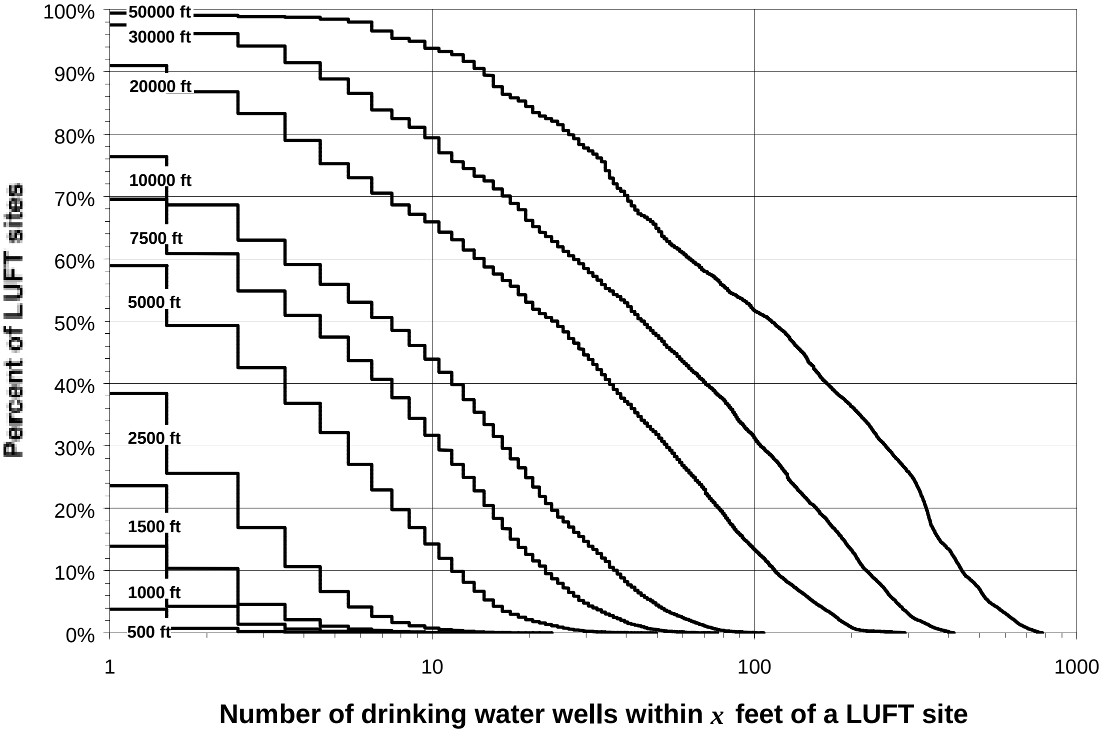

Figure 8-26. Distribution of the number of drinking water wells within *x* feet of a LUFT site.

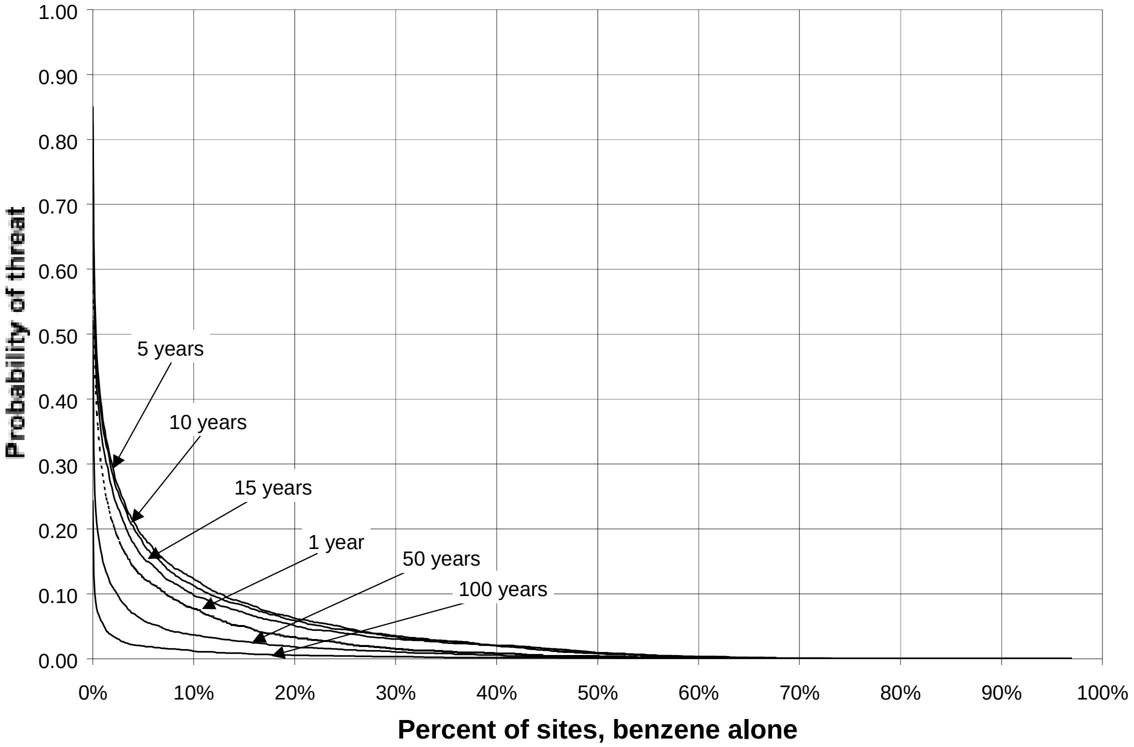

Figure 8-27. Distribution of the absolute probability of threat for LUFT sites with benzene alone.

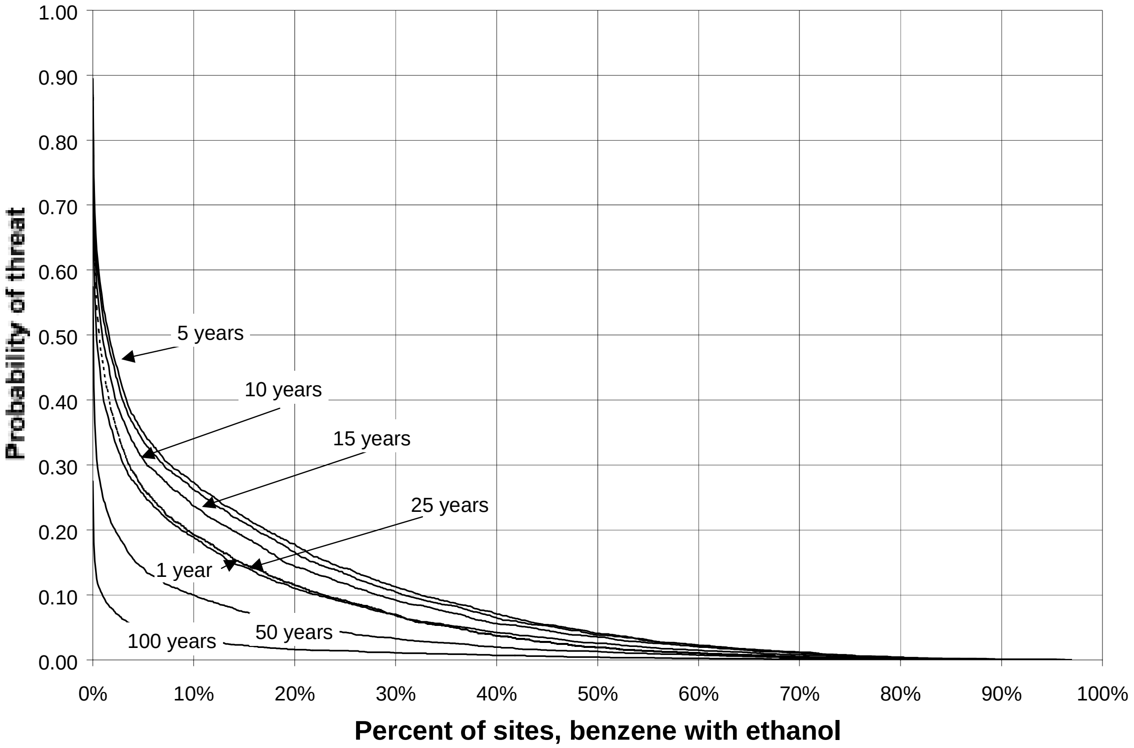

Figure 8-28. Distribution of the absolute probability of threat for LUFT sites with benzene and ethanol.

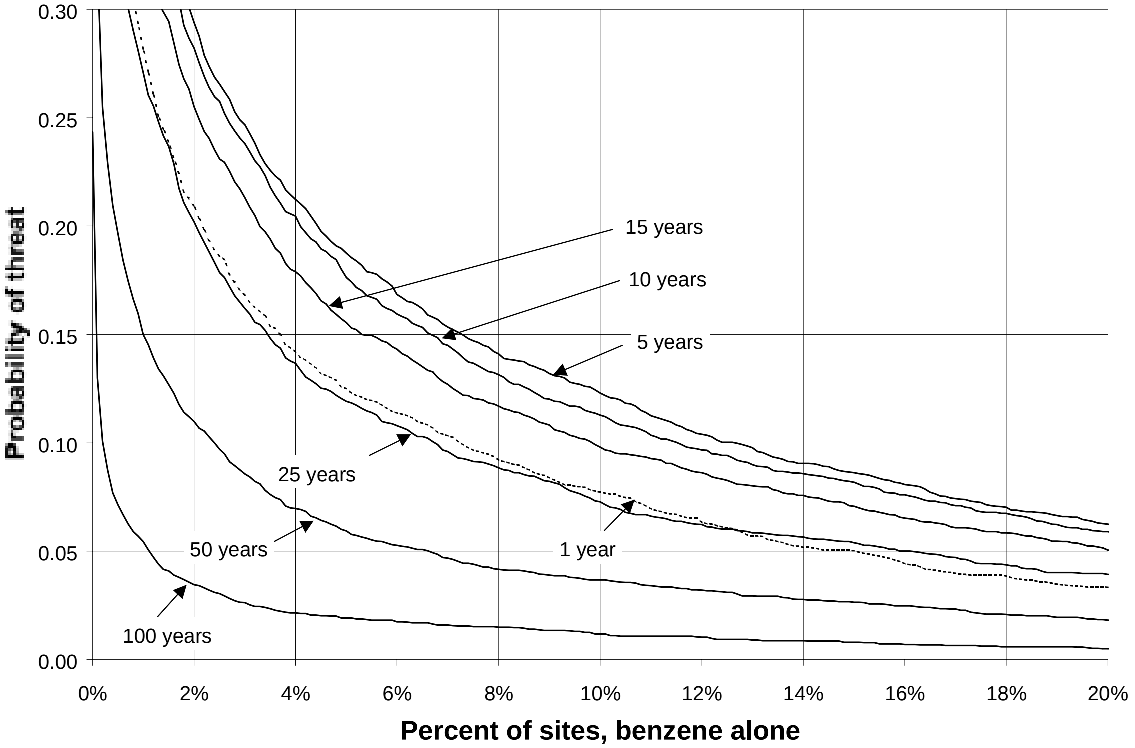

Figure 8-29. Close view of the distribution of the absolute probability of threat for LUFT sites with benzene alone.

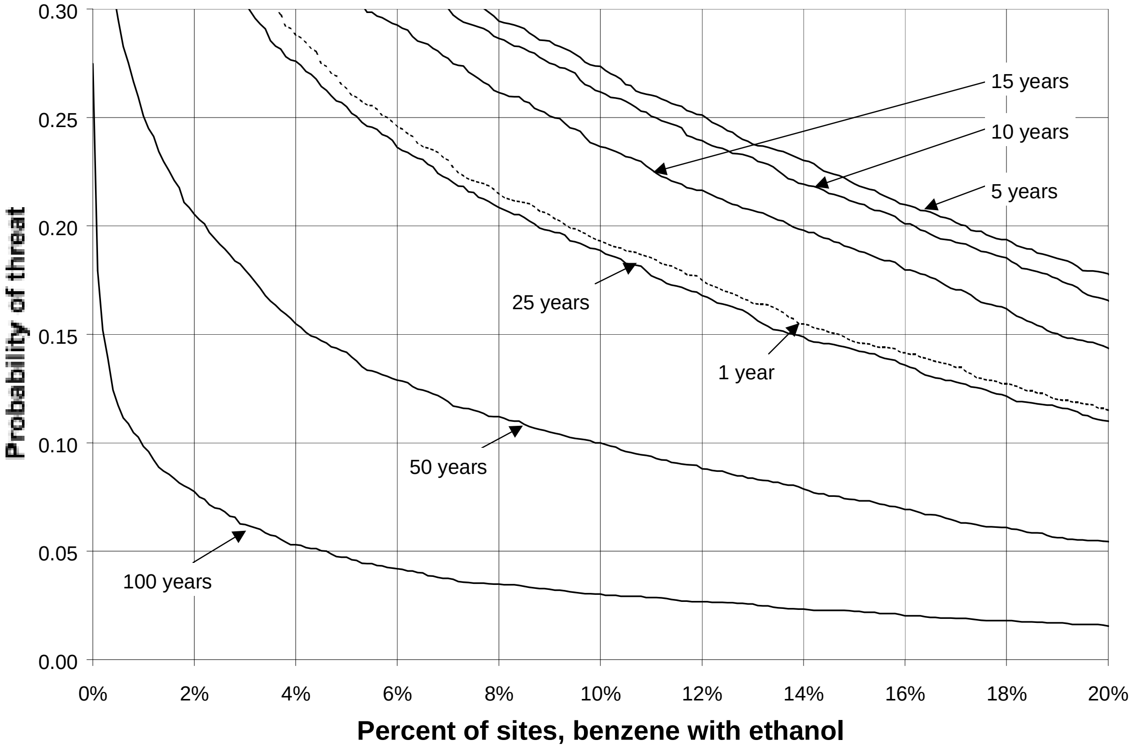

Figure 8-30. Close view of the distribution of the absolute probability of threat for LUFT sites with benzene and ethanol.

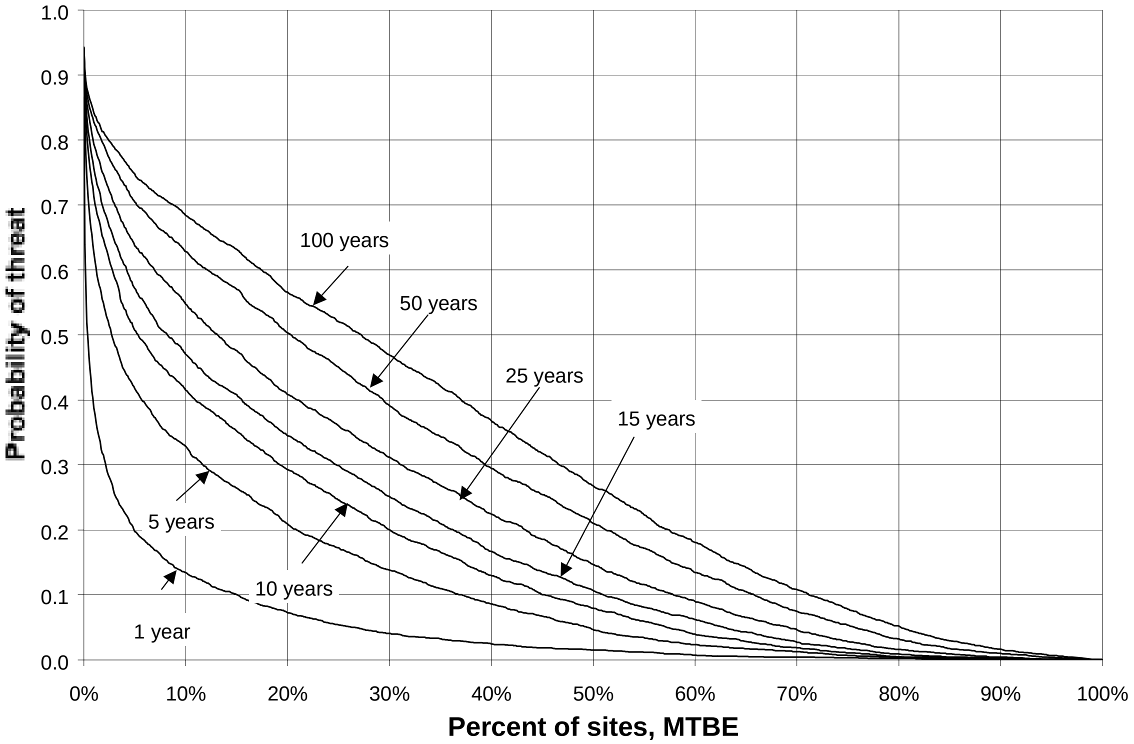

Figure 8-31. Distribution of the absolute probability of threat for LUFT sites with MTBE.

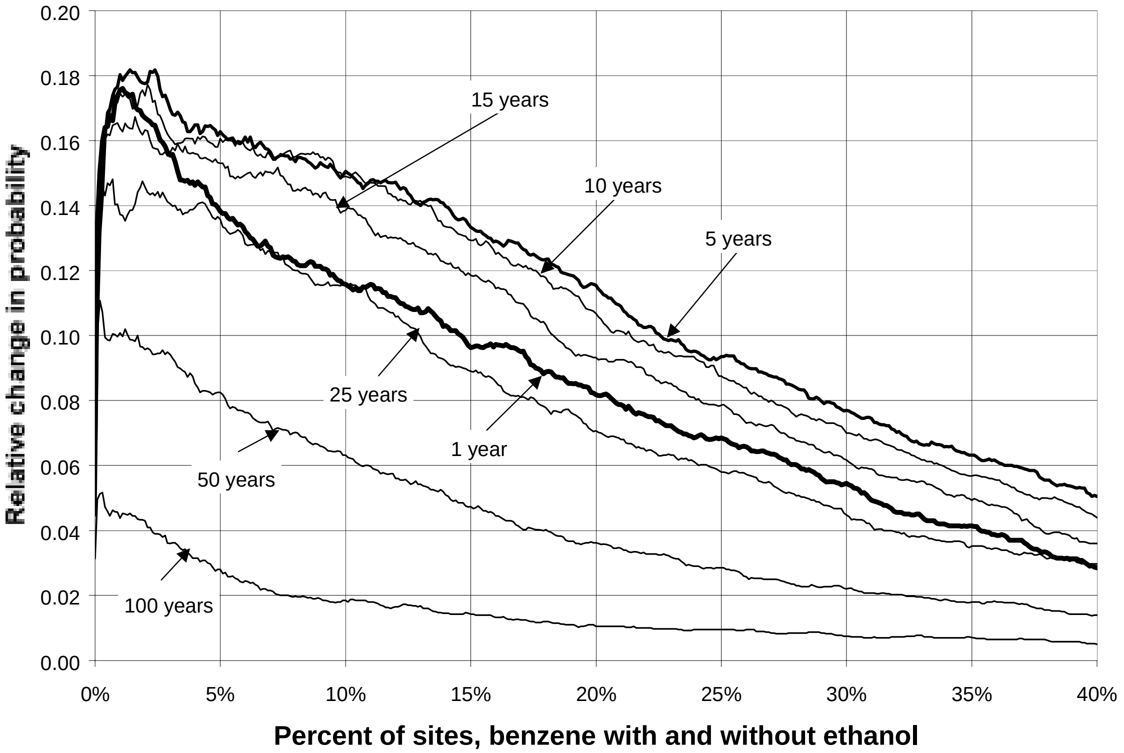

Figure 8-32. Relative probability of threat for LUFT sites for benzene with and without ethanol.

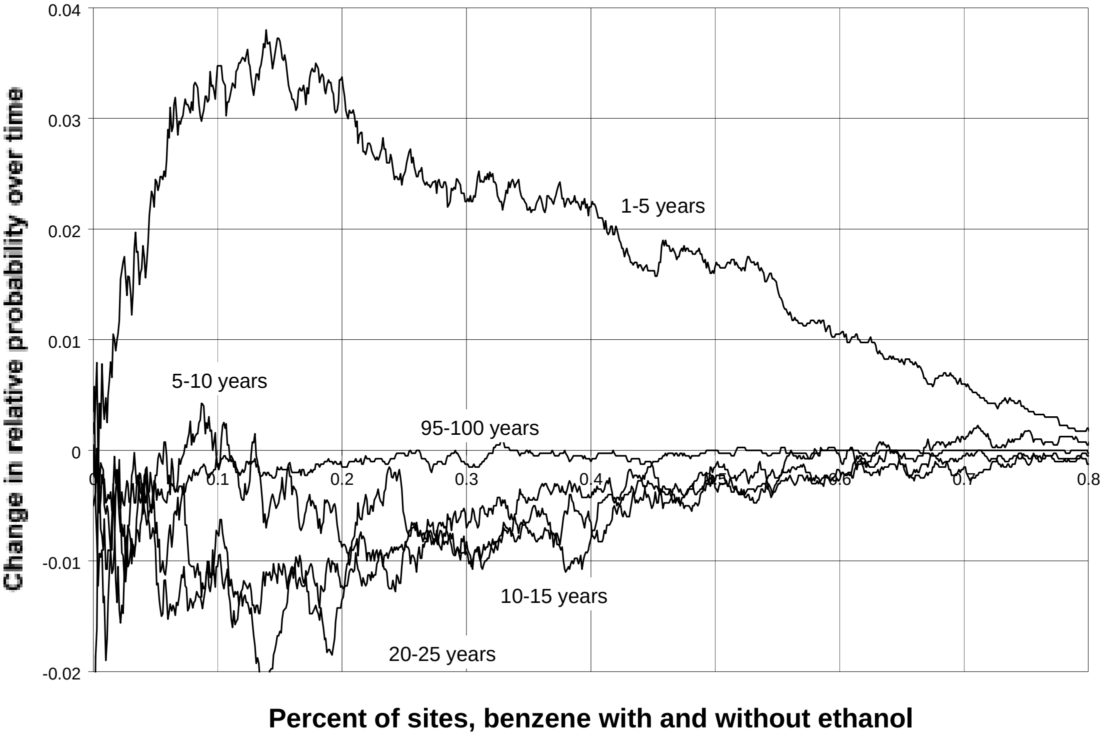

Figure 8-33. Temporal relative change in probability of threat for LUFT sites for benzene with and without ethanol.

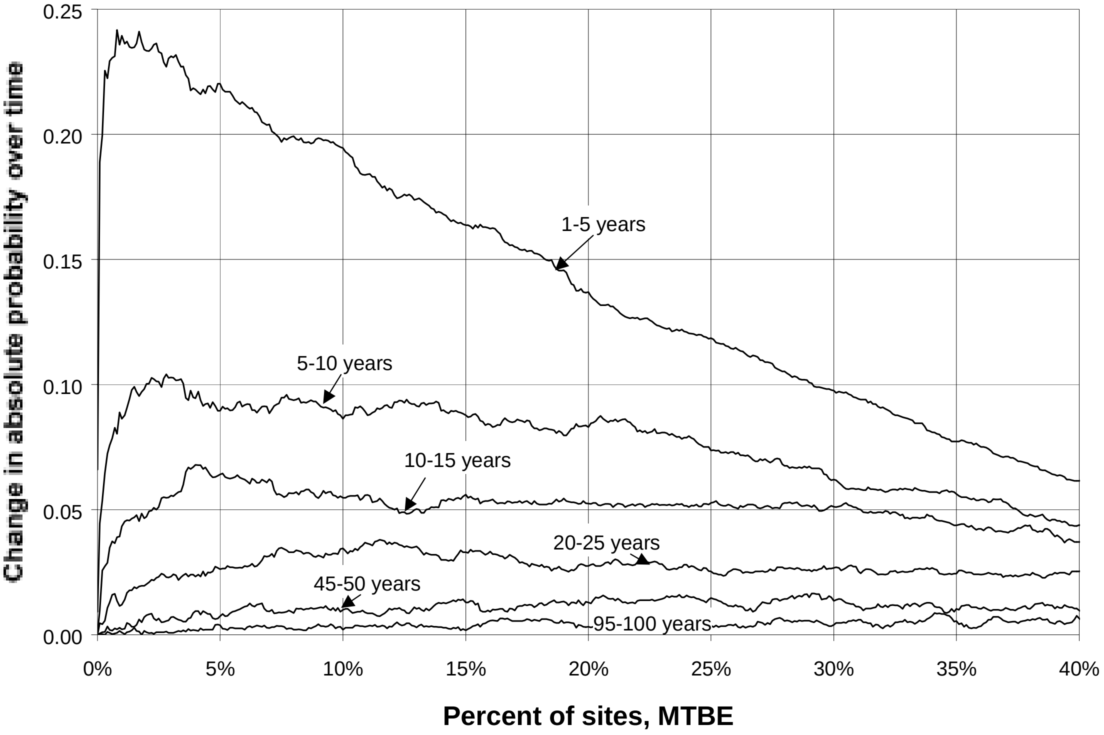

Figure 8-34. Temporal change in absolute probability of threat for LUFT sites for MTBE.

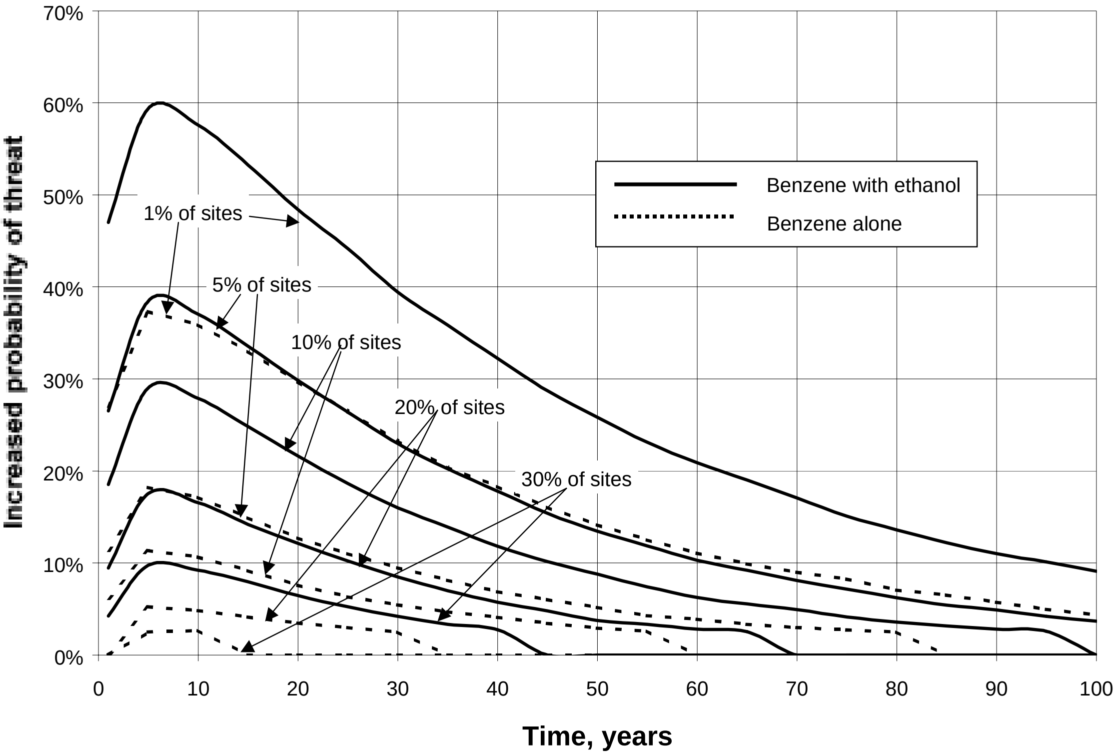

Figure 8-35. Absolute probability of a site threatening any well using de Morgan's law, benzene and benzene with ethanol.

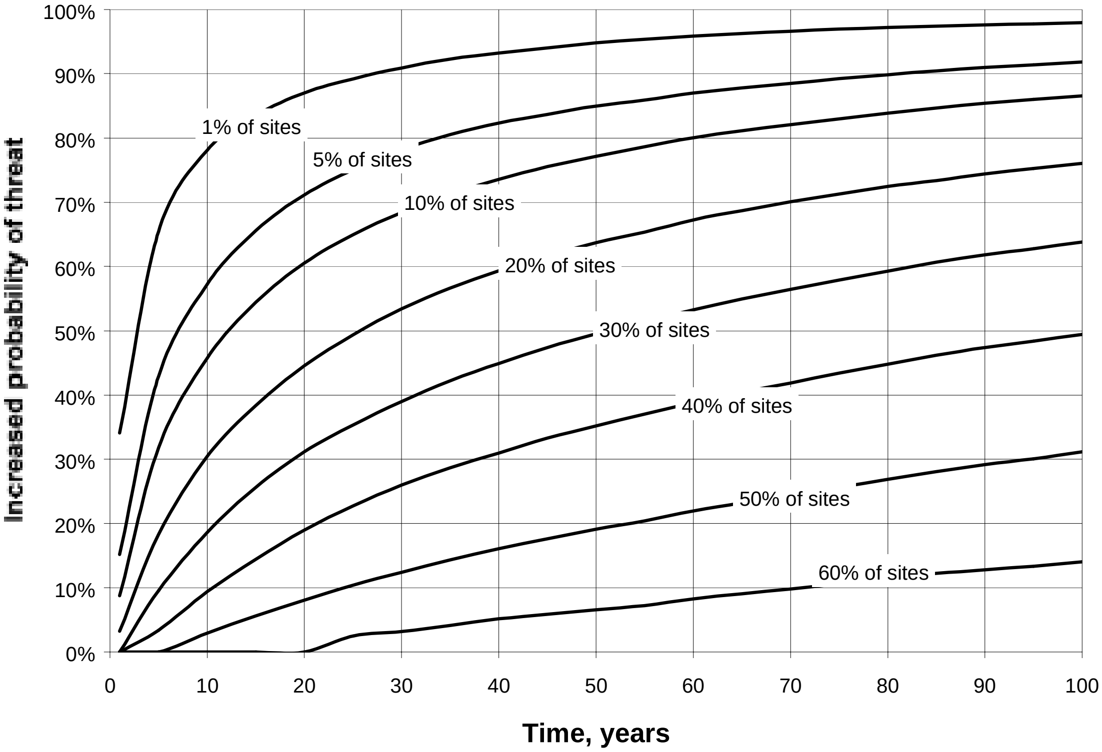

Figure 8-36. Absolute probability of a site threatening any well using de Morgan's law, MTBE.

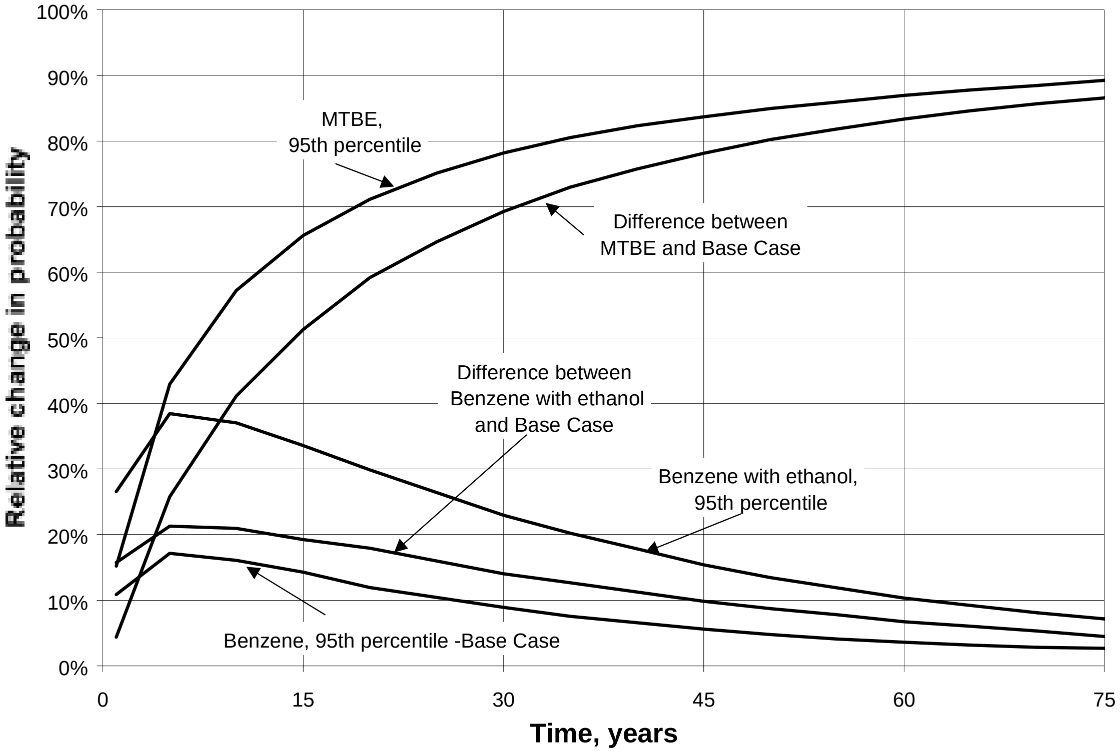

Figure 8-37. Relative probability of a site impacting any well using de Morgan's law.

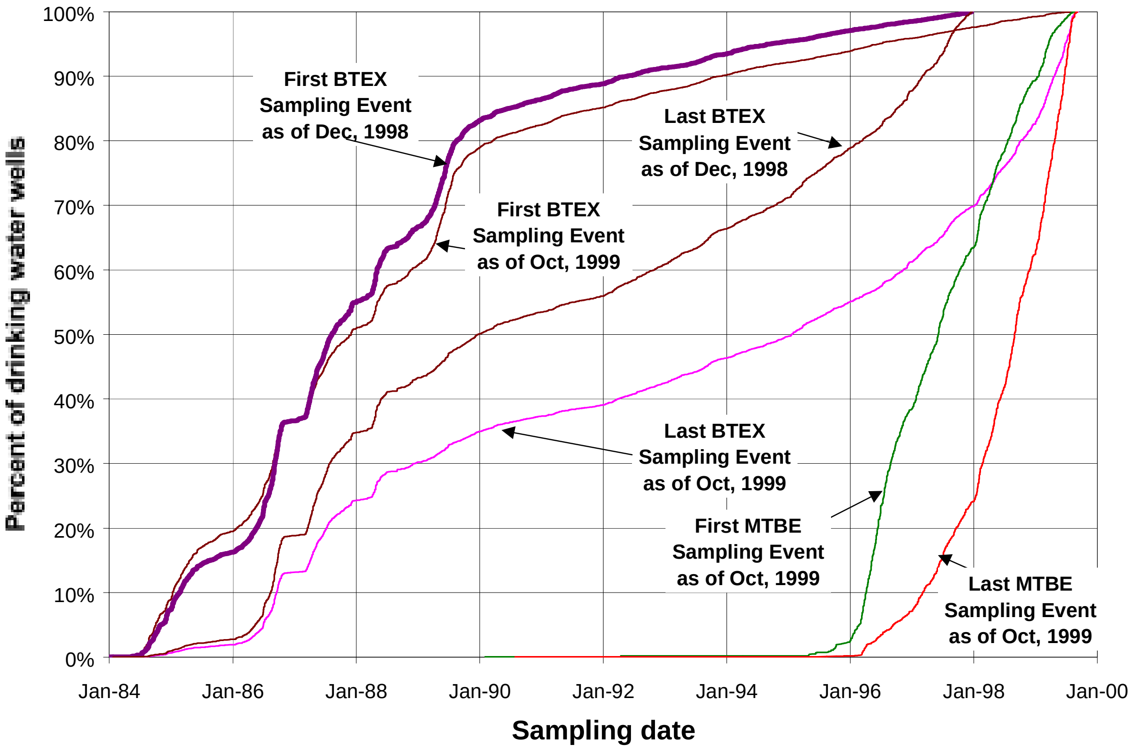

Figure 8-38. First and last sampling event dates for BTEX and MTBE in drinking water wells.

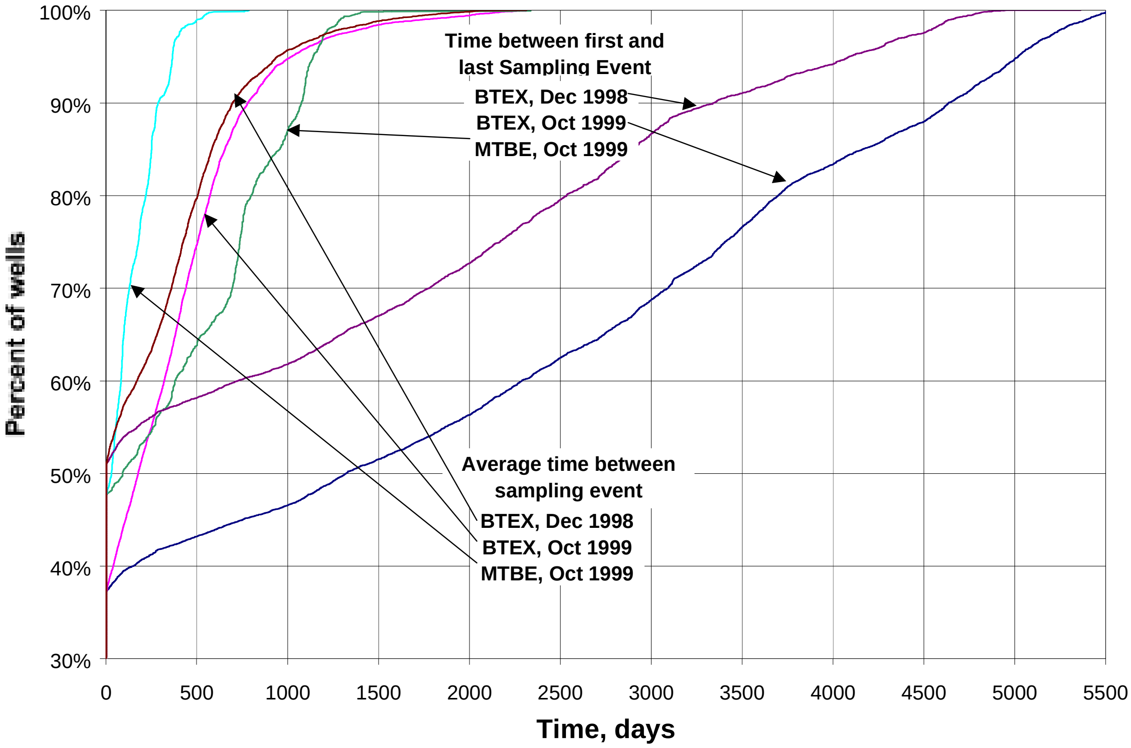

Figure 8-39. Time between first and last sample event and the average time between sample events.

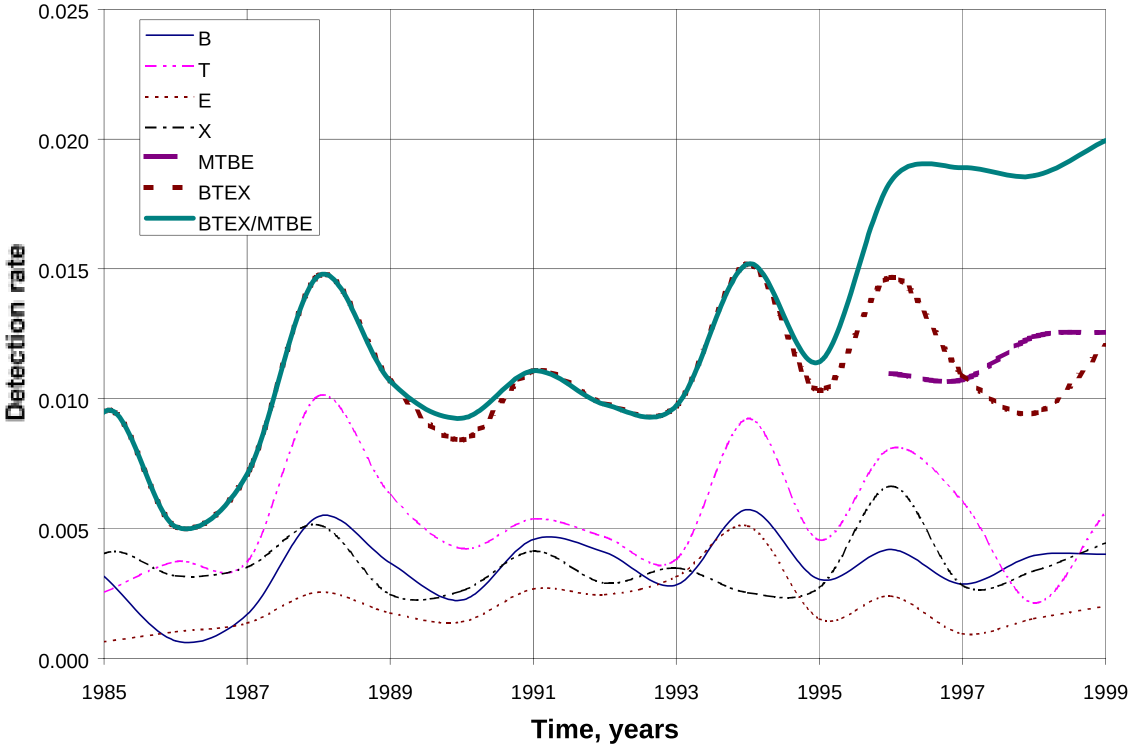

Figure 8-40. Rate of detetections per year of BTEX and MTBE in California public drinking water sources.

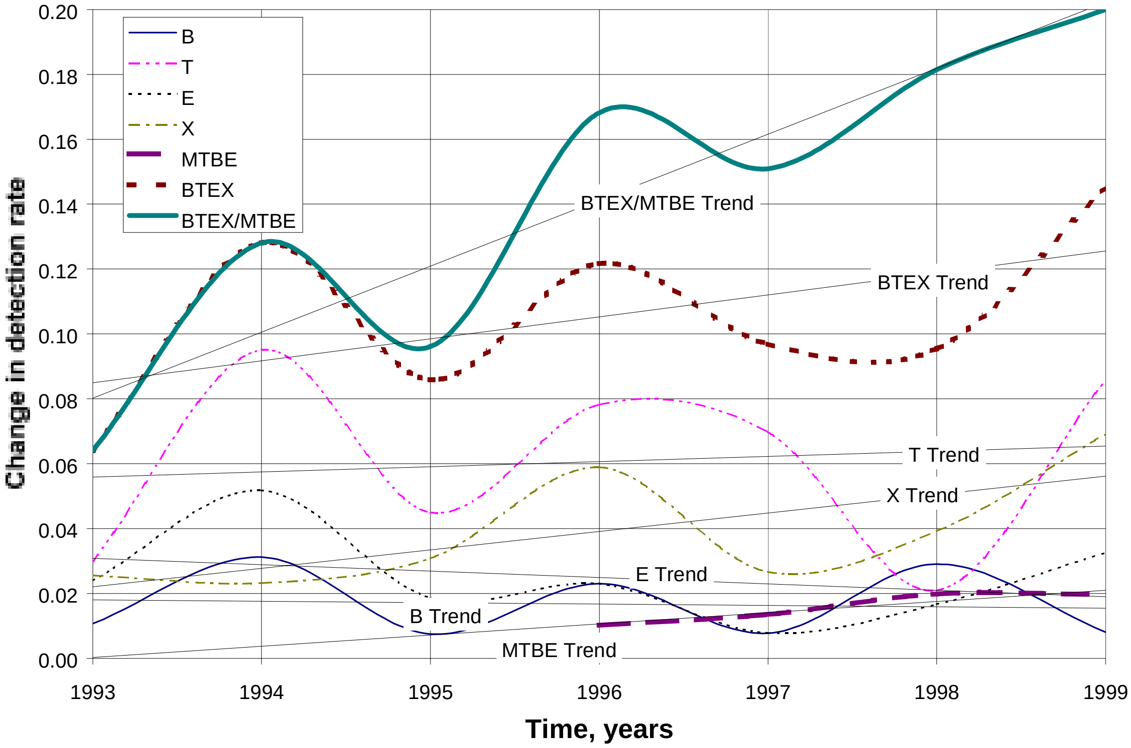

Figure 8-41. **Change in detetection rate per year of BTEX and MTBE in California public drinking water sources.**

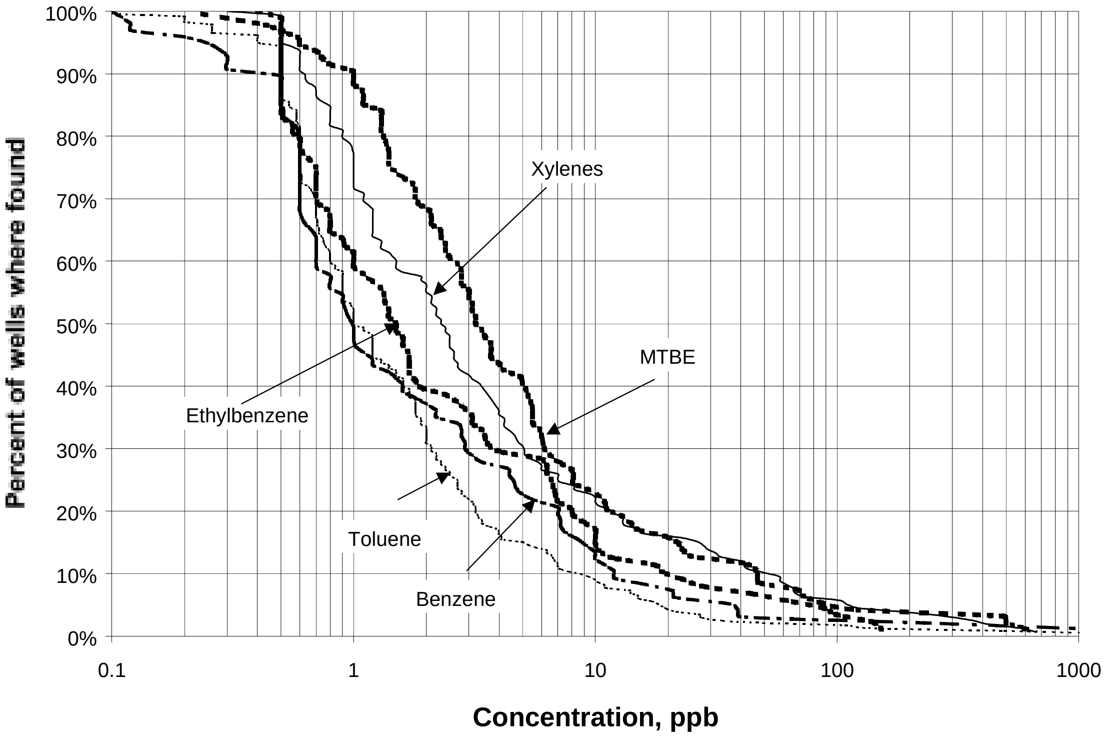

Figure 8-42. **Complementary cumulative distribution of BTEX and MTBE detections at impacted drinking water wells in California.**

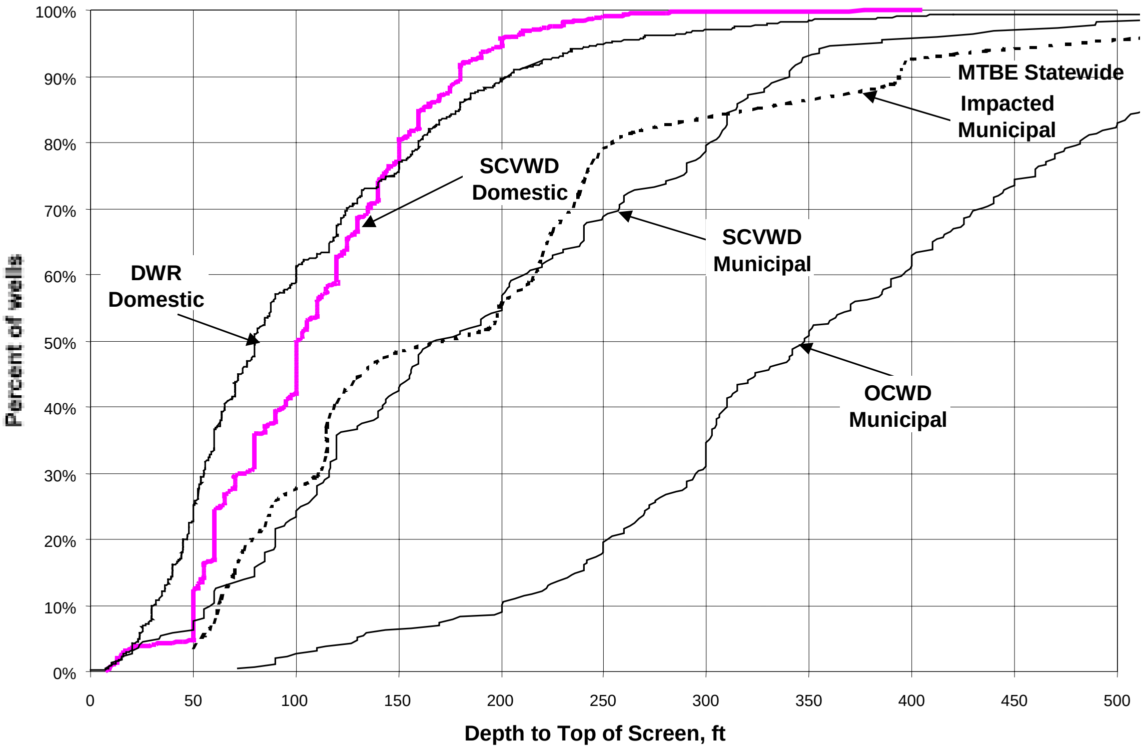

Figure 8-43. Cumulative distribution of depth to top of screen for various public and private drinking water wells in California.

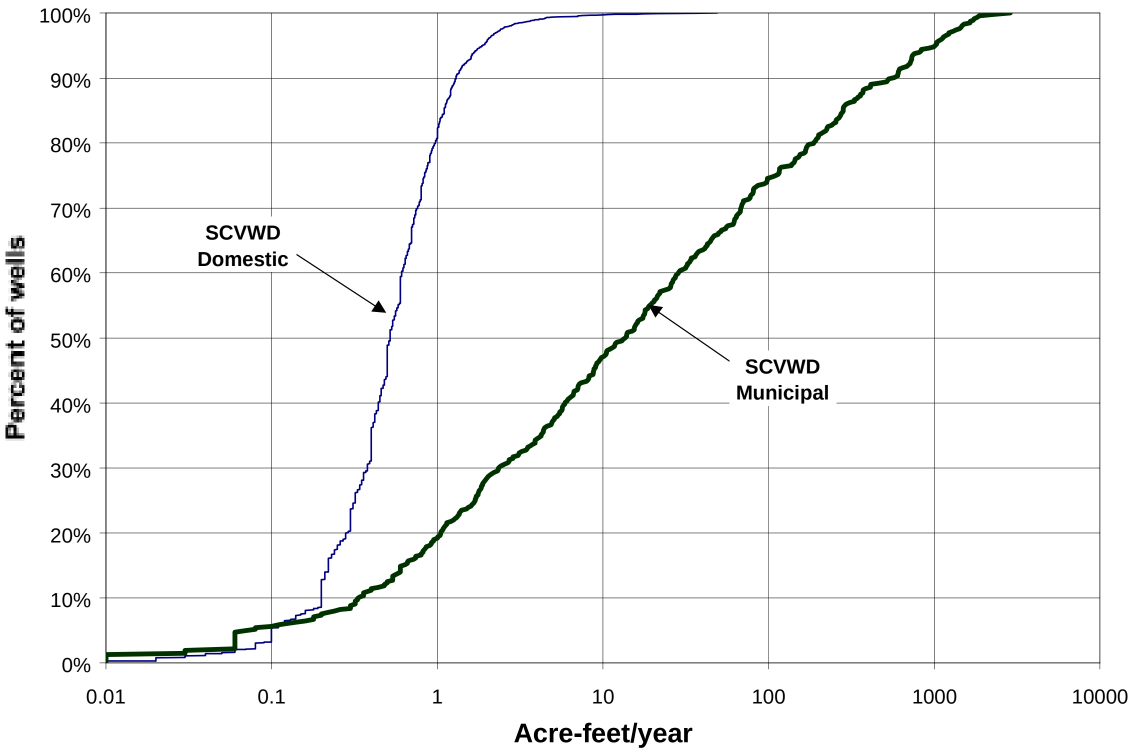

Figure 8-44. Cumulative distribution of well yield for public and private drinking water wells.

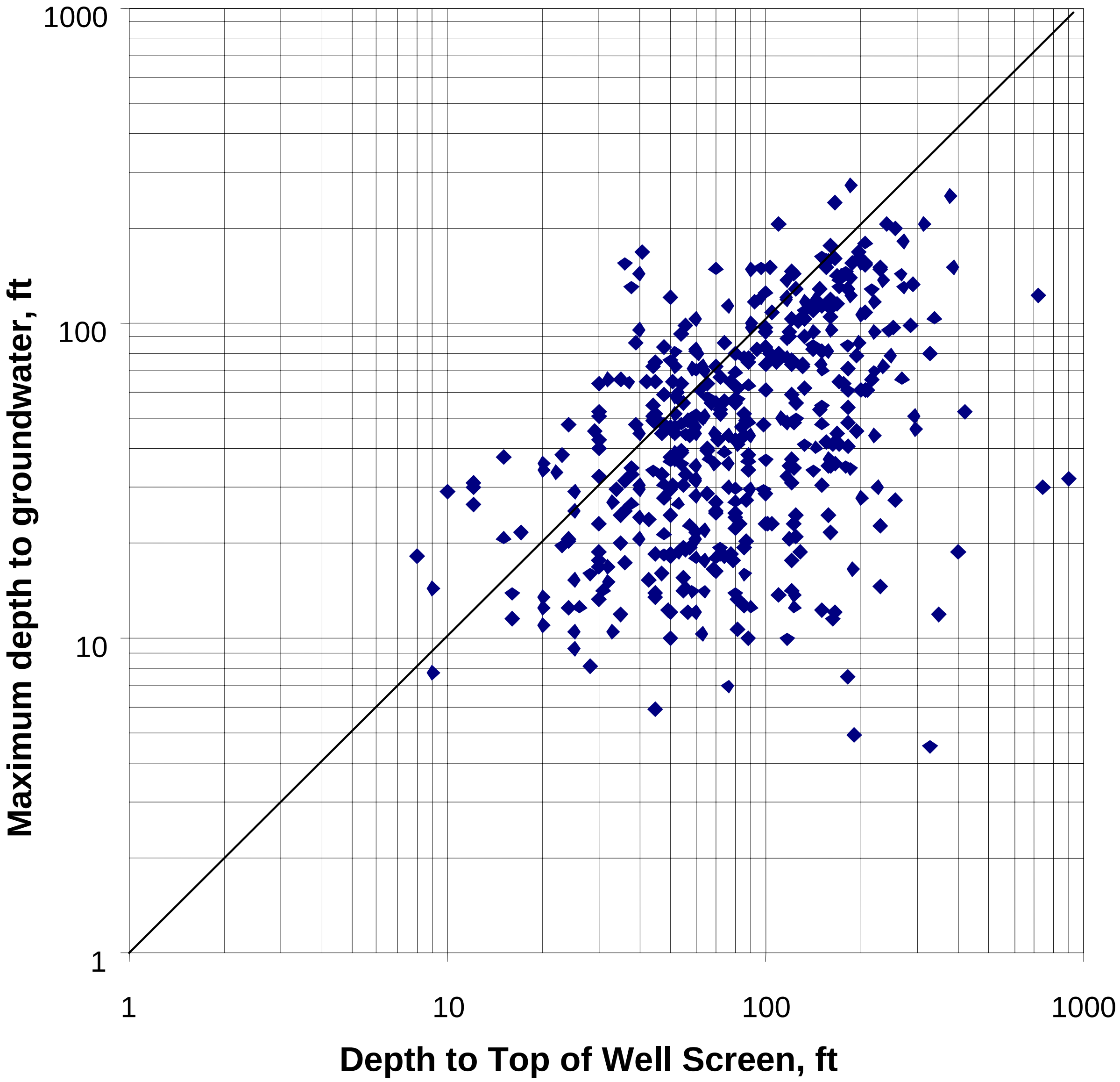

Figure 8-45. Correlation of top of screen interval to maximum groundwater depth for private wells.

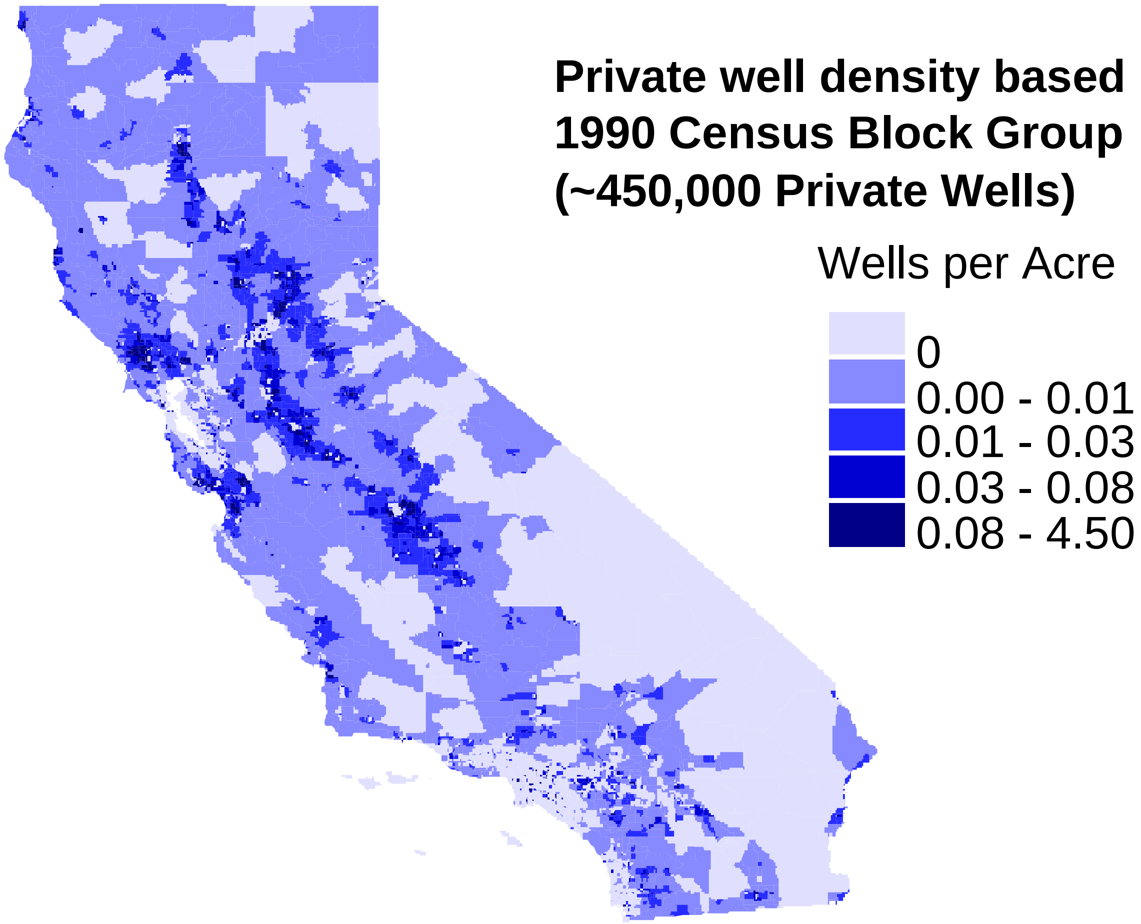

Figure 8-46. Drinking water well density in California (private wells). Darker areas indicate higher densities.

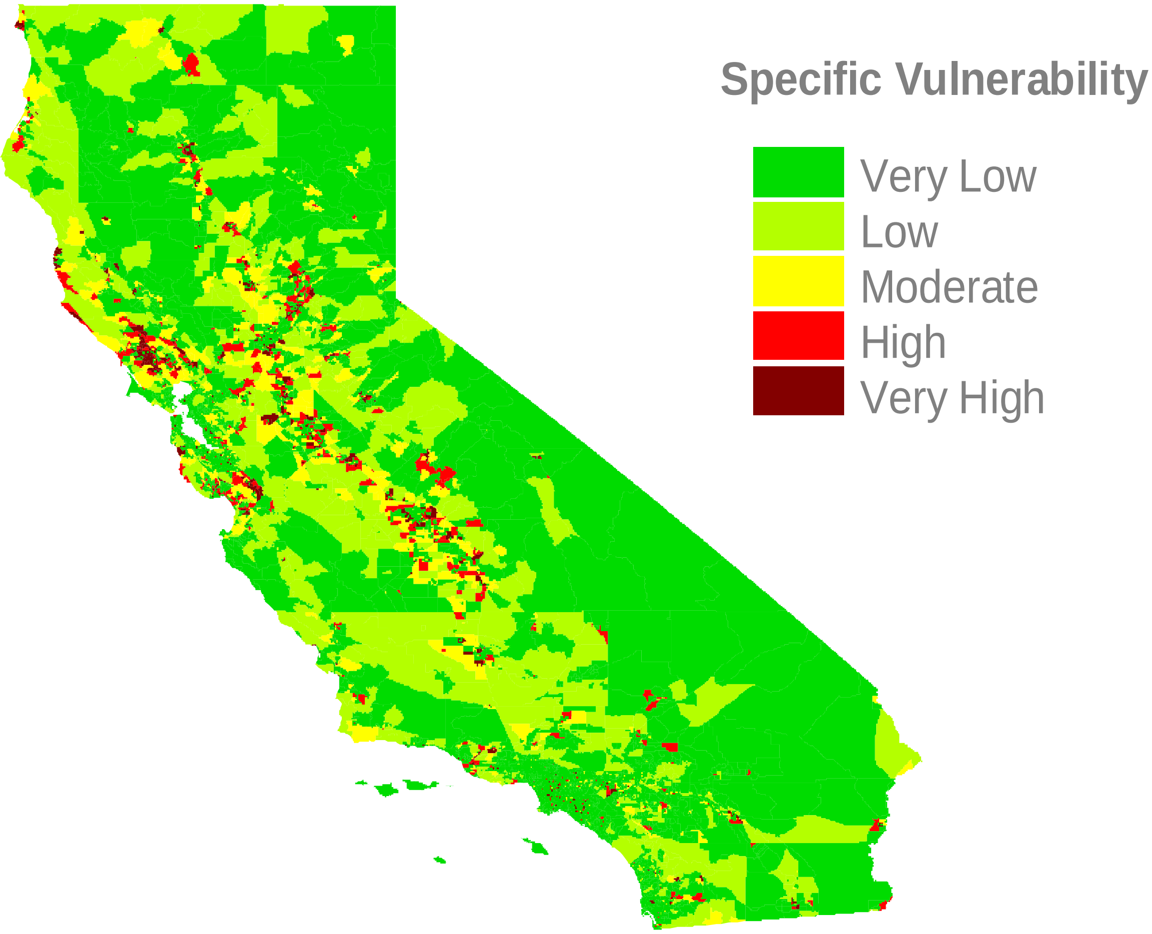

Figure 8-47. Specific vulnerability to private drinking water wells in California at the block group level. Darker areas indicate higher densities of LUFT sites and private wells.

Tables

Table 8-1. Notation of Parameters Used in Cleary and Ungs (1978) Equation.

Symbol	Notation Description
C	Concentration
C_P	Maximum or Peak Concentration of Gaussian Source
D_x	Dispersion coefficient in the x (longitudinal) direction
D_y	Dispersion coefficient in the y (horizontal) direction
D_z	Dispersion coefficient in the z (vertical) direction
f_{oc}	Organic carbon content of soil
k_{oc}	Partition coefficient of chemical
R	Retardation
t	Time
v_x	velocity component, x direction
v_y	velocity component, y direction
v_z	velocity component, z direction
x	Distance in the x direction
y	Distance in the y direction
Y_0	Center location of Gaussian source in the y direction
z	Distance in the z direction
Z_0	Center location of Gaussian source in the z direction
α_L	Dispersivity coefficient in the x (longitudinal) direction
α_H	Dispersivity coefficient in the y (horizontal) direction
α_V	Dispersivity coefficient in the z (vertical) direction
η	Dummy integration variable
γ	First order decay/growth coefficient for an exponential boundary source
θ	Porosity
λ	First order decay constant for the plume
ρ_b	Bulk density of soil
ρ	Correlation coefficient of the source
σ_y	Standard deviation of the Gaussian Source in the y direction
σ_z	Standard deviation of the Gaussian Source in the z direction

Table 8-2. Population Input Parameters for Monte Carlo Forecasts.

Parameter	Description	Remarks	Prescribed distribution
t	Elapsed time since source initiation	Captures a range of typical ages encountered at LUFT sites.	Lognormal distribution. 5th percentile = 730 days (2 years) mean = 3260 days (8.9 years) 95th percentile = 14,600 days (40 years)
σ_y	Source width	Captures a range of possible release types, from small LUFT tank and pipeline leaks to releases from large industrial facilities. Mean is based on typical 10,000-gal tank length. Assumed to correlate with elapsed time, R = +0.75.	Lognormal distribution. 5th percentile = 1.9 m mean = 10.7 m 95th percentile = 29.6 m
γ	Source depletion rate (first-order)	Pseudo-first-order decay coefficient which accounts for volatilization, engineered source removal, and other mechanisms of source depletion (Dooher, 1998).	Lognormal distribution. 5th percentile = 7.35×10^{-5} day^{-1} ($t_{1/2}$ = 9,420 days or 25.8 years) mean = 2.78×10^{-4} day^{-1} ($t_{1/2}$ = 2500 days or 6.8 years) 95th percentile = 6.67×10^{-4} day^{-1} ($t_{1/2}$ = 1040 days or 2.8 years)
C_{0FP}	Maximum concentration associated with free product sites (38.2% of sites)	Results of MC forecasts are raised to the power of 10 and divided by 1000 (Dooher, 1998). $C_{0FP} = \frac{10^{\beta(20.05,6.84,5.55)}}{1000}$	Beta Distribution. a = 20.05 b = 6.84 scale = 5.55
C_{0L}	Maximum concentration associated with sites where FP is detected (61.8% of sites)	Results of MC forecasts are raised to the power of 10 and divided by 1000 (Dooher, 1998). $C_{0L} = \frac{10^{T(-0.48,3.93,5.09)}}{1000}$	Triangular Distribution Minimum = -0.48 Likeliest = 3.93 Maximum = 5.09
K	Hydraulic conductivity	Values typifying California hydrogeology (Dooher, 1998). Values supported by by Mackay *et al.* (1985) and Guven *et al.* (1984).	Lognormal distribution. 5th percentile = 3.82×10^{-6} m/s (0.33 m/day) mean = 1.25×10^{-4} m/s (10.8 m/day) 95th percentile = 4.75×10^{-4} m/s (41 m/day)
h	Hydraulic gradient	Values typifying California hydrogeology (Dooher, 1998). Values supported by by Mackay *et al.* (1985) and Guven *et al.* (1984).	Lognormal distribution. 5th percentile = 1.42×10^{-3} mean = 1.66×10^{-2} 9th percentile = 5.58×10^{-2}

Table 8-2. Population Input Parameters for Monte Carlo Forecasts (continued).

Parameter	**Description**	**Remarks**	**Prescribed distribution**
φ	Porosity	Based on 252 samples taken at the Lawrence Livermore National Laboratory Superfund Site (Dooher, 1998) and Jury (1985).	Normal distribution. mean = 0.42 standard deviation = 0.07
α_x:L ratio	Ratio of longitudinal dispersivity to plume length	Based on results presented in Gelhar *et al.* (1992) fitted to the equation $\alpha_x = 1.022(\log L)^{3.1179} 10^{N(0,0.7}$	Normal distribution. mean = 0.0 standard deviation = 0.74
α_y:L ratio	Ratio of horizontal transverse dispersivity to plume length	Based on results presented in Gelhar *et al.* (1992) fitted to the equation $\alpha_y = 0.017 L^{0.75269} 10^{N(0,0.8)}$	Normal distribution. mean = 0.0 standard deviation = 0.80
λ	First-order degradation rate	Median value may be fairly typical as a macroscopic average for many sites (e.g., Buscheck *et al.*, 1996).	Lognormal distribution. 5th percentile = 4.62×10^{-4} day^{-1} ($t_{1/2}$ = 1500 days or 4.1 years) mean = 9.47×10^{-3} day^{-1} ($t_{1/2}$ = 73.2 days or 0.20 year) 95th percentile = 3.47×10^{-2} day^{-1} ($t_{1/2}$ = 20 days or 0.055 year)
f_{oc}	Fractional organic carbon content	Based on 278 samples taken at the Lawrence Livermore National Laboratory Superfund Site (Dooher, 1998).	Lognormal distribution. 5th percentile = 1.37×10^{-4} mean = 1.4×10^{-3} 95th percentile = 4.6×10^{-3}
ρ_b	Bulk density	Based on 595 samples taken at the Lawrence Livermore National Laboratory Superfund Site (Dooher, 1998).	Normal distribution. mean = 1.75 g/cm^3 standard deviation = 0.22 g/cm^3

Table 8-3. Count of sampled public water sources, by year.

YEAR	B	T	E	X	MTBE	BTEX	BTEX/MTBE
1980	1	1	1	1	0	1	1
1981	1	1	1	0	0	1	1
1982	2	2	2	0	0	2	2
1983	0	0	0	0	0	0	0
1984	1,196	1,188	1,188	1,169	0	1,196	1,196
1985	1,580	1,573	1,571	1,486	0	1,580	1,580
1986	2,957	2,950	2,941	2,828	0	2,957	2,957
1987	2,951	2,960	2,949	2,848	0	2,960	2,960
1988	2,375	2,375	2,357	2,334	0	2,375	2,375
1989	5,708	5,710	5,709	5,687	0	5,710	5,710
1990	3,563	3,547	3,561	3,470	3	3,565	3,568
1991	2,619	2,609	2,618	2,421	0	2,619	2,619
1992	3,676	3,635	3,672	3,452	9	3,672	3,681
1993	3,182	3,143	3,188	3,164	0	3,188	3,188
1994	3,141	3,143	3,141	3,160	1	3,160	3,160
1995	3,294	3,292	3,291	3,292	129	3,294	3,326
1996	3,338	3,338	3,337	3,319	2,279	3,338	3,589
1997	3,149	3,147	3,144	3,198	2,888	3,198	3,493
1998	3,285	3,279	3,281	3,266	3,635	3,285	3,982
1999	2,491	2,483	2,488	2,474	2,310	2,491	2,707

Table 8-4. Cumulative count of sampled public water sources, by year.

YEAR	B	T	E	X	MTBE	BTEX	BTEX/MTBE
1980	5	3	4	3	0	5	5
1981	6	4	5	3	0	6	6
1982	8	6	7	3	0	8	8
1983	8	6	7	3	0	8	8
1984	1,202	1,192	1,193	1,172	0	1,202	1,202
1985	2,614	2,601	2,601	2,499	0	2,614	2,614
1986	4,920	4,907	4,904	4,718	0	4,920	4,920
1987	6,857	6,850	6,845	6,687	0	6,857	6,857
1988	8,212	8,201	8,191	8,112	0	8,212	8,212
1989	10,971	10,971	10,962	10,896	0	10,971	10,971
1990	11,533	11,529	11,522	11,459	3	11,533	11,536
1991	11,924	11,917	11,914	11,839	3	11,924	11,927
1992	12,331	12,327	12,324	12,243	12	12,331	12,343
1993	12,706	12,696	12,700	12,635	12	12,706	12,718
1994	12,995	12,980	12,990	12,937	13	12,995	13,007
1995	13,263	13,247	13,258	13,197	142	13,263	13,288
1996	13,567	13,554	13,563	13,486	2,301	13,567	13,609
1997	13,825	13,812	13,820	13,749	3,853	13,825	13,874
1998	14,066	14,051	14,060	14,004	5,418	14,066	14,144
1999	14,190	14,179	14,183	14,134	6,081	14,190	14,274

Table 8-5. Change in count of sampled public water sources, by year.

YEAR	B	T	E	X	MTBE	BTEX	BTEX/MTBE
1980							
1981	1	1	1	0	0	1	1
1982	2	2	2	0	0	2	2
1983	0	0	0	0	0	0	0
1984	1,194	1,186	1,186	1,169	0	1,194	1,194
1985	1,412	1,409	1,408	1,327	0	1,412	1,412
1986	2,306	2,306	2,303	2,219	0	2,306	2,306
1987	1,937	1,943	1,941	1,969	0	1,937	1,937
1988	1,355	1,351	1,346	1,425	0	1,355	1,355
1989	2,759	2,770	2,771	2,784	0	2,759	2,759
1990	562	558	560	563	3	562	565
1991	391	388	392	380	0	391	391
1992	407	410	410	404	9	407	416
1993	375	369	376	392	0	375	375
1994	289	284	290	302	1	289	289
1995	268	267	268	260	129	268	281
1996	304	307	305	289	2,159	304	321
1997	258	258	257	263	1,552	258	265
1998	241	239	240	255	1,565	241	270
1999	124	128	123	130	663	124	130

Table 8-6. Count of detections in sampled public water sources, by year.

YEAR	B	T	E	X	MTBE	BTEX	BTEX/MTBE
1980	0	0	0	0	0	0	0
1981	0	0	0	0	0	0	0
1982	0	0	0	0	0	0	0
1983	0	0	0	0	0	0	0
1984	0	0	0	1	0	1	1
1985	5	4	1	6	0	15	15
1986	2	11	3	9	0	15	15
1987	5	11	4	10	0	21	21
1988	13	24	6	12	0	35	35
1989	21	36	10	14	0	61	61
1990	8	15	5	9	3	30	33
1991	12	14	7	10	0	29	29
1992	15	17	9	10	0	36	36
1993	9	12	10	11	0	31	31
1994	18	29	16	8	0	48	48
1995	10	15	5	9	4	34	38
1996	14	27	8	22	25	49	66
1997	9	19	3	9	31	35	66
1998	13	7	5	11	45	31	74
1999	10	14	5	11	29	30	54

Table 8-7. Cumulative count of detections in sampled public water sources, by year.

YEAR	B	T	E	X	MTBE	BTEX	BTEX/MTBE
1980	0	0	0	0	0		
1981	0	0	0	0	0		
1982	0	0	0	0	0		
1983	0	0	0	0	0		
1984	0	0	0	1	0	1	1
1985	5	4	1	6	0	15	15
1986	7	15	4	15	0	30	30
1987	12	26	8	25	0	51	51
1988	25	50	14	37	0	85	85
1989	44	84	24	49	0	140	140
1990	48	99	28	57	3	166	169
1991	54	110	34	65	3	187	190
1992	65	125	42	73	3	218	221
1993	69	136	51	83	3	242	245
1994	78	163	66	90	3	279	282
1995	80	175	71	98	7	302	309
1996	87	199	78	115	29	339	363
1997	89	217	80	122	50	364	403
1998	96	222	84	132	81	387	452
1999	97	233	88	141	94	405	478

Table 8-8. Change in count of detections in sampled public water sources, by year.

YEAR	B	T	E	X	MTBE	BTEX	BTEX/MTBE
1980							
1981	0	0	0	0	0	0	0
1982	0	0	0	0	0	0	0
1983	0	0	0	0	0	0	0
1984	0	0	0	1	0	1	1
1985	5	4	1	5	0	14	14
1986	2	11	3	9	0	15	15
1987	5	11	4	10	0	21	21
1988	13	24	6	12	0	34	34
1989	19	34	10	12	0	55	55
1990	4	15	4	8	3	26	29
1991	6	11	6	8	0	21	21
1992	11	15	8	8	0	31	31
1993	4	11	9	10	0	24	24
1994	9	27	15	7	0	37	37
1995	2	12	5	8	4	23	27
1996	7	24	7	17	22	37	54
1997	2	18	2	7	21	25	40
1998	7	5	4	10	31	23	49
1999	1	11	4	9	13	18	26

Table 8-9. Yearly public water source detection rate.

YEAR	B	T	E	X	MTBE	BTEX	BTEX/MTBE
1980							
1981							
1982							
1983							
1984				0.00086		0.00084	0.00084
1985	0.00316	0.00254	0.00064	0.00404		0.00949	0.00949
1986	0.00068	0.00373	0.00102	0.00318		0.00507	0.00507
1987	0.00169	0.00372	0.00136	0.00351		0.00709	0.00709
1988	0.00547	0.01011	0.00255	0.00514		0.01474	0.01474
1989	0.00368	0.00630	0.00175	0.00246		0.01068	0.01068
1990	0.00225	0.00423	0.00140	0.00259		0.00842	0.00925
1991	0.00458	0.00537	0.00267	0.00413		0.01107	0.01107
1992	0.00408	0.00468	0.00245	0.00290		0.00980	0.00978
1993	0.00283	0.00382	0.00314	0.00348		0.00972	0.00972
1994	0.00573	0.00923	0.00509	0.00253		0.01519	0.01519
1995	0.00304	0.00456	0.00152	0.00273	0.03101	0.01032	0.01143
1996	0.00419	0.00809	0.00240	0.00663	0.01097	0.01468	0.01839
1997	0.00286	0.00604	0.00095	0.00281	0.01073	0.01094	0.01889
1998	0.00396	0.00213	0.00152	0.00337	0.01238	0.00944	0.01858
1999	0.00401	0.00564	0.00201	0.00445	0.01255	0.01204	0.01995
Average	0.00348	0.00534	0.00203	0.00360	0.01553	0.01149	0.01745

Table 8-10. Yearly public water source detection rate, based on cumulative count.

YEAR	B	T	E	X	MTBE	BTEX	BTEX/MTBE
1980							
1981							
1982							
1983							
1984				0.00085		0.00083	0.00083
1985	0.00191	0.00154	0.00038	0.00240		0.00574	0.00574
1986	0.00142	0.00306	0.00082	0.00318		0.00610	0.00610
1987	0.00175	0.00380	0.00117	0.00374		0.00744	0.00744
1988	0.00304	0.00610	0.00171	0.00456		0.01035	0.01035
1989	0.00401	0.00766	0.00219	0.00450		0.01276	0.01276
1990	0.00416	0.00859	0.00243	0.00497		0.01439	0.01465
1991	0.00453	0.00923	0.00285	0.00549		0.01568	0.01593
1992	0.00527	0.01014	0.00341	0.00596		0.01768	0.01790
1993	0.00543	0.01071	0.00402	0.00657		0.01905	0.01926
1994	0.00600	0.01256	0.00508	0.00696		0.02147	0.02168
1995	0.00603	0.01321	0.00536	0.00743	0.04930	0.02277	0.02325
1996	0.00641	0.01468	0.00575	0.00853	0.01260	0.02499	0.02667
1997	0.00644	0.01571	0.00579	0.00887	0.01298	0.02633	0.02905
1998	0.00682	0.01580	0.00597	0.00943	0.01495	0.02751	0.03196
1999	0.00684	0.01643	0.00620	0.00998	0.01546	0.02854	0.03349
Average	0.00467	0.00995	0.00354	0.00617	0.02106	0.02603	0.02888

Table 8-11. Yearly public water source detection rate, based on count change.

YEAR	B	T	E	X	MTBE	BTEX	BTEX/MTBE
1980							
1981							
1982							
1983							
1984	0.00000	0.00000	0.00000	0.00086		0.00084	0.00084
1985	0.00354	0.00284	0.00071	0.00377		0.00992	0.00992
1986	0.00087	0.00477	0.00130	0.00406		0.00650	0.00650
1987	0.00258	0.00566	0.00206	0.00508		0.01084	0.01084
1988	0.00959	0.01776	0.00446	0.00842		0.02509	0.02509
1989	0.00689	0.01227	0.00361	0.00431		0.01993	0.01993
1990	0.00712	0.02688	0.00714	0.01421		0.04626	0.05133
1991	0.01535	0.02835	0.01531	0.02105		0.05371	0.05371
1992	0.02703	0.03659	0.01951	0.01980		0.07617	0.07452
1993	0.01067	0.02981	0.02394	0.02551		0.06400	0.06400
1994	0.03114	0.09507	0.05172	0.02318		0.12803	0.12803
1995	0.00746	0.04494	0.01866	0.03077	0.03101	0.08582	0.09609
1996	0.02303	0.07818	0.02295	0.05882	0.01019	0.12171	0.16822
1997	0.00775	0.06977	0.00778	0.02662	0.01353	0.09690	0.15094
1998	0.02905	0.02092	0.01667	0.03922	0.01981	0.09544	0.18148
1999	0.00806	0.08594	0.03252	0.06923	0.01961	0.14516	0.20000
Average	0.01267	0.03732	0.01522	0.02360	0.01883	0.06570	0.08271

Appendix A
Cleary and Ungs (1978) 3-D Solution

Appendix A
Cleary and Ungs (1978) 3-D Solution

A-1. Exact Analytical Solutions to the Advection-Dispersion Equation

Exact analytical solutions are available for some simple geometries. These solutions are useful in developing the model of the plume probability domain, as they give approximations that range from extremely conservative and simple (one-dimensional) to much more realistic (three-dimensional). In the following solutions, the initial condition is one in which there is a rate constant γ, which can apply either to a source growth or attenuation rate.

In the following equations, retardation may be added by dividing the velocity or dispersivity coefficients by *R*, which is

$$R = 1 + \frac{k_{oc} f_{oc} \rho_b}{\gamma} \qquad \text{(A-1)}$$

where k_{oc} is the partition coefficient for the chemical species in question. (Table 8-1 has the symbols for the following equations.)

For a three-dimensional bivariate gaussian distributed boundary source (represented spatially in Figures A-1 and A-2), the change in concentration over time,

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} - v_x \frac{\partial C}{\partial x} - v_y \frac{\partial C}{\partial y} - v_z \frac{\partial C}{\partial z} - \lambda C \qquad \text{(A-2)}$$

subject to the boundary and initial conditions,

$$\begin{aligned}
&C = C_o \exp\left\{ -\gamma t - \frac{1}{2\left(1-\rho^2\right)} \left[\frac{\left(y - Y_0\right)^2}{2\sigma_y^2} - \frac{2\rho\left(y - Y_0\right)\left(z - Z_0\right)}{\sigma_y \sigma_z} + \frac{\left(y - Y_0\right)^2}{2\sigma_y^2} \right] \right\} \\
&\frac{\partial C}{\partial x} \to 0 \qquad x \to +\infty \\
&\frac{\partial C}{\partial y} \to 0 \qquad y \to \pm\infty \qquad\qquad \text{(A-3)} \\
&\frac{\partial C}{\partial z} \to 0 \qquad z \to \pm\infty \\
&C = 0 \qquad t = 0
\end{aligned}$$

the equivalent analytical solution is

$$\begin{aligned}C(x,y,z,t)={}&\frac{C_P x\sigma_y\sigma_z\left(1-\rho^2\right)}{4\sqrt{\pi D_x}}\exp\left[\frac{v_x x}{2D_x}-\gamma t+\frac{v_z\left(z-Z_0\right)}{2D_z}+\frac{\sigma_x^2\left(1-\rho^2\right)}{2}\left(\frac{v_y}{2D_y}+\frac{y-Y_0}{\sigma_x^2\left(1-\rho^2\right)}\right)^2\right.\\&\left.-\frac{\left(y-Y_0\right)^2}{2\sigma_x^2\left(1-\rho^2\right)}\right]\times\int_{\eta=0}^{\sqrt[4]{t\psi}}\Bigg\{\frac{4\sqrt{\psi}}{\eta^3}\exp\left[-\eta^4-\frac{x^2\psi}{4D_x\eta^4}-\frac{\left(z-Z_0\right)^2}{4D_z\eta^4/\psi}+\frac{\beta^2}{4\alpha^2}\right]\\&\times\left[\left(\sigma_z^2\left(1-\rho^2\right)+2D_z\frac{\eta^4}{\psi}\right)\left(2\sigma_y^2\left(1-\rho^2\right)+4D_y\frac{\eta^4}{\psi}\right)-8D_yD_z\frac{\rho^2\eta^8}{\psi^2}\right]^{-1/2}\\&\times\exp\left[-\frac{\sigma_y^4\left(1-\rho^2\right)^2}{4D_y\eta^4/\psi+2\sigma_y^2\left(1-\rho^2\right)}\left(\frac{v_y}{2D_y}+\frac{y-Y_0}{\sigma_x^2\left(1-\rho^2\right)}\right)^2\right]\Bigg\}d\eta\end{aligned}\tag{A-4a}$$

$$\alpha=\sqrt{\frac{1}{2\sigma_z^2\left(1-\rho^2\right)}+\frac{\psi}{4D_y\eta^4}-\frac{2D_y\rho^2\eta^4}{\psi\sigma_z^2\left(1-\rho^2\right)\left(4D_y\eta^4/\psi+2\sigma_y^2\left(1-\rho^2\right)\right)}}\tag{A-4b}$$

$$\beta=\frac{v_z}{2D_z}-\frac{\left(z-Z_0\right)}{2D_z\eta^4/\psi}-\frac{\rho\left(y-Y_0\right)}{\sigma_y\sigma_z\left(1-\rho^2\right)}+\frac{4D_y\sigma_y\rho\eta^4}{\psi\sigma_z\left(4Dy\eta^4/\psi+2\sigma_y^2\left(1-\rho^2\right)\right)}\left(\frac{v_y}{2D_y}+\frac{y-Y_0}{\sigma_x^2\left(1-\rho^2\right)}\right)\tag{A-4c}$$

$$\psi=\lambda-\gamma+\frac{v_x^2}{4D_x}+\frac{v_y^2}{4D_y}+\frac{v_z^2}{4D_z}\tag{A-4d}$$

When there is uni-directional flow, the above becomes

$$\begin{aligned}C(x,y,z,t)={}&\frac{C_P x\sigma_y\sigma_z\left(1-\rho^2\right)}{4\sqrt{\pi D_x}}\exp\left(\frac{v_x x}{2D_x}-\gamma t\right)\int_{\eta=0}^{\sqrt[4]{t\psi}}\Bigg\{\frac{4\sqrt{\psi}}{\eta^3}\exp\left[-\eta^4-\frac{x^2\psi}{4D_x\eta^4}-\frac{\left(z-Z_0\right)^2}{4D_z\eta^4/\psi}+\frac{\beta^2}{4\alpha^2}\right]\\&\times\left[\left(\sigma_z^2\left(1-\rho^2\right)+2D_z\frac{\eta^4}{\psi}\right)\left(2\sigma_y^2\left(1-\rho^2\right)+4D_y\frac{\eta^4}{\psi}\right)-8D_yD_z\frac{\rho^2\eta^8}{\psi^2}\right]^{-1/2}\\&\times\exp\left[-\frac{\left(y-Y_0\right)^2}{4D_y\eta^4/\psi+2\sigma_y^2\left(1-\rho^2\right)}\right]\Bigg\}d\eta\end{aligned}\tag{A-5a}$$

$$\alpha = \sqrt{\frac{1}{2\sigma_z^2\left(1-\rho^2\right)} + \frac{\psi}{4D_H\eta^4} - \frac{2D_H\rho^2\eta^4}{\psi\sigma_z^2\left(1-\rho^2\right)\left(4D_H\eta^4/\psi + 2\sigma_y^2\left(1-\rho^2\right)\right)}} \qquad \text{(A-5b)}$$

$$\beta = \frac{4D_H\rho\eta^4\left(y-Y_0\right)}{\psi\sigma_y\sigma_z\left(4D_H\eta^4/\psi + 2\sigma_y^2\left(1-\rho^2\right)\right)\left(1-\rho^2\right)} - \frac{\left(z-Z_0\right)}{2D_V\eta^4/\psi} - \frac{\rho\left(y-Y_0\right)}{\sigma_y\sigma_z\left(1-\rho^2\right)} \qquad \text{(A-5c)}$$

$$\psi = \lambda - \gamma + \frac{v_x^2}{4D_L} \qquad \text{(A-5d)}$$

Where α, β, and ψ are temporary variables.

A-2. References

Cleary, R.W., and M.J. Ungs (1978). *Analytical Models for Groundwater Pollution and Hydrology*. Princeton University, Princeton, NJ. Water Resources Program Report 78-WR-15.

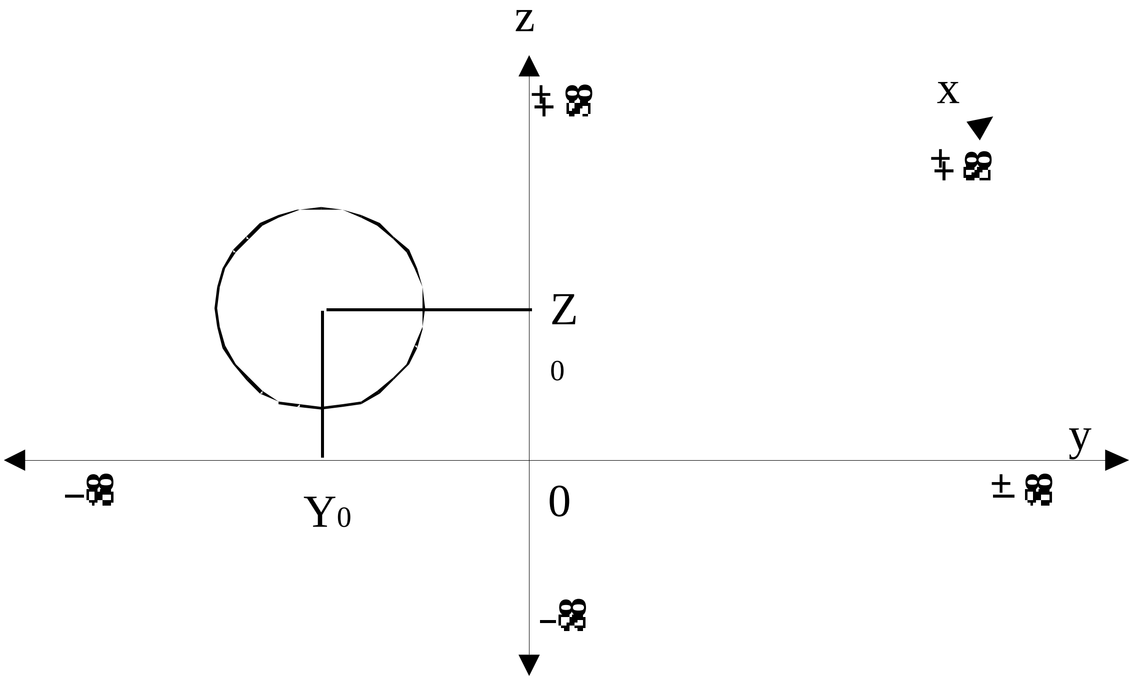

Figure A-1: Bivariate Gaussian source of infinite areal extent for three-dimensional flow.

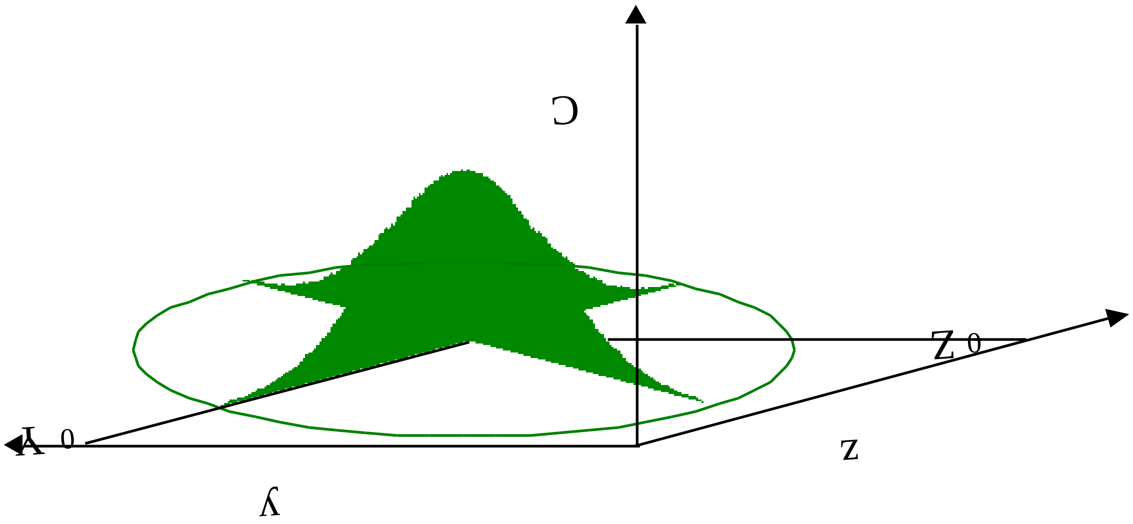

Figure A-2. Bivariate Gaussian source of infinite areal extent for three-dimensional flow – concentration distribution.

Appendix B
Results of Public Water Sources throughout California

Appendix B
Results of Public Water Sources throughout California

Tables 8-3 to 8-5 show the yearly count of tested public water sources throughout California. Table 8-3 shows the count of tested water sources by year. Public water sources include public drinking water wells and also surface water sources. Public drinking water wells are the vast majority of sources represented. The use of the results of this testing as part of an evaluation of potential groundwater impacts will yield conservative results because groundwater impacts will be overestimated somewhat.

The BTEX column is the combined count of wells tested for BTEX alone; the BTEX/MTBE is the combined count for BTEX and MTBE. There are a small number of water sources that have not been tested for BTEX, but that have been tested for MTBE. This likely reflects small systems that have been asked to report MTBE testing, but are not required to report BTEX sampling unless there is a detection. Table 8-4 is the year cumulative total of the sampled water sources, and Table 8-5 shows the yearly change in the number of water sources sampled. Tables 8-6 to 8-8 show the same counts for sources reporting BTEX and MTBE detections.

Tables 8-9 to 8-11 combine the above six tables. Table 8-9, also seen as Figure 8-40, shows the yearly detection rate for benzene, toluene, ethylbenzene, total xylenes, MTBE, and the combined count. Figure 8-40 shows a fairly constant pattern of BTEX detections, with a slight upward trend in MTBE. Figure 8-41 looks at the change in these trends on a yearly basis. There is a large upward trend in total xylenes and MTBE, and a small upward trend in toluene detections. Both benzene and ethylbenzene exhibit negative detection trends over time. The upward trend in BTEX detections is driven by the large total xylenes detection trend. The cyclic trend can be partially explained through a cyclic source sampling trend, but the cycling needs to be examined more closely.

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Volume 4: Potential Ground and Surface Water Impacts

Chapter 9: Knowledge Gaps Regarding the Ground and Surface Water Impacts of Ethanol-containing Gasoline and Recommendations for Future Research

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Table of Contents

List of Tables

9. Knowledge Gaps Regarding the Ground and Surface Water Impacts of Ethanol-containing Gasoline and Recommendations for Future Research

9.1. Introduction

A comprehensive understanding of the effects of ethanol on the fate and transport of gasoline compounds is needed to determine if the economic and air-quality benefits of adding such fuel alcohols to gasoline outweigh their potential detrimental effects on groundwater pollution and related health risks. An important consideration, which is related to the decision to use ethanol, is the potential effect it may have on the fate and transport of toxic gasoline components (in particular, benzene, toluene, ethylbenzene, and xylenes [BTEX]). For example, while California has implemented improved containment practices for underground storage tanks (USTs), releases of gasoline that may impact ground- and surface-water resources can still be expected. This fate-and-transport information is important for evaluating the impact that ethanol may have on the cleanup of gasoline releases and on California's water resources in general.

The chapters in this volume have summarized the possible release scenarios associated with the use of ethanol as a fuel oxygenate (Chapter 1: Rice *et al.*, 1999), and the effect of ethanol on the fate and transport of BTEX compounds (Chapter 2: Powers and Heermann, 1999) and on their natural attenuation and biodegradation (Chapter 3: Alvarez and Hunt, 1999). We reported the results of the predictive modeling performed to compare BTEX groundwater plumes in the presence of ethanol (Chapter 4: McNab *et al.*, 1999). We considered the potential impacts of the use of ethanol-containing gasoline on surface-water resources (Chapter 5: Layton and Daniels, 1999) and compared possible nonoxygenated fuel formulation to MTBE- and ethanol-containing gasoline (Chapter 6: Marchetti *et al.*, 1999). We evaluated the analytical methods available for the detection of ethanol in the environment (Chapter 7: Koester, 1999). We performed a comparative analysis of potential groundwater resource impacts for gasoline containing methyl tertiary butyl ether (MTBE) or ethanol (Chapter 8: Dooher, 1999).

As a result of the assessment contained in this volume, we have identified important knowledge gaps regarding the anticipated environmental behavior of gasoline containing ethanol. This chapter summarizes those knowledge gaps and provides recommendations for future research that would improve decision-making regarding the use of ethanol in oxygenated and reformulated gasolines in California.

9.2. Knowledge Gaps in the Life-cycle Analysis of Ethanol and Nonoxygenated Fuel Compounds

During the evaluation of ground- and surface-water impacts, we began the development of a comprehensive life-cycle model (Chapter 1: Rice *et al.*, 1999). This life-cycle model systematically addresses impacts from fugitive and accidental releases associated with the production, distribution, and use of gasoline containing ethanol. Time constraints for producing this particular assessment limited its focus only to those scenarios of chronic or accidental releases of ethanol that are most likely to impact ground and surface waters. Therefore, we were unable to fully consider other scenarios related to releases of substances as a consequence of the transportation and use of feedstocks required for ethanol production as well as from activities conducted at centralized blending centers. Also not considered were the additional implications of agricultural-related impacts from ethanol-fuel production. For example, increased corn-production for ethanol in California and elsewhere will require the application of additional herbicides/pesticides which may impact the environment. Including such scenarios will improve the breadth of understanding concerning the impacts of ethanol use in motor fuels and, therefore, may warrant more complete evaluation in the future.

We also examined the salient environmental properties of alkylates, which are nonoxygenated compounds that are likely to be used in greater amounts in gasoline after an MTBE phaseout. However, the limited analyses conducted were not completed within the context of an integrated life-cycle analysis concerning their production, storage, and use. Alkylates are complex solutions of isoalkanes, and some properties, such as biodegradability, may not be easily extrapolated to all alkylate components. In general, alkylate biodegradation rate is relatively slow compared to other organic compounds, and some components may not biodegrade in reasonable timeframes.

There is no toxicity data on the chronic effects of isooctane in humans. Additionally, cancer risk and reproductive and developmental effects have not been addressed. Surface releases of alkylates, either on water or land, would probably result in the evaporation of most alkylate into the atmosphere. Overall, it appears that alkylates would not affect dramatic changes in the way gasoline behaves in the environment and, thus, in the treatment of accidental releases.

9.3. Knowledge Gaps in Fate-and-transport Processes Associated with the Use of Ethanol as a Fuel Oxygenate

9.3.1 Subsurface Abiotic Processes

Chapter 2 of this volume identified abiotic processes or mechanisms that affect the fate of ethanol and ethanol-gasolines in the subsurface. These processes include infiltration, spreading at the capillary fringe, and leaching of chemicals into groundwater. They can potentially impact the retention and distribution of gasohol (gasoline containing 10% ethanol) or other petroleum products in the unsaturated zone, the size and the shape of a gasoline pool at the water table, and the flux of contaminants from the gasoline to the groundwater.

The extent of our knowledge about these processes ranges from sufficient to inadequate. For example, we now have a relatively large database quantifying the gasoline-water-ethanol partitioning behavior and cosolvency effect. On the other hand, we have very little information on the behavior of an ethanol gasoline as it infiltrates through the unsaturated zone. We used three categories to summarize the level of understanding of each of the abiotic processes or mechanisms affecting the fate and transport of gasoline containing ethanol:

- Sufficient information for prediction.

- Sufficient information for a rough, first-order approximation.
- Insufficient information.

There is substantial knowledge about many of the mechanisms affecting saturated zone transport of gasoline containing ethanol. The net effect of ethanol on the length and longevity of a contaminant plume, however, requires an understanding of each of the steps that define the complete transport pathway. Rather than just deal with each of these steps individually, it is important to understand the complex interrelationships among the processes involved with the ultimate transport of gasoline components to a potential downgradient receptor.

9.3.1.1. Unsaturated Zone

One of the most critical knowledge gaps is the nature of the interaction of groundwater and air (multiphase flow) with ethanol-containing gasoline in the unsaturated zone. The introduction of ethanol affects the migration and distribution of gasoline in the unsaturated zone in two primary ways:

- Capillary forces are reduced, thereby changing multiphase flow characteristics.
- Pore structure of some mineral types is altered by chemical interactions with ethanol.

Table 9-1 summarizes the knowledge level for the mechanisms associated with multiphase flow through the unsaturated zone. In the presence of ethanol, hydrocarbons can enter smaller pore spaces and drain more easily from unsaturated zone soils. This may impact the distributions of residual fuel hydrocarbons in the unsaturated zone and the periphery of free-product pools that may exist. Among the impacts may be the mobilization of existing unsaturated zone contamination. As a result of the reduction in capillary forces, the height of the capillary fringe may also be reduced. The depth and the area of hydrocarbon pool on top of the water table may be altered (although 10% ethanol in gasoline is expected to have a very minor effect). Further, the dehydration of clays and formation of micro-fractures will increase permeability. The importance of these factors in multiphase flow has not been quantified.

Understanding this process is crucial because knowledge gaps about the early stages of the overall flow and transport make adequate prediction of the important impacts of ethanol on BTEX contamination difficult. A high level of predictive uncertainty will remain until the relationship of each step to the overall process is understood sufficiently. Thus, although first-order assessments can be conducted and are widely cited, conclusions drawn from this type of assessment will be applicable to a only a small subset of environmental conditions that may be associated with potential releases scenarios.

9.3.1.2. Saturated Zone

Ethanol in gasoline will affect the concentrations of BTEX that dissolve into groundwater and the residence time of fuel hydrocarbons in contact with the water table (saturated zone). Although the dissolved equilibrium concentrations of gasoline components—benzene, toluene, ethylbenzene, and xylenes—increase in the presence of high concentrations of ethanol, the 10% ethanol expected to be added to gasoline in California should have only a minor effect on the dissolution of these gasoline components. Relatively hydrophobic compounds, such as xylenes, will be more affected than less hydrophobic compounds, such as benzene. Table 9-2 summarizes the levels of knowledge on the mechanisms affecting the dissolution of gasoline components in groundwater.

The presence of ethanol in groundwater may alter the processes of sorption and retardation and could contribute to increased benzene plume lengths. As summarized in Table 9-3, the possible impact of these effects is dependent on the quantity of ethanol at the source. For gasoline containing 10% ethanol, these processes will likely be insignificant, whereas for neat-ethanol spills, these processes may become important.

To better assess the overall impact of oxygenated and reformulated gasolines on the length and the longevity of a BTEX groundwater plume, we need a better understanding of the significance of the size, the shape, and the composition of free-product gasoline in contact with the water table. A thorough modeling effort to assess the sensitivity of the overall predictions to these unknown parameters would be an appropriate first step. If the predictions are sensitive to these parameters, then further experimental or modeling studies would be required to improve our ability to estimate them.

9.3.2. Subsurface Biodegradation Processes

The exploitation of natural attenuation processes, within the context of a carefully controlled and monitored site cleanup program, is often the preferred approach to deal with petroleum product releases (National Research Council, 1993). However, current bioremediation and risk-management practices may have to be adapted to the increasing possibility of encountering ethanol as a co-contaminant of a gasoline release. As a first step, additional laboratory and field research is needed to delineate the applicability and limitations of natural attenuation for different release scenarios of BTEX-ethanol mixtures.

Natural attenuation of BTEX contamination relies heavily on anaerobic biodegradation processes (Rifai *et al*., 1995). In such processes, indigenous microbial communities often degrade BTEX using electron acceptors preferentially in order of decreasing reduction potential (Chapelle, 1993). Sequential depletion of electron acceptors often leads to successive transitions from aerobic to denitrifying, iron-reducing, sulfate-reducing, and methanogenic conditions (see Figure 3-1 in Chapter 3). Biodegradation of fuel alcohols contributes to the depletion of electron-acceptor pools, and this depletion is likely to affect temporal and spatial transitions in electron-acceptor conditions during natural attenuation of releases of ethanol-containing petroleum product. Such geochemical transitions are important to study because they affect both BTEX degradation and migration rates. For example, both the changes in electron-acceptor availability and the presence of easily degradable ethanol could affect catabolic diversity and the relative abundance of specific BTEX-degrading bacteria.

Little is known about the effect of ethanol on microbial population shifts (that is, microbial ecology) and the resulting catabolic diversity. Among the possible effects are enrichment of ethanol-degrading bacteria in relation to BTEX-degrading bacteria, fortuitous enrichment of bacteria that can degrade both ethanol and BTEX compounds, and decreases in populations of certain bacteria as a result of toxicity. Because the efficiency of bioremediation depends, in part, on the presence and expression of appropriate biodegradative capacities of the subsurface microbes, studying the microbial ecology of aquifers contaminated with gasoline-ethanol mixtures could be a fruitful avenue of research. Such studies should address response variability as a function of a release scenario and site specificity to facilitate risk assessment and remedial action decisions.

To date, little research has been conducted on substrate interactions between BTEX and ethanol. Often, target pollutants are degraded by inducible enzymes whose expression can be repressed when easily degradable substrates (for example, ethanol) are present at high concentrations. Although biodegradation of contaminant mixtures is not very well understood at the biochemical level, preferential substrate degradation appears to be a concentration-dependent phenomenon related to repression of the enzymes needed to degrade the target compounds (Egli *et al.*, 1993). Currently, little is known about the conditions leading to sequential or simultaneous degradation of BTEX in the presence of ethanol. This knowledge gap suggests the need to investigate the concentration-dependent effect that ethanol may have on the induction or repression of enzymes that catalyze BTEX degradation. However, considering that the co-occurrence of BTEX and ethanol may be a short-lived phenomenon relative to the overall duration of a gasoline plume, it is likely that the depletion of oxygen and other electron acceptors resulting from ethanol degradation will be a more important effect of ethanol than the substrate interactions between ethanol and BTEX.

Much of the relevant research to date reflects a reductionist approach to studying the effect of ethanol on natural attenuation. For example, to study the effect of ethanol on specific biodegradation activities, batch studies have often been used that eliminate confounding effects from other variables, such as BTEX and electron-acceptor concentration gradients, as well as mass-transport limitations. Similarly, pure cultures have been used to eliminate confounding effects of microbial population shifts. This work on individual processes generally facilitates hypothesis testing and yields results that are easier to interpret but may do so at the expense of oversimplifying the complex conditions encountered in the field. To determine how ethanol affects BTEX plume dimensions and treatment end points, future research should take on a more holistic approach that considers transport and degradation processes interactively.

Ethanol stimulates microbial processes that may affect aquifer porosity and hydraulic conductivity (for example, biofilm growth, mineral precipitation or dissolution, and nitrogen or methane gas generation). Therefore, it is important to study how the presence of ethanol influences the dynamics of anaerobic microbial communities and related processes that affect the hydraulic and chemical properties of the aquifer. Such research should delineate the conditions that lead to a significant accumulation of volatile fatty acids (VFA, potential degradation products of ethanol), that could decrease the pH to levels that inhibit bioremediation. Emphasis should be placed on evaluating the potential for ethanol-induced methane production to restrict groundwater flow (thus, hindering the replenishment of nutrients and electron acceptors) and to pose an explosion hazard (which raises the possibility of requiring unique corrective action measures).

Because the presence of as little as 1% water can cause “phase separation” of an ethanol-gasoline mixture into an alcohol-rich and a hydrocarbon-rich phase (Bauman, 1999), pure ethanol must be stored at terminals in separate tankage and blended at the distribution terminal just prior to delivery to the end user. Releases of pure ethanol at distribution terminals could magnify the negative effects of many of the issues discussed above. In addition, such releases could occur at sites that are already contaminated with hydrocarbons. Therefore, the effect of neat-alcohol releases on natural attenuation of pre-existing BTEX and MTBE contamination should also be investigated.

9.3.3. Historical-case Studies

The lack of BTEX and ethanol concentration data at gasohol leak sites is a major knowledge gap. Although 10% gasohol is widely used in Iowa and Nebraska, the ethanol concentrations associated with gasohol releases are typically not measured because ethanol is not a regulated pollutant. There is a perception that no important differences exist between gasoline with and without 10% ethanol, but potential differences have not been evaluated rigorously.

Based on laboratory studies and theoretical considerations, we expect that ethanol may increase BTEX plume length by hindering BTEX biodegradation, enhancing light nonaqueous phase liquid (LNAPL) dissolution, and facilitating BTEX migration due to a decrease in sorption-related retardation during transport. Nevertheless, there is very little information about the subsurface characteristics of ethanol plumes or about the variability of their effect on BTEX fate and transport.

9.3.4. Modeling Uncertainties

9.3.4.1. Benzene Plume Lengths

Several modeling efforts evaluating the behavior of benzene groundwater plumes in the presence of ethanol have been undertaken by a variety of organizations (Chapter 4: McNab *et al.*, 1999; Malcolm Pirnie, Inc., 1998; Ulrich, 1999; Schirmer *et al.*, 1999). These modeling studies indicate that benzene plumes are likely to increase in length under such conditions. The amount of this increase is not determined. Because of the conservative assumptions used regarding unknown transport processes, the models used to forecast benzene plume lengths in the presence of ethanol systematically overestimate plume lengths. Each of these modeling efforts has taken a different approach and has used a different set of simplifying assumptions that may not reflect actual subsurface conditions. A key simplifying assumption that these studies have in common is that the biodegradation rate of benzene is constant in space and in time and for all concentrations of benzene with in the plume. This assumption is very conservative; and if benzene biodegradation rates do actually increase downgradient from the ethanol degradation zone, then these modeling predictions significantly overestimate the extent of future benzene plumes. As information from laboratory, field, and historical-case studies becomes available, these simplifying assumptions can be refined, and more accurate and representative forecasts of gasohol-release plumes may be prepared. Improved modeling will aid in the identification of efficient and cost-effective cleanup approaches and resource-management priorities.

9.3.4.2. Impacts to Groundwater Resources

During our analysis of potential groundwater impacts, we used a distance approach combined with known impact probabilities and estimated plume lengths to compare the probabilities of threat to public drinking water wells in California from MTBE or benzene releases (with or without ethanol) from leaking underground fuel tanks (LUFTs). This method provides an important advantage because it allows comparative estimates of potential future impacts between MTBE and benzene in the presence of ethanol. For comparative purposes only, this analysis develops a modeled estimated baseline for benzene impacts. This baseline estimate is then used to compare potential impacts from MTBE and benzene with ethanol present. The methodology described in Chapter 8 can act as a screening-level approach to identify vulnerable groundwater resource areas.

Based on the results of our analysis, an approximately 20% peak relative increase in public drinking water wells impacted by benzene was estimated if MTBE is replaced by ethanol. The percent relative increase in impacts to public drinking-water wells is estimated to decline from this peak increase at about ten years after the initiation of the use of ethanol. However, the estimated, potential future increase in public wells impacted by MTBE is significantly higher if MTBE were to remain the primary fuel oxygenate. By the conclusion of the first ten-year period, estimated MTBE-well impacts increase by as much as 45% and continue to increase thereafter. This analysis is very conservative, especially with regard to MTBE. Known concentrations of MTBE at LUFT sites were not used in the analysis because only a limited number of LUST sites have a known concentration associated with them.

This approach may be subject to misinterpretations. Because we are examining an absolute probability, there is a concern that the results can be taken out of context. It is important that the relative probabilities be used, using the benzene-alone distributions as the baseline. These estimates are not intended to be used to predict or forcast actual impacts. The results of these estimates are to be used for relative comparison only.

Overall, the average yearly public drinking water source benzene detection rate is under 0.35%. Both toluene and total xylenes have a higher rate, 0.53% and 0.36% respectively. MTBE shows a 1.17% yearly detection rate, much higher than any of the BTEX constituents alone, although similar to the combined BTEX detection rate (1.15%). The evaluation of known detection levels in public water sources is to provided some perspective to the magnitude of benzene or MTBE impacts in the past. Benzene shows a fairly constant detection rate over time, with a slight downward trend when yearly rates are compared. The use of ethanol as a fuel oxygenate would likely increase this detection rate which may stabilize at some higher level. MTBE shows definite upward detection trends; its continued use could, based on the trend results, result in more detections in water sources than benzene within the foreseeable future.

In assessing the probability that MTBE, or benzene with or without the presence of ethanol may affect a drinking-water well or degrade a water supply, several unknowns must be estimated. These include the concentration of benzene, MTBE, or ethanol at a gasoline-release site, the local hydrogeological regime, and the construction of nearby drinking-water wells and their radius of groundwater capture during use. The availability of this data is very limited, and existing data often have significant inaccuracies and errors.

Database location information on public drinking-water wells is often poor. Having accurate locations of public drinking-water wells is important to this effort. Additionally, data on well construction and yield—necessary items to determine a well's intrinsic vulnerability—are not readily available, and collecting that data is costly although recent legislation has made the data more accessible to groups performing environmental assessments.

9.3.4.3. Surface Water Impacts

On the basis of our evaluation and screening-calculations concerning the fate of ethanol in surface-water resources, we conclude that its persistence in surface water will be governed by its biodegradation rate. Screening-level calculations for a scenario that simulates a discrete, seven-day period of watercraft discharges of fuel-borne ethanol (that is, 40 kg/d) to Donner Lake in northern California[1] showed that the peak concentration of ethanol was only 2 µg/L, compared to about 8 µg/L for MTBE under the same release scenario. The difference in levels is due to the elevated biodegradation loss rate assumed to occur for ethanol—compared with the slower volatilization-driven losses for MTBE. For accidental tank-car releases of ethanol to a river or stream, toxic levels of ethanol could occur in the immediate downstream area of a spill. The toxic levels of ethanol would be expected to occur at variable distances downstream from the hypothesized spill with the extent of such toxic concentrations depending on volumetric-discharge conditions. If only a portion of the tank-car inventory were released, the resulting concentrations would also be reduced proportionately.

Aside from the acute toxicity for aquatic species that might be associated with a spill and their associated recovery, it is unlikely that there would be any long-term toxic effects because the ethanol will not persist in water due to its rapid degradation. However, we were only able to identify one study of the biodegradation kinetics of ethanol in a surface water sample (Apoteker and Thévenot, 1983). The key uncertainty with regard to assessments of the impacts of ethanol releases to surface waters is the magnitude of the range of ethanol biodegradation rates.

Rainout of ethanol to surface waters is considered to be more than a factor of 40 greater than for MTBE (by mass per unit-volume), as a result of the large difference between the Henry's law constants for these two compounds. The quantity of ethanol in rainout will only be about 10 µg/L for every part per billion by volume (ppb[v]) of ethanol in air compared to only 0.17 µg/L for MTBE. However, ethanol will biodegrade rapidly in surface water, but MTBE is recalcitrant to such removal.

Nevertheless, for more accurate estimates of the levels of ethanol in rain, temperature-dependent values of the Henry's law constant need to be quantified in laboratory experiments. Compared to ethanol and MTBE, the concentration of isooctane (a representative alkylate) in rain is going to be negligible (estimated to be 0.000036 µg/L per 1 ppb[v] in air). Other isoalkanes are also likely to have very low concentrations in rainwater.

9.3.5. Extracting Ethanol from Aqueous Samples

Having accurate data from field sites is crucial; however, as discussed in Chapter 7 of this volume, ethanol is a small, polar molecule difficult to remove from water. The literature reviewed in Chapter 7 indicates that the technology currently exists to enable researchers to detect ethanol at spill sites. Sufficient methods also exist to determine ethanol at its taste threshold of 50 parts per million (ppm) in water (50 mg/L). However, no routine methods are currently able to detect ethanol below 50 ppb in water. The literature reviewed for this study indicates that either direct injection of an aqueous solution or injection of the headspace above an aqueous liquid can be used to obtain detection limits of 10 ppm or less. The poor extraction

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[1] For reference: epiliminatic depth was 8 m, and wind speed was 3 m/s.

efficiency of ethanol from water is the main contributor to its relatively high analytical detection limits**.** Improved extraction methods will result in better detection limits.

A novel method for ethanol analysis capable of 15-ppb detection limits has been reported. However, this solid-phase microextraction method requires validation before it can be applied routinely to the analysis of environmental samples. Thus, much time and effort must be invested to enable the detection of trace concentrations of ethanol. Until this is accomplished on a routine basis, it will be difficult to monitor effectively the fate and transport of ethanol in the environment.

9.4. Recommendations to Address Knowledge Gaps

9.4.1. Expanded Life-cycle Analysis of the Use of Ethanol and Nonoxygenated Fuel Compounds

A comprehensive life-cycle assessment of ethanol should include the evaluation of release scenarios associated with all stages of its manufacture, distribution, and utilization, including transportation and use of feedstocks and activities at blending centers. This complete analysis would account not only for the mass balance of ethanol in the environment but also for its direct and indirect impacts with respect to issues related to the environment, health, and safety. Accordingly, the objective of a complete life-cycle analysis is to provide a scientifically sound characterization of its input feedstocks and related byproducts as well as their potential impacts. A life-cycle analysis was not prepared for alkylates, but preparing one would also be beneficial in order to understand the nature and magnitude of environmental releases and their impacts.

9.4.2. Additional Field and Laboratory Research

Additional field and laboratory research is recommended as a first step in delineating the applicability and limitations of natural attenuation for the different release scenarios of gasoline containing ethanol.

9.4.2.1. Detailed Field Studies to Refine Conceptual Models

Modeling based on detailed site-specific information is needed. Data from a thoroughly studied field site would refine our conceptual models of critical processes controlling the net fate of gasohol in the subsurface. Because the results of these estimates are largely dependent on the input-parameter probability distributions, historical-case data that better constrain the uncertainty in these probability distributions will improve the predictive capability of any future modeling. The uncertainty inherent in using the complete distribution of benzene concentrations and velocities increases substantially the increase in expected probability for well impacts. Site-specific, maximum concentrations should be used, as opposed to a generic distribution that assumes no knowledge of the specific LUFT site.

A representative site where gasoline containing ethanol has been released should be evaluated in detail, including the collection and analysis of additional soil and groundwater samples needed to support microcosm and column studies. Additional sampling of field sites might be used to provide field verification of microcosm results and increase the number of sites upon which decision-making is based.

Groundwater capture zones should be included in the analysis. The approach we used to evaluate potential groundwater-resource impacts assumes that all plumes move toward a nearby well but with no influence from the well itself. Further probabilistic modeling should be performed to ascertain the sensitivity of this approach to well-capture zones and known groundwater-flow directions.

9.4.2.2. Microcosm and Aquifer Column Studies Using Field Study Materials

Microcosm and associated aquifer column studies are recommended to address knowledge gaps regarding the effect of ethanol on the biodegradation of BTEX compounds. The microcosm studies, which would involve aquifer solids and groundwater from several sites with different histories of fuel contamination, would address the following:

- Microbial ecology/catabolic diversity—assessment of changes in the relative abundance of BTEX-degrading bacteria resulting from exposure to gasoline with and without ethanol under various electron-accepting conditions (based on analysis of DNA that codes for specific aerobic and anaerobic BTEX-degrading enzymes).
- Degradation kinetics—generation of kinetic data (lag periods and degradation rates) for BTEX compounds and ethanol under various electron-accepting conditions in aquifer materials from areas with different histories of gasoline and oxygenate exposure.

The results from such studies will also show whether ethanol metabolism results in marked pH changes in naturally buffered systems as a result of VFA accumulation. The column studies will provide a means to examine whether the kinetic results for the microcosms (for one selected site) are generally consistent with the results in a more realistic, flow-through system. The column studies will also allow researchers to examine how the integrated effects of bacterial metabolism (for example, depletion of electron acceptors and variations in BTEX degradation rates under different electron-accepting conditions) and physical processes (for example, advection and dispersion) result in spatial heterogeneity in degradation processes. The kinetic BTEX and ethanol degradation data could be used in conjunction with existing laboratory data to derive input parameters for predictive modeling.

Although the recommended studies will address some of the most critical knowledge gaps identified during the literature review, they cannot address all knowledge gaps because of time and cost constraints. As discussed earlier, a primary consequence of releases of ethanol-containing gasoline into the subsurface will be the rapid consumption of oxygen and the accelerated development of anaerobic conditions. Long lag times and relatively slow BTEX degradation rates characteristic of anaerobic conditions will constrain the scope of microbiological studies.

9.4.2.3. Historical-case Studies to Develop Statistical Analyses

Additional data should be collected from sites where ethanol-containing gasoline has been released. These data should be used to develop parameter frequency distribution statistics to support the predictive modeling efforts and interpret how the release scenario affects ethanol-plume characteristics. Emphasis should be placed on statistically analyzing BTEX data to determine how ethanol affects the stability and the dimensions of individual BTEX plumes. Such a survey would provide an integrated picture of the overall effects of ethanol on groundwater pollution from other gasoline components and the natural attenuation of these components. This information would also provide a stronger basis for the selection and operation of appropriate remediation strategies.

A possible outcome of the historical-case analysis would be a statistical comparison of gasoline-release plume lengths at locations where ethanol is present or absent as a fuel component. A reasonable objective is to gather at least 25 cases where ethanol was released as a gasoline component. This population of plume lengths would then be compared to existing historical-case data available for gasoline releases without ethanol.

9.4.2.4. Laboratory Studies to Improve Henry's Law Constants

To improve the prediction of the concentrations of ethanol in rainfall and in surface waters, we recommend that temperature-dependent values of the Henry's law constant be determined in laboratory studies. Additionally, we recommend that further studies be conducted to predict more accurately the biological half-lives of ethanol in different kinds of surface waters in California. This is particularly important because of the important role that rapid natural biodegradation can play for the removal of ethanol from surface waters.

9.4.2.5. Development of Laboratory Analytical Methods

Analysis methods must be improved to meet the data quality requirements contributor to relatively high analytical detection limits. Improved extraction methods will result in better detection limits.

In order to eliminate problems with potential interferences, we recommend that gas chromatographic (GC) separation be used in all future ethanol analyses. There are two practical strategies that can be used for the sensitive detection of ethanol in the presence of interfering compounds. The first is to use the best possible GC procedure to separate ethanol from any interferences and then to detect ethanol with a nonspecific detector, such as a flame ionization detector. The second strategy is to perform a less rigorous GC separation coupled with a detector that would respond specifically to ethanol but would not respond to potentially interfering compounds (for example, an atomic emission detector or a mass spectrometer). Both of these strategies merit careful consideration and comparison.

9.4.2.6. Development of Central Database

More knowledge is required concerning the subsurface environment in California. One of the major unknowns in any hydrogeological investigation is the lack of knowledge of subsurface geology. A great deal can be learned even from the moderate to poor quality of data available in well logs of the California Department of Water Resources. This data should be transcribed into electronic format for use by researchers attempting to draw conclusions on the subsurface.

As part of ethanol studies, we should use GeoTracker and the Geographic Environmental Information Management System (GEIMS) database as a central repository of data. The State Water Resources Control Board (SWRCB) already intends to use this system to help regulators assess sites. Other agencies should be encouraged to supply their data to the system so that interagency cooperation may be fostered. As Senate Bill 989 (1999)[2] allows responsible parties to access well construction and other details when under order from a regulatory agency, the associated data for wells in the state of California (lithologic logs, well construction, location, and yield) should be placed in an electronic database to expedite site assessments and decrease costs. This information can also assist in the evaluation of vulnerable groundwater areas as stated elsewhere in the same bill.

Drinking water well and LUFT data already collected by various state organizations should be systematically organized for use in decision analysis. This would permit further comparative analysis of public drinking water wells impacted by gasoline containing ethanol or MTBE from LUFTs. For example, Rempel's 1995 report should be updated to help to understand what factors result in well impacts throughout California.

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[2] *Section 13752 of the Water Code is amended to read:* Reports made in accordance with paragraph (1) of subdivision (b) of Section 13751 shall not be made available for inspection by the public, but shall be made available to governmental agencies for use in making studies, or to any person who obtains a written authorization from the owner of the well. However, a report associated with a well located within two miles of an area affected or potentially affected by a known unauthorized release of a contaminant shall be made available to any person performing an environmental cleanup study associated with the unauthorized release, if the study is conducted under the order of a regulatory agency. A report released to a person conducting an environmental cleanup study shall not be used for any purpose other than for the purpose of conducting the study.

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Tables

Table 9-1. Knowledge level for individual properties/mechanisms associated with multiphase flow through the unsaturated zone.

Properties/mechanisms	Knowledge level
Equilibrium composition of the water and hydrocarbon phases	Sufficient information for prediction, but predictive ability has not yet been adequately validated.
Capillary forces—reduction in surface and interfacial tension	Sufficient information for rough, first-order analysis, but significance has not yet been evaluated for this problem.
Effective permeabilities	
– Volume changes as ethanol partitions into water	Insufficient information, extent of volume change understood, but rates and significance are unknown.
– Dehydration and cracking of clay strata	Sufficient information for rough, first-order analysis if typical geological strata can be defined.

Table 9-2. Knowledge level for individual properties/mechanisms associated with the dissolution of gasoline components into groundwater.

Properties/mechanisms	Knowledge level
Equilibrium composition of the two phases	Sufficient information for prediction. Data and modeling available for predicting phase partitioning.
Mechanisms of transport of chemical species through the gasoline pool	Sufficient information for rough, first-order analysis but depends on the size and shape of gasoline pool. Understanding has not yet been adequately applied to this problem.
Mass-transfer rates across the gasoline-water interface	Sufficient information for rough, first-order analysis but depends on the size and the shape of gasoline pool.

Table 9-3. Knowledge level for individual properties/mechanisms associated with the transport of BTEX and ethanol with groundwater.

Properties/mechanisms	Knowledge level
Sorption and retardation	Sufficient information for a rough, first-order analysis. Quality of prediction will depend on ethanol concentrations at the source.
Precipitation of gasoline droplets	Sufficient information for a rough, first-order analysis. Overall impact currently being studied. Quality of prediction will depend on knowledge of ethanol concentrations at the source.

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Volume 4: Potential Ground and Surface Water Impacts

Chapter 10: Response to Comments

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Table of Contents

Chapter 10: Response to Comments

10. Response to Comments

10.1. Peer Review Comments

The following responses address independent peer review comments on the draft State Water Resources Control Board (SWRCB) Volume 4, *Potential Ground and Surface Water Impacts*, which is part of the report to the California Environmental Policy Council titled, *Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate.*

10.1.1. Peer Review Comments from Dr. Patricia Holden, Donald Bren School of Environmental Science and Management, University of California, Santa Barbara.

Patricia Holden (Ph.D. University of California at Berkeley, 1995) is an Assistant Professor in environmental microbiology and microbial ecology. Dr. Holden researches the biotic mechanisms of hydrocarbon pollutant transformation in unsaturated systems. She is currently studying factors influencing the formation of biofilms in the vadose zone and the role of extracelluar polymeric matrices in biodegradation kinetics. More recently, Dr. Holden has also been studying the phylogenetic composition and diversity of microbial communities in contaminated urban runoff. In this area of research, her laboratory group is trying to understand how urbanization affects water quality during dry and wet seasons in the south coast of California. She has eight years of professional experience in environmental engineering, design, and project management, and two years of similar experience during her postdoctoral research.

Volume 4, Chapter 1 Comments:

Comment: Figure 1: L in the UST is not shown. This is, in fact, a likely release scenario based on historical precedence. Show it; it is discussed in the text.

Response: The intent of the figure was to graphically show the steps in the production, distribution and use of ethanol in gasoline. Not all underground storage tanks (UST) leak. This is why the UST in the figure is not labeled as leaking “L.”

Comment Table 1: no mention of safety issues in addition to toxicity issues. Ethanol is a flammable substance.

Response: This is a good comment. Safety issues have not been addressed as part of this evaluation because of time constraints to meet the required report delivery date of December 31, 1999. The evaluation of safety issues would be included in a complete life cycle analysis.

Comment Table 1: Where the word “degraded” is used to describe the fate of ethanol, it is hard to justify the use of this term because there is no supporting data provided in the chapter. Rather, distribution and loss should be used to describe the Risk Assessment issues.

Response: Comment noted. Table 1-1 edited to refer to “loss” where appropriate.

Comment Table 1: The Release assumptions for “Release during bulk ethanol transport by marine cargo tanker” should emphasize infinite solubility and not just the density difference.

Response: Comment noted. Table 1 edited to reflect this comment.

Comment Table 1-1: For Release Scenario “Release from watercraft emissions into surface waters,” the risk assessment issues section regarding expected rapid biodegradation and volatilization should be supported by citing literature in the text (see below) that demonstrates the importance of these fates in the presence of BTEX (even if it is bench scale data). Also, is there not a “Risk Management Option” here (for watercraft emissions) that is missing?---.e.g. regulating / restricting watercraft usage on surface waters. If this is an inevitable release point, then there are only two ways to avoid it-either stop using the additive or stop using the watercraft to the current extent permitted.

Response: Comment noted. The risk management option of regulating / restricting watercraft usage on surface waters has been added to Table 1-1.

Comment: I strongly suggest listing physicochemical characteristics of ethanol up front in this section, describing its properties and delineating safety issues. This will also help readers follow the logic in later sections of this first chapter (e.g. 1.5.2).

Response: Volume 2, *Background Information on the Use of Ethanol as a Fuel Oxygenate*, provides this information. This information is provided as a separate volume because all the subsequent California Air Resources Board (CARB), SWRCB, and Office of Environmental Health Hazard Assessment (OEHHA) volumes draw upon this information, and repeating it in each volume would be redundant.

Comment Section 1.2.2.: The chemical composition of the corrosion inhibitors and detergents should be identified in the text and in Table 1-3. Additionally, the percent by weight should be provided in the text (it is a footnote in the table).

Response: Much of this information is proprietary and is not available at this time.

Comment Section 1.3.1.: Given the predicted reliance on marine bulk transport of EtOH, the risk to marine organisms from spilled tankers will need to be addressed.

Response: We agree with this comment and this issue should be addressed as part of a complete life-cycle analysis.

Comment Section 1.5.1: What is the basis for stating that biodegradation and /or volatilization were the important fates for ethanol in a bulk spill? Given its solubility in water, it seems more likely that ethanol would dissolve in groundwater and disperse. If there is a basis for emphasizing biodegradation here, it is better to provide a citation to the proper reference.

Response: Volatilization will likely be important if bulk ethanol is released to the ground surface, and significant amounts do not infiltrate into the subsurface.

Comment Section 1.5.2.: To the untrained reader, the reason for suspecting increased concentrations of hydrocarbons at existing subsurface petroleum spills is not obvious. If physicochemical characteristics are tabulated and described earlier, then the proper introduction to the "cosolvent effect" will have been done and the reasoning in this section would be more understandable to the reader.

Response: Comment noted.

Comment Section 1.5.5.: The preceding reviews of existing spills is very well done. If there is another or additional way to make a stronger recommendation to evaluate the Tacoma spill data, as was recommended in this section, then it is advised to do so. This seems critical-why not evaluate the data now, then make the decision regarding another fuel additive that may or may not be disastrous to water quality? Another point for this section-do local fire departments keep an inventory of gasohol versus gasoline in USTs? Page 1-9 of this section---a typographical error (perceive, not perceived).

Response: The focus of this report has been to perform a literature review, identify potential data sources, and perform as much screening analysis as possible in time permitted before the report was due to the Environmental Policy Council. A recommendation has been made to gather and evaluate available historical-case field data and this will likely occur once this report has been submitted.

Comment Appendix A: when did these releases occur? State either in the Appendix or in the text of section 1.5.4.

Response: The Nebraska contact that provided this information is unavailable to respond to this comment.

Volume 4, Chapter 2 Comments:

Comment: The emphasis on this Chapter is effects of ethanol on BETX in the environment. However, in Chapter 1, an additional important point is made: that BTEX and MTBE in existing spills are both potentially affected by the addition of ethanol to the spill site. Can this also be addressed in Chapter 2?

Response: The impact of an ethanol spill on benzene, toluene, ethylbenzene and the xylenes (BTEX) was described in Section 2.2.5.1. No mention of the impact of an ethanol spill on methyl tertiary butyl ether (MTBE) was included in this discussion because there is no data available to address this issue. A speculative comment regarding MTBE has been added to this section after the second paragraph.

Comment Section 2.2.2.1: The third paragraph in this section is confusing. It is not clear from Figure 2-5 where the 19.7 dyes/cm line is.

Comment Figure 2-5: Recommend a different symbol for isooctane because of the error bars. The index and the text in section 2.2.2.1 are difficult to co-interpret. In the legend, is the "surface tension-air" measured at the air/solvent interface (must be, since the solvent is expected to float)? It would help to clarify this in the text.

Response: We have improved Figure 2-5 and revised the third paragraph in Section 2.2.2.1. to improve the clarity.

Comment Section 2.2.2.2.: Unless I am mistaken, the word "cosolvent" first appears on pg 2-7, although the description of the effect occurs in the pages preceding. The word should be clearly defined early in the chapter with some additional background literature presented on colsolvency and what compounds generally show this behaviour. The phase diagrams are good, not easy to read by everyone and either a table of reported solubilities as a function of cosolvent effect or some language in the next would be useful.

Response: Section 2.1 had been edited to address to better define "cosolvent."

Comment Section 2.2.2.3.: Typographical error: "Direct measurement(s) do...." It may not be appropriate to mention in this section, but an outcome of the reduced entrapment of gasoline in the vadose zone is that the remediation strategies that have been so well-developed for jet fuel and gasoline (venting and bioventing) will have a lessor utility for cleanup. Again, this is not relevant to the technical presentation here, but is an outcome of the possible effects of ethanol on hydrocarbon distribution.

Response: Comment noted. A recent report prepared by J. M. Davidson and D. N. Creek, Alpine Environmental, Inc., for the Western States Petroleum Association, evaluated several technologies commonly used at gasoline spill sites to determine how effective they would be for remediating ethanol-impacted sites and for treating ethanol-impacted water and soil.

Comment Section 2.2.3.2.1.: Here is where cosolvency is introduced and the background suggested in the above comments appears in 2.2.3.2.5. It would be easier to follow this if the background appeared early in the chapter. Perhaps the organization can be changed so that the physicochemical factors influencing distribution are first delineated, then each is defined then described in detail. Instead, we learn about the effects of cosolvency before the concept is introduced.

Response: Changes have been made earlier in this chapter to introduce the concept of cosolvency.

Comment Section 2.2.3.3.2: Typographical error: "Inherent in these models (are) the assumptions..."

Response: Comment noted.

Comment Section 2.2.4.1.: It would be useful to define the word "sorption" so that the untrained reader can understand. This definition would include / differentiate adsorption and absorption, if possible.

Comment Section 2.2.4.2.: From the above recommendation it follows that isotherms are mathematical relationships that describe the proportions of sorbing compound in either phase. Some isotherm models are more theortically (e.g., Langmuir) than empirically (Freundlich) based.

Response: Reference to "sorption" has been changed to "adsorption" for clarity.

Comment Section 2.2.6.2: 2nd paragraph from bottom: Do the authors mean "overestimates" instead of "underestimates"?. Wouldn't the processes of sorption and biodegradation diminish the extent of the plume?

Response: We agree with this comment. The section has been edited to improve clarity.

Comment: I would recommend a summary section at the end of this chapter. This chapter is very well done with considerable detail regarding the possible interphase behaviours of ethanol/gas/water mixtures. However, there are several occasions where we are informed that not enough is known. It seems really important to punctuate what is not known in a summary section because all of the uncertainties ultimately lead to an overall uncertainty in BTEX migration if EtOH is added to fuel. Particularly since this report is to the CA government where decisions can be made regarding funding of research to resolve the uncertainties.

Response: To facilitate the California Environmental Policy Council's review of important decision making information, the summary conclusions and recommendations for further research have been gathered into a separate chapter, Chapter 9, "Critical Knowledge Gaps Regarding the Ground and Surface Water Impacts of Ethanol-containing Gasoline and Recommendations for Further Research."

Comment Appendix A: HSA (pg A-2) was defined but how it is determined is not provided. Can one sentence be added here, or should the reader go to the reference?

Response: This is too detailed for the scope of this report. The reader is referred to the appropriate reference.

Comment: A final note about Chapter 2. This chapter is difficult for the untrained. Considering that this is a report to the Governor, it might be worth taking some of the analytical treatments of cosolvency and mass transfer back to the appendices and simplifying the language in the main chapter while being careful not to leave out any important concepts. It appears that there is redundancy between the text and the appendices anyway and thus improving the readability of the text should not require elimination of any important theory or analyses.

Response: We agree that this chapter is intended for a knowledgeable audience. The "condensed" version can be found in the Executive Summary, Volume 1, of the report.

Comment: Lastly, it seems worthwhile to examine the effects of EtOH on MTBE distribution-especially since MTBE already exists in the subsurface and is likely to be further distributed by the cosolvent effect. Is ethanol going to make MTBE cleanup more difficult?

Response: Ethanol is probably not going to make MTBE cleanup more difficult: 1) Although it has not been studied yet, the cosolvent effect for MTBE is likely to be very small because MTBE is hydrophilic. 2) Ethanol will most likely disappear before remediation of MTBE begins because the ethanol is readily biodegradable.

Volume 4, Chapter 3 Comments:

Comment Section 3.2.1 pg 3-3: check the spelling of the genera Alcaligen(e)s ?, Noca(r)dia ? What is the toxicity of ethanol to microbes? This could be clarified in the last paragraph of this section by stating that ethanol is toxic at high concentrations in water (70% ?) but is nontoxic at concentrations in water resulting from gasohol and water in equilibrium (?). This is important because in Chapter 2, the main reference regarding mobility of gasohol was related to an 85% methanol blend.

Response: Those two genera are indeed misspelled in the text and need to be “Alcaligenes” and “Nocardia.” See comment below.

Comment Section 3.2.4.2: pg 3-5: Typographical error: Paul and Clark, 1989. (also in references)

Response: Comment noted.

Comment: The comments above (related to toxicity) are addressed in later sections of the chapter.

Response: Comment noted.

Comment Section 3.4.1.3: It would be helpful to the untrained to also provide the aqueous concentrations in units of % (w/w) as these are the units in earlier chapters (and in specification for reformulated gasoline) and thus provide a frame of reference for these toxicity discussions.

Response:

Comment: What about the effects of ethanol on MTBE biodegradation in the presence of BTEX? Preceding chapters acknowledged the existence of prior contamination and that there would be a potential interaction between MTBE and ethanol.

Response: We agree with this comment. The potential interaction between MTBE and ethanol should be evaluated as part of future laboratory and field studies. The postulation would be that ethanol could affect MTBE biodegradation in the same fashion as BTEX degradation.

Comment: There are a few misspellings in the References section-worth running a spell check and looking at authors’ names.

Response: Comment noted.

Comment: As with the other chapters, it would be useful to have a summary section that summarizes what is known (ethanol should biodegrade), what is not known and what should be known to provide better predictive capabilities.

Response: To facilitate the California Environmental Policy Council’s review of important decision-making information, the summary conclusions and recommendations for further research have been gathered into a separate chapter, Chapter 9, “Critical Knowledge Gaps Regarding the Ground and Surface Water Impacts of Ethanol-containing Gasoline and Recommendations for Further Research.”

Comment: The primary message carried into Chapter 4 from this section is that biotransformation of ethanol will remove electron acceptors and thus negatively affect BTEX biodegradation. How would this effect be potentially counterbalanced by the higher aqueous availability of BTEX due to the cosolvency effects (and the higher population sizes overall due to ethanol presence)?

Response: Possible beneficial effects are mentioned. How much the positive effects would balance the negative effects is unknown and one of the reasons for more research to be done.

Comment: The rate constants in Table 3-2 seem low (1/day), but are taken from other studies so must have been carefully confirmed. The reason this comes up is that in Chapter 5, the 1st order rate constant for biodegradation in surface water is 0.22 per hour in aerobic conditions. It would be useful in Chapter 3 to stress that aerobic rate constants in porous media are expected to be lower than rate constants in surface waters, because....

Response: The numbers in Table 3-2 are correct. This is addressed indirectly in Section 3.3.3.3.

Comment: Lastly, is ethanol involved in cometabolic processes at all?

Response: This question has been identified as an important knowledge gap in Chapter 9, “Critical Knowledge Gaps Regarding the Ground and Surface Water Impacts of Ethanol-containing Gasoline and Recommendations for Further Research,” and will be a focus on ongoing research during the coming year. Some alcohol dehydrogenase enzymes that work primarily on ethanol do act on other alcohols. For example, the alcohol dehydrogenase of the human liver will convert methanol to formaldehyde (which is why methanol is toxic to people).

Volume 4, Chapter 4 Comments:

Comment Pg 4-3 (Section 4.2.1): Top of page is a lone right “parentheses”. Next paragraph (1st full on this page) repeats the text in next to last paragraph of page 4-2. Next paragraph: define BOD in first use. Further in this paragraph, it seems unimportant to qualify the impossible model as “(analytical or numerical)”-suggest removing this clause as unessential. Next paragraph: It seems that the justification neglects retardation because of mechanical (not in previous model, validity of calculations) reasons. The next sentence seems to be the more important justification (low adsorption, so not important to include retardation term). Next page, next paragraph: “hydrophilic”, not “hydrophillic”.

Response: Comment noted.

Comment Section 4.2.1.: What is the basis for the first order rate constant of 0.01 per day, when the previous chapter (Table 3-2) provides a lowest rate of 0.1 per day? Some explanation for this 10-fold conservatism would be useful.

Response: The rate constant of 0.01 per day was used as part of a side calculation, separate from the main analysis, that was used to evaluate ethanol concentrations near the groundwater/LNAPL interface to assess the potential for cosolvency effects. The very conservative rate constant was used simply to illustrate the point that even if biotransformation of ethanol at the interface is minimal (which could be argued, based on toxicity effects at high concentrations), ethanol concentrations are still not high enough to produce an appreciable cosolvency effect on benzene.

Comment Section 4.2.2.: If only ethanol biodegradation is modeled (preceding paragraph), then why convert to BOD? It would help in a preceding paragraph to show stoichiometry assumed for BOD conversion so that the nearly non-technical reader can see the relationship. Ah-this shows up in the Appendix. It might also help to have it here.

Response: Comment noted.

Comment: The results and model are quite interesting and dramatic. Would there be any benefit to increasing the 10% EtOH concentration and seeing how this changes the plume length? I realize that there is considerable effort in doing these simulations, but it seems that either here or at some point in the future it would be worthwhile to perform a sensitivity analysis with varying EtOH concentrations.

Response: We agree with this comment.

Comment: As with comments on the other chapters, a quick summary section at the end of this chapter would be useful-to encapsulate the figures and tables into a couple of capstone messages.

Response: To facilitate the California Environmental Policy Council’s review of important decision making information, the summary conclusions and recommendations for further research have been gathered into a separate chapter, Chapter 9, “Critical Knowledge Gaps Regarding the Ground and Surface Water Impacts of Ethanol-containing Gasoline and Recommendations for Further Research.”

Comment: As with comments on the preceding chapters, it seems an important question is the effect of ethanol on MTBE distribution. Granted it will not be added, but residual pollution will be mixed with new spills. This may be impossible to model, but might be worth discussing.

Response: At this point additional laboratory data would useful to support any future modeling efforts. Any discussion at this time would be very speculative at best.

Volume 4, Chapter 5 Comments:

Comment: Is rainout the preferred term or is wet deposition? Perhaps the latter is used to describe particulates only-but “rainout” is not a familiar term.

Response: We have indicated in the first paragraph of Section 5.3 that for purposes of discussing washout from the atmosphere of ethanol and MTBE, rainout and wet deposition are synonymous. Specifically, “... significant rainout (i.e. wet deposition) can potentially impact surface waters.”

Comment: The biodegradation rates in the model are much higher than what was presented in Chapter 3. It would be useful to make the comparison between the two environmental compartments and their associated rate constants in this chapter as the biodegradation rate heavily influences the results in the analyses.

Response: We were able to find only one reference (Apoteker and Thévenot [1983]. Experimental simulation of biodegradation in rivers. *Water Res.* 17: 1267-1274; referenced in Chapter 5) that quantified the degradation of ethanol in surface water (i.e., Seine River), so it is difficult to draw strong conclusions from this one article regarding the differences in the biodegradation rates for ethanol in soil, groundwater, and surface water. Consequently, we have noted that additional biodegradation experiments are needed for ethanol in surface waters. Typically, however, the biodegradation rate of ethanol will be faster in surface water because generally, surface water will possess an increased oxygen content compared to soils and ground waters. As noted by Alexander ([1999]. "Chapter 16. Bioremediation Technologies. In Situ and Solid Phase." In *Biodegradation and Bioremediation,* Second Edition [Academic Press, San Diego, CA], p. 341; §*In Situ* Groundwater Biorestoration), biodegradation typically is carried out most rapidly by aerobic bacteria, and little oxygen is present in groundwater, even under the best conditions. [Note: In comparison to ethanol and most other gasoline components, MTBE is considered resistant to aerobic microbial degradation (Sulfita and Mormile, [1993]. Anaerobic biodegradation of known and potential gasoline oxygenates in the terrestrial subsurface. *Env. Sci. Technol.* 27: 976-978). Because Section 5.4 only addresses surface water, no changes were made to the text, except to add the footnote in Section 5.4.1 (prior to Equation [5-4]) that as just mentioned, according to Sulfita and Mormile (1993), MTBE is considered resistant to microbial degradation.

Comment: In Table 5-1, provide reference temperature for solubility data.

Response: We address this point by citing the original measurement performed by Stephenson (1992). According to Stephenson (1992), the solubility of MTBE is 42 g/L at 19.8˚C, and we report this value as 476 mol/m^3 at 20˚C in Table 5-1.

Volume 4, Chapter 6 Comments:

Comment Section 6.2.: A footnote defining the "Reid" vapor pressure would be useful.

Response: A footnote was added as suggested in page 6-1.

Comment Section 6.5.4.: Gasoline is indeed a complex mixture, despite it having been modeled as "one compound."

Response: Comment noted.

Comment: Early in this section it is important to state how much alkyate must be added to gasoline to boost the octane rating when ethanol is the fuel oxygenate. An evaluation of gasoline from 1996 (pg 6-4) is provided, but what really seems important here is how much would be added and how that additional fraction of alkylates will change the environmental consequences of gasoline release into the environment.

Response: There is not a simple answer to this question because there are other requirements that gasoline formulations must meet besides octane rating, and many of the specification parameters (including octane and vapor pressure) are not linearly additive properties. However, we did make a very rough estimation and incorporated this result to the introduction. Because the physicochemical properties of alkylate components resemble those of other hydrocarbons in gasoline, we would not expect that this increase could effect dramatically the way gasoline behaves in environmental releases.

Comment: Does the increase in alkylates increase the overall toxicity of gasoline? What are the consequences of elevated groundwater concentrations? Given their low solubility and high volatility, would we expect these compounds to be biodegraded in the vadose zone and thus fairly amenable to well-proven vadose zone cleanup strategies such as vapor venting? Is the addition of these compounds important or inconsequential in the scheme of the entire hydrocarbon spectrum in gasoline? Overall, this chapter seemed a bit sparse in these areas. The reader is left a bit uncertain as to whether or not the concentrations actually added to gasoline would result in any substantial change in overall distribution of gasoline and/ or fate.

Response: No information is available on the chronic effects of isooctane—a major alkylate component—in humans. At acute doses, isooctane is a nervous system depressant, as are many other hydrocarbon solvents. *A priori*, there is no reason to believe that alkylates will affect—much less increase—the overall toxicity of gasoline. As a matter of fact, this is a complex problem because an increase of alkylate percentage implies a decrease in the percentage of other hydrocarbons (e.g., BTEX) and toxicity should be evaluated in an integral manner. The low solubilities of alkylate components in water and their high Henry's law constants seem to suggest that vapor venting would be a viable cleanup strategy.

Volume 4, Chapter 7 Comments:

Comment: Physicochemical properties of ethanol are provided in this chapter; they were also provided in other preceding chapters. In Chapter 1, it was recommended that the properties be provided up front. It seems really important that all authors are consistent with the use of values for physicochemical properties.

Response: Detailed explanations of physicochemical properties of ethanol are not provided in this chapter. Sufficient discussion was included so that Chapter 7 could be used as a "standalone" document and provide a context for the following discussion. Volume 2, *Background Information on the Use of Ethanol as a Fuel Oxygenate,* provides information on the physicochemical properties of ethanol. This information is provided as a separate volume because all the subsequent CARB, SWRCB, and OEHHA volumes draw upon this information and to have it repeated in each volume would be redundant.

Comment Section 7.4.3.2.: Are there any data with AED detectors for ethanol?

Response: No data is available for AED detectors; that is why it might be of interest to explore the use of an AED in the future.

Comment Section 7.4.4.: Explain what cryofocusing is and how it is perceived to be beneficial.

Response: A brief footnote explaining cryofocussing and its benefits has been added to Chapter 7.

10.1.2. Dr. Michael K. Stenstrom, Civil and Environmental Engineering Department, University of California, Los Angeles

Professor Stenstrom is the Assistant Dean for Computing Resources for the School of Engineering and Applied Science (SEAS), and has developed the SEASnet Computing Facility. His research and teaching are in the environmental engineering area with emphasis on biological treatment methods and applications of computing technologies to environmental engineering research. Professor Stenstrom's research interests center around process development for water and wastewater treatment systems, including mathematical modeling and optimization. More recently he has applied these mathematical techniques to urban runoff and groundwater modeling. In the past two years, he has developed a land-use and drainage model for the Santa Monica Bay Water Shed. From this model it is possible to predict pollutant emissions to the Bay and how changes in land-use regulations will affect pollutant emissions. He is also conducting an experimental study to access toxicity in urban runoff.

General Cover Letter Comments:

This letter and attachments are my review of Volume 4 Potential Ground and Surface Water Impacts. I wrote the attached comments as I read the report. In this letter I provide more general comments and an overview.

Professor Jenkins of UCB contacted me about this review. I am not sure if you have seen my resume. I am enclosing a short one. Also I worked two years for Amoco, which at that time was the refining and marketing subsidiary of Standard Oil (Indiana). At Amoco I worked as an environmental engineer designing end-of-pipe treatment plants as well as investigating various environmental aspects of refining. I recall we evaluated tertiary butyl alcohol (TBA) as a gasoline additive. This review reminded me of some of the things I did for Amoco.

I found the review informative and interesting. I have learned something from the review. Before I received it, I though the exchange of ethanol (EtOH) for MTBE would be relatively simple, since health effects ingestion of EtOH are well known. After reading the review I understand it better and I think it is much more complicated.

Chapters 1 and 2 relate more to groundwater modeling. I have supervised two students to the completion of their Ph.D.'s in this area; however it is not my strongest area and you will find my comments directed more towards improving clarity than questioning the writers position or the results. I know Susan Powers is well respected in this area.

Response: Comment noted.

Comment: Chapter 3 relates to biodegradation. I found this chapter to focus on potential degradation of EtOH in the subsurface environment. It ignores a great deal of work on EtOH degradation in treatment plants. EtOH is very degradable and it is never considered a problem in treatment plants. In my own laboratory we have degraded EtOH in fixed film reactors in waste streams with 3 to 5% EtOH concentration (volume percent). The authors discussed EtOH degradation but soon turned to the potential changes in contaminant movement due to physical or chemical changes in the subsurface. I feel even more strongly than the authors that a large spill of EtOH containing gasoline can modify the movement of the more environmental significant constituents of gasoline, such as benzene. The EtOH can overwhelm the ability of the subsurface to degrade gasoline components. The metabolism can change from aerobic to anaerobic, which will reduce degradation rates and may even change the degradability of a constituent. In ground waters that are used as a potable supply, objectionable taste and odor may be created due to residual concentrations of compounds produced during anaerobic condition.

I do not think the writers can accomplish very much on this aspect because it is a difficult and unknown topic. It seems to me that we are all speculating. I think we will need empirical results to better understand the potential impacts of a spill. I am surprised that we cannot find more information on EtOH-gasoline spills. I saw the list of Nebraska spills. I wonder if the writers have checked the international literature. I suspect that EtOH has been used in other countries. Lots of strange things were done in Europe due to war necessity. Perhaps there is some experience there that we do not know about. I have found direct contact with professors or researchers the most useful way to ferret out information about spills.

I urge you to continue your search for empirical results, or to recommend in the conclusions of the report that others continue to search for empirical results. Future projects should be created to study EtOH spills in order to verify the speculations in the report, and improve our understanding of potential mitigation techniques.

Response: We agree with the comment that field studies of ethanol spills is important to verify screening model predictions and improve our understanding of gasoline component migration in the presence of ethanol.

Comment: Chapter 5 describes scenarios for release to surface waters (I know Dr. Daniels well). It seems to me this chapter is typical of accidental release studies of a number of chemicals. I did not see all that I expected. They conclude that the extreme biodegradability of ethanol will prevent its widespread transport. I agree, however, I also wonder about the scenario of an EtOH spill, perhaps without a gasoline spill, into a potable water supply. I think it would be useful to answer this “acute” question. How much EtOH can be tolerated in a public water supply? What will be the rate controlling parameter?

After reading the documents, it occurs to me that the risks of replacing MTBE with EtOH are greater than I originally thought. I think this is in part because the review does its job and explores effects than we might not have considered. Also I think it results because in reading the chapters one continually learns about what we do not know about EtOH spills. One looses site of the problem we are trying to fix-- MTBE contamination of drinking water supplies. In order for the various chapters and volumes to have the appropriate impact, the risk of adding EtOH must be compared to the risks we reduce by eliminating MTBE. At someplace in this document, I believe it is important to indicate what we know about the risk of exposure to MTBE and other chemicals. I know this is difficult because of uncertain transport mechanisms and all the other phenomena that might reduce or facilitate EtOH transport to humans. I believe it important to balance this impression by including some other section or discussion (perhaps this is included in another volume I have not reviewed). One tends to loose track of the benefits of replacing MTBE with EtOH, and we need to correct this impression in some way.

Response: We agree with the perspective articulated by these points. However, a quantitative risk assessment is not the focus or intention of Chapter 5 and 6 in Volume 4, or the volume itself. Indeed, health-protective concentrations for benzene, ethanol, MTBE, toluene, and xylenes are summarized and explained by the State of California Environmental Protection Agency, Office of Environmental Health Hazard Assessment (CalEPA/OEHHA) in *Volume 5, Potential Health Risks of Ethanol in Gasoline* of this report. For this reason, we have made a general statement in Section 5.6 (Summary) that generally relates our results to health-protective concentrations for MTBE and ethanol identified in *Volume 5: Potential Health Risks of Ethanol in Gasoline* of this report (see response to "*Stenstrom Comments #2" below*).

Comment: Chapter 8, which I read after the other chapters, helps put risks associated with the compounds into perspective. It is I made some specific suggestions about continuing this work in the attachment.

Response: Comment noted.

Comment: Chapter 9 functions as a summary or conclusions section. I suggest you consider a title change to indicate this function. Also there is little information from Chapter 8 in Chapter 9. Perhaps this is due completion dates of the chapters. In either case, I think Chapter 9 needs to include results from Chapter 8.

Response: The results from Chapter 8 have been incorporated into Chapter 9.

Specific Notes on LLNL Review of Ethanol–Gasoline

General Note: This document shows its varied authorship. Style changes from chapter to chapter (although there is good consistency for basic issues such as style of citing references). It occurs to me as I review Vol. 4, that there will be a need for an overall summary, which is acceptable to all authors. I have not seen Vol. 1, but it will be challenging to write such a summary.

Volume 4, Chapter 1 Comments:

Comment 1: What about exposures via small uses of gasohol, such as gardeners, gas lantern, stoves, hand warmers. Figure 1.

Comment 2: Copper content of gasohol is 0.1 mg/kg (1 ppm). Do a calculation to see what impact this will have on urban runoff. Table 1-2

Response: Both these issues are good ones to be addressed as part of a complete life cycle analysis.

Comment 3: Provide as much detail as possible on impurities in the EtOH so that one can calculate the impurities after a gasoline release or other spill. Can Table 1-3 be quantitative?

Response: Little quantitative information is available on the variation in ethanol impurities. Further many of the additives are proprietary and information is not available at this time.

Comment 4: Page 1-5. A good point is made about MTBE in Lake Tahoe from 2 stroke engines. Then the discussion just stops. What's the implication for EtOH? Will their ban on 2-stroke engines continue? Does it need to be continued? What are the rest of the writers' thoughts in this paragraph? Finish the idea.

Response: The risk management option to restrict watercraft use is a local and area specific decision. A discussion of the effectiveness of the current ban on gasoline containing MTBE in the Lake Tahoe area is presented in Appendix C of Chapter 5, Potential Impact of Ethanol-containing Gasoline on Surface Water Resources.

Comment 5: I live in Southern California, and it seems that every house uses a gardener who has at least two gasoline-powered tools - a weed whacker and a leaf blower. Gasoline powered leaf blowers have been outlawed by the LA City council, but there seems to be no impact on professional gardeners. Most of these tools use 2-stroke engines and blue smoke trails are abundant. It seems to me that this is probably a larger source than boaters in Lake Tahoe, and merits equal time in the review.

Response: We agree with this comment and this issue should be addressed as part of a complete life cycle analysis.

Comment 6: The search on Nebraska is a little surprising. It seems like a useful thing to do, and why is only Nebraska represented? Are they no other states that have kept such records?

Response: None that we could find in the time allowed for our literature search.

Volume 4, Chapter 2 Comments:

Comment 1: The reference is provided for the surface tensions (Figure 2-5), but I think you should still mention the method of measurement in the text.

Response: Comment noted.

Volume 4, Chapter 3 Comments:

Comment 1: It seems that one could put some bounds on concentrations that would create inhibitory conditions, as cited in 3.3.2.

Comment 2: In Section 3.3.3.2, 4th paragraph, it states that pH was observed from 4.5 to 7.8. Is this correct? 4.5 is very low, and if this is correct, it answers the speculation in the preceding paragraphs about low pH inhibition. Surely pH=4.5 would inhibit ethanol degradation and most other biodegradation. Also, groundwater at pH=4.5 would solublize many other contaminants, metals for example, that could inhibit biodegradation or facilitate their transport.

Comment 3: On page 3-12, just above section 3.3.3.3, the authors conclude that ethanol degradation is so rapid that that degradation is bound to occur, independent of electron acceptor, given favorable conditions of pH etc. One question that has not yet been addressed in the text, but seems obvious to me, is the impact of the gasoline components on ethanol degradation. Some of the compounds in gasoline, at higher concentrations, are inhibitory. The question of how rapid ethanol degradation will be in gasoline/ethanol spill, as compared to just ethanol, should be addressed.

Response: We agree that this is an important issue that should be addressed by further research.

Comment 4: Later on this page, the authors suggest that ethanol degradation may be favored over degradation of compounds such as benzene. In wastewater treatment plants, where ethanol is considered so degradable that one doesn't worry about it very much, its presence will inhibit other degradation almost completely. In fact, the microbial populations can change so much in the presence of ethanol that physical properties change sufficiently to impede the process. The hydraulic conductivity of the soil and retention of gasoline components could be changed for the worse. A scenario comes to mind where degradation of the more toxic compounds in gasoline is reduced because organisms degrading ethanol out compete gasoline-degrading organisms, and deplete available nutrients and the most desirable electron acceptors.

Response: Comment noted. This information will be useful in designing future laboratory research experiments.

Comment 5: On page 3-14, the authors report toxicity o ethanol. My own experience, of microbial reactors degrading ethanol using nitrite and nitrate as electron acceptors, is that inhibition begins at about 4% EtOH concentration (e.g., 40,000 mg/L). This is for an acclimated culture. A non-acclimated culture can be inhibited at much lower concentrations.

Response: Comment noted. This information will be useful in designing future laboratory research experiments.

Comment 6: I see (Section 3.4.2.1) that the authors have also thought about a highly degradable substrate depleting nutrients and oxygen.

Response: Comment noted. This information will be useful in designing future laboratory research experiments.

Comment 7: Methanogens are not inhibited equally by all VFA's. Acetate is the least inhibitory. The pioneering work of McCarty describing anaerobic digesters is still generally accepted. However, his values of VFA's (measured in the days when Gas and Liquid Chromatography could not be routinely used), are predominately acetic acid. Several hundred mg/L of propionate can be more inhibitory that several thousand mg/L of acetate.

Response: Comment noted. This information will be useful in designing future laboratory research experiments.

Comment 8: On page 3-17 the authors speculate on methane production and the production of gas bubbles. We have some experience here that may be helpful. Anaerobic digesters, typically treat biosolids in the 3 to 8% range and produce gas, on a dry basis that is 65% methane and 35% carbon dioxide, with traces of other gases. The rates of production of carbon dioxide and methane are equal, but sufficient carbon dioxide dissolves to elevate the gas phase methane mole fraction. For low strength applications, the dissolved methane, even though it is a sparingly soluble gas, becomes important, and very little methane is observed in the gas phase. For systems treating 200 to 300 mg/L of COD, methane mole fraction is very low, under 20%. The nitrogen is not displaced, which accounts for the remainder of the gas.

Response: Comment noted. This information will be useful in designing future laboratory research experiments.

Comment 9: I question the value of Table 3-3. Various conditions mean different things. In reactors acclimated to ethanol, 100 mg/L can be degraded in a matter of hours, for both aerobic and anaerobic conditions. The table needs to be more restrictive. Also it seems to conflict with Table 3-2 (even though they are from the same reference). What is the difference between carbon dioxide as an electron acceptor in 3-2 and methanogenic conditions in 3-3? The rate coefficients do not correlate between the two tables. The products of λ and half-lives agree in Table 3-2; however, applying the values of l in Table 3-3 produces removal rates of 78, 80, 89, 92 and 77%. The rates for sulfur and carbon dioxide reducing conditions are reversed. It takes longer in Table 3-3 than in Table 3-2. Perhaps these are associated with the original reference, but even so, it needs to be clarified. I suspect most of these differences have simple explanations and are not out right errors, but they should be corrected or explained.

Response: Table 3-3 has been omitted and the text edited to improve clarity.

Comment 10: An effect not considered in the report is the content of biodegradable organic carbon in drinking water. Recent work in disinfection of potable waters has stressed the importance of removing biodegradable organic carbon (e.g. BDOC) from drinking supplies. The premise, which seems correct, is that indicator organisms and pathogens can persist or regrow in distribution systems in the presence of substrate. BDOCs in the range of 200 ug/L become important. EtOH would probably be an excellent substrate for regrowth. If potable water supplies are contaminated with EtOH, a consequence, which may not be apparent, is greater difficulty in disinfection.

Response: Comment noted.

Volume 4, Chapter 4 Comments:

Comment 1: This chapter needs a small conclusion.

Response: To facilitate the California Environmental Policy council's review of important decision making information, the summary conclusions and recommendations for further research have been gathered into a separate chapter, Chapter 9. *Critical Knowledge Gaps Regarding the Surface Water and Groundwater Impacts of Ethanol-containing Gasoline and Recommendations for Further Research.*

Comment 2: Graphs in color would be helpful.

Response: Figures are intentionally developed to be duplicated in black and white copiers. Color figures often do not copy in black and white well.

Volume 4, Chapter 5 Comments:

Comment 1: The introduction of this chapter might be shortened a little. This is not critical, but would improve the review. The current introduction was written as if the chapter were "stand alone."

Response: Comment noted, but no changes were made to text because authors felt it important that the chapter does stand alone, if necessary.

Comment 2: When I first started reading this review, I was expecting to see something of the relative risks of EtOH and the alternatives in this chapter. Perhaps it has been written before, but I think it would be useful to say something about the relative risk of MTBE and ethanol in drinking water. One could provide the risk of drinking water associated with the measured values of MTBE in water supplies. Perhaps Santa Monica groundwater would be a good choice. Then the authors could compare this risk with the risk of ethanol-contaminated water risk. The chapter now does a good job of trying to project EtOH concentrations for various conditions; however, there is no mention or way of understanding just how much risk is associated with MTBE, EtOH and the "do nothing" alternative (e.g. ordinary gasoline). The writers of this section are familiar to risk assessment; therefore they should be able to do this with relative ease.

Response: We agree with this comment in principle, but did not perform the suggested analysis because “quantifying health risk” was not the objective for Chapter 5 or Chapter 6, but such risk analyses certainly should be done comprehensively in the future. Nevertheless, we have added a statement to Section 5.6 (Summary), that generally links our results to health-protective concentrations for MTBE and ethanol in drinking water summarized by the State of California Environmental Protection Agency, Office of Environmental Health Hazard Assessment (CalEPA/OEHHA) in *Volume 5: Potential Health Risks of Ethanol in Gasoline* of this report.

Volume 4, Chapter 6 Comments:

Comment 1: The cover page is different.

Response: Comment noted.

Comment 2: What about the relative risk of alkylates? It makes sense to study their transport, but what are the risks associated with ingestion? The authors state they may not be so degradable. I think more information is needed to indicate whether these compounds are more or less risky that MTBE. If we do not know the risks, then we need to say it.

Response: No information is available on the chronic effects of isooctane—a major alkylate component—in humans. At acute doses, isooctane is a nervous system depressant, as are many other hydrocarbon solvents. *A priori*, there is no reason to believe that alkylates will affect—much less increase—the overall toxicity of gasoline. As a matter of fact, this is a complex problem because an increase of alkylate percentage implies a decrease in the percentage of other hydrocarbons (e.g. BTEX) and toxicity should be evaluated in an integral manner. The low solubilities of alkylate components in water and their high Henry’s law constants seem to suggest that vapor venting would be a viable cleanup strategy. (Also see Dr. Holden’s general comment on Chapter 6).

Volume 4, Chapter 7 Comments:

Comment 1: I suggest separating Table 7-1 into useful and non-useful methods by placing a bold line across the table and putting less useful methods below it. A column could be eliminated. Also change ppm to mg/L or appropriate unit. Are there no LC methods? I would have guessed a normal phase LC might be useful.

Response: Editorial comments noted. No information was found in the course of our literature search on the use of liquid chromatography (LC) techniques for analyzing ethanol. Further development of these methods may be useful.

Comment 2: The distinction of “useful” seems to be based upon detection limit. What about detection of EtOH in gasoline? Isn’t it conceivable that a researcher might want to determine the EtOH in a field sample from a spill? This might be an analysis for percentage EtOH concentrations, as opposed to very low concentrations. There is no method listed for this application.

Response: Our review considered only the measurement of environmental concentrations of ethanol. While we acknowledge that methods for the detection of high (percent) concentrations of ethanol in gasoline are currently used by the gas industry, we chose to focus on methods which could be used to access the impact of ethanol to the environment and which could be used to determine ethanol contamination of water supplies.

Volume 4, Chapter 8 Comments:

Comment: This chapter came last, after Chapter 9, but potentially is the most useful in understanding the overall risk. I have not had time to review the methodology, so I cannot critique its validity, but if I assume it is correct, the results provide a basis for more quantitative decision making. If one couples the probabilities of spills reaching wells with risk associated with specific concentrations in drinking water, one has a method to show that ethanol is or is not riskier than MTBE. If future work is to be done by this group on this problem, continuing the work from this chapter is a good starting point.

Response: We agree with this comment.

Volume 4, Chapter 9 Comments:

Comment 1: This chapter is almost a conclusions or executive summary of the earlier chapters. Consider using "conclusions" or similar word in a modified title.

Response: Comment noted. A title change in this chapter is not possible at this time. Such a change would have significant impact on meeting the December 31, 1999 deadline for submittal of this report to the California Environmental Policy Council.

Comment 2: Section 9.3.4.2 might be a good place to put risk information mentioned earlier. The average reader (I do not) will not know the risk of 10 ug/L of ethanol.

Response: Issues of risk to human health are covered in Volume 5: Potential Health Risks of Ethanol in Gasoline.

Comment 3: I generally agree with the conclusions and recommendations in this chapter. It in the second mailing, but it would have been useful to read first, before the other chapters. I have a couple of other suggestions. The first is to continue to look for information on previous spills. Perhaps there is some foreign information that might be useful. I do not know how long you had to develop this review, but I suspect it was relatively short. Given such time, it is unlikely to that you had time to conduct a through search. An approach might be to identify researchers who might have encountered ethanol spills from their publications. The references from each chapter are a starting point. Next go through each set of authors to identify senior authors who might have experience will spills. Next write or email them. The second is more specific. I think it might be easier to develop an extraction (SPE) and LC technique that might be a better than a GC approach (I do not recommend eliminating the GC approach).

Response: We agree with these suggestions.

10.1.3. Dr. Michael R. Hoffman, Executive Officer of Environmental Engineering Science, James Irvine Professor of Environmental Science, California Institute of Technology.

Professor Hoffmann received his B.S. from Northwestern University in 1968 and his Ph.D. from Brown University in 1974. Professor Hoffmann has been active in the subject areas of applied chemical kinetics, aquatic chemistry, atmospheric chemistry, catalytic oxidation, heterogeneous photochemistry, sonochemistry, pulsed plasma chemistry, and hazardous waste treatment. His recent research has been focused on the development of advanced technologies for water and wastewater treatment. These approaches involve the application of metal-catalyzed autoxidation, semiconductor electrocatalysis and photocatalysis, ultrasonic irradiation, pulsed-plasma discharges, and the use of highly potent oxidants, such as hydrogen peroxide, ozone, perosymonosulfate, and periodate for the oxidative and reductive elimination of chemical contaminants from water. His atmospheric chemistry research has been focused on the chemical speciation of iron in clouds and aerosol, on the chemical characterization of aerosols over the remote Indian Ocean and Atlantic Oceans, and on the chemistry of carbonyl sulfide and other sulfur compounds in sulfuric acid aerosol.

Overall Comments

The nine chapters of Volume 4 of the "*Report to the Governor of the State of California in response to Executive Order D-5-99*" collectively represent a very commendable effort to provide a state-of-the-art analysis of the potential environmental impacts of ethanol and ethanol-containing gasoline on surface and ground waters. This volume examines in detail current knowledge pertaining to our understanding of the behavior and eventual fate of ethanol in the aquatic environment. Primary and secondary effects of the intrinsic physicochemical properties of ethanol and the subsurface transport characteristics of gasoline-ethanol mixtures are explored in detail. It is too bad that this type of thorough analysis was not undertaken before the widespread introduction of MTBE into reformulated gasoline. Perhaps some of the current problems related to the apparent persistence of MTBE in the aquatic environment could have been predicted if this type of pre-use analysis had been performed.

Specific Comments by Chapter

Volume 4, Chapter 1 Comments:

Chapter 1 provides a general background perspective on ethanol production, usage, distribution and potential environmental release pathways.

Comment: However, this chapter contains too many ‘gray’ literature references that are not academically satisfying. Some primary refereed literature articles should be included.

Response: The extensive use of ‘gray’ literature reflects the absence of peer-reviewed literature regarding life-cycle issues associated with the use of ethanol as a fuel oxygenate.

Volume 4, Chapter 2 Comments:

Chapter 2 provides a critical review of the effects of ethanol in gasoline on the fate and transport of the BTEX family of compounds in the subsurface aquatic environment. This chapter gives an excellent systematic overview of the physical organic chemistry of ethanol and ethanol-BTEX mixtures with appreciable attention focused on the physicochemical phenomenon of co-solvency. Mass transfer and mass transport considerations are also addressed in a thorough manner.

Comment: However, I question the use of the Greek symbol lamda, λ, to represent the apparent first-order rate constant for biodegradation. Traditionally, microbiologists have used the Monod kinetic terminology of μ (i.e., specific growth rate constant, t^{-1}), μ_{max}, and K_s. Schwarzenbach et al. (Environmental Organic Chemistry, Wiley, New York, 1993), use k_{bio} to denote the apparent first-order biodegradation rate constant. Why the switch away from more conventional terminology?

Response: We used “lambda” for biodegradation because it was used by the Malcolm Pirnie, Inc., report that we were referencing. The monod kinetics would be inappropriate to use here, but k_{bio} could be used in place of λ. This change in notation would require editing a number of chapters to be consistent and do the late receipt of Dr. Hoffmann’s comments, this change has not been made.

Volume 4, Chapter 2, Appendix A Comments:

Comment: On pg. A-1, eq. A-1b: g’s in eq. A-1b should be gamma’s, γ‘s. (i.e., change g into γ).

Response: Comment noted.

Comment: Techniques for the determination of γ for methanol, ethanol, isopropanol, THF, and methanol-hexane mixtures are presented by Pividal et al. in the *J. Chem. Eng. Data*, **37**, 484-487, 1992.

Response: Comment noted. There are many means of estimating gamma.

Comment: It should also be noted that much of Appendix A is repeated verbatim in the main body of chapter 2.

Response: We agree that there is redundancy between Appendix A and the main text, but there is much more detail (approximately three times the length) in the appendix in comparison with the main text. This approach was adopted in order to allow readers who did not wish the detail supplied in the Appendix to nonetheless receive a useful level of detail.

Volume 4, Chapter 2, Appendix B Comments:

Comment: On pg. B-2, pg. 4, ln. 4: Cussler (~~1997~~) should read Cussler (1984).

Response: Comment noted.

Comment: In transforming eq. B6 into B7 explain or justify the formal logic behind the substitution of x = L/4. In addition, some logic is needed in going from eq. B7 to B9. Some assumptions about τ_z and α_z need to be stated to make the aforementioned transformation obvious to the reader.

Response: Comment noted. The “Tau” and “Alpha” transformation are very standard in contaminant transport. We felt that it was too elementary to elaborate further, especially in an appendix.

Comment: Why is the term, $\partial^2 C_i^u / \partial y^2$, ignored is the plume dispersion equation of eq. B11? It is subsequently included in the Appendix of chapter 8. This needs to be explained as a 2-D model. Assumptions in model development should be stated clearly, because later on a 3-D model is presented as the frame of reference for the Monte Carlo analysis.

Response: This is a good comment The two sections should have been made consistent, but unfortunately, due to the late receipt of Dr. Hoffmann’s comments, these editorial changes cannot be made in time to deliver the report on December 31, 1999. However, to clarify that when a two-dimensional model is used (p. B-4, second paragraph), we have edited the following sentence: “Holman and Javandel (1996) extended the complexity of the mass transfer problem in a two-dimensional vertical cross section to include. . . . “

Volume 4, Chapter 3 Comments:

Comment: The initial background material on microbial ecology and metabolism is quite elementary, too lengthy, and perhaps unnecessary given the level of treatment by the authors of the other chapters.

Response: Comment noted. Unfortunately, the author is unavailable to respond due to the late receipt of Dr. Hoffmann’s comments.

Comment: There definitely needs to be a discussion of co-metabolism. The authors define enzymes as “polymers of amino acids.” This definition is overly simplistic and limited. A more realistic definition of enzymes is desirable.

Response: Unfortunately, the author is unavailable to respond due to the late receipt of Dr. Hoffmann's comments.

Comment: The authors state that the average pH of groundwater is 7? If this is in reality true, then the authors need to provide an authoritative reference. The pH of groundwater should cover a much broader range depending on the specific mineral content of the aquifer solids. For example, would the authors expect that groundwater flowing through limestone or calcite to have a pH of 7? The pH of groundwater could vary from pH 5 to 9 depending on local influences and the level of alkalinity.

Response: Author unavailable to respond due to the late receipt of Dr. Hoffmann's comments.

Comment: On pg. 3-7, pr. 3, ln. 4: insert a '**the**' between operate and Krebs (operate **the** Krebs cycle).

Response: Comment noted. Editorial corrections have been made.

Comment: On pg. 3-10, pr. 0, ln. 1: please subscript the naught on concentration (i.e., C_o). This should also be done in eq. 3-3 and in ln. 4.

Response: Comment noted. Editorial corrections have been made.

Comment: pg. 3-10, pr. 4, last line: delete 'removal of' before "alcohol was removed by washing."

Response: Comment noted. Editorial corrections have been made.

Comment: pg. 3-16, pr. 3, sec. 3.4.2.3 on Bioavailability: the authors need to refer back to chapter 2 on co-solvent effects and then re-evaluate their last statement of this section which reads "the extent to which ethanol might hinder these processes, however, is unknown.

Response: Comment noted. Editorial corrections have been made.

Comment: There appear to be some relevant recent references that are missing. For example,

C. Goudar, K. Strevett, and J. Grego (1999) "Competitive substrate (BTEX) biodegradation during surfactant-enhanced remediation," *J. Environ. Eng. ASCE*, **125**, 1142-1148.

F. Domenech, P. Christen, J. Paca, and S. Rehah (1999) "Ethanol utilization for metabolite production by Candida utilis strains in liquid medium," *Acta Biotechnol.*, **19**, 27-36.

J. E. Landmeyer, F. H. Chapelle, P. M. Bradley, J. F. Pankow, C. D. Church, and P. G. Tratynek, (1998) "Fate of MTBE relative to benzene in a gasoline-contaminated aquifer (1993-98)," *Ground Water Monitoring and Remediation*, **18**, 93-102.

Another useful reference source for ethanol metabolism is available at http://www.labmed.umn.edu

Response: Unfortunately, the author is unavailable to respond due to the late receipt of Dr. Hoffmann's comments.

Volume 4, Chapter 4 Comments:

Chapter 4 focuses on the determination of the effects of ethanol on benzene plume lengths in the subsurface.

Comment: Why were the calculations done in terms of the somewhat archaic BOD instead of more relevant compound-specific transformation rates?

Response: BOD, reflecting electron acceptor depletion as a result of ethanol transformation, is a convenient means for quantifying the total electron acceptor demand at some location in the model. We can assume that the rate of benzene transformation will be inversely proportional to the BOD to some extent (based on the abundant literature from field and laboratory studies suggesting this, as well as simple thermodynamic arguments), hence the inverse correlation between the benzene biotransformation rate and the BOD in the model. We do not understand what is meant by relying on compound-specific transformation rates; these data for different redox regimes in the presence of ethanol is not available.

Comment: There are two consecutive pages numbered as the same 4-7. The second in that series should be 4-8.

Response: Comment noted.

Comment: Why were the calculations done in English units. Metric units would have been more appropriate. In addition, IUPAC approved chemical units should have been used throughout.

Response: This was to maintain consistency with other studies that also used English units.

Volume 4, Chapter 5 Comments:

Chapter 5 addresses potential problems associated with ethanol-containing gasoline usage and its possible effects on surface water resources.

Comment: I would prefer to see in eq. 5-1, units of concentration in rain in terms of moles / L or μM, air units in moles / m^3 and pressure in units of atm (atmospheres).

Response: Preferred units have been added to text. However, it is agreed that Equation (5-1) could be simplified, but in its present form yields units that the authors feel are more representative and perhaps useful. Therefore, Equation (5-1) was not changed.

Comment: On pg. 5-5, eq. 5-5: Something appears to wrong with eq. 5-5 as written. The use of the factor of 10^6 in the denominator needs to be explained better. In Jobsen's paper (*vide infra*), C_u is defined as the unit concentration with units of reciprocal time, which is 10^6 times the observed river concentration at a particular cross section times the river discharge divided by the total mass to pass the cross section. The units used in the glossary below eqs. 5-5 and 5-6 differ from the units used in the subsequent paragraphs. For example, in the written paragraphs Q is in m^3/s while in the glossary it is given in L/s. The original paper by Jobsen (H. E. Jobsen, "Predicting Travel, Time, and Dispersion in Rivers and Streams, *J. Hydraul. Eng.*, **123**, 971-978, 1997) uses units of m^3/s.

Furthermore, in the subsequent paragraph's river velocity, v, is given in km/h while in the glossary v is in units of m/s. What further transformations did the authors of chp. 5 make to arrive at eq. 5-5? Please check for self-consistency. Also, the authors should reference the formal Jobsen paper (*vide supra*).

Response: Comment noted. We followed the methodology described in the technical report by Jobs"o"n (1996). The factor of 10^6 shown in Equation (5-5) arises from the fact that Jobson (1996) arbitrarily defines the "unit concentration" (identified now as k_{pc} in Equation (5-5) as 10^6 times the concentration produced in a unit discharge due to the injection of a unit mass of substance. Jobson (1996) further relates the "unit concentration" to a mass flux of solute (mass/time) per unit of mass injected. This statement now appears as a footnote to the new term in Equation (5-5), "nf" that replaces $1x10^6$. The journal article cited by Dr. Hoffmann in his comment was not available at the time this chapter was prepared.

Comment: On pg. 5-8, eq. 5-7: I believe that there is a factor of 10^9 missing from the numerator of eq. 5-7. For example, the LHS of this equation has units of μg's while the input, E_r, on the RHS of the equation is in kilograms per day, kg/d. Thus, there are 10^3 g per kg and 10^6 μg's per g yielding the factor of 10^9.

Response: The calculations were performed correctly using Equations (5-7) and (5-8); however, a units conversion factor was omitted from Equation (5-7) (typographically). That conversion factor has been restored and is noted as "cf", which is equal to 10^9 μg/kg.

Volume 4, Chapter 5, Appendix C-1 Comments:

Comment: On pg.C-4, pr. 1., ln. 4: the i.e. needs a **comma** after it (e.g., i.e.**,**).

Response: Comment noted, and the paragraph has been changed. There is no longer an (i.e.,) starting parenthetical statement and instead (that is, …) now appears.

Comment: On pg. C-5, pr. O, last line: It would be nice to actually know the analytical methods employed (not just a personal communication from an unknown person) and the QA/QC procedures used to have any faith in the numbers presented.

Response: Comment has been addressed by adding additional analytic method and QA/QC information following the statement "personal communication citation (Koester, 1999)".

Volume 4, Chapter 6 Comments:

Chapter 6 deals with the possible environmental consequences of an increased usage of branched alkanes as additives.

Comment: On pg. 6-3, pr. 2, ln. 2: 'registry number' should read registry number**s**.

Response: Comment noted.

Comment: On pg. 6-4, pr. 1, eq. 6-2: The units of equation 6-2 are not given. The terms are defined but the units are missing. They should be given.

Response: The units of Equation (6-2) have been added.

Comment: pg. 6-5, pr. 2, ln. 7: In urban, near urban, and continental regions, the hydroxyl radical concentrations on average may be 10^7 molec cm^3 or higher. Thus, the projected lifetimes of isooctane and related molecules would be shorter by a factor of ten. The mean global OH concentration may not be the most appropriate in this case.

Response: Good comment. The text of this Chapter 7 section has been modified to reflect this comment.

Comment: The authors of this Appendix should reference the book by Schwarzenbach et al. (1993).

Response: This comment is unclear. There is no appendix in Chapter 6.

Chapter 7:

This chapter addresses the need for appropriate analytical methods for the precise, accurate, and reliable determination of ethanol in natural water samples.

Comment: This chapter is the least thorough and least satisfying of Volume 4.

Response: Comment noted. This points to the lack of good analytical methods for trace-level ethanol analysis.

Comment: One obvious analytical technique that was not mentioned is APS-ES-MS (i.e., atmospheric pressure ionization electrospray mass spectrometry). It may also be possible to couple APS-ES-MS with HPLC to determine ethanol at extremely low concentrations (See: Nishikawa et al., *J. Chromatogr. B,* **726**, 105-110, 1999).

Response: Ethanol is not usually considered to be a candidate for LC/MS analyses--primarily because it is volatile and detected easily by GC/MS. It appears from examining the complete title of the article that LC/MS is used primarily for the analysis of ethyl glucuronide (ethanol's metabolite). However, LC/MS might merit additional investigation as an analysis technique because it might eliminate the necessity of extraction prior to GC/MS analysis.

Comment: It may also be possible to employ Laser Raman spectroscopy (see: Giles, et al., *J. Raman Spectroscopy,* **30**, 767-771, 1999), FT-NIR, or FT Raman Spectroscopy for the determination of oxygenates (see: Choquette et al., *Anal. Chem.*, **68**, 3525-3533, 1996).

Response: The primary objective of Chapter 7 is to review methods applicable to the routine analysis of ethanol in environmental waters. The above reference discusses the use of Raman spectroscopy to "determine whether near-IR and/or Raman methods could quantitate oxygen species in SRM (standard reference material, i.e., gasolines) ampules." While this method might be amenable to quantitate percent concentrations of ethanol in gasoline, it probably would not be suitable to the determination of trace quantities of ethanol in water (Raman spectroscopy is not a very sensitive technique). For this reason, the reference was not included in this chapter. In addition, we realize that there exist some papers describing the use of nuclear magnetic resonance (NMR) spectroscopy for the determination of oxygenates in fuel--however, these references were also omitted because they did not pertain to the analysis of ethanol in environmental waters.

Comment: Another recently reported technique for the determination of ethanol in water uses a gold-coated unclad optical fiber system (see: Misushio and Kamata, "Alcohol analysis using a gold-coated unclad fiber sensor system," *Bunseki Kagaku*, 48, 757-762, 1999).

Response: This article is written in Japanese and would require translation. To meet the required report delivery date of December 31, 1999, our literature search was biased towards the selection of articles that were written in English.

Volume 4, Chapter 8 Comments:

Chapter 8 focuses on the use of a detailed Monte Carlo analysis of the dispersion equation employed in Chapter 3 to analyze the parametric effects of a variety input variables on the BTEX plume lengths.

Comment: On pg. 8-11: Were any variations in the solids/mineral characteristics factored into account in this analysis? Was the sensitivity of the plume length (vis-à-vis retardation) on the organic carbon content (OC) of the aquifer solids examined?

Response: Stochiometric calculations were not assessed in this section (although this method is discussed in McNab and Dooher, 1998) due to, what we believe are, a reasonable approximation of the degradation population associated with benzene throughout California. Details of these rates are available in references provided in Chapter 8. Retardation is one of the sensitivity parameters examined. Please see the response to Dr. Hoffmann's comment on Table 8-2, below.

Comment: On pg. 8-14, Section 8.5 Conclusions: A summary of the effects of variations in parameter space on plume lengths and durations should be presented.

Response: This is discussed in detail in Dooher, 1998.

Comment: On Table 8-1 – no page number given: Units must be given for each term in the glossary of parameters given in Table 8-1.

Response: The program described used metric units, which were then translated into English for uniformity of the presentation of results.

Comment: On Table 8-2 – no page number given: The fractions of organic carbon, f_{OC}, seem to be too low. Are they truly realistic for a typical California subsurface environment?

Response: These data were developed from several sources. The distribution itself was developed in Dooher (1998) from data collected around the Lawrence Livermore National Laboratory (LLNL) Superfund site. This data was compared to data compiled in Domenico and Schwartz (1990) for a 'reality check.' The maximum organic carbon described therein is a 0.0226 measurement from a river sediment environment, described as fine silts, at Oconee River (exact location unknown). The author attempted to contact the one of the originator's of these measurements to get more information, but the source was generally unresponsive. Others in the Ontario area ranged from 0.00017 to 0.00102—all in glacial-fluvial environments, ranging from sands and gravels to fine sands. A measurement of 0.01 was referenced from Palo Alto Baylands, California, described as a silty sand. LLNL's environment is alluvial, encompassing many soil types, and is typical of coastal valleys in California. Although the 99th percentile for that environment is approximately 0.01, we believe it is representative of a great number of sites in California. We could expand the distribution as part of future work, but this should have little effect on the potential for well impacts, especially for MTBE. Of greater importance is knowledge of the LUFT site's maximum concentration.

Volume 4, Chapter 9 Comments:

Chapter 9 summarizes the apparent knowledge, science, and engineering gaps that need to be bridge to provide a more reliable assessment of the potential aquatic impacts of gasoline containing ethanol.

Comment: On pg. 9-3, pr. 1, ln. 4: Although California has 'implement**ed**' improved

Response: Comment noted.

Comment: On pg. 9-3, pr. 2, ln. 1: This is a bad sentence. Perhaps it can be salvaged as follows:

"An important consideration, which is related to the decision to use ethanol, is the potential effect that it may have on the fate and transport of toxic gasoline components."

Response: Comment noted.

Comment: On pg. 9-6, pr. 1, ln. 4: 'adaptedto' should read, "**adapted to**"

Response: Comment noted.

Comment: On pg. 9-6, pr. 2, ln. 7: 'transitionsin' should read, "**transitions in**"

Response: Comment noted.

Comment: On pg. 9-6: The possibility of co-metabolism should be noted.

Response: We have discussed lack of information regarding the effect of ethanol on microbial population shifts (that is, microbial ecology) and the resulting catabolic diversity. We indicate that among the possible effects are enrichment of ethanol-degrading bacteria in relation to BTEX-degrading bacteria, fortuitous enrichment of bacteria that can degrade (co-metabolize) both ethanol and BTEX compounds, and decreases in populations of certain bacteria as a result of toxicity.

Comment: On pg. 9-11: I would favor APS-ES-MS techniques for ethanol determination.

Response: Comment noted.

10.2. Public Review Comments

The following responses address external review comments on the draft State Water Resources Control Board (SWRCB) Volume 4, "Potential Ground and Surface Water Impacts", which is part of the report to the California Environmental Policy Council titled, "Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate." The following Organizations and individuals have submitted comments:

Michael C. Kavanaugh, Ph.D., P.E., and Andrew Stocking, P.E., Malcom Pirnie, Inc.; Western States Petroleum Association;

10.2.1. Michael C. Kavanaugh, Ph.D., P.E., and Andrew Stocking, P.E., Malcolm Pirnie, Inc.: Comments and LLNL Responses

I recently attended the public workshop in Sacramento regarding the fate and transport of ethanol in the environment. As part of the public comment process, we are providing written comments to you on issues that we recommend should be further addressed in the study being conducted by the Lawrence Livermore National Laboratory (LLNL).

Malcolm Pirnie, Inc has been retained by the American Methanol Institute to prepare these comments on the LLNL analysis of potential impacts of the use of ethanol in gasoline on the fate and transport in groundwater of other constituents in gasoline, namely the aromatic compounds, benzene, toluene, ethylbenzene and the xylenes (BETX). We believe that these comments will help to clarify and expand the LLNL conclusions presented at the Sacramento public workshop regarding impacts on the BETX plumes due to the use of ethanol-blended gasoline.

Using a screening-level model, LLNL concluded that the use of ethanol-blended gasoline could extend BTEX plumes by approximately 25%. These results presented by LLNL are consistent with two other recently completed modeling efforts to assess this issue. As referenced in the LLNL presentation, Malcolm Pirnie completed a detailed analysis of ethanol fate and transport in the environment last year entitled, “Evaluation of the Fate and Transport of Ethanol in the Environment.” Included in that analysis was a preliminary modeling evaluation of the effect of 10% ethanol in gasoline (gasohol) on the fate of BETX plumes.

The Malcolm Pirnie report concluded that a primary disadvantage of adding ethanol to gasoline is the potential impact of ethanol biodegradation on the natural biodegradation of other gasoline constituents present in the groundwater. Ethanol is known to readily biodegrade under a variety of aerobic and anaerobic conditions. Under these conditions, ethanol is a preferred substrate and will be preferentially utilized in the presence of BTEX. However, as ethanol is aerobically biodegraded, oxygen and other electron acceptors, as well as nutrients will become depleted in the groundwater. As a result, BTEX plumes may be lengthened due to the delay in biodegradation in the presence of ethanol. Based on modeling results, the presence of ethanol is expected to increase BTEX plume lengths by approximately 27% under typical California groundwater conditions (ranging from 16% to 34% increase in BTEX plume lengths). The potential impact of increasing BTEX plume lengths is either a greater probability that drinking water well fields could be impacted by BETX or higher BTEX concentrations at wells that are already contaminated. Additional migration of the BETX plumes could also cause greater property damage due to plumes extending beyond the boundaries of the source property. These impacts would result in higher cleanup costs for BTEX plumes, if cleanup is warranted.

Finally, the University of Waterloo, Ontario, Canada has recently completed a modeling effort to evaluate the use of ethanol-blended gasoline on gasoline in groundwater. Preliminary results from this research have been presented at the National Ground Water Association meeting in Houston, Texas, 1999 at the Petroleum Hydrocarbon Conference. This study concludes that the use of ethanol in gasoline could extended BTEX plumes 24 to 33%. Thus, three independent assessments using different groundwater modeling approaches have reached similar conclusions regarding the impact of ethanol on BTEX plumes, namely, that BTEX plumes may be extended 24 to 33%.

A second scenario not evaluated in the Malcolm Pirnie report or the LLNL analysis, but of importance for fully understanding the impact on groundwater of the use of ethanol, is the expected BTEX plume elongation resulting from a release of pure ethanol onto an existing BTEX plume with some residual gasoline containing BETX in the soil or groundwater. The University of Waterloo has also presented preliminary results from this research at the National Ground Water Association meeting in Houston, Texas, 1999 at the Petroleum Hydrocarbon Conference. The Waterloo model evaluated the effects of increased benzene dissolution, rapid depletion of electron acceptors due to the biodegradation of ethanol, and more rapid ethanol biodegradation rates. The scenario involved a release of pure ethanol onto a 10-year old BTEX release. The results indicate that BTEX plumes could be elongated from 55% to 142%, relative to non-ethanol conditions. The highest BTEX elongation occurred in soil with low organic carbon content, which results in limited retardation of the benzene in the groundwater. Results from Waterloo suggest that BTEX plume elongation will increase as the contact time between the ethanol and BTEX increases, i.e., the longer ethanol remains in contact with the BTEX plume, the more the BTEX plume will elongate.

The results from these evaluations of ethanol’s impact on BETX plumes pose two questions. First, are these predicted BTEX plume extensions significant? Second, are there limitations with these modeling efforts that may underestimate the actual impacts under field conditions? The following presents a list of three factors that have not been addressed in any of the modeling analyses, which could result in BTEX plumes extending beyond what has been predicted in these three modeling studies.

1. Due to the complexity of modeling real systems, all of the models have ignored subsurface heterogeneities, which may prove to be their most significant limitation. Subsurface heterogeneities can result in preferential groundwater pathways, where the impact of ethanol on BTEX compounds is unknown. Similarly, the fate of BTEX compounds in fractured bedrock is likely to change when exposed to ethanol. Under both of these conditions, i.e., preferential pathways and fractured media, groundwater velocities are high and the fraction of organic carbon is low. Under these conditions, the Waterloo results suggest that BTEX plumes could be extended up to 142 % of the plume length without ethanol compared to the 30-50% predicted by models that ignore preferential pathways.

2. A second factor that could result in further elongation of BTEX plumes occurs when multiple discrete releases of gasohol occur over several years. Under these conditions, ethanol will be released in pulses to the subsurface over a period of several years and thus, will remain in contact with the BTEX over several years. As the Waterloo results suggest, a long contact time between ethanol and BTEX could lead to increased BTEX plume elongation.

3. Due to the lack of field data to verify modeling, dissolution kinetics of gasoline in groundwater have been estimated from controlled lab, modeling, and limited field experiments. Based on an evaluation of the properties of ethanol, ethanol dissolution should occur very quickly under ideal mixing conditions; however, if dissolution occurs slowly, ethanol will remain in contact with BTEX longer and BTEX plumes may experience greater elongation. A similar issue has been addressed with respect to MTBE. One would expect MTBE to dissolve from the source area rapidly, resulting in detached MTBE plumes. However, in the field, MTBE plumes remain attached to the source for extended periods. Recently, Dr. Bill Rixey at the University of Houston estimated that over 100 pore volumes could be required for complete MTBE dissolution in a heterogeneous source area with minimal groundwater/NAPL interfacial contact. Ethanol is expected to behave similarly to MTBE in heterogeneous environments, and thus, ethanol dissolution may occur over a much longer period than theoretically predicted.

Each of these factors could result in BTEX plumes that are extended beyond their non-ethanol maximum length. The relevant question is whether these elongated BTEX plumes are more likely to impact drinking water wells. We suggest that this issue should be addressed quantitatively by the LLNL study.

In conclusion, there are significant unknowns regarding the real impact of ethanol on BTEX plumes; however, it is generally acknowledged that the use of ethanol in gasoline will extend BTEX plumes. Three independent modeling assessments have consistently concluded that the use of ethanol-blended gasoline will extend BTEX plumes 24 to 33% on average, relative to gasoline without ethanol under presumed homogeneous aquifer conditions. In addition, modeling results at the University of Waterloo suggest that a pure release of ethanol on an existing BTEX plume could extend the BTEX plume up to 142%, relative to non-ethanol conditions. As noted, however, it is likely that release and subsurface factors exist where BTEX plumes could be extended even further. Thus, the use of ethanol in gasoline and the increased transport of pure ethanol are expected to increase the probability of detecting benzene in drinking water wells as well as exacerbating property impact issues. We therefore recommend that LLNL carefully consider the potential impacts of these findings on costs of soil and groundwater cleanup in California, and on the potential for impacts of drinking water wells. The effects of heterogeneous aquifer conditions on BETX plume lengths in the presence of ethanol should be further evaluated. Finally, the potential impacts on groundwater quality of denaturants that must be added to ethanol should be considered to provide a more comprehensive assessment of the relative merits of ethanol in gasoline compared to other options.

Response: The observation that the various modeling efforts referenced in the comment all indicate approximately the same general results for predicted benzene plume behavior in the presence of ethanol is important. These similar results in spite of the different modeling approaches taken, suggests that there is an important common assumption in the modeling that dominates the results. This common assumption is likely associated with the interaction of biodegradation rates between ethanol and benzene. All the models referenced assume that there is no biodegradation of benzene within the ethanol groundwater plume and that once benzene migrates beyond this ethanol biodegradation zone, that a constant benzene biodegradation rate can be applied. These assumptions are made because very little is known about the spatial distribution of degradation rates with either ethanol or benzene groundwater plumes.

Because the biodegradation factors may be a dominant factor, it is important to note that, if biodegradation of benzene is later found to be occurring within the ethanol biodegradation zone, or if benzene biodegradation rates are higher at the margins of the benzene groundwater plume, then benzene plumes lengths measured in the field could be much shorter than the referenced modeled predictions.

Fracture flow is very unpredictable and is difficult to compare to a benzene plume in sedimentary porous media. It is important to recognize that the issue of fractured flow raised by the comment is also true for MTBE. The significant difference between benzene and MTBE is that benzene will likely biodegrade in a much shorter period of time compared to MTBE and, thus, will not travel as far through fractured flow as MTBE.

Regarding the dissolution rates of ethanol, if dissolution is slower, then the concentrations of ethanol in the aqueous phase will be very small and will have relatively little effect. There should be almost no cosolvency effect. The impact on biodegradation will depend on how fast the electron acceptors are replenished. It is premature to attempt to quantify the significance of these effects, but a comprehensive modeling study will address some of these concerns.

Regarding the comparative dissolution of MTBE, there are some very different properties between ethanol and MTBE that could result in vastly different dissolution rates. First of all, ethanol is completely miscible with water. This results in a much higher driving force for mass transfer than for MTBE and, therefore, a higher flux. Secondly, preliminary results suggest that free convection is an important mechanism that increases the flux of ethanol from the gasoline to the water. This phenomenon results from the higher density of ethanol than standard gasoline. MTBE, on the other hand, has a density very similar to gasoline and would, therefore, not be subject to this transport mechanism. The net effects of these phenomena are unknown. It might be true that ethanol dissolves slower in a natural setting than in a laboratory column although the differences described above illustrate that we cannot extrapolate the behavior of MTBE to ethanol.

10.2.2. Western States Petroleum Association (WSPA): Comments and LLNL Responses

The Western States Petroleum Association (WSPA), is a nonprofit trade association, representing approximately 30 companies that explore, produce, transport, refine and market petroleum and petroleum products in the six western states.

WSPA has reviewed the eight chapters[1] of Volume 4 prepared by Lawrence Livermore National Laboratory (LLNL) that were posted on the World Wide Web on

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[1] Chapters 1-7 were read, as was Chapter 9. At the time of this review, Chapter 8 was not yet available. Once Chapter 8 becomes available, WSPA and other reviewers will need adequate time to provide review and comment.

12/10/99. WSPA has several general concerns regarding these water chapters, and they are as follows:

Cover Letter Comment 1: The Volume is a useful and accurate compilation of the data available to date. However, there are numerous knowledge gaps, uncertainties and data gaps identified in the eight Chapters which we believe need to be addressed. Indeed, in Chapter 9, LLNL lists over 20 significant knowledge gaps identified throughout the Volume. WSPA agrees that these gaps exist, and that additional research is needed to fill them. Collectively, these gaps reflect the uncertainty in many of the water analyses presented in this Volume. WSPA is concerned that ethanol data, in general, is quite limited at this time. WSPA also believes there are additional gaps which were not mentioned in Volume 4, including:

a. UST compatibility

b. Distribution system changes required for ethanol

c. Ethanol remediation & treatment, and

d. Impacts of benzene plume elongation.

We encourage the State to continue to seek answers to these and other issues. In that regard, WSPA and its members are committed to assist the SWRCB in answering some of these outstanding concerns.

Response: We agree that additional knowledge gaps exist and UST compatibility, distribution system changes required for ethanol, and ethanol remediation and treatment need to be addressed. These are among the issues have not been addressed as part of this evaluation because of time constraints to meet the required report delivery date of December 31, 1999. The evaluation of these would be included in a complete life-cycle analysis.

A preliminary analysis of the impact of possible benzene plume elongation in the presence of ethanol is presented in Chapter 8, which WSPA had not reviewed at the time these comments were prepared.

Cover Letter Comment 2: Not all of the Chapters have a definitive “Conclusion” or “Summary” section. Likewise, there is no executive summary or interpretation of Volume 4 as a whole; we believe this to be a significant oversight. As such, the report does not provide a comprehensive overview of the potential water impacts of extensive ethanol use. As with many reports, the executive summary is the most read section of the report. Not having an executive summary can easily mislead the reader who does not have the time or technical background to review the remainder of the report. Lastly, WSPA requests that the executive summary be available for prior review before its presentation to the Environmental Policy Council.

Response: To facilitate the California Environmental Policy Council’s review of important decision-making information, the summary conclusions and recommendations for further research that normally would be part of individual chapters have been gathered into a separate chapter, Chapter 9, “Critical Knowledge Gaps Regarding the Ground and Surface Water Impacts of Ethanol-containing Gasoline and Recommendations for Further Research.”

The Volume 1, *Executive Summary,* has been created using text from the report's technical volumes. This information has been peer reviewed and open for public comment, and no new information has been introduced in the Executive Summary.

Cover Letter Comment 3: Several studies on possible benzene plume length increases due to ethanol usage are discussed, but there is no consideration of the possible impacts of longer benzene plumes. The possible impacts (eg: remediation methodology changes, impacted receptors, altered plume management, legal & policy issues, etc.) must be considered if benzene plumes might indeed become 20-100% longer as the modeling indicates. In addition, it needs to be emphasized in the report that the modeling results should be considered preliminary as they are based on limited laboratory data and not field data.

WSPA believes these concerns are significant and need to be addressed if ethanol is to be used extensively in California for gasoline blending. Specific comments that demonstrate and support the above-listed general concerns are presented in Attachment A. Attachment B is a report recently prepared for WSPA entitled "A Preliminary Evaluation of Ethanol Remediation and Treatment" by Davidson and Creek of Alpine Geophysics. WSPA requests that this report be entered in the record and utilized in the SWRCB studies.

Response: A preliminary analysis of the impact of possible benzene plume elongation in the presence of ethanol is presented in Chapter 8, which WSPA had not reviewed at the time these comments were prepared.

The comment that the modeling results are preliminary and based on laboratory data and not field data is an important one that we agree with. The evaluation of field data will be important to improving the predictive value of future modeling efforts.

Specific WSPA Comments on "Volume 4: Potential Ground and Surface Water Impacts," December 17, 1999

Introduction: WSPA has provided comments on the SWRCB ethanol studies since the initial presentation of the agency's work plans. In extensive written comment (dated 08/24/99), WSPA requested the development of key information, some of which still remains unanswered. A few of those unaddressed issues are briefly reiterated below, but most of our specific comments are new and relate directly to the Volume 4 technical analyses conducted by LLNL and SWRCB. WSPA has focused our comments on major issues and significant data gaps, rather than provide lengthy comments on minor points.

Volume 4, Chapter 2 Comments:

Comment: There is insufficient data (i.e., limited experimental data and extremely limited field data) to fully determine how ethanol will impact several important abiotic subsurface processes.

Comment Explanation: In Chapter 2, the technical review of how ethanol might affect numerous subsurface processes was well done, considering the limited amount of information available. However, there are only a few laboratory studies that directly relate to these ethanol issues, and almost no field studies with which to correlate the limited experimental data. As such, there is still much uncertainty about how ethanol might impact the subsurface fate and transport of gasoline components (e.g., cosolvency, changes in attenuation capacities of soil, alterations of protective clay layers, etc.). These important subsurface processes need to be understood much better if ethanol is to be used much more extensively for gasoline blending.

Response: This comment is also one of the uncertainties identified in Chapter 9, "Critical Knowledge Gaps Regarding the Ground and Surface Water Impacts of Ethanol-containing Gasoline and Recommendations for Further Research." We agree that additional field studies clearly are needed.

Volume 4, Chapter 3 Comments:

Comment: Chapter 3 lacks a conclusion section regarding probable ethanol impacts on BTEX biodegradation.

Comment Explanation: The Chapter 3 biodegradation literature review presents several different reasons why BTEX biodegradation will be delayed, slowed, or inhibited in most subsurface locales when ethanol is present. As a result, it seems likely that BTEX plumes will be lengthened to some degree. When the possible BTEX plume-lengthening effects of co-solvency and reduced retardation are also added in, an increase in BTEX plume length and in plume longevity both seem highly likely. Because no summary, or integration, of all these factors is presented, the discussion is not complete.

Response: A screening analysis of the impacts of ethanol biodegradation on plume length are provided in Chapter 4, Screening Model Evaluation of the Effects of Ethanol on Benzene Plume Lengths and the potential impact of increased benzene plume lengths in the presence of ethanol are evaluated in Chapter 8, Screening Analysis of Potential Groundwater Resource Impacts From Gasoline Containing Ethanol.

Volume 4, Chapter 4 Comments:

Comment: The results of LLNL's modeling effort are not applicable to most ethanol-gasoline spills and most neat ethanol releases.

Comment Explanation: In Chapter 4, the authors present their screening model of how ethanol may impact benzene plume length. Their approach is valid, but only for the narrow set of conditions they model. They did not vary biodegradation rates and they greatly simplified the spatial oxygen deficiency created by the ethanol (i.e., they assumed a high Biological Oxygen Demand due to ethanol degradation only by the source area). Also, only a single spill condition was modeled (an ethanol-gasoline blend release at "less than 3 gallons/day"). As a result, the LLNL modeling results are not applicable to many of the possible release scenarios defined in Chapter 1.

Response: We agree that the screening modeling performed for Chapter 4 is not applicable to many of the possible release scenarios defined in Chapter 1. This release scenario was selected because it is one of the most likely to occur. The other release scenarios have not been addressed as part of this evaluation because of time constraints to meet the required report delivery date of December 31, 1999. The evaluation of these scenarios would be included in a complete life-cycle analysis.

Comment: The LLNL modeling results are not put into context.

Comment Explanation: The LLNL modeling predicted that benzene plumes would get 20% longer (50 feet longer) at the 10-ppb benzene level, and 100% (200–250 feet) longer, when defined at the 1-ppb benzene level. The possible 100% increase in benzene plume lengths (at 1-ppb level) may be the most applicable in California as the benzene MCL is 1-ppb in California. The Chapter should clarify which results of the LLNL modeling effort, and which results of modeling done by others, is most pertinent in California, i.e., the results need to be put into context.

Response: The LLNL model is intended as a screening tool and makes a variety of simplifying assumptions, as does the modeling recently performed by a variety of others. In particular analytical solution treats the dispersion phenomena in a simplistic manner. Caution should be exercised in applying the results of these models too broadly. The screening analysis is for comparative purposes and should not be used for absolute predictions. Predictive analysis pertinent to other release scenarios would likely be part of a more comprehensive life-cycle analysis that we recommend be performed.

Comment: Possible increased benzene plume lengths are not put into context.

Comment Explanation: Several modeling studies on possible benzene plume length increases due to ethanol usage are presented and discussed[2], and the models predict a 20%–100% increase (i.e., 50–250 feet longer than non-ethanol gasoline). The general agreement among the models is promising, but these modeling efforts must be considered preliminary as none could be verified against field data. The significance of the possible (probable) increased benzene plume lengths is not put into context or summarized.

Response: Chapter 8, “Screening Analysis of Potential Groundwater Resource Impacts from Gasoline Containing Ethanol or MTBE,” which WSPA had not reviewed at the time these comments were prepared, places possible increased benzene plume lengths in to context from a resource impact perspective.

Volume 4, Chapter 5 Comments:

Comment: The ethanol concentrations predicted to occur in urban precipitation (37-64 (g/L) imply a strong need for more in-depth research on this topic.

Comment Explanation: Modeling of air in the Los Angeles basin indicates that ethanol concentrations in precipitation could reach 37–64 (g/L. Although it appears that the methods and assumptions used for this analysis are reasonable, it is a preliminary analysis. This important issue requires more in-depth study under a wider variety of conditions, and with temperature-specific Henry’s Constants.

Response: We strongly agree with this point and recommendation.

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[2] Another pertinent study has recently been released: Molson, John W., James F. Barker, Mario Schirmer, and Emil O. Frind, 1999. Modeling the Impact of Ethanol on the Persistence of BTEX Compounds in Gasoline-Contaminated Groundwater, DRAFT, National Water, Resource Institute, Fountain, Valley, CA, 64 pages. That modeling study found generally similar results, but by considering more variables and more different spill scenarios, Molson et al. (1999) predicted that in a few cases, benzene plume lengths could increase significantly more.

Comment: The results of the surface water spill modeling are not well described in the text.

Comment Explanation: After modeling a surface water release of ethanol, Chapter 5 described the impacts as being limited to “immediately downstream.” However, this conflicts with the accompanying graphs that appear to indicate that toxic levels will reach 27 to 33 km downstream. A revised or more detailed discussion is needed of ethanol fate in rivers and streams. In addition, it’s not clear how the fate of ethanol (as predicted by the model) compares to that of other compounds, like MTBE. As such, it’s difficult to judge the significance of the results for ethanol.

Response: To address this comment we have modified the text in Section 5.4.2 to describe the potential extent of downstream toxicity from a catastrophic spill of ethanol.

Volume 4, Chapter 8 Comments:

Comment: Not Reviewed - At the time of this review, Chapter 8 was not yet available.

Response: Chapter 8 was available December 17, 1998.

Volume 4, Chapter 9 Comments:

Comments & Explanations: WSPA agrees with the gaps identified, but WSPA believes there are additional knowledge/data gaps that were not mentioned. Specifically:

- UST Compatibility - This issue was only mentioned briefly in Table 1-1 of Volume 4, and yet it is a critical topic if ethanol-gasoline releases are to be avoided/minimized.
- Distribution System Changes Required for Ethanol - There are numerous procedures that are needed to adapt the gasoline transport, storage and distribution systems (i.e., pipelines and USTs) for ethanol-blended gasoline. These issues, and their costs, should be recognized.
- Ethanol Remediation and Treatment - Volume 4 did not discuss the remediation or treatment of ethanol, whether from a neat ethanol spill, or from a release of ethanol-blended gasoline. To start discussion of this important topic, WSPA has had a preliminary ethanol remediation report prepared[3] (see Davidson and Creek, 1999 in Attachment B).

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[3] In Davidson and Creek (1999), several technologies commonly used at gasoline spill sites were evaluated to determine how effective they would be for remediating ethanol-impacted sites and for treating ethanol-impacted water and soil. The report concluded:

- At the present time, there is very little monitoring, remediation, or treatment data available for ethanol.
- Based on ethanol’s physiochemical properties, and upon the reviewed technologies’ performance on gasoline compounds, the following technologies are expected to be effective for remediating subsurface ethanol contamination: ground-water extraction (for plume control); soil vapor extraction; enhanced bioremediation; and, monitored natural attenuation.
- Biotreatment and advanced oxidation process are both expected to be effective for above-ground treatment of ethanol-impacted water. Conversely, the more common water treatment methods of air stripping and granulated activated carbon are not expected to be effective for ethanol.

- Impacts of Benzene Plume Elongation - Ethanol's presence might make addressing ethanol-enriched gasoline spills more complex or costly if the longer benzene/BTEX plumes mandate a technology change (eg: make natural attenuation less applicable), complicate plume mangement (as the plume expands), raise costs (due to the plume's greater size and volume), or increase the chances of benzene/BTEX impacting a receptor.

Response: We agree that additional knowledge gaps exist and underground storage tank compatibility, distribution system changes required for ethanol, and ethanol remediation and treatment need to be addressed. These are among the issues have not been addressed as part of this evaluation because of time constraints to meet the required report delivery date of December 31, 1999. The evaluation of these would be included in a complete life-cycle analysis.

A preliminary analysis of the impact of possible benzene plume elongation in the presence of ethanol is presented in Chapter 8, which WSPA had not reviewed at the time these comments were prepared.

- The most effective above-ground technologies for treating ethanol-impacted soils are expected to be biotreatment and thermal desorption.
- Until greater fate and transport knowledge of ethanol-gasoline mixtures is obtained, the remediation and treatment of ethanol-gasoline mixtures are difficult to evaluate in detail.

Davidson, James M. and Daniel N. Creek, 1999. A Preliminary Evaluation of Ethanol Remediation and Treatment, prepared for Western States Petroleum Association, Sacramento, CA, 36 pages.

Acronyms, Glossary, and Authors

Acronym List

2D-GC	Two-dimensional gas chromatography
3-D	Three-dimensional

A

ACE	American Coalition for Ethanol
AED	Atomic emission detector
AFDC	Alternative Fuels Distribution Center
API	American Petroleum Institute
AQMD	Air Quality Management District
AST	Above-ground storage tank

B

BG	Block group
BOD	Biochemical oxygen demand
BPJ	Best professional judgement
BRP	Blue Ribbon Panel
BTEX	Benzene, toluene, ethyl benzene, and xylene
BTX	Benzene, toluene, and xylenes

C

CAA	Clean Air Act
CalCVRWQCB	California Central Valley Regional Water Quality Control Board
CAL-DHS	California Department of Health Services
CAL-DWR	California Department of Water Resources
CAL-EPA	California Environmental Protection Agency
CARB	California Air Resources Board
CAS	Chemical Abstract Service
CBG	Cleaner Burning Gasoline (Program)
CEC	California Energy Commission
COC	Contaminant of concern
COD	Chemical oxygen demand
CRFA	Canadian Renewable Fuels Association

D

DL	Detection limits
DOE	U.S. Department of Energy

F

FHC	Fuel hydrocarbon
FID	Flame ionization detectors
FP	Free product

G

GC	Gas chromatography
GC/FID	Gas chromatography with flame ionization detection
GC/MS	Gas chromatograph with a mass spectrometer
GEIMS	Geographic Environment Information Management System
GIS	Geographic Information System

H

HOC	Hydrophobic organic compound

I

IFT	Interfacial tension

L

LC_{50}	Lethal concentration for 50% of a population
LLNL	Lawrence Livermore National Laboratory
LNAPL	Light nonaqueous phase liquid
LOD	limit of detection
LPA	Local primary agency
LUST	Leaking underground storage tank
LUSTIS	Leaking Underground Fuel Tank Information System

M

MC	Monte Carlo
MCI	Maximum contaminant level
MCL	maximum contaminant levels
MIR	Maximum Incremental Reactivity
MRI	Magnetic resonance imaging
MS	Mass spectrometer
MTBE	Methyl tertiary butyl ether

N

NAPL	Nonaqueous phase liquids
NDEQ	Nebraska Department of Environmental Quality
NESCAUM	Northeast States for Coordinated Air Use Management
NIST	National Institute of Science and Technology
NFP	Non-free product
NOM	Natural organic material

NRTL	Non-random-two-liquid (model)
NSTC	National Science and Technology Council

O

OCWD	Orange County Water District
OEHHA	Office of Environmental Health Hazard Assessment
ONWR	Outstanding National Water Resource

P

PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PDF	Probability distribution function
PICME	Permitting, Inspections, Compliance, Monitoring, and Evaluation (database)

Q

QA	Quality assurance
QC	Quality control

R

RFA	Renewable Fuels Association
RFG	Reformulated gasoline
RVP	Reid vapor pressure
RWQCB	Regional Water Quality Control Board

S

SB	Senate Bill
SCVWD	Santa Clara Valley Water District
SPCC	Spill prevention and containment contingency
SPME	Solid-phase microextraction
SRC	Syracuse Research Corporation
SWRCB	State Water Resources Control Board

T

TCE	Tri-chloroethylene
TNC	Transient non-community
TPH	Total petroleum hydrocarbons
TRG	Tahoe Research Group
TRPA	Tahoe Regional Planning Agency

U

UNIFAC	UNIQUAC functional-group activity coefficients
UNIQUAC	Universal quasi chemical
UNR	University of Nevada at Reno

US EPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

V

VFA	Volatile fatty acid
VOA	Volatile organic analysis
VOC	Volatile organic chemicals (BTX, etc.)

W

WQM	Water Quality Monitoring (database)

Ethanol Glossary

Accuracy	The agreement between the measured value and the accepted or "true" value.
Activation	The conversion of nontoxic chemicals to products harmful to humans, animals, plants, or microorganisms
Advection	The principal means of transporting hydrocarbons horizontally away from the gasoline-pool boundary with the flowing groundwater
Aerobic	Living or active in the presence of free oxygen; and aerobic process is one taking place in the presence of free oxygen. A state in which oxygen dissolved in water acts as an oxidizing agent.
Analyte	The specific component or element measured in a chemical analysis.
Anaerobic	Living or active in absence of oxygen. The remaining oxygen may be combined in the form of some organic or inorganic compound. Sulphate-reducing bacteria, though present in rivers, are normally inhibited by the presence of dissolved or free oxygen.
Biodegradation	The process of destruction or mineralization of either natural or synthetic materials by the microorganisms of soils, waters, or wastewater treatment systems.
Bioremediation	Use of indigenous microorganisms (or the catalysts that they produce) to degrade the target pollutants
Constitutive enzymes	Enzymes that are always produced (at some level) regardless of environmental conditions
Conventional gasoline	refers to gasoline used nationwide before 1995. Conventional gasoline typically does not contain any oxygenates, except in quantities of about 2 to 3% by volume, when refiners have chosen to add them as octane boosters. Conventional gasoline typically has higher benzene content than reformulated gasoline.
Desorption	The release of ions, molecules, or atoms from the surface of a solid.
Dispersion	The process whereby concentration of a dissolved chemical is reduced by dilution, and the contaminant front spreads faster than the average rate of ground water movement.
Detection limit	The minimal concentration of a substance which analytical techniques can detect with some degree of accuracy in various environmental samples, such as ground water. A detection level varies between substances, environmental conditions, samples, and laboratory equipment and technique.

Diffusion	The movement of suspended or dissolved particles from a more concentrated to a less concentrated region as a result of the random movement of individual particles; the process tends to distribute them uniformly throughout the available volume; a transport process.
Epilimnion	The relatively warm, upper layer of water in a body of water
False negative	An error where the incorrect decision is made that an analyte is not present (is not detected) when, in fact, it is present.
False positive	An error where the incorrect decision is made that an analyte is present (is detected) when, in fact, it is not present.
Flame Ionization Detector (FID)	A sensitive, general-purpose detector for most organic compounds.
Free convection	the process where bulk fluid flow occurs as a result of an unstable condition created when the fluid density increases vertically upwards. It occurs when a density gradient exists within a single fluid. If the gradient is such that the fluid is less dense near the bottom, a physically unstable fluid profile is created. As a result, a convective flow is established within the fluid, typically as “fingers,” thereby blending the high and low density portions of the fluid.
Gas chromatography	An analytical technique that employs separation of components of a gas phase mixture by passing the mixture through a column.
Gasohol	Gasoline containing alcohol, such as ethanol.
Groundwater	All subsurface water that occurs beneath the water table in rocks and geologic formations that are fully saturated.
Henry’s law constant	A mathematical description of the propensity for a compound to volatilize to air from water, or conversely, to enter water and remain in the water phase.
Hydrophobicity	Lacking an affinity for, repelling, or failing to adsorb or absorb water.
Hydrodynamic dispersion	The principal means for vertical transport away from the gasoline pool.
Hypolimnion	The colder, denser water layer at the bottom of a body of water.
In situ	In the original location.
Inducible enzymes	Enzymes that are produced only when an inducer (for example, toluene) is present at a higher concentration than the minimum threshold for induction
Intrinsic bioremediation	Natural conditions at contaminated sites meet all the essential environmental requirements so that bioremediation can occur at high rates without human interference
Isotherms	Mathematical relations between the concentration of a compound dissolved in water and its equilibrium concentration sorbed to a solid.

Mass-transfer velocity	The rate with which a compound moves from water to air as a function of its physicochemical properties and environmental conditions, such as water velocity of a stream, water temperature, and wind velocity.
Oxygenates	Organic molecules that contain oxygen. Oxygenates are typically alcohols (such as ethanol) or ethers (such as MTBE). The main purpose for adding oxygenates to fuels is to promote more efficient combustion under adverse conditions in the engine, such as cold starts or fuel-rich operations, when a substantial amount of fuel may escape the engine unburned. The extra oxygen in the fuel helps to convert carbon monoxide (CO, a product of incomplete combustion) to carbon dioxide. To a lesser extent, the extra fuel-bound oxygen may help to convert hydrocarbons, also formed as products of incomplete combustion, to carbon dioxide and water.
Oxyfuels	Oxygenated fuels that contain oxygenates at concentrations on the order of 10 to 15% by volume.
pH	Water with pH values between 0 and 7 is acidic; with pH value of 7 is neutral; with pH values between 7 and 14 is alkaline.
Plume	A visible or measurable discharge of a contaminant from a given point of origin. A plume can be visible or thermal in water.
Precision	A measure of data reproducibility. It is assessed by replicate measurements of reference materials, samples, or method performance samples
Reformulated gasoline (RFG)	RFG differs from conventional gasoline with respect to several fuel parameters. RFG is intended to reduce automotive pollutant formation, especially evaporative emissions and exhaust emissions of photochemical ozone precursors. The most important targeted ozone precursors are volatile organic compounds (VOCs). RFG is also intended to reduce air toxic emissions, specified in the Clean Air Act Amendments as benzene, 1,3-butadiene, formaldehyde, and acetaldehyde. Compared to conventional gasoline, RFG has reduced vapor pressure (to lower evaporative emissions), reduced sulfur content (to prevent poisoning of catalytic converters), and reduced aromatic and benzene content (to decrease evaporative and exhaust emissions of these compounds). Reformulated fuel may or may not include oxygenated compounds; the term “reformulated gasoline” does NOT itself imply the presence of oxygenates.
Sorption	Temporary retention of the contaminant on soil and sediment particles
Substrates	In biochemistry, the substance with which an enzyme reacts.

Surface water	Natural water bodies, such as rivers, streams, brooks, and lakes, as well as artificial water courses, such as irrigation industrial and navigational canals, in direct contact with the atmosphere.
Volatile fatty acids	Produced by anaerobic metabolism of ethanol
Volatilization	The loss of a substance to the air from a surface or from solution by evaporation.
Xenophores	Organic compounds (Cl, NO2, CN, and SO_3) that make the molecule difficult to be recognized by these pathways

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Authors

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Dr. Alvarez is a P.E. (registered in Michigan and Iowa), a certified groundwater professional, and a Diplomate of the American Academy of Environmental Engineers with Diplomate status (DEE). His honors include the Collegiate Excellence in Teaching Award from the University of Iowa (1998); the Alejo Zuloaga Medal from the Universidad de Carabobo, Venezuela (1996); a Career Award from the National Science Foundation (1995); the Best Paper Award from the EPA/HSRC for Regions 7 and 8 (1995); and the Outstanding Achievement Award in Environmental Engineering from the University of Michigan (1991).

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Stephen E. Heermann holds a M.S. in hydrology from the New Mexico School of Mining and Technology and a B.S. in geology from the University of Maryland. He is a doctoral candidate in the environmental engineering program at Clarkson University in New York state. For his dissertation, Mr. Heermann is studying the potential for ethanol in gasoline to enhance the groundwater transport of aromatic gasoline compounds following an accidental release of gasohol into the subsurface. He is investigating a number of physiochemical processes governing the fate and transport of ethanol and gasoline compounds in the subsurface, including cosolvency effects, the mass transfer of ethanol and gasoline compounds between gasoline and ground water, and the transport of ethanol and gasoline compounds via ground water.

Mr. Heermann previously worked as a hydrogeologist for S.S. Papadopulos and Associates and Bechtel Corporation.

Craig S. Hunt is a post-doctoral researcher with the Civil and Environmental Engineering Department of the University of Iowa. He received a Ph.D. in environmental engineering in 1999 from the University of Iowa. He studied the effects of supplementary substrates on the biodegradation of monoaromatic hydrocarbons under the guidance of Associate Professor Pedro J. Alvarez. He has co-authored two papers in this area. Currently, Dr. Hunt is investigating the effect of ethanol on the bioremediation of underground gasoline contamination with the use of aquifer column and chemostat studies.

Carolyn J. Koester, Ph.D., is a research chemist with Lawrence Livermore National Laboratory (LLNL). She received a doctorate in analytical chemistry in 1991 from Indiana University, where she studied the atmospheric fate and deposition of chlorinated dioxins and furans under the direction of Distinguished Professor Ronald A. Hites. During a postoctoral appointment with Trent University and Ontario Ministry of Environment and Energy, she studied environmental applications of liquid chromatography/mass spectrometry and ion trap mass spectrometers.

Dr. Koester's current interests include the study of extraction and mass spectrometric techniques for the determination of trace concentrations of polar organic compounds, including methyl tertiary butyl ether (MTBE), perchlorate, and various pesticides, in water. She has co-authored 13 papers in the area of environmental chemistry, including four recent "Environmental Analysis" review articles for *Analytical Chemistry*.

David Layton is the Division Leader of the Health and Ecological Assessment Division at Lawrence Livermore National Laboratory (LLNL).

During the early part of his 24-year career, his research focused on the health and environmental impacts of geothermal energy development in the western United States. Later, he led a major assessment of the information available on conventional ordnance (i.e., explosives and propellants) in order to support studies of the impacts of weapons demilitarization. He was also one of the lead investigators of a U.S. Department of Defense–funded project to revise the field–water quality standards used by the U.S. military.

After these projects, his research emphasis gradually shifted to the development of quantitative risk assessments of environmental contaminants. He has prepared risk assessments of hazardous gas releases, residual groundwater contamination at a Superfund site, plutonium-contaminated soils, heterocyclic amines in cooked foods, and nuclear wastes dumped in the Arctic Ocean. In addition, he has worked to improve exposure parameters for use in risk assessments. For example, he developed a metabolically-based method for determining breathing rates and conducted research on the resuspension of particles indoors. More recently, he has initiated projects dealing with the assessment of additives for transportation fuels.

Walt W. McNab, Jr., Ph.D., is an environmental scientist with Lawrence Livermore National Laboratory (LLNL). He received his doctorate in hydrogeology in 1995 from the University of California at Berkeley, where he studied reactive transport modeling through groundwater systems under T.N. Narasimhan.

Dr. McNab has worked on projects involving the analyses of multi-site groundwater contamination data. These have included serving on an expert panel convened by the U.S. Department of Defense, Petroleum Hydrocarbon Cleanup Demonstration Program. This project assessed the role of bioattenuation in limiting the risks posed by subsurface fuel releases at California military. Dr. McNab has also been the data analysis task leader for U.S. Department of Energy/LLNL's chlorinated hydrocarbon historical case analysis initiative. He has authored a number of papers on issues related to groundwater contamination, including articles in *Environmental Monitoring and Assessment*, *Ground Water*, and *Water Resources Research*, which discussed modeling and statistical approaches for understanding fuel hydrocarbon bioattenuation signatures in aquifers.

Alfredo A. Marchetti is a research chemist with Lawrence Livermore National Laboratory (LLNL). He received a License in Analytical Chemistry from the University of Buenos Aires, Argentina, in 1984, and a Ph.D. in nuclear chemistry in 1991 from the University of Maryland.

Since 1992, he has worked in LLNL's Health and Ecological Assessment Division. He is the LLNL principal investigator in a collaborative project addressing the Hiroshima neutron dose discrepancy. He has been a key contributor to the Chernobyl radiiodine dose reconstruction project. He has devised methods of iodine analysis in biological and soil samples using gas chromatography. He has developed the target chemistry for the determination by accelerator mass spectrometry of nickel-63, technetium-99, iodine-129, and chlorine-36 in a variety of environmental matrices. He is co-author in 17 peer-reviewed publications and is a member of the American Chemical Society.

Susan E. Powers is an Associate Professor in the Department of Civil and Environmental Engineering at Clarkson University in upstate New York. She received her Ph.D. in environmental engineering from the University of Michigan in 1992, where she studied the dissolution of nonaqueous phase liquids (NAPLs) entrapped within porous media under the guidance of Drs. Walter Weber and Linda Abriola. She received a B.S. and a M.S. in chemical engineering and environmental engineering, respectively, from Clarkson University.

Dr. Powers's current research focuses on understanding the physical and chemical phenomena associated with multiphase flow and contaminant transport in subsurface systems, with specific emphasis on the fate, transport, and remediation of NAPLs in complex systems. Her current research projects include the complexities associated with aquifer heterogeneities and nonideal chemical mixtures, such as coal tars and oxygenated gasoline.

David W. Rice is the Environmental Chemistry and Biology Group Leader for the Environmental Protection Department at Lawrence Livermore National Laboratory (LLNL). He is an expert in the fate and transport of contaminants in subsurface sediments, groundwater, and the marine environment. Mr. Rice has a B.A. in biology and a Life Secondary Education Credential from San Jose State University, and a M.A. in marine biology through the California State University Moss Landing Marine Science Institute.

During his 23 years at LLNL, Mr. Rice has participated in the management of the LLNL Superfund sites and directed and performed research on environmental decision-making, information management, and the application of natural process to environmental remediation. Mr. Rice has acted as Project Director for Chlorinated VOC Historical Case Analysis Initiative, Department of Defense Petroleum Hydrocarbon Cleanup Demonstration Program, and the Revision of California Leaking Underground Fuel Tank Cleanup Process. He is presently the Project Director for evaluating the potential surface and ground water impacts that may result from the use of ethanol as a replacement for MTBE in gasoline.

Mr. Rice has authored or co-authored over 50 publications. He is a member of the World Federation of Scientists Monitoring Panel on Water and Pollution and the Scientific Advisory Board for the Association for the Environmental Health of Soils. He is a recipient of the Lawrence Livermore National Laboratory Director's Performance Award.

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Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate

Report to the
California Environmental
Policy Council
in Response to
Executive Order
D-5-99

VOLUME 5

Potential Health Risks of Ethanol in Gasoline

Office of Environmental Health Hazard Assessment

December 1999

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California Environmental Protection Agency
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Table of Contents

List of Tables

1. Introduction

On March 25, 1999, Governor Gray Davis issued Executive Order D-5-99 which stated that, while the gasoline additive, methyl *tertiary*-butyl ether (MTBE), has benefited California by decreasing air pollution, it also poses an environmental threat to groundwater and drinking water. Weighing all of the evidence, the Governor declared that there is significant risk to the environment from using MTBE in gasoline in California. As a result, the Governor assigned tasks, by way of the Executive Order, to various designated state agencies, regarding the reformulation of gasoline in the State. Task 10 requires the California Air Resources Board (CARB) and the State Water Resources Control Board (SWRCB) to conduct an environmental fate and transport analysis of ethanol in air, surface water, and ground water. It further requires the Office of Environmental Health Hazard Assessment (OEHHA) to 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. This draft report, prepared by OEHHA, is the analysis of the potential public health impacts of ethanol as an oxygenate in gasoline.

1.1. Objective

The objective of this document is to present an evaluation of the public health impacts of ethanol as an oxygenate in gasoline. In order to give the analysis a frame of reference, the potential health impacts of ethanol in gasoline have been evaluated in comparison to the current MTBE formulation, as well as to gasoline with no oxygenate. This evaluation includes an analysis of evaporative emissions, tailpipe (exhaust) emissions, as well as atmospheric transformation products that are produced as a result of the use of ethanol in gasoline. Four gasoline formulations were selected by CARB for analysis, all formulations fully complying with existing air pollution regulations. The formulations are as follows:

- Current MTBE-based California Phase 2 Reformulated Gasoline (CaRFG),
- Ethanol-based (with oxygen content of 3.5%),
- Ethanol-based (with oxygen content of 2.0%), and
- A non-oxygenated fully complying fuel.

The CARB model produced estimates of the total concentrations of specific pollutants in ambient air from all sources (emissions from stationary and mobile sources, and atmospheric transformation products). Generation of these estimates is described in detail in the report contributed by CARB: the results are cited here without modification. Rather than evaluating the health impact of each fuel-related pollutant, this report focuses on the differences in combustion by-products, evaporative emissions, and atmospheric transformation products that occur from use of one fuel versus another. It is not intended to assess the overall impact of gasoline usage regardless of type, or the adequacy of current regulatory controls in limiting the impacts of this usage on public health.

In conducting a quantitative assessment of the relative health impacts of the different fuel formulations, we used estimates of total air concentrations modeled by CARB, and calculated the risk levels associated with these concentrations. However, our confidence in these lifetime cancer risk estimates, and acute and chronic hazard indices, is lower than our confidence in the relative differences in risk estimate or hazard index associated with the different fuel scenarios. This arises because of the intrinsic uncertainties in the CARB exposure modeling and the risk assessment processes.

While this assessment focuses primarily on the potential impacts from emissions into the ambient air, an evaluation of potential risks from groundwater contamination by fuel components is also included. This evaluation centers primarily on the differences between MTBE and ethanol in groundwater.

2. Hazard Identification: Chemicals of Concern

In examining the health risks of ethanol in gasoline, we considered the impacts from evaporative emissions, exhaust (tailpipe) emissions, as well as secondary transformation products formed in the atmosphere. Evaporative emissions of unburned gasoline occur primarily during refueling at the pump, from fuel spills, and directly from carburetors and other fuel system components of automobiles. Exhaust emissions include unburned fuel and other products of incomplete combustion. Many of these products, particularly emissions of hydrocarbons and nitrogen oxides (NO_X), together are critical precursors in the formation of ozone and other atmospheric transformation products.

CARB provided the speciation profiles for the air emissions and modeling to determine concentrations of key chemicals from the four fuels. OEHHA focused this analysis on key chemicals associated with fuel use and potential changes in air concentration of those chemicals. Selection of chemicals of concern initially relied on the identification of representative fuel constituents and atmospheric contaminants by CARB, and a preliminary assessment of toxicological data available from secondary sources in the literature. The chemicals determined to be the most important in terms of public health risks which were selected for more detailed evaluation in this report are: 1) the oxygenates MTBE, ethanol; 2) Combustion products 1,3-butadiene, formaldehyde, acetaldehyde, carbon monoxide; 3) Evaporative emittents benzene, hexane, and toluene; and 4) Atmospheric transformation products peroxyacetyl nitrate (PAN) and ozone. Summaries of the toxicity of each of these compounds are included with this document as Appendix A.

3. Dose-Response Assessment

In a risk assessment, health impacts are quantified using health assessment values. These values characterize the dose-response relationship, that is the relationship between exposure to an agent and the incidence of an adverse health effect in an exposed population. In this risk analysis, health assessment values used to quantify risks are those currently available from Cal/EPA and U.S. EPA as described below. In the absence of adopted health assessment values suitable for estimating potential health impacts from the chemicals of concern, OEHHA used 'proposed' numbers that have been developed under other California regulatory programs that are currently undergoing scientific peer review. In cases where 'proposed' numbers were not available, OEHHA calculated 'health protective concentrations' for the purpose of this report. The sources of adopted values and proposed values currently undergoing scientific and public peer review, as well as the methodology used to calculate draft 'health protective concentrations,' are all described below. The health assessment values used in this report are shown in Tables 1-3. The derivation of all proposed numbers and draft numbers are included in the chemical summaries in Appendix A.

3.1. Values for Assessing Potential Health Impacts from Inhalation Exposures

3.1.1. Carcinogenic Endpoints

Risks from exposure to a carcinogen are quantified using potency values. A carcinogenic potency is an estimate of the slope of the dose-response curve at low exposure concentrations. Potency values are expressed in units of inverse dose, either as a cancer potency or *slope factor* (i.e., units of $(\text{mg/kg-day})^{-1}$) or, for inhalation exposures, as a *unit risk factor* (i.e., units of $(\mu\text{g/m}^3)^{-1}$). These values represent the theoretical probability of extra cancer cases occurring in an exposed population assuming a 70-year lifetime exposure. Potencies may be derived from animal or human data, and their derivation takes into account the available information on pharmacokinetics, mechanism of carcinogenic action, and the effects of different models on low dose extrapolation. The unit risk or cancer potency factors used in this report are a 95% upper confidence limit of the slope of the dose-response curve, and thus represent an upper estimate of the risk.

For this risk assessment, unit risk factors used in inhalation risk calculations are those currently available from Cal/EPA and U.S. EPA. These values, and information on how they were derived, are documented in the "Air Toxics Hot Spots Program Risk Assessment Guidelines, Part II: Technical Support Document for Describing Available Cancer Potency Factors" (OEHHA, 1999b).

3.1.2. Noncancer Endpoints

3.1.2.1. Acute, One-Hour Inhalation Exposures

Potential health impacts from acute, one-hour exposures were estimated using acute reference exposure levels (RELs). An REL is a concentration in air at or below which no adverse health effects are anticipated for a specified exposure duration. RELs are based on the most sensitive, relevant, adverse health effect reported in the medical and toxicological literature. They are designed to protect the most sensitive individuals in the population by the inclusion of margins of safety. Acute RELs used in the present risk analysis were obtained from the "Air Toxics Hot Spots Program Risk Assessment Guidelines, Part I: The Determination of Acute Reference Exposure Levels for Airborne Toxicants" (OEHHA, 1999a). As mandated by state legislation, these guidelines underwent public and scientific peer review prior to approval by the

Scientific Review Panel and adoption by OEHHA (Senate Bill 1731, Statutes of 1992, Ch. 1162 of the California Health and Safety Code).

In the absence of adopted acute RELs, OEHHA calculated draft ‘health protective concentrations’ following the adopted methodology for developing acute RELs. Details on the methodology are provided in OEHHA (1999a).

3.1.2.2. Annual Average Inhalation Exposure Concentrations

Potential health impacts from chronic inhalation exposures were estimated using several types of health assessment values.

a) U.S. EPA’s Reference Concentrations (RfCs). U.S. EPA has developed reference concentrations (RfC) for many airborne toxicants. An RfC is defined by U.S. EPA as “an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious noncancer effects during a lifetime.”

b) Proposed Chronic Reference Exposure Levels. In the absence of a U.S. EPA RfC, OEHHA used the proposed chronic reference exposure levels currently being developed by the Air Toxics Hot Spots Program risk assessment guidelines process. These values, as well as the methodology used to develop them, are in the process of undergoing public and scientific peer review. The methodology and proposed values are described in the “Air Toxics Hot Spots Program Risk Assessment Guidelines, Part III: Technical Support Document for the Determination of Noncancer Chronic Reference Exposure Levels” available on our web page (www.oehha.ca.gov).

c) Reference Exposure Levels for Toxic Air Contaminants. OEHHA has developed RELs for some chemicals evaluated in the Toxic Air Contaminant (TAC) program, mandated by Assembly Bill 1807 (California Health and Safety Code 39660 et seq.) These numbers underwent public and scientific peer review. One chemical in the present analysis, acetaldehyde, has an REL that was developed under the TAC process.

In the absence of a U.S. EPA RfC, a proposed chronic REL, or an REL developed under the TAC process, OEHHA calculated draft health protective concentrations using the chronic REL methodology.

Table 1. Health Assessment Values and Draft "Health Protective Concentrations" (HPCs)

	Non-cancer		**Cancer**	
	1-hour (mg/m^3)	***Annual Average (mg/m^3)***	***Unit risk (mg/m^3)$^{-1}$***	***Air concentration corresponding to10^{-6} lifetime risk (mg/m^3)***
Acetaldehyde	**115** **(65 ppb)** [draft HPC]	**9** **(5 ppb)** [TAC]	**2.7 E-6** **(4.8 E-6 ppb^{-1})** [TAC]	**3.7 E-1** **(2.1 E-1 ppb)**
Benzene	**1300** **(400 ppb)** [acute REL]	**60** **(20 ppb)** [proposed chronic REL]	**2.9 E-5** **(9.3 E-5 ppb^{-1})** [TAC]	**3.5 E-2** **(1.1 E-2 ppb)**
Butadiene	**310** **(140 ppb)** [draft HPC]	**8** **(4 ppb)** [U.S. EPA RfC]	**1.7 E-4** **(3.7 E-4 ppb^{-1})** [TAC]	**5.9 E-3** **(2.7 E-3 ppb)**
Ethanol	**100,000** **(53,000 ppb)** [draft HPC]	**100,000** **(53,000 ppb)** [draft HPC]	No evidence of carcinogenicity by inhalation	
Formaldehyde	**94** **(76 ppb)** [acute REL]	**3** **(2 ppb)** [proposed chronic REL]	**6.0 E-6** **(7.0 E-6 ppb^{-1})** [TAC]	**1.7 E-1** **(1.4 E-1 ppb)**
MTBE	**25,000** **(7000 ppb)** [draft HPC]	**3000** **(800 ppb)** [U.S. EPA RfC]	**2.6 E-7** **(9.3 E-7 ppb^{-1})** [TAC]	**3.9 E0** **(1.1 ppb)**
PAN	**8.8** **(1.8 ppb)** [draft HPC]	**3.2** **(0.6 ppb)** [draft HPC]	No evidence of carcinogenicity / inadequate data	

Draft HPC: health protective concentration; In the absence of adopted health assessment values OEHHA developed draft numbers for use in this analysis. The basis of these numbers is described in Appendix A in the toxicity summaries. These numbers are not in regulation.

TAC: toxic air contaminant; peer-reviewed value developed under the TAC program mandated by AB 1807

Acute REL: acute reference exposure level; peer-reviewed value developed as part of the legislatively mandated Air Toxics Risk Assessment Program risk assessment guidelines process (SB 1731; Statutes of 1992; California Health and Safety Code, Chapter 1162)

Proposed chronic REL: chronic reference exposure level; currently being developed as part of the legislatively mandated Air Toxics Risk Assessment Program risk assessment guidelines process (SB 1731; Statutes of 1992; California Health and Safety Code, Chapter 1162); these numbers are currently undergoing various stages of a scientific peer review and public comment process.

Table 2. Health Assessment Values for the Criteria Air Pollutants

	1 hour	8 hour	24 hour	Annual Average
Carbon monoxide	**23000 $\mu g/m^3$ (20 ppm)** [acute REL; CA AAQS]	**10,000 $\mu g/m^3$ (9.0 ppm)** [CA and federal AAQS]		
NO_X	**470 $\mu g/m^3$ (0.25 ppm)** [acute REL; CA AAQS]			**100 $\mu g/m^3$ (0.053 ppm)** [federal AAQS]
Ozone	**180 $\mu g/m^3$ (0.09 ppm)** [acute REL; CA AAQS]	**157 $\mu g/m^3$ (0.08 ppm)** [federal AAQS]		
Particulate Matter < 10 microns (PM_{10})			**50 $\mu g/m^3$** [CA AAQS]	**30 $\mu g/m^3$** [CA AAQS]

Acute REL: Acute Reference Exposure Level **CA AAQS: California Ambient Air Quality Standard**

Federal AAQS: Federal Ambient Air Quality Standard

3.2. Values for Assessing Potential Health Impacts from Exposure via Drinking Water

3.2.1. Public Health Goals (PHGs)

The PHG describes concentrations of contaminants in drinking water at which adverse health effects are not expected to occur, even over a lifetime of exposure. PHGs have been developed by OEHHA under the California Safe Drinking Water Act of 1996 (amended Health and Safety Code, Section 116365). PHGs are based solely on scientific and public health considerations, unlike many other state and federal drinking water standards which take into account other considerations (e.g., technological feasibility and economic factors).

Table 3. Health Assessment Values and Draft "Health Protective Concentrations" for Assessing Potential Health Impacts of Ethanol in Gasoline – Oral exposures from Drinking Water.

	Health Assessment Value	Endpoint	Source	Reference
Benzene	**1.4×10^{-4} mg/L (0.14 ppb)**	**cancer**	**draft public health goal**	**OEHHA (1999c)**
Ethanol	**1100 mg/L (1.1×10^{6} ppb)**	**noncancer**	**draft HPC**	**---**
Methyl *t*-butyl ether (MTBE)	**0.013 mg/L (13 ppb)**	**cancer**	**public health goal**	**OEHHA (1999d)**
Toluene	**0.150 mg/L (150 ppb)**	**noncancer**	**public health goal**	**OEHHA (1999e)**
Xylenes	**1.8 mg/L (1800 ppb)**	**noncancer**	**public health goal**	**OEHHA (1997)**

Public Health Goal (PHG): developed under the California Safe Drinking Water Act of 1986 (amended Health and Safety Code, Section 116365)

Draft HPC: health protective concentration; In the absence of adopted health assessment values OEHHA developed draft numbers for use in this analysis. The basis of these numbers is described in Appendix A in the toxicity summaries. These numbers are not in regulation.

4. Exposure Assessment: Sources of Exposure Data

The CARB conducted modeling analyses of the air quality impacts of use of one fuel versus another. The South Coast airshed was selected as the basis of their modeling efforts since the South Coast is a severely impacted area of the State and one which has been extensively studied. The CARB analysis includes consideration of the changes in ambient air concentrations of specific toxic components of exhaust, evaporative components, and subsequent reaction products that would result from substituting ethanol-blended gasoline for gasoline blended with MTBE. The modeled air concentrations incorporate all sources of emissions within the South Coast airshed, including stationary source emissions, mobile source emissions and background emissions. However, stationary source and background emissions are not expected to change between the various fuel scenarios. As noted above, the fuels modeled include the current MTBE formulation, two formulations containing ethanol, and a formulation containing no oxygenate. These were considered in exposure scenarios based on the predicted emissions inventory for the year 2003. A scenario of the 1997 emissions inventory and MTBE-containing fuel was used to calibrate the model against actual measured data for that year. The model predictions of one-hour and 24-hour peak concentrations of pollutants are worst case estimates, but the population-weighted annual averages are best estimates calibrated against actual measurements for 1997, the baseline year. CARB's modeling analysis is described in more detail in their report and the accompanying appendices of this document. CARB developed speciation profiles of volatile organic compounds (VOC) for each fuel under varying conditions (e.g., start exhaust, hot stabilized exhaust, etc.). The modeling results provide one-hour peak concentrations for all compounds, eight-hour concentrations for ozone and CO, 24-hour average concentrations for PM_{10}, and population-weighted annual average concentrations for all compounds of interest. These modeled air concentrations are summarized in Table 4 and form the basis of the health impacts analysis. The concentrations are input into simple arithmetic equations to estimate health risks.

As shown in Table 4, measurable air concentrations of ethanol are present even under the non-ethanol-containing fuel scenarios. These ethanol emissions result primarily from stationary sources. However, there are no detectable levels of MTBE under the non-MTBE-containing fuel scenarios because stationary source emissions of MTBE are negligible and result in non-detectable air concentrations of the chemical.

The SWRCB contracted with Lawrence Livermore National Laboratories to model a variety of scenarios related to release of ethanol-containing gasoline onto soil or into surface waters. The main purpose of the modeling is to estimate potential water quality impacts of using ethanol as an oxygenate in gasoline. The modeling focused on predicting the movement of ethanol through the soil and into groundwater as well as the effects ethanol may have on the movement of other gasoline constituents (primarily benzene, toluene, and xylenes; also referred to as BTEX) through soil and into groundwater. Although the modeling analyses are not yet complete, information to date indicates that ethanol readily undergoes microbial degradation in the environment. This is in contrast to MTBE, which is resistant to microbial degradation. As a result, it appears unlikely that ethanol will contaminate groundwater to any degree approaching a public health concern. At this time, OEHHA is awaiting results of the modeling being conducted on the effects of ethanol on the movement of other gasoline constituents (BTEX). The results of the modeling will be used to ascertain whether the probability of well-water contamination by BTEX will increase, decrease, or stay the same relative to baseline MTBE-containing fuels. If possible, we may be able to obtain modeled concentrations of BTEX and ethanol to compare to existing PHGs or estimated health-protective concentrations as described in the following section.

Table 4. Atmospheric Concentration Estimates: Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin[a]

		1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 Non-Oxy
Acetaldehyde (ppb)						
Population-Weighted Annual Exposure						
	Upper	1.8	1.6	1.6	1.8	1.6
	Lower	1.8	1.5	1.5	1.7	1.5
Maximum Daily Average						
	Upper	6.2	6.2	6.2	6.2	6.2
	Lower	5.1	5.1	5.1	5.1	5.1
Maximum 1 Hour Average						
	Upper	17.7	16.7	16.9	17.1	16.9
	Lower	13.8	13.1	13.2	13.4	13.2
Benzene (ppb)						
Population-Weighted Annual Average						
	Upper	1.19	0.80	0.78	0.81	0.76
	Lower	1.07	0.72	0.70	0.73	0.69
Maximum Daily Average						
	Upper	9.5	6.8	6.5	6.8	6.4
	Lower	7.4	5.3	5.1	5.3	4.9
Maximum 1 Hour Average						
	Upper	22.4	14.3	14.3	14.3	14.3
	Lower	11.6	7.4	7.4	7.4	7.4
Butadiene (ppb)						
Population-Weighted Annual Average						
	Upper	0.36	0.20	0.20	0.20	0.20
	Lower	0.34	0.19	0.19	0.19	0.19
Maximum Daily Average						
	Upper	2.9	1.2	1.2	1.2	1.2
	Lower	2.0	0.8	0.8	0.8	0.8
Maximum 1 Hour Average						
	Upper	6.7	3.4	3.4	3.4	3.4
	Lower	3.1	1.6	1.6	1.6	1.6
Ethanol (ppb)						
Population-Weighted Annual Average						
	Best	5.4	5.1	7.6	8.8	5.1
Maximum Daily Average						
	Upper	51	49	71	81	49
	Lower	47	45	64	75	45
Maximum 1 Hour Average						
	Upper	108	101	145	165	101
	Lower	78	74	114	140	74

Table 4 (continued). Atmospheric Concentration Estimates: Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin[a]

		1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 Non-Oxy
Formaldehyde (ppb)						
Population-Weighted Annual Average						
	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	14.0	12.2	11.8	12.1	11.7
Maximum 1 Hour Average						
	Upper	37.8	38.3	37.8	38.1	37.8
	Lower	20.3	20.6	20.3	20.5	20.3
MTBE (ppb)						
Population-Weighted Annual Average						
	Upper	3.9	2.6	0	0	0
	Lower	3.6	2.4	0	0	0
Maximum Daily Average						
	Upper	29	20	0	0	0
	Lower	13	9	0	0	0
Maximum 1 Hour Average						
	Upper	67	46	0	0	0
	Lower	19	13	0	0	0
PAN (ppb)[b]						
Maximum Daily Average						
	Upper	5.0	4.8	4.8	4.9	4.7
	Lower	2.5	2.4	2.4	2.4	2.4
Maximum 1 Hour Average						
	Upper	10.0	9.5	9.3	9.5	9.1
	Lower	5.0	4.8	4.7	4.8	4.5

Table 4 (continued). Atmospheric Concentration Estimates: Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin[a]

	1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 Non-Oxy
Carbon Monoxide (ppm)					
Maximum 8 Hour Average					
Best	**17.5**	**14.3**	**14.3**	**13.4**	**14.7**[c]
Maximum 1 Hour Average					
Best	**22.5**	**19.2**	**19.2**	**18.0**	**19.7**[c]
Nitrogen Dioxide (ppm)					
Maximum Annual Average					
Best	**0.043**	CARB reported, “No difference expected among 2003 scenarios” [d]			
Maximum Daily Average					
Best	**0.117**	**0.098**	**0.097**	**0.097**	**0.097**
Maximum 1 Hour Average					
Best	**0.255**	**0.235**	**0.235**	**0.235**	**0.235**
Ozone (ppm)					
Maximum 8 Hour Average					
Best	**0.206**	**0.196**	**0.196**	**0.196**	**0.196**
Maximum 1 Hour Average					
Best	**0.244**	**0.230**	**0.228**	**0.228**	**0.228**
Particulate Matter (10 microns or less) (μg/m^3)					
Maximum Annual Geometric Mean					
Best	**56**	CARB reported, “No difference expected among 2003 scenarios” [d]			
Maximum Daily Average					
Best	**227**	CARB reported, “No difference expected among 2003 scenarios” [d]			

[a] Source: Table 4.6 of “Staff Report: Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline. November 18, 1999. California Air Resources Board, Cal/EPA”

[b] A population-weighted annual average for PAN was not determined because consistent long-term measurements of atmospheric PAN have not been performed. See CARB report for details.

[c] This 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.

[d] No significant change compared to 1997 MTBE-fuel scenario. See CARB report for details.

5. Methodology Used for Quantifying Cancer and Noncancer Risks

Risk characterization is the process of integrating data on exposure with dose-response in order to estimate public health impacts. In quantifying risks of exposure, cancer and noncancer endpoints are considered separately. Please refer to the toxicity summaries in Appendix A for further details on estimating cancer and noncancer risks for individual chemicals.

5.1. Estimating Cancer Risk

Typically, carcinogenesis is treated as a "nonthreshold" toxicological phenomenon. In other words, there is some finite risk to any finite dose. It may be so small as to be indistinguishable from zero at very low doses. In order to estimate cancer risk, we multiply the unit risk factor by the modeled concentration in air to obtain a unitless probability of cancer occurring in a population thus exposed.

$$\text{Risk} = \text{concentration} \times (\text{URF or potency slope})$$

So, for example, if the unit risk factor is 1×10^{-6} for chemical "X", and the concentration of chemical "X" is 5 $\mu g/m^3$, then the risk is calculated as :

$$\text{Risk} = [(1 \times 10^{-6})\ (\mu g/m^3)^{-1}] \times 5\ \mu g/m^3 = 5 \times 10^{-6}$$

The cancer risks thus estimated reflect high-end estimates (usually a 95% upper confidence limit or UCL95) of the potential cancer cases in a population exposed to chemical "X" at 5 $\mu g/m^3$ over a lifetime. In other words, there is the potential for five extra cancer cases to occur over a 70 year period in a population of one million persons exposed to that level of chemical "X".

In cases where there is exposure to multiple carcinogens, the risk of each carcinogen is added. The implicit assumption is that the effect on cancer risk in the population exposed to multiple carcinogens is additive. It is possible that some carcinogens might be synergistic and some antagonistic, although at low exposure levels these mechanisms may be unimportant.

5.2. Estimating Noncancer Risk

Noncancer health endpoints are assumed to have a threshold for effect. If the exposure is below the individual's threshold for effect, then no adverse impact would be expected. To quantify potential noncancer health impacts resulting from exposure to hazardous substances, a *hazard index* approach is used. In using this approach, measured or modeled exposure concentrations are compared to calculated health assessment values such as the Reference Exposure Level (REL). The Hazard Quotient (HQ) for a chemical is the ratio of the modeled concentration in air to the REL. If the HQ exceeds one, a 'red flag' is raised with regard to exposure to that chemical and possible adverse health impacts. Exceedance of an HQ of one does not necessarily mean that a health impact will occur. It implies that the margin of safety built into the REL is being eroded. The higher the ratio, the closer the exposure is to an adverse level. It is generally impossible to calculate the exact concentration at which anyone in a diverse population would respond. Interindividual differences in response and limited information on the toxicant preclude such a determination. Uncertainty factors are included in the calculation of the RELs to protect sensitive members of the population.

To assess the cumulative impact of several chemicals present at the same time, it is important to consider the interaction of the effects of the toxicants. Unless specific information is available to the contrary, the interaction of two or more chemicals that affect the same target organ is assumed to be additive. An underlying issue in chemical interactions and additivity is the concept of threshold. Exposure to a single chemical may not result in a toxic response if it is below the threshold necessary to elicit a response. However, simultaneous exposure to two or more chemicals that impact the same target organ at sub-threshold concentrations may result in a toxic response. This is taken into account by adding the individual HQs for chemicals that impact the same target organ or system. Thus, if more than one toxicant is present that impacts the same target organ or system (e.g., respiratory system, cardiovascular system), then the HQ for individual compounds is added to produce the Hazard Index (HI). As such, the *hazard index* approach assumes that multiple sub-threshold exposures to chemicals acting on the same target organ could result in an overall risk of developing adverse effects. This may underestimate the effect in the cases in which interactions are synergistic, or overestimate it if the interactions are not additive or are antagonistic.

6. Risk Characterization

6.1. Inhalation – Cancer and Noncancer Effects

The following section refers to data presented in Tables 5a-c. Please refer to the toxicity summaries in Appendix A for relevant citations and information pertaining to the basis and the development of the health assessment values for individual chemicals.

6.1.1. Acetaldehyde

The lifetime cancer risk is the toxicological endpoint of concern for exposure to acetaldehyde in the South Coast Air Basin. Toxic endpoints may include nasal and pulmonary cancers, with a cancer unit risk value of 2.7×10^{-6} $(\mu g/m^3)^{-1}$ or 4.8×10^{-6} ppb^{-1}. Several sources of uncertainty result in a lower level of confidence in this estimate for acetaldehyde than for some of the other carcinogenic potency estimates, for example, the benzene and butadiene cancer risk estimates. The sources of uncertainty are similar to those facing other cancer potency estimates. They include reliance on animal studies due to the lack of human data, and the five orders of magnitude extrapolation from experimental animal exposure concentrations to current ambient levels. In the case of acetaldehyde, the extensive metabolism of the compound *in vivo* (and its occurrence as a normal intermediary metabolite) is an additional source of uncertainty with respect to the standard assumption in risk assessment that the dose-response curve is linear down to the low ambient levels of the compound.

The upper bound estimate of the cancer risk resulting from exposure to the maximal predicted levels of acetaldehyde over a 70 year lifespan is seven to nine excess cancer cases per million people exposed. The real risk may in fact be considerably lower than this upper bound estimate. There are increased ambient concentrations of acetaldehyde from the ethanol-based fuel containing 3.5% oxygen, compared to the other formulations evaluated for the year 2003. This results in an increase of up to two in a million excess lifetime cancer cases in the upper bound estimate. However, in view of the uncertainties both in the emission and exposure predictions, and in the acetaldehyde lifetime cancer risk estimate, this predicted increase in risk may be regarded as of marginal significance when comparing the other consequences of the different fuel formulations. None of the predicted ambient levels of acetaldehyde for the year 2003 exceeds the levels in the 1997 model.

The acute (one-hour maximal average) and chronic (maximum annual exposure) noncancer Hazard Quotients (HQs) for acetaldehyde generated by each of the fuel scenarios are well below one. In general, the air concentrations are three- to five-fold below the reference exposure levels and there is little difference in HQ values among the five fuel types. Toxicological endpoints considered include eye, skin, and respiratory tract irritation with acute exposure, and inflammation of the respiratory tract and degeneration of the olfactory epithelium with chronic exposure.

6.1.2. Benzene

The lifetime cancer risk is the toxicological endpoint of concern for exposure to benzene in the South Coast Air Basin. Health effects other than cancer are not expected to occur at maximal ambient levels. The primary toxic endpoint in humans is acute myelogenous leukemia, but strong evidence exists to suggest that benzene causes other forms of leukemia as well (OEHHA, 1999c). The current cancer unit risk value for California, 2.9×10^{-5} $(\mu g/m^3)^{-1}$ or 9.3×10^{-5} ppb^{-1}, is based on total leukemia (i.e. all forms of leukemia as a related class of diseases). There is a moderate to high level of confidence in the estimate of this value. Principally, there exists sufficient evidence to consider benzene a carcinogen in both humans and experimental animals. The cancer risk value is the upper 95 percent confidence level estimate from the analysis of human data and falls within the range of estimates derived from numerous epidemiological and animal studies. However, the approximate five orders of magnitude extrapolation from human occupational exposure concentrations to current ambient levels represent a major source of uncertainty for the benzene cancer risk estimate. Although some experts have postulated that the mechanism by which benzene causes leukemia may have a threshold, there are also substantial reasons for considering that benzene is acting as a nonthreshold genotoxic carcinogen (reviewed in OEHHA, 1999c). Based on this latter interpretation, benzene is treated as a substance without a carcinogenic threshold in humans (OEHHA, 1999c; U.S. EPA, 1999).

Comparing the 1997 fuel scenario to the year 2003 formulations, the upper bound estimate of the cancer risk resulting from exposure to the maximal predicted levels of benzene over a 70 year lifespan is expected to drop from 110 to 75 or less excess cancer cases per million people exposed. Given the uncertainty in the cancer risk estimate, the differences in cancer risks between the various year 2003 fuel scenarios are small and insignificant.

The most sensitive toxicological endpoint under acute exposures may include reduced birth weights in newborns. Chronic exposure and high acute exposure to benzene may result in hematotoxicity, including aplastic anemia. However, with acute and chronic noncancer HQs generated for benzene by each of the five fuel scenarios well below one, these noncancer health effects are not expected to occur even at maximum ambient levels. The upper bound concentrations in air are between 17- and 25-fold below the REL and there is essentially no difference in HI values among the year 2003 formulations.

6.1.3. Butadiene

The lifetime cancer risk is the toxicological endpoint of concern for exposure to butadiene in the South Coast Air Basin. Butadiene has been shown to induce cancers in animals at multiple sites including, heart, lung, mammary gland, ovaries, liver, pancreas, Zymbal gland, thyroid, testes, and hematopoietic system. The cancer unit risk value is 1.7×10^{-4} $(\mu g/m^3)^{-1}$ or $3.7 \text{ x } 10^{-4}$ ppb^{-1}. There is a moderate level of confidence in the estimate of this value. Recent epidemiological studies suggest a connection between excess cases of leukemia and lymphoma and butadiene exposure, although this provides only limited evidence to support the carcinogenic effects observed in experimental animals. Mice are known to develop lymphomas following butadiene exposure, although this has not been observed in the rat. This interspecies difference is a significant source of uncertainty in the risk estimate, and may reflect differences seen between mice and rats regarding butadiene metabolism. Another uncertainty results from the necessity to extrapolate from experimental animal exposure concentrations to current ambient levels. However, the evidence on metabolism and carcinogenicity suggests that butadiene is a genotoxic carcinogen acting via metabolically generated reactive intermediates. Hence, no threshold is thought to exist for this substance.

Comparing the1997 fuel scenario to the year 2003 formulations, the upper end estimate of the cancer risk resulting from exposure to the maximal predicted levels of butadiene over a 70 year lifespan is expected to drop from 130 to about 74 excess cancer cases per million people exposed. The real risks may be lower than these upper bound estimates. Given the uncertainty in the cancer risk estimates, the differences in cancer risks between the various year 2003 fuel scenarios are small and likely to be of little significance.

The most sensitive toxicological endpoint under acute exposures may include reduced birth weights in newborns. Chronic exposure to butadiene may result in ovarian atrophy. However, with acute and chronic noncancer HQs generated for butadiene by each of the five fuel scenarios are well below one, these noncancer health effects are not expected to occur even at maximal ambient levels. There is essentially no difference in HQ values among the year 2003 formulations, though the year 2003 formulations have significantly lower chronic HQs than the 1997 formulation. The upper and lower bound one-hour average concentrations are between 20- and 100-fold below the acute REL.

6.1.4. Ethanol

Health effects due to ethanol exposure under any of the five fuel scenarios are not expected to occur at modeled ambient levels. There is no evidence that ethanol is carcinogenic via the inhalation route. Exposure to high concentrations of ethanol vapor may result in transient irritation to eyes and the respiratory system under either acute or chronic conditions. However, the acute and chronic noncancer HQs generated for ethanol by each of the five fuel scenarios are 0.002 or less, indicating that modeled concentrations are at least 500-fold below the HPCs.

As discussed in Appendix A, OEHHA concluded that ethanol exposure via the inhalation route at the low ambient concentrations predicted by CARB is unlikely to present a carcinogenic hazard. However, in order to further explore the possible impact of atmospheric pollution by ethanol, OEHHA evaluated the implications of a proposed unit risk factor (R. Wilson, 1999; comment on a draft of this document) and found that even if ethanol were regarded as a human carcinogen by the inhalation route, with linear low-dose response, the cancer risks predicted on this basis from ethanol are negligible. This analysis is described in detail in the attached listing of public comments.

6.1.5. Formaldehyde

The lifetime cancer risk is the toxicological endpoint of concern for exposure to formaldehyde in the South Coast Air Basin. The primary toxic endpoint is nasal cancer, but may also include other respiratory tract cancers. The cancer unit risk is 6.0×10^{-6} $(\mu g/m^3)^{-1}$ or 7.0×10^{-6} ppb^{-1}. The sources of uncertainty in this estimate are similar to those facing other cancer potency estimates. They include reliance on animal studies due to insufficient human data, and three to four orders of magnitude extrapolation from experimental animal exposure concentrations to current annual average exposure levels. Another uncertainty involves cross-species scaling calculations. The evidence indicates formaldehyde is a contact carcinogen (i.e., formaldehyde generally reacts with the first tissues it contacts) so that whole-body scaling factors may not be appropriate. Because the formaldehyde cancer unit risk is based on studies in rats, there is uncertainty in extrapolating to humans due to potentially significant differences in the anatomy and physiology of the respiratory systems between rats and humans.

Comparing the 1997 fuel scenario to the year 2003 scenarios, the upper bound estimate of the cancer risk resulting from exposure to the maximal predicted levels of formaldehyde over a 70 year lifespan is expected to drop from 33 to about 28-29 excess cancer cases per million people exposed by 2003. There is no apparent difference between year 2003 fuel formulations regarding cancer risk from formaldehyde.

The chronic (maximum annual exposure) noncancer HQ generated by the 1997 fuel scenario is 2.4. The 2003 fuel scenarios have lower HQs, but indicate that the concentrations of formaldehyde are almost two-fold above the REL. There is no apparent difference between fuel formulations for year 2003 of possible chronic health effects of formaldehyde. Toxicological endpoints include eye and respiratory system irritation. It is possible that some sensitive individuals may develop these chronic adverse effects at the maximal predicted annual exposure. Simultaneous exposure to other sensory irritants, such as acetaldehyde, may exacerbate the eye and respiratory irritation caused by formaldehyde (see section 6.4). However, it should be noted that the proposed chronic REL is undergoing revision and the value may change. The acute health effects from formaldehyde, primarily due to eye irritation, are not anticipated to occur at the predicted maximal ambient levels. The upper bound maximum one-hour average concentrations for all five fuel scenarios were two-fold below the acute REL.

Significant indoor exposures to formaldehyde are known to occur. However, the emission estimates determined in this report for all pollutants, including formaldehyde, do not address potential additional exposure to indoor sources of formaldehyde. Unlike the formaldehyde TAC document, the estimated cancer risk and noncancer hazards reported here do not reflect the potential for indoor exposure to formaldehyde.

6.1.6. Methyl t-Butyl Ether (MTBE)

The lifetime cancer risk is the toxicological endpoint of concern for exposure to MTBE in the South Coast Air Basin. Toxic endpoints in animal studies included leukemia, lymphoma, and testicular, kidney, and liver cancer. The cancer unit risk estimate is 2.6×10^{-7} $(\mu g/m^3)^{-1}$ or 9.3×10^{-7} ppb^{-1}. The sources of uncertainty include those facing other cancer potency estimates, such as reliance on animal studies due to the lack of human data, and the extrapolation from experimental animal exposure concentrations to current ambient levels. Some additional sources of uncertainty apply in this particular case since the mechanism of action of MTBE as a carcinogen is unknown. The estimate therefore relies on health protective default assumptions as to the applicability of the findings in animals to humans, resulting in the use of a non-threshold model for the low-dose region.

The upper bound estimate of the cancer risk resulting from exposure to the annual average levels of MTBE predicted in the 1997 scenario, over a 70 year lifespan, is 3.6 excess cancer cases per million people exposed. In the 2003 scenario with the same MTBE-containing fuel, the resulting cancer risk estimate of 2.4 excess cancer cases per million people exposed is approximately one-third lower. The cancer risk via inhalation of MTBE is zero for scenarios where the fuel formulation does not contain MTBE.

The acute and chronic noncancer HQs generated by each of the MTBE-containing fuel scenarios are at least 0.01, indicating that modeling concentrations are at least 100-fold below the RELs. Noncancer health effects due to acute or chronic MTBE exposure are not expected to occur at maximal ambient levels. The most sensitive toxicological endpoints for acute inhalation exposure may include eye irritation, respiratory irritation and CNS effects (headache, nausea, vomiting, dizziness, and disorientation). The most sensitive toxicological endpoints for chronic exposure may include eye irritation, kidney damage, and CNS depression.

6.1.7. Peroxyacetyl Nitrate (PAN)

The acute noncancer HQs for PAN based on the results of the air modeling are above the threshold at which toxic effects may occur. Acute noncancer effects are the toxicological endpoints of concern for this pollutant in the South Coast Air Basin; the most sensitive of these is eye irritation. The one-hour maximum predicted HQ is 5.5 or less under all fuel scenarios. It appears that none of the scenarios for the year 2003 involves an exacerbation of the adverse health impact of PAN compared to the 1997 data. While these HQs are above one, it should be recognized that the air modeling results for short-term exposures reflect unfavorable meteorology. However, it is possible that some sensitive individuals may develop acute adverse effects at the maximum predicted exposure. Simultaneous exposure to other sensory irritants, such as formaldehyde, may exacerbate the eye irritation caused by PAN. As mentioned above, the CARB notes that they have much more confidence in the relative values than the absolute values of concentrations of the modeled chemicals.

Notably, there has been a consistent downward trend in the observed average acute PAN concentrations in the South Coast Air Basin. Twenty-four hour average PAN concentrations have declined from 15-20 ppb in the late 1960s, to 5-12 ppb in 1985-1990 and 2-5 ppb in 1993. Therefore, it may be concluded that the irritant effects due to exposure to PAN have decreased proportionally in the South Coast Air Basin since the 1960s.

A population-weighted annual average exposure to PAN has not been determined because consistent long-term measurements of atmospheric PAN have not been measured. Therefore, a chronic HQ cannot be adequately determined. The most sensitive endpoint from chronic exposure to PAN may include inflammation, epithelial metaplasia and hyperplasia in the respiratory tract.

Currently, there is inadequate evidence to determine if PAN is carcinogenic in either experimental animals or humans.

Table 5a. Range of Estimated Maximum Noncancer Hazard Quotients (HQ) for Various Scenarios in the South Coast Air Basin

		1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 NonOxy
Acetaldehyde						
Chronic HQ	Upper	0.4	0.3	0.3	0.4	0.3
	Lower	0.4	0.3	0.3	0.3	0.3
Acute HQ	Upper	0.3	0.3	0.3	0.3	0.3
	Lower	0.2	0.2	0.2	0.2	0.2
Benzene						
Chronic HQ	Upper	0.06	0.04	0.04	0.04	0.04
	Lower	0.05	0.04	0.04	0.04	0.03
Acute HQ	Upper	0.06	0.04	0.04	0.04	0.04
	Lower	0.03	0.02	0.02	0.02	0.02
Butadiene						
Chronic HQ	Upper	0.09	0.05	0.05	0.05	0.05
	Lower	0.09	0.05	0.05	0.05	0.05
Acute HQ	Upper	0.05	0.02	0.02	0.02	0.02
	Lower	0.02	0.01	0.01	0.01	0.01
Ethanol						
Chronic HQ	Best	0.0001	0.0001	0.0001	0.0002	0.0001
Acute HQ	Upper	0.002	0.002	0.003	0.003	0.002
	Lower	0.001	0.001	0.002	0.003	0.001
Formaldehyde						
Chronic HQ	Upper	2.4	2.1	2.1	2.1	2.0
	Lower	2.4	2.1	2.0	2.0	2.0
Acute HQ	Upper	0.5	0.5	0.5	0.5	0.5
	Lower	0.3	0.3	0.3	0.3	0.3
MTBE						
Chronic HQ	Upper	0.005	0.003	0.0	0.0	0.0
	Lower	0.005	0.003	0.0	0.0	0.0
Acute HQ	Upper	0.01	0.007	0.0	0.0	0.0
	Lower	0.003	0.002	0.0	0.0	0.0
PAN*						
Acute HQ	Upper	5.5	5.3	5.2	5.3	5.1
	Lower	2.7	2.7	2.6	2.7	2.5

* A population-weighted annual average for PAN was not determined because consistent long-term measurements of atmospheric PAN have not been performed. See CARB report for details.

Table 5b. Range of Estimated Maximum Noncancer Hazard Quotients (HQ) for Various Scenarios in the South Coast Air Basin – Criteria Air Pollutants

	1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 NonOxy
Carbon Monoxide					
Acute 8 hour HQ	1.9	1.6	1.6	1.5	1.6
Acute 1 hour HQ	1.1	1.0	1.0	0.9	1.0
Nitrogen Dioxide					
Chronic HQ	0.8	concentrations not estimated by CARB since no significant change in Maximum 1-Hour*			
Acute 1 hour HQ	1.0	0.9	0.9	0.9	0.9
Ozone					
Acute 8 hour HQ	2.6	2.5	2.5	2.5	2.5
Acute 1 hour HQ	2.7	2.6	2.5	2.5	2.5
Particulate Matter (PM10)					
Chronic HQ	1.9	CARB reported, “No significant change expected among 2003 scenarios” for both annual and daily concentrations*			
Acute 24 hour HQ	4.5				

* compared to exposure estimates for the 1997 MTBE-fuel scenario (see CARB report for details)

Table 5c. Range of Estimated Maximum Lifetime Cancer Risk Values for Various Scenarios in the South Coast Air Basin

		1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 NonOxy
Acetaldehyde						
Lifetime Cancer Risk	**Upper**	8.6×10^{-6}	7.6×10^{-6}	7.6×10^{-6}	8.6×10^{-6}	7.6×10^{-6}
	Lower	8.6×10^{-6}	7.2×10^{-6}	7.6×10^{-6}	8.1×10^{-6}	7.2×10^{-6}
Benzene						
Lifetime Cancer Risk	**Upper**	1.1×10^{-4}	7.4×10^{-5}	7.3×10^{-5}	7.5×10^{-5}	7.1×10^{-5}
	Lower	1.0×10^{-4}	6.7×10^{-5}	6.5×10^{-5}	6.8×10^{-5}	6.4×10^{-5}
Butadiene						
Lifetime Cancer Risk	**Upper**	1.3×10^{-4}	7.4×10^{-5}	7.4×10^{-5}	7.4×10^{-5}	7.4×10^{-5}
	Lower	1.3×10^{-4}	7.0×10^{-5}	7.0×10^{-5}	7.0×10^{-5}	7.0×10^{-5}
Formaldehyde						
Lifetime Cancer Risk	**Upper**	3.3×10^{-5}	2.9×10^{-5}	2.9×10^{-5}	2.9×10^{-5}	2.8×10^{-5}
	Lower	3.3×10^{-5}	2.9×10^{-5}	2.8×10^{-5}	2.8×10^{-5}	2.8×10^{-5}
MTBE						
Lifetime Cancer Risk	**Upper**	3.6 x 10-6	2.4 x 10-6	0.0	0.0	0.0
	Lower	3.3 x 10-6	2.2 x 10-6	0.0	0.0	0.0

6.2. Risk Characterization for Other Compounds of Concern: Toluene, Xylenes, Isobutene, n-Hexane.

A number of compounds were evaluated for possible adverse health impacts, besides those for which detailed atmospheric model data were developed by the CARB. In particular, the toxicological properties of toluene, xylenes, isobutene and *n*-hexane were considered since they have been identified as substantial fuel components. A detailed discussion of the potential toxicity for each of these chemicals is summarized in Appendix A. CARB provided measured or modeled concentrations of these compounds in the South Coast airshed for the year 1997 during which MTBE-containing fuel was used.

In each of these cases the annual average concentrations found or estimated were substantially below the chronic REL or other health protective concentrations, with a projected HQ of 0.1 or less (see Table 6 for details). None of these materials is a suspected human carcinogen. For acute exposures to toluene, *m*/*p*-xylene and *o*-xylene, the one-hour and 24-hour peak concentrations were also substantially below the corresponding health risk values. No acute health protective concentrations have been determined for isobutene and *n*-hexane, but since the predicted concentrations for acute episodes did not exceed the chronic protective levels for these compounds, no adverse acute health consequences are anticipated.

The emissions data and atmospheric model outputs for these compounds were not developed using the 2003 scenario. However, it was anticipated that there would be little or no change between the different fuel types, and a modest improvement relative to the 1997 (MTBE) scenario. Since no plausible variations in the model output would alter the conclusion that these compounds present no significant risk, it was not considered necessary to predict the 2003 outcomes in greater detail.

Table 6. Comparison of Estimated Maximum Pollutant Levels in California (based on South Coast Air Basin Data for 1996-1997) and Health Assessment Values

	Toluene (ppbV)	m/p-Xylene (ppbV)	o-Xylene (ppbV)	Isobutene (ppbV)	n-Hexane (ppbV)
Annual Average *					
Maximum Measured Value **	5.1	2.2	0.77	---	---
Projected Range of Maximum based on CO levels	5.6-11.4	2.8-4.7	1.0 - 4.4	2.2 - 3.9	1.2 - 2.6
Chronic REL	100	170	170	1100	60
Maximum 1 hour Average					
Extrapolated from Measured 24-Hour Maximum **	29.7	14.3	5.5	---	---
Projected Range of Maximum based on CO levels	51 - 103	25 - 45	8.8 - 40	22 - 35	11 - 23
Acute REL	9800 (6h)	5000 (0.5h)	5000 (0.5h)	NA	NA

* Overall Statewide Population-Weighted Annual Exposure typically would be between ½ and ¾ of the Maximum

** There is currently some uncertainty in measurement techniques; actual values may be higher.

6.3. Cumulative Cancer Impact of Multiple Chemical Exposures

The cumulative impact due to exposure to multiple cancer-causing chemicals is determined by the addition of all the corresponding lifetime risks of the chemicals involved. The lifetime risk is expressed as the estimated excess risk that results from lifetime exposure (i.e. 70 years) to a specific air concentration of a cancer-causing chemical. Unlike the cumulative impact methodology for noncancer toxicological endpoints, the lifetime risk from exposure to multiple cancer-causing chemicals is assumed to be additive regardless of the toxicological endpoint or target organ. This is because chemically induced cancer is considered predominantly a non-threshold event that is irreversible once initiated and because the target tissue may vary from species to species.

Table 7 displays 95 percent upper confidence limit estimates of lifetime cancer risk based on the predicted exposure concentration of each chemical, and the aggregate lifetime risk attributable to exposures to all these chemicals, for each fuel scenario in the South Coast Air Basin. Risk estimates were calculated using the range of atmospheric concentration estimates provided by CARB. These exposure estimates are best estimates of the population-weighted annual average exposures, with variations in model assumptions as described earlier by CARB. The last row displays the estimated range of excess cancer cases per million people that can be expected from lifetime exposure to the aggregate of cancer-causing pollutants.

Comparison among the individual pollutants shows that, regardless of the fuel scenario, benzene and butadiene are the major contributors to excess cancers due to airborne exposure to cancer-causing pollutants in the South Coast Air Basin. The contribution of excess cancer cases by acetaldehyde and MTBE by comparison is relatively minor. A small increase in acetaldehyde concentration in the Et3.5% 2003 scenario has no effect on the overall cancer risk, due to the lower potency of acetaldehyde compared to other pollutants such as benzene and butadiene, and to minor reductions in butadiene- or MTBE-related risks relative to the other 2003 scenarios.

Comparing the 1997 fuel scenario to the year 2003 fuel scenarios, the upper bound estimate of the excess cancer cases per million individuals is expected to drop from 270 - 290 to 170 - 190 excess cancer cases by 2003. There are very minor differences in the predictions for 2003 (170 - 180 excess cases per million for 2.5% ethanol and non-oxy fuels, compared to 180 - 190 for 3.5% ethanol and MTBE). But these appear to be much less than the uncertainty in the estimates, indicating that there is no difference among the year 2003 fuel scenarios regarding cancer risk. The conclusion that can be drawn from the cumulative exposure to airborne cancer-causing pollutants in the South Coast Air Basin is that the reduction in excess cancers, from the 1997 fuel scenario to the 2003 fuel scenarios, results from expected reductions in overall emissions, rather than a reduction in cancer causing emissions due to the use of any single fuel scenario.

Table 7. Lifetime Cancer Risk from Individual Chemicals and Cumulative Lifetime Cancer Risk for Each of the Five Fuel Scenarios.

Chemical		1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 NonOxy
Acetaldehyde	Upper	8.6 E-6	7.6 E-6	7.6 E-6	8.6 E-6	7.6 E-6
	Lower	8.6 E-6	7.2 E-6	7.6 E-6	8.1 E-6	7.2 E-6
Benzene	Upper	1.1 E-4	7.4 E-5	7.3 E-5	7.5 E-5	7.1 E-5
	Lower	1.0 E-4	6.7 E-5	6.5 E-5	6.8 E-5	6.4 E-5
Butadiene	Upper	1.3 E-4	7.4 E-5	7.4 E-5	7.4 E-5	7.4 E-5
	Lower	1.3 E-4	7.0 E-5	7.0 E-5	7.0 E-5	7.0 E-5
Formaldehyde	Upper	3.3 E-5	2.9 E-5	2.9 E-5	2.9 E-5	2.8 E-5
	Lower	3.3 E-5	2.9 E-5	2.8 E-5	2.8 E-5	2.8 E-5
MTBE	Upper	3.6 E-6	2.4 E-6	0	0	0
	Lower	3.3 E-6	2.2 E-6	0	0	0
Cumulative Lifetime Risk	Upper	2.9 E-4	1.9 E-4	1.8 E-4	1.9 E-4	1.8 E-4
	Lower	2.7 E-4	1.8 E-4	1.7 E-4	1.7 E-4	1.7 E-4
Excess Cancer Cases Per Million Individuals	Upper	290	190	180	190	180
	Lower	270	180	170	170	170

An inherent uncertainty resulting from addition of multiple lifetime cancer risks is that this may underestimate the cancer risk in cases where the interactions are synergistic, or overestimate the cancer risk in cases where the interactions are not additive or are antagonistic. Also, the aggregate risk prediction may exaggerate the confidence bounds on the estimate, since it is obtained by adding individual upper 95 percent confidence limits on the contributing risks. Since it is not known how the various risks and the uncertainties in their estimates interact, it has not been possible to allow for this effect.

The sources of uncertainty that are incorporated into the estimate of lifetime cancer risks, such as reliance on animal data and extrapolation from experimental exposure concentrations to ambient exposure concentrations, imply that the real aggregate risk may in fact be lower than the upper bound estimates. On the other hand, the exposure concentrations provided by CARB's model that serve as the basis for the cancer calculations are population-weighted annual averages. Certain individuals or communities located in areas where pollutant emissions are concentrated (such as those near freeways or fuel storage and handling facilities) may experience greater increments in risk from some fuel-related pollutants, whereas the impacts in other areas may be less. As noted above, there is more confidence in the relative differences between fuels than the absolute magnitude of the risk faced by the exposed population under the various scenarios considered. Therefore, comparison of the aggregate cancer risks among the five fuel scenarios gives a reasonably good indication of the relative impact of each fuel on the cancer risk from airborne pollutants in the South Coast Air Basin.

6.4. Cumulative Noncancer Impact of Multiple Chemical Exposures

By definition, exposure to a single chemical in the air will not result in a toxic response if it is below the threshold necessary to elicit a response. However, simultaneous exposure to two similar chemicals at sub-threshold levels may result in a toxic response. Under the noncancer cumulative impact methodology, the combined impact of several chemicals present at the same time are assessed by assuming the interaction of the chemicals will be additive for a given toxicological endpoint, unless information is available to the contrary.

The cumulative impact is determined by simply adding the HQs for chemicals that impact the same target organ or system. If either the HQ for an individual chemical or the cumulative hazard index (HI) for a particular toxicological endpoint exceeds one, the margin of safety implicit in the REL is eroded. As noted in the introduction, this does not automatically imply that adverse health effects will occur. Rather, it indicates that there is an increasing possibility that more sensitive individuals may be affected. For the airborne pollutants of concern in the South Coast Air Basin, cumulative HIs for a given toxicological endpoint can be determined under each fuel scenario and for each predicted exposure period (maximum one-hour average and maximum population-weighted annual exposure).

For the maximum one-hour average exposure, the cumulative toxicological endpoints of concern are eye irritation and respiratory irritation. Table 8 displays the individual HQs for each chemical where eye irritation is a primary toxicological endpoint. PAN, ozone, and nitrogen dioxide are the major pollutants that cause the eye irritant effects. Under the cumulative impact methodology, sub-threshold pollutants such as acetaldehyde and formaldehyde may also participate by exacerbating the eye irritation primarily due to PAN, ozone, and nitrogen dioxide.

For acute respiratory irritation, ozone and nitrogen dioxide are the major pollutants of concern. Acetaldehyde may also exacerbate the respiratory irritation caused by ozone and nitrogen dioxide (Table 9). The ethanol and MTBE contribution to both eye and respiratory irritation tend to be so small that these pollutants are not likely to have a significant impact on these toxicological endpoints.

The primary pollutants involved in chronic respiratory irritation are formaldehyde and PM_{10}, both of which are individually above the threshold for this toxicological endpoint (Table 10) and may result in chronic respiratory effects at the maximum exposure level. A limitation in using the cumulative impact approach for pollutants that cause either acute or chronic respiratory irritation is that their primary site of action within the respiratory system may differ. For example, formaldehyde is known to produce nasal and upper respiratory irritation while PM_{10} produces inflammation principally in the lower airways. Therefore, the cumulative impacts for these two pollutants may be less than additive.

Table 8. Maximum Acute Hazard Quotients (HQ) and Cumulative Acute Hazard Indices (HI) for Eye Irritation for Each of the Five Fuel Scenarios

Chemical		1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 NonOxy
Acetaldehyde	Upper	0.3	0.3	0.3	0.3	0.3
	Lower	0.2	0.2	0.2	0.2	0.2
Ethanol	Upper	0.002	0.002	0.003	0.003	0.002
	Lower	0.001	0.001	0.002	0.003	0.001
Formaldehyde	Upper	0.5	0.5	0.5	0.5	0.5
	Lower	0.3	0.3	0.3	0.3	0.3
MTBE	Upper	0.01	0.007	0	0	0
	Lower	0.003	0.002	0	0	0
PAN	Upper	5.5	5.3	5.2	5.3	5.1
	Lower	2.7	2.7	2.6	2.7	2.5
Nitrogen dioxide	Best	1.0	0.9	0.9	0.9	0.9
Ozone	Best	2.7	2.6	2.6	2.5	2.6
Cumulative HI	Upper	10.0	9.6	9.5	9.5	9.4
	Lower	6.9	6.7	6.6	6.6	6.5

Table 9. Maximum Acute Hazard Quotients (HQ) and Cumulative Acute Hazard Indices (HI) for Respiratory Irritation for Each of the Five Fuel Scenarios

Chemical		1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 NonOxy
Acetaldehyde	Upper	0.3	0.3	0.3	0.3	0.3
	Lower	0.2	0.2	0.2	0.2	0.2
Ethanol	Upper	0.002	0.002	0.003	0.003	0.002
	Lower	0.001	0.001	0.002	0.003	0.001
MTBE	Upper	0.01	0.007	0	0	0
	Lower	0.003	0.002	0	0	0
Nitrogen dioxide	Best	1.0	0.9	0.9	0.9	0.9
Ozone	Best	2.7	2.6	2.6	2.5	2.6
Cumulative HI	Upper	4.0	3.8	3.8	3.7	3.8
	Lower	3.9	3.7	3.7	3.6	3.7

Table 10. Maximum Chronic Hazard Quotients (HQ) and Cumulative Chronic Hazard Indices (HI) for Respiratory Irritation for Each of the Five Fuel Scenarios

Chemical		1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 NonOxy
Acetaldehyde	Upper	0.4	0.3	0.3	0.4	0.3
	Lower	0.4	0.3	0.3	0.3	0.3
Ethanol	Best	0.0001	0.0001	0.0001	0.0002	0.0001
Formaldehyde	Upper	2.4	2.1	2.1	2.1	2.0
	Lower	2.4	2.1	2.0	2.0	2.0
Nitrogen dioxide	Best	0.8	0.8	0.8	0.8	0.8
PM_{10}	Best	1.9	1.9	1.9	1.9	1.9
Cumulative HI	Upper	5.5	5.1	5.1	5.2	5.0
	Lower	5.5	5.1	5.0	5.0	5.0

Other limitations may exist for determining the cumulative toxicological impacts of airborne pollutants. Combining HIs may underestimate the effect in the cases where interactions on a given target organ are synergistic, or overestimate the effect in the cases in which interactions are not additive or are antagonistic.

A limitation concerning the acute HIs is that the peak one-hour airborne concentrations for each of the chemicals may not have occurred in the same hour. However, given that the one-hour maximum average is a worst case scenario for an episodic event, it is appropriate to assume for the purposes of the cumulative impact analysis that peak one-hour concentrations occur during the same time period.

The modeling conducted by CARB to evaluate the differences in air quality impacts from using the various fuel formulations provided the concentrations in air that we have used in this analysis. The concentrations for acute exposures (e.g., 1, 8, 24 hour averages) reflect a scenario with relatively adverse meteorological conditions. In addition, the model is based on the South Coast Airshed, in which pollutant concentrations from vehicular and other sources are typically somewhat higher than in some other areas of the State of California. Therefore, the absolute values of the annual average concentrations may not reflect an average in other parts of the State. There is more confidence assigned to the relative values of the concentrations representing the various fuel usage scenarios.

Overall, OEHHA finds that the modest reduction in HIs for the 2003 fuel scenarios compared to the 1997 fuel scenario is encouraging. The cumulative HIs imply that at times some individuals may experience eye and respiratory irritation. However, given the above limitations in the cumulative impact methodology, as well as uncertainties in modeled exposure and toxicological risk methodology, the very minor differences in the predicted cumulative noncancer impacts among the year 2003 fuel scenarios are not significant enough to warrant a recommendation for any one fuel based solely on airborne exposure to eye and respiratory irritants.

6.5. Health Impacts of Drinking Water Contamination by Gasoline Components

Health protective concentrations for drinking water for various components of gasoline are shown in Table 3.

The compounds of greatest concern from the point of view of potential low-level contamination of drinking water are benzene (a known human carcinogen) and MTBE. MTBE is a suspected carcinogen, and also has highly objectionable taste and odor which render drinking water unpalatable even at very low concentrations. Its breakdown product, TBA, is also a suspected carcinogen and has similarly objectionable organoleptic (i.e. noxious) properties. Other compounds for which some adverse health effects might be anticipated are toluene, xylene, formaldehyde, and various aliphatic hydrocarbons. These are not considered carcinogenic by the oral route, but higher concentrations are toxic, and some may also adversely effect taste and odor. Ethanol and its oxidation products such as acetaldehyde are toxic only at very high levels and are also very rapidly biodegraded, so in general these are not expected to present major long-term contamination problems.

Contamination of ground and surface waters by gasoline components, as a result of leakage, spills and transportation accidents is an established fact, and likely to continue in spite of efforts to prevent such occurrences. However, the organizations responsible for providing public drinking water supplies have monitoring and control measures in place for contaminants with potentially adverse impacts on public health. OEHHA has been advised by the State Water Resources Control Board (SWRCB) that it is the policy of the California Department of Health Services' (DHS) Drinking Water Program to avoid contamination of any public water supply by gasoline components in excess of the health protective levels. This may include closing down wells or surface water sources that show signs of contamination. They also monitor the movement of known plumes from gasoline spills and leaks. These measures are intended by the SWRCB to ensure that public drinking water supplies remain free of contamination by gasoline components, and thus prevent adverse public health consequences for consumers of the public drinking water supply. This would be the case either with continued use of MTBE, or with its replacement by ethanol or non-oxygenated gasoline. There may be extensive economic consequences and resource availability problems if well closures are widespread. These consequences, and their differential impact in scenarios with use of different fuel compositions, are the subject of a separate report by SWRCB (Volume 4).

There is a concern for public health impacts of different fuel formulations for those using private wells or other sources of drinking water not subject to the monitoring and regulatory oversight of the DHS Drinking Water Program. OEHHA has so far been unable to determine the number and location of such sources that may be threatened by gasoline spills, or the number of people using them as their drinking water sources. There appears also to be little quantitative information on the differential impact of alternative fuel formulations on contamination levels in affected wells. It has not therefore been possible to provide a quantitative risk assessment for this situation. Qualitatively, it would appear that MTBE is already a problem for groundwater users, and its removal would be an unqualified benefit. Direct effects of ethanol would appear to be minimal even in cases of severe contamination, although the adverse consequences of contamination by the hydrocarbon fraction of the gasoline would remain. Research is currently being undertaken to determine whether any secondary effects of ethanol, such as enhancement of migration through soil, or acceleration or inhibition of biodegradation, would alter the concentrations of compounds of concern (such as benzene) in impacted wells.

No investigations of the systemic effects of oral exposure to very low levels of ethanol, such as might be anticipated if groundwater contamination were to occur, were identified in the literature. It is known that ethanol is rapidly biodegraded, and expected exposures are low. This issue is the subject of more detailed investigations currently being undertaken for the SWRCB. Since the results of this investigation are not yet available, the CalTox model was used as a preliminary approach for a typical situation of contaminated soil, with literature values for ethanol degradation, etc. Starting with 10,000 ppm in soil and 5,000 ppm in the vadose zone, the predicted values in ground water and tap water at one year were 2.3×10^{-6} and 1.9×10^{-6} ppm, respectively. Human exposure was 8% by inhalation, 91% by oral and 1% by dermal routes. As an extreme worst-case scenario, the values for half-lives of ethanol in soil and water were increased by an order of magnitude and the exposure time shortened to begin at 50 days instead of one year. In this case, the water concentrations were 0.24 and 0.20 ppm, respectively. Human exposure via tap water was assumed to be 10% by inhalation, 89% by oral, and 1% by dermal routes. These concentrations are well below the health protective concentrations developed in Appendix A and are also well below concentrations normally found in foods.

Overall, these findings indicate that ethanol contamination of the water due to use of ethanol in gasoline should present very minimal toxic and carcinogenic risk and no objectionable taste or smell problems for public drinking water.

6.6. Uncertainties and Data Gaps

6.6.1. Uncertainties in Dose-Response Assessment

Risk assessment involves a number of assumptions. Due to data limitations, it is not possible to ascertain all the uncertainties inherent in any cancer potency or unit risk factor. As a result of a number of uncertainties (e.g., in the cases where human data were inadequate for risk assessment, applicability of animal data to humans, variability in response in the general population, presence of susceptible subpopulations, etc.), the unit risk factor represents generally the 95 percent upper confidence limit of the slope of the dose-response curve. As such it may be considered a high-end estimate of the risks. The RELs for non-carcinogenic effects also have similar associated uncertainties. In developing RELs, uncertainty factors are applied to animal or human data to arrive at a concentration of the chemical in question that we are reasonably confident will not be associated with adverse health effects from long-term exposure. Thus, there is a built in margin for health-protection in the REL. These types of uncertainties are not readily quantifiable and in some instances, not quantifiable at all.

Most of the health values (unit risk factors, cancer potency factors, reference exposure levels) used in the evaluation were peer-reviewed numbers currently in use in a number of regulatory and advisory programs. In several instances, there was no available regulatory number. For example, there is no acute REL for butadiene and OEHHA has provided an interim value for a one-hour averaging time. Likewise, there is no regulatory value for ethanol in either air or water.

OEHHA has evaluated secondary literature and the key primary studies to develop interim values for use in this assessment as reference exposure levels in air and water.

A similar situation exists for other important chemicals of interest. The atmospheric transformation product, peroxyacetyl nitrate or PAN, is an irritant gas due to its oxidant properties. Despite the fact that PAN was identified as an irritating component of smog decades ago, no peer-reviewed regulatory numbers exist to use in a health effects assessment. We developed interim health protective concentrations for PAN for one hour and annual averaging times. A related compound, peroxypropionyl nitrate or PPN, is also an irritant gas formed via atmospheric reactions. However, we could not locate adequate toxicity information on this chemical and so have not included formation of PPN in this evaluation.

Other chemicals of interest lack key toxicity data. Nonoxygenate formulas of gasoline will likely have increased levels of alkylates relative to fuels with an oxygenate, including 2-methylpentane, 3-methylpentane, methylcyclopentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 2,2,4-trimethylpentane, 2,3,4-trimethylpentane, 2-methylhexane, and 3-methylhexane. These branched chain hydrocarbons function much the same as an oxygenate by increasing the efficiency of combustion. There are almost no toxicological data on these compounds. We are therefore unable to estimate potential public health risks from increasing the concentrations of these motor fuel components in the non-oxygenate fuels. However, the concentrations of these compounds modeled for the South Coast Air Basin for existing fuel speciation profiles are in the low parts per billion range as an annual average and in the tens of ppb range as one-hour peaks. Thus the alkylates would need to be fairly potent toxicants (e.g., be about equivalent to the cancer potency of benzene, have much greater acute noncancer toxic potential than benzene, and have greater chronic toxic potential than benzene) in order for these concentrations to be of concern. Our inability to estimate public health impacts of alkylates due to the almost complete lack of toxicological data is an uncertainty in this evaluation.

Finally, this evaluation focused on the key differences resulting from use of four different fuels. We used available evidence to decide which chemicals are important in assessing the air quality impacts differences. Although we believe we have focused on the key primary and secondary pollutants that impact air quality as a result of fuel usage, there is a slight possibility that the air quality impacts analysis from use of different fuels omitted a significant chemical.

6.6.2. Uncertainties in Exposure Assessment

The concentrations in air modeled by the CARB modeling effort also have inherent uncertainties. The uncertainty in speciation profiles of the various VOCs in the different fuels carries into the modeling results. The modeled concentrations are thus subject to uncertainties due to potential inaccuracies in the species profiles as well as inherent model uncertainties. It is evident from a comparison of the 1997 and 2003 scenarios with the same MTBE-containing fuel that the predicted emissions inventory has a substantial dependence on the expected numbers and types of vehicles. Since the types of vehicles in service and the mileage driven in 2003 are estimates with a significant level of uncertainty, this uncertainty will carry through to the exposure estimates for key pollutants. Uncertainty also exists in CARB’s assumption that reduced air emissions for 2003 are based on a total reduction of overall fuel emissions. As in the dose-response assessment, uncertainties in modeling may be difficult to quantify. However, they are likely considerably less than the uncertainties inherent in dose-response assessment. All of the models used by CARB in this exercise have had some validation studies to characterize their accuracy and guide their improvement. Whatever uncertainty exists in the assessment of exposure carries into the assessment of risk.

Aside from the air modeling, there are exposure assumptions implicit in some of the health values used in assessing risk. For instance, the unit risk factors and some of the reference exposure levels generally contain default assumptions that the average 70 kg person breathes 20 cubic meters per day. A recent analysis of breathing rate distribution conducted by OEHHA under the Air Toxics Hot Spots program indicates that the value of 20 cubic meters for a 70 kg person is about the 85th percentile of the distribution of breathing rates. As such it represents an above-average breathing rate. If the basis of the unit risk factor is a human inhalation study, this assumption results in a lower estimate of the potency if in fact the subjects were breathing less air and thus less chemical to produce the observed effect.

There is a very considerable degree of uncertainty over the level of exposure to fuel components and breakdown products occurring as water contaminants. A primary concern is exposure via drinking water. (In scenarios involving water as the pathway of exposure, it is generally assumed that people consume about two liters of water per day. For compounds that are volatile, they have inhalation exposures equivalent to drinking at least another liter by virtue of household water use.) We have been unable to perform a quantitative analysis of the risk from drinking water since estimates of contamination of the sources most likely to be affected, *i.e.* private wells, are not available. It is assumed that the DHS Drinking Water Program's regulatory and monitoring activities are sufficient to prevent actual delivery of contaminated water via public distribution systems, in which case there will not be health impacts from this source. We do not have access to a quantitative evaluation or failure analysis for this expectation. Some of these uncertainties may be addressed by research currently being undertaken by the SWRCB.

There may be low-probability scenarios for contamination of water which we have not evaluated. For example, since ethanol will be transported by truck, train, or barge, the possibility exists that a transportation accident might contaminate a surface-water drinking water supply. However, while the aquatic life immediately at the site of the spill might be affected by the ethanol, it is unlikely that such a scenario would impact public health due to the biodegradability and relatively low toxicity of ethanol. Similar accidents might also occur with a vessel transporting already-blended fuel. However, it does not appear useful to focus on that scenario for the comparative evaluation of ethanol-containing gasoline with other fuels since other components of fuels of interest (e.g. benzene, toluene, hexane, xylenes) are more toxic and more slowly degraded in the environment than ethanol and would become water contaminants in a blended-fuel spill into surface water.

Finally, it is not yet determined which denaturants will be used to denature the ethanol, as required by law. Initial proposals include the use of naphtha or similar gasoline-like materials, so these are unlikely to have a substantial effect on the health impacts of the combined fuel. However, since both the actual composition of such additives and their toxicological properties are unknown to us at present, we have not evaluated potential health risks of denaturants in the ethanol used for gasohol.

7. Research Needs

As noted earlier in this report there are several issues which cannot be addressed, or for which our assessment is subject to very substantial uncertainties, due to lack of information which would be required to better define expected risks. Whereas some of the uncertainties are intrinsic to the process of risk assessment, some could be substantially reduced by further research. Potential areas for further research relate to both the toxicological properties of presently identified pollutants and the assessment of exposure to these materials (and perhaps to others as yet unidentified). These are summarized in Tables 11 and 12.

Table 11. Research Needs for More Complete Understanding of the Potential Health Effects of Ethanol in Gasoline.

Basic Toxicologic Information Needed:

Alkylates, including but not limited to

2-methyl pentane
3-methylpentane
methylcyclopentane
2,3-dimethylpentane
2,4-dimethylpentane
2,2,4-trimethylpentane
2,3,4-trimethylpentane
2-methylhexane
3-methylhexane

Other compounds:

ethanol (at low concentrations)
isobutene
peroxyacetyl nitrate (PAN)
peroxyproprionyl nitrate (PPN)

Development of Health Assessment Values Needed:

acetaldehyde (acute exposures)
butadiene (acute exposures)
ethanol (acute and chronic exposures)
MTBE (acute exposures)
PAN (acute and chronic exposures)
PPN (acute and chronic exposures)

Table 12. Key Issues to be Resolved in Order to Further Our Understanding of the Potential Health Effects of Ethanol in Gasoline

Water contamination issues:
what are the gasoline breakdown products?
what is the likelihood of contamination of public / private wells?
what are the impacts of transportation accidents?
what are the impacts of watercraft use?
General risk assessment issues:
what denaturants will be used in the new formulations?
what are the risks posed by, and interactions of, complex mixtures associated with motor fuels?
need to conduct life-cycle analysis to determine overall exposure from production, use and disposal of motor fuels; this will include air emissions as well as contamination of water and soil
need more information on localized 'hot spots'
address remaining uncertainties in emissions and atmospheric chemistry

The components of existing and proposed gasoline formulations include several compounds for which there is relatively little toxicological information available. This applies particularly to the branched-chain alkanes and alkenes classified as "alkylates". Whereas these compounds occur to some extent in all of the fuel formulations considered in this report, they are specifically increased in the proposed non-oxygenated RFG3 fuel. There appears to be only very limited acute toxicological information on a few of these compounds, and none at all on many. Further investigation of those specific chemicals identified as major "alkylate" components of the new fuels is warranted, to include investigation of both short-term and long-term effects. Studies need to be performed on specific isomers, rather than on generic fractions such as pentanes, hexanes, octanes etc., because the toxicological properties of different isomers may differ substantially. There are some reports on the toxicological properties of generic mixtures, including previous formulations of unleaded gasoline (U.S. EPA, 1987). While these have assisted in quantifying the risk from fuels in general, they do not provide sufficient information on individual components to allow analysis of the differential impact of alternative fuel formulations.

In spite of the very large literature on the effects of consumption of alcoholic beverages, there is also a surprising lack of information on the toxicity of ethanol by inhalation, and on the effects of low level oral ingestion. This may reflect a consensus that ethanol occurs in many foods and the toxicity of ethanol is not considered a substantial problem under these circumstances. Nevertheless, it would be preferable to have more complete studies of acute and chronic effects, performed according to modern experimental design principles. Continued research on the toxicity of ethanol-containing gasoline also would have merit.

The toxicological information available on the photochemical reaction product PAN is limited. Although there are data on acute effects, there has been no evaluation for carcinogenic effects. Some genotoxic effects have been observed, and studies of up to six months duration identified squamous metaplasia in the respiratory tract of mice. While these latter findings were not considered evidence of neoplasia, they do raise the concern for possible carcinogenicity of this compound, suggesting a more exhaustive investigation using a lifetime bioassay protocol would be desirable. We were unable to locate any toxicological information on the related compound PPN. Since both these photochemical reaction products appear to have the potential for significant health impacts after both acute and chronic exposures, more information on their effects would be highly desirable.

Actual exposures to chemicals associated with fuels most commonly occur as exposures to complex chemical mixtures, rather than to isolated chemicals; thus, it is important that the health effects of interactions between individual components of these mixtures be characterized, in addition to the health effects of the individual components. There are presently large gaps in our knowledge of the health effects of exposures to complex mixtures associated with gasoline, as well as the health effects associated with some individual compounds. There is a need to conduct original research and to further develop and evaluate existing epidemiological data on the human health effects from complex mixtures associated with fuel components.

Additional research is also needed to address uncertainties in the exposure assessment. While the emissions and atmospheric chemistry have already been the subjects of extensive study, and a sophisticated model is available, significant uncertainties remain. It is important that monitoring of the actual atmospheric pollutant levels be continued, to observe the outcome of changes in vehicle type and usage and fuel composition, and thereby to confirm the accuracy of the model predictions.

It is also evident that at present our knowledge of the possible exposures via drinking water is limited. This needs to be augmented in several respects. An analysis of the likelihood of contamination of the public drinking water supply, in spite of the regulatory and monitoring efforts in place to avoid this, should be undertaken. This needs to reflect the number of sources potentially affected, the frequency of monitoring of these sources, and the size of the potentially impacted populations. This analysis also needs to provide indications of the possible concentration ranges and duration of exposures that might arise in the event of a failure of the control measures. An equally pressing concern is the lack of information of the likelihood and severity of exposures to gasoline components due to contamination of private wells at risk from contamination.

Life-cycle analysis integrates the multi-media risks associated with production, use, and disposal of substances. This is a resource intensive proposition; none the less it should be attempted for reformulated fuels. Life-cycle analysis would look at such issues as contamination of the environment from production, transportation, use, dissemination (e.g., at gasoline stations), and disposal. It is understood that work is at present being undertaken by SWRCB to address the likelihood of contamination from watercraft engine emissions, leaks, spills, and transportation accidents. The conclusions of these current efforts are clearly important. In addition, there is a need to investigate the concentrations of pollutants (gasoline components and their breakdown products) that might occur in drinking water as a result of such events. While it may not be possible to predict actual outcomes from likely sources of contamination, it would be useful to have some information as to the severity of plausible incidents.

8. Summary / Conclusions

Predicted levels of atmospheric pollutants for different fuel composition scenarios were provided by the CARB. Fuel compositions represented currently available MTBE-containing oxygenated fuel, two formulations of ethanol-containing fuel with either 2 or 3.5 percent oxygen content, and a non-oxygenated fuel formulated to comply with the proposed RFG3 requirements. These were considered in exposure scenarios based on the predicted emissions inventory for the year 2003. A scenario of the 1997 emissions inventory and MTBE-containing fuel was used to calibrate the model against actual measured data for that year.

Health protective concentrations in air and water for compounds of concern in the gasoline formulations, primary exhaust emissions or transformation products were selected from current California or United States regulatory standards where these were available. In the absence of suitable regulatory levels, draft levels currently under development for California programs were used, or else draft health protective levels were developed for this report using standard methodology.

The health protective levels for air contaminants were compared to the model predictions for these compounds provided by CARB, and risk characterizations developed for individual compound impacts. Risk characterizations of the cumulative impacts of carcinogens and irritant compounds were also developed.

It appears that there are no substantial differences in the public health impacts of the different non-MTBE fuel formulations considered in the scenarios for the year 2003. MTBE-containing fuels still pose a risk to water resources due to the high water solubility coupled with slow environmental degradation of MTBE. For all of these fuels the concentrations of irritants (including both air toxics and criteria pollutants) may achieve levels at which the safety margins for short-term and long-term exposures are reduced. At these levels, adverse health effects are not necessarily expected, but more sensitive members of the population may be affected. The 2003 scenarios are based on relatively adverse meteorological conditions in a region (the South Coast Airshed) of California severely impacted by vehicle-generated pollution, so effects in other parts of the State and under different meteorological conditions will likely be less severe. Due to the reduction in overall emissions, all the scenarios for year 2003 show a significant improvement over the predicted averages for 1997. The pattern for airborne carcinogens is similar in that the overall estimated risks do not differ between fuel formulations, but show some improvement for 2003 relative to 1997. The absolute values of the risk estimates are not regarded as reliable indicators of the actual risks faced by the population in the South Coast region, but are regarded as useful in indicating the relative impacts of the different scenarios.

Due to the lack of quantitative information on possible public exposures as a result of fuel-related groundwater, surface water or drinking water pollution, it was not possible to provide risk estimates for public health impacts of water contamination. However, consideration of the relative toxicity of ethanol, MTBE and their degradation products suggests that the direct effects of ethanol (if any public exposure were to occur) would be substantially less severe than the effects of MTBE. Secondary effects, including alterations in distribution and biodegradation of other fuel components, are currently being evaluated by the SWRCB. They are also examining the possible impacts of various contamination scenarios, such as spills, leakage, transportation accidents and the use of gasoline-powered watercraft, on water contamination by fuel components. Further analysis of the relative effects on water of the different fuel formulations may be possible once these studies are complete.

Our analysis of the health effects of ethanol in gasoline is dependent on the modeled concentrations provided by the CARB. As CARB updates their atmospheric concentration estimates, this report will be updated to reflect any possible new findings and conclusions.

9. References

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APPENDIX A. TOXICITY SUMMARIES

ACETALDEHYDE

CAS No: 75-07-0

INTRODUCTION

Acetaldehyde is directly emitted into the atmosphere as a product of incomplete combustion. It is also formed in the atmosphere as a result of photochemical oxidation of hydrocarbons and free radical reactions involving hydroxyl radicals. Photochemical oxidation is estimated to contribute 56% of the ambient acetaldehyde, as predicted by the Urban Airshed model. Concentrations of acetaldehyde formed via photochemical oxidation can vary significantly depending on the season, location, meteorological conditions, and time of day. Reactive organic gases such as ethyl peroxide and ethoxy radicals are precursors of photochemically generated acetaldehyde, while products of its atmospheric degradation include formaldehyde and peroxyacetyl nitrate (PAN). Acetaldehyde is regulated in California as a Toxic Air Contaminant, and is monitored by the statewide California Air Resources Board (CARB) toxics monitoring network.

KEY TOXICOLOGIC EFFECTS

Acute Toxicity

Acute exposure to acetaldehyde vapor leads to eye, skin and respiratory tract irritation (Reprotext, 1997). Eye irritation has occurred at airborne concentrations as low as 45 mg/m^3 and is seen in all persons exposed to 360 mg/m^3 (Clayton and Clayton, 1993; Grant, 1993). With higher airborne concentrations or extended exposure, corneal epithelium damage may occur producing photophobia, a foreign body sensation, and persistent lacrimation (Clayton and Clayton, 1993; HSDB, 1999). Concentrations of 12 µg/m^3 in air have caused changes in light sensitivity of the eye (Grant, 1993). Changes in auditory sensitivity were noted in one study at airborne exposure levels of approximately 50 µg/m^3 (Grant, 1993). Exposure to an airborne concentration of 241 mg/m^3 for 30 minutes resulted in upper respiratory tract irritation (Hathaway et al., 1991). Acetaldehyde may also cause bronchitis. Acetaldehyde exposure decreased pulmonary macrophage number (Clayton and Clayton, 1993). Higher concentrations can cause a build-up of fluid in the lungs (pulmonary edema), with severe shortness of breath.

Chronic Toxicity

No epidemiological exposure studies were located that specifically examined the effects of acetaldehyde in humans. In experimental animals, chronic exposure has caused growth retardation, upper respiratory tract irritation, mild anemia, increased urinary glutamic-oxaloacetic transaminase (SGOT/AST) activity, increased urinary protein content, increased kidney weights (without renal pathology), and histopathological changes in the nasal mucosa and trachea (including hyperplasia, squamous metaplasia, and inflammation) (ACGIH, 1991; Hathaway et al., 1991). Rats exposed to high concentrations (> 2880 mg/m^3) exhibited acute bronchopneumonia, occasionally accompanied by tracheitis and severe respiratory distress that included salivation, labored breathing, and mouth breathing.

Carcinogenicity

An increased incidence of nasal tumors in rats and laryngeal tumors in hamsters has been observed following inhalation exposure to acetaldehyde. The International Agency for Research on Cancer (IARC) classified acetaldehyde in Group 2B, possible human carcinogen, based on sufficient evidence in animals and inadequate evidence in humans (IARC, 1987). U.S. EPA (1997a) classified acetaldehyde in Group B2, probable human carcinogen, on the basis of sufficient evidence for carcinogenicity in animals and inadequate evidence in humans. OEHHA (1993) developed a cancer unit risk value of 2.7×10^{-6} $(\mu g/m^3)^{-1}$ for acetaldehyde under the Toxic Air Contaminant program. Acetaldehyde is listed as a carcinogen by the State of California under Proposition 65, California’s Safe Drinking Water and Toxic Enforcement Act of 1986.

Reproductive and Developmental Toxicity

No information is available regarding adverse reproductive or developmental effects of acetaldehyde in humans (U.S. EPA, 1994b). In studies with rodents, acetaldehyde has been shown to cross the placenta and cause growth retardation, to cause skeletal malformations, and to kill embryos. *In vitro* reproductive toxicity studies have shown that acetaldehyde is an inhibitor of testicular testosterone production (OEHHA, 1993). Acetaldehyde is not listed as a reproductive or developmental toxicant by the State of California under Proposition 65.

DOSE-RESPONSE ASSESSMENT

The following table contains available health assessment values used by California regulatory programs for acetaldehyde.

Table 1. Health assessment values for acetaldehyde

	Health Assessment Value	Reference
Acute reference exposure level (REL)	NA	--
Chronic reference exposure level (REL)*	9 mg/m^3	OEHHA (1993)
Cancer potency factor	1.0×10^{-2} (mg/kg-day)$^{-1}$	OEHHA (1999b)
Unit risk factor	2.7×10^{-6} $(\mu g/m^3)^{-1}$	OEHHA (1999b)
No significant risk level (NSRL)	90 mg/day	OEHHA (1994b)
U.S. EPA reference dose (RfD)	NA	---
U.S. EPA reference concentration (RfC)	9 mg/m^3	U.S. EPA (1991)
Public health goal	NA	---

*** This chronic REL was adopted from the Toxic Air Contaminant document approved by the Scientific Review Panel in 1993.**

NA = not available

Since adopted health assessment values suitable for assessing potential health impacts from short-term inhalation exposures are not available for acetaldehyde, OEHHA calculated a draft health protective concentration (HPC) for the purpose of this report. In calculating the HPC, OEHHA followed the risk assessment methodology used for developing the acute reference exposure levels (RELs) under the Air Toxics Hot Spots Program risk assessment guidelines process (OEHHA, 1999a). As mandated by state legislation, these guidelines underwent scientific and public peer review, prior to approval by the Scientific Review Panel (Senate Bill 1731, Statutes of 1992, Ch. 1162 of the California Health and Safety Code) and adoption by OEHHA. The derivation of the HPC is summarized below. Further details on the methodology are provided in OEHHA (1999a).

Derivation of Health Protective Concentration

Silverman et al. (1946) found that a 15-minute exposure to acetaldehyde induced eye irritation in male and female human volunteers at a concentration of 46 mg/m^3 (26 ppm). This concentration was identified as a lowest-observed-adverse-effect level (LOAEL); a no-observed-adverse-effect level (NOAEL) was not observed in this study. Application of “Haber’s Law” to extrapolate from a 15 minute exposure to 1 hour results in an adjusted LOAEL of 11.5 mg/m^3 (6.5 ppm), as shown below.

$$\begin{aligned} C^nT &= K \\ C^n_1T_1 &= C^n_2T_2 \text{ where n=1 for extrapolation from 15 min. to 60 min.} \\ (46\text{ mg/m}^3)\ (15\text{ min}) &= (C)\ (60\text{ min}) \\ C &= 11.5\text{ mg/m}^3 \end{aligned}$$

An acute 1-hour draft HPC can be calculated for acetaldehyde using the formula:

$$\text{Draft HPC} = \text{LOAEL} / \text{UF} = 11.5\text{ mg/m}^3 / 100 = 115\ \mu\text{g/m}^3\ (65\text{ ppb})$$

The uncertainty factor (UF) for this calculation is 100, which incorporates uncertainty contributions for extrapolation from a LOAEL to a NOAEL (10) and for potentially sensitive human subpopulations (10).

BENZENE

CAS No.: 71-43-2

INTRODUCTION

Except for cigarette smoking, vaporization of gasoline and automobile exhaust are the primary sources of benzene exposure in the general population (Wallace, 1996). Past formulations of gasoline contained about one to two percent benzene; however, current formulations are required to contain no more than one percent benzene by volume (CARB, 1997; CARB, 1998).

The California Air Resources Board (CARB) routinely monitors ambient air concentrations of benzene throughout California through its air toxics network. In 1982, when the monitoring program began, estimates of the population-weighted annual concentration of benzene was roughly 5 ppb (16 $\mu g/m^3$) (CARB, 1984). These concentrations have declined steadily over time such that in 1994 average estimates across the state were approximately 1.2 ppb (3.8 $\mu g/m^3$) (CARB, 1995). Since the statewide use of oxygenated gasoline in 1996, the ambient air concentrations of benzene have dropped to less than 1 ppb.

In studies of human exposures to benzene, the primary sources of exposure among non-smokers were auto exhaust and gasoline vapor emissions. Most of the benzene in outdoor air comes from auto and gasoline vapor emissions; inhalation of ambient air accounts for a large percentage of an individual’s total benzene exposure. Also, indoor air exposures due to intrusion of evaporative gasoline fumes in homes with attached garages and personal activities such as driving can contribute significantly to an individual’s total exposure to benzene (Wallace, 1996). Other sources of exposure to benzene include contaminated drinking water, which can arise for example from contamination of water sources by leaking from underground fuel storage tanks. In addition to direct ingestion, exposure routes of concern for benzene-contaminated drinking water include inhalation and dermal absorption from showering, cooking, and other household activities.

KEY TOXICOLOGIC EFFECTS

Acute Toxicity

Exposure to air concentrations of benzene of approximately 20,000 ppm for five to ten minutes, 7500 ppm for 30 minutes, or 1500 ppm for 60 minutes is estimated to cause death or severe toxicity in humans. Causes of death include pulmonary hemorrhage, renal congestion, and cerebral edema. Acute exposures to benzene have also resulted in less severe symptoms including headaches, lethargy, and weakness. These symptoms have been reported from exposure to 50 to 150 ppm benzene for 5 hours, whereas exposure to 25 ppm for eight hours showed no clinical effect (IPCS, 1993; Paustenbach et al., 1993).

Chronic Toxicity

Long-term exposure of humans to benzene is associated with numerous adverse effects including bone marrow damage, changes in circulating blood cells, developmental and reproductive effects, immunological effects, mutation, chromosomal damage, and cancer.

In humans, the blood forming organs (i.e., the lymphohematopoietic system) appear to be the most sensitive to the toxic effects of benzene. Many blood disorders, including aplastic anemia, pancytopenia, thrombocytopenia, granulocytopenia, lymphocytopenia, and leukemia have been associated with chronic exposure to inhaled benzene. Statistically significant increases in myelodysplastic syndromes and acute non-lymphocytic leukemia have been observed among workers exposed to average air concentrations of less than 10 ppm benzene (Hayes et al., 1997; OEHHA, 1999e).

Carcinogenicity

Benzene has been clearly established as a known human carcinogen. In 1987, benzene was listed as a carcinogen by the State of California under Proposition 65, the Safe Drinking Water and Toxic Enforcement Act of 1986. The International Agency for Research on Cancer (IARC) has classified benzene as Group 1, known to be carcinogenic to humans (IARC, 1982). U.S. EPA classifies benzene as a Group A, human carcinogen (U.S. EPA, 1999a).

The carcinogenic activity of benzene in humans has been established through numerous occupational epidemiological studies and case series reports (ATSDR, 1997; OEHHA, 1999e). It is well established that benzene can cause acute myelogenous leukemia and myelodysplastic syndromes. Strong evidence exists to implicate benzene in causing other forms of leukemia as well. There is some evidence to suggest that benzene also causes lymphoma and multiple myeloma in humans but these associations are less clear. Benzene has also been implicated as a potential risk factor for childhood leukemia (OEHHA, 1997b; Smith and Zhang, 1998).

Benzene also has been shown to be carcinogenic in numerous animal studies by either the inhalation or oral route of administration. Statistically significant increased incidences of cancer were observed at multiple sites, including Zymbal gland, mammary gland, ovary, uterus, nasal cavity, oral cavity, skin, Harderian gland, preputial gland, liver, and lung. Leukemias and lymphomas were also reported (ATSDR, 1997; OEHHA, 1999e).

Reproductive and Developmental Toxicity

Benzene causes reproductive and developmental effects including reduced fetal weight, delayed ossification, fetal chromosomal damage, altered fetal hematopoiesis, and alterations to sperm. OEHHA (1997b) extensively reviewed the available literature on benzene’s reproductive and developmental toxicity. Benzene was listed in 1997 as a reproductive and developmental toxicant by the State of California under Proposition 65, the Safe Drinking Water and Toxic Enforcement Act of 1986.

DOSE-RESPONSE ASSESSMENT

The following table contains current health assessment values used by California regulatory programs for benzene.

Table 2. Health assessment values for benzene

	Health Assessment Value	Reference
Acute reference exposure level (REL)	1300 µg/m^3 (for 6 hr)	OEHHA (1999a)
Proposed chronic reference exposure level (REL)	60 µg/m^3	OEHHA (1999c)
Cancer potency factor	1.0×10^{-1} (mg/kg-day)$^{-1}$	OEHHA (1994a)
Unit risk factor	2.9×10^{-5} (µg/m^3)$^{-1}$	OEHHA (1994a)
No significant risk level (NSRL)	7 µg/day	DHS (1988)
Proposed maximum contaminant level (PMCL)*	1.8×10^{-4} mg/L	DHS (1987)
Proposed public health goal (PHG)	0.00014 mg/L (0.14 ppb)	OEHHA (1999e)

Adopted health assessment values suitable for estimating potential non-cancer public health impacts from chronic benzene inhalation exposures, as well as any impacts from oral exposures from drinking water, are not available. Therefore, OEHHA used draft numbers developed under other California regulatory programs for the purpose of this report. To quantify non-cancer risks from chronic inhalation exposures, OEHHA used the proposed chronic reference exposure level (REL) currently being developed under the Air Toxics Hot Spots Program risk assessment guidelines process (Senate Bill 1731, Statutes of 1992, Ch. 1162 of the California Health and Safety Code). The methodology used to derive the proposed chronic REL for benzene, as well as the number itself, have undergone an initial round of public and scientific peer review, and are currently being considered by the State's Scientific Review Panel (1999c). In addition, OEHHA used the proposed public health goal (PHG) developed by OEHHA under the California Safe Drinking Water Act of 1996 (amended Health and Safety Code, Section 116365) to estimate potential health impacts from exposures via drinking water. The proposed PHG for benzene is also currently undergoing scientific and public review and comment. The derivation of both the proposed chronic REL and PHG for benzene is briefly summarized below. More detailed information is provided in OEHHA (1999c) and OEHHA (1999e), respectively.

Derivation of the Proposed Chronic Reference Exposure Level

Tsai et al. (1983) examined hematologic parameters in a population of male workers exposed to benzene in a refinery. This study provided a no-observed-adverse-effect level (NOAEL) of 0.53 ppm. The Tsai et al. study was based on occupational exposures; however, the chronic REL is intended to protect the general public who could be exposed continuously. Therefore, an equivalent time-weighted average concentration (C_{AVE}) was estimated from the observed concentration (C_{OBS}) as follows:

$$C_{AVE} = C_{OBS} \times (10\ \text{m}^3\text{/day occupational exposure} / 20\ \text{m}^3\text{/day total exposure}) \times (5\ \text{days} / 7\ \text{days})$$

In addition, an uncertainty factor of ten was applied to account for sensitive human subpopulations. Therefore:

Proposed chronic REL = C_{AVE} / UF = 0.02 ppm (20 ppb; 0.06 mg/m^3; 60 $\mu g/m^3$)

Derivation of the Proposed Public Health Goal

The proposed public health goal (C) for benzene in drinking water (in units mg/L) was calculated as follows:

$$C = \frac{BW \times R}{CSF \times L/day} = mg/L$$

where

BW = Adult body weight (a default of 70 kg)

R = De minimis level for lifetime excess individual cancer risk (a default of 10^{-6})

CSF = Cancer slope factor was estimated from the upper 95 percent confidence limit on the lifetime risk of total leukemia estimated for general population exposure to benzene, 24 hr/d, 365 d/yr. This estimate comes from the geometric mean of estimates derived from two cohorts, the Pliofilm Cohort (Paxton et al., 1994) and the Chinese Worker Cohort (Hayes et al., 1997). The mean lifetime risk estimate (0.050 ppm^{-1}) has been converted to a population-based cancer potency in units of $(mg/kg\text{-}day)^{-1}$:

$$risk/(mg/kg\text{-}d) = (0.050/ppm)*(ppm/3190\ \mu g/m^3\ air)*(70\ kg)*(1/20\ m^3/d)* (1/0.5\ absorbed)*(1000\ \mu g/mg) = 0.11$$

where 70 kg is the standard adult male body weight, and 20 m^3/d is the default estimate for the volume of air inhaled per day. This computation is based on absorption efficiencies of 50 percent for inhalation and 100 percent for oral ingestion of benzene, which were derived from the available literature on benzene uptake and metabolism in humans and animals (Appendix C of OEHHA, 1999e).

L/day = Daily volume of water consumed by an adult. Although the standard default is 2.0 L/day, studies of household use of benzene-contaminated drinking water (Lindstrom et al., 1994; Beavers et al., 1996) indicate that additional exposures via inhalation (e.g., from stripping of benzene to air via showering, dish washing) and via dermal absorption (e.g., bathing, showering) are expected. A best estimate of the daily water consumption equivalents is 4.7 L (Lindstrom et al., 1994, adjusted values). This value is supported by an estimate obtained from CalTox (DTSC, 1999) of 4.6 L-equivalents. This estimate includes adjustments for differences in absorption by route of exposure.

Therefore:

$$C = \frac{70\ kg \times 10^{-6}}{0.11\ (mg/kg\text{-}d)^{-1} \times 4.7\ Leq/day} = 1.4 \times 10^{-4}\ mg/L, \text{ or } 0.14\ ppb$$

The proposed PHG is 0.14 ppb based on carcinogenicity (total leukemia) which is also protective of non-cancer hematological effects from chronic exposure.

BUTADIENE

1,3-butadiene; CAS No.: 106-99-0

INTRODUCTION

Butadiene is an important industrial chemical used in the production of styrene-butadiene copolymers (SBR rubber) and chloroprene/neoprene. It is primarily released into the environment via emissions from gasoline- and diesel-powered vehicles and equipment. Lesser releases occur via production processes (fugitive leaks), tobacco smoke, gasoline vapors, burning plastic or rubber, and occasionally drinking water (Miller, 1978). Butadiene has low solubility in water, thus environmental release results primarily in air contamination. Airborne butadiene is subject to photodegradation and reaction with ozone and nitrate radicals. The main photooxidation products are acrolein and formaldehyde (Maldotti et al., 1980). Butadiene is regulated in California as a Toxic Air Contaminant, and is routinely monitored by CARB's statewide toxics monitoring network. The mean concentration of butadiene in 1996, as monitored by CARB from January through December of that year, was 0.214 ppb.

KEY TOXIC EFFECTS

Acute Toxicity

Butadiene is only mildly acutely toxic. In rats and mice, the median lethal concentrations (LC_{50}) for butadiene are above 100,000 ppm for two to four hours inhalation. The oral LD_{50} values for rats and mice are 5480 mg/kg and 3210 mg/kg, respectively. Acutely toxic effects of butadiene exposure in experimental animals progressed from light anesthesia, to running movements and tremors, to deep anesthesia and death (NIOSH, 1991).

Chronic Toxicity

Among workers in the styrene-butadiene rubber manufacturing industry, chronic exposure to butadiene was reported to contribute to an increase in overall mortality, emphysema, and cardiovascular diseases in a retrospective epidemiological study (McMichael et al., 1976). In another study, a survey of rubber workers exposed to a mean concentration of 20 ppm butadiene exhibited slightly lower levels (but within normal range) of red blood cells, hemoglobin, platelets, and neutrophils (Checkoway and Williams, 1982). Workers in both of these studies were exposed to mixtures of chemicals. Therefore, the specific contribution of butadiene to the adverse respiratory and hematopoietic effects remain unclear.

In a comprehensive study conducted by the National Toxicology Program, chronic inhalation exposure of mice to concentrations as low as 20 ppm 1,3-butadiene resulted in decreased survival, primarily due to the development of malignant neoplasms (NTP, 1993). Exposure to higher concentrations (60-650 ppm) resulted in significant changes in hematological parameters (i.e., decreased erythrocyte counts, hemoglobin concentrations and packed cell volume); these changes were attributed to significant adverse effects on the bone marrow. In addition to changes in bone marrow, adverse non-neoplastic or pre-neoplastic effects were observed in liver, thymus, lung, testes, ovary, heart, mammary gland, upper respiratory tract, and other organs.

Carcinogenicity

Results of epidemiological studies regarding the effects of butadiene on human populations have shown an association between butadiene exposure and the occurrence of leukemias (Santos-Burgoa et al., 1992; Matanoski et al., 1993; Delzell et al., 1995 and 1996).

In mice and rats, inhalation of butadiene has been shown to induce tumors at multiple sites (OEHHA, 1992b; 1999b). These sites include heart, lung, mammary gland, ovaries, fore-stomach, liver, pancreas, Zymbal gland, thyroid, testes, and hematopoietic system (NTP, 1993; Melnick et al., 1990a, 1990b, 1990c; Melnick and Huff, 1992; Owen et al., 1987). Butadiene is only one of two chemicals known to induce cancer of the heart in laboratory animals.

The Occupational Safety and Health Administration (OSHA, 1990) has classified butadiene as a “potential occupational carcinogen”. U.S. EPA (1985) and IARC (1987) have concluded that the evidence for carcinogenicity of butadiene in animals is sufficient. These organizations have classified the chemical as Group B2 and 2B, respectively, in their schemes of ranking potential human carcinogens (OEHHA, 1999b).

Reproductive/Developmental Toxicity

No reproductive or developmental toxicity studies were located that specifically examined the effects of butadiene in humans. However, butadiene has been shown to cause reproductive and developmental effects in rodents (OEHHA, 1992b). Reproductive effects have been reported in male and female mice (i.e., testicular and ovarian atrophy, respectively) (NTP, 1993). Developmental effects reported in the literature consist primarily of reduced fetal body weight (observed in both rats and mice) and minor skeletal defects (i.e., abnormal ossifications, abnormal sternebrae, and supernumerary ribs) observed in mice (IISRP, 1982; Hackett et al., 1987b; Anderson et al., 1993). In a 1992 review of the available literature by OEHHA, the no-observed-adverse-effect level (NOAEL) for developmental toxicity in rats was found to be 1000 ppm, while a NOAEL could not be determined for mice since effects were seen in the lowest doses of all available studies (OEHHA, 1992b).

Dose-Response Assessment

The following table contains health assessment values used by California regulatory programs for 1,3-butadiene.

Table 3. Health assessment values for 1,3-butadiene.

	Health Assessment Value	Reference
Acute reference exposure level (REL)	NA	---
Proposed chronic reference exposure level (REL)	8 mg/m^{3}	OEHHA (1999c)
Cancer potency factor	3.4 E+0 (mg/kg-day)$^{-1}$	OEHHA (1999b)
Unit risk factor	1.7 ´ 10^{-4} (mg/m3)$^{-1}$	OEHHA (1999b)
No significant risk level (NSRL)	0.4 mg/day	OEHHA (1989)
U.S. EPA reference dose (RfD)	NA	--
U.S. EPA reference concentration (RfC)	NA	--
Public health goal (PHG)	NA	---

NA = not available

Since adopted health assessment values suitable for assessing potential non-cancer health impacts from short-term inhalation exposures to butadiene are not available, OEHHA calculated draft health protective concentration (HPC) for the purpose of this report. In calculating the HPC, OEHHA followed the risk assessment methodology used for developing the acute reference exposure levels (RELs) under the Air Toxics Hot Spots Program risk assessment guidelines process (OEHHA, 1999a). As mandated by state legislation, these guidelines underwent scientific and public peer review, prior to approval by the Scientific Review Panel (Senate Bill 1731, Statutes of 1992, Ch. 1162 of the California Health and Safety Code). In addition, in the absence of an adopted health assessment value suitable for assessing chronic inhalation exposures, OEHHA used the proposed chronic reference exposure level (REL) to assess potential public health impacts from chronic inhalation exposures. Chronic RELs are being developed under the legislatively mandated Air Toxics Hot Spots Program risk assessment guidelines process; however, the chronic RELs have not been adopted at this time. The methodology used to derive the proposed chronic REL for butadiene, as well as the number itself, have undergone an initial round of public and scientific peer review, and are currently being considered by the State's Scientific Review Panel (1999c). The derivation of the draft HPC and the proposed chronic REL are summarized below. The adopted risk assessment methodology used for deriving the HPC is provided in OEHHA (1999a), and a more detailed analysis of the chronic REL is provided in OEHHA (1999c).

Derivation of Health Protective Concentration

The short-term inhalation value for butadiene is derived from developmental and reproductive studies evaluated by U.S. EPA (1998). Hackett *et al.* (1987a and b) examined the developmental toxicity of butadiene in mice and rats. Animals were exposed via inhalation at 0, 40, 200, and 1,000 ppm on gestation days 6-15 for 6 hours per day. No effects were seen in rats. A no-observed-adverse-effect level (NOAEL) of 200 ppm was identified for maternal toxicity in rats. In mice, reduced fetal weights were observed in all exposure levels with 40 ppm considered a lowest-observed-adverse-effect level (LOAEL). Using a benchmark dose analysis, an LEC$_{10}$ of 13.67 ppm was derived for reduction in mean fetal weight per litter. Using the LEC$_{10}$, the HPC was calculated as follows:

draft health protective concentration = LEC_{10} / UF = 13.67 / 100 = 0.14 ppm
(140 ppb, rounded)

The cumulative uncertainty factor of 100 is based on a factor of 3.16 for extrapolation from a LOAEL to a NOAEL, 3.16 for interspecies differences, and 10 for interindividual differences. The factor of 3.16 represents the geometric mean between 1 and 10.

In comparison, applying an uncertainty factor to the observed LOAEL (instead of the LEC_{10} derived from the benchmark dose) gives a similar value as the benchmark dose calculation. In this case, the cumulative uncertainty factor is 300 based on a factor of 10 for extrapolation from the LOAEL to NOAEL, 3.16 for interspecies differences, and 10 for interindividual difference. A factor of 3.16 instead of 10 is used for extrapolation from the LOAEL to the NOAEL because use of the benchmark dose methodology reduces some of the uncertainty by utilizing the dose response curve to estimate a threshold for effects. Therefore, 40 ppm / 300 yields a value of 130 ppb (rounded).

Derivation of Proposed Chronic Reference Exposure Level

The proposed chronic REL is based on NTP (1993), which reported an increased incidence of ovarian atrophy in mice exposed to butadiene. In this study, mice were exposed to 0, 6.25, 20, 62.5, 200, or 625 ppm butadiene by inhalation 6 hours per day, 5 days per week for 103 weeks. The lowest exposure concentration (6.3 ppm) was identified as a LOAEL, while a NOAEL was not identified. Adjusting for the discontinuous exposure pattern, the average experimental concentration was calculated to be 1.1 ppm for the LOAEL group (6.3 ppm × 6/24 hours × 5/7days). An uncertainty factor of 300 was applied which incorporates uncertainty contributions for use of a LOAEL (10), interspecies scaling (3) and intraspecies scaling (10). Therefore, the proposed chronic REL is 4 ppb (0.004 ppm; 0.008 mg/m^3; 8 $\mu g/m^3$).

ETHANOL

CAS No.: 64-17-5

INTRODUCTION

Ethanol is formed by the fermentation of carbohydrates by various microorganisms. It is also produced synthetically from various petrochemical feedstocks, especially ethylene. The most quantitatively important source of human exposure to ethanol is consumption of alcoholic beverages. Due to the ubiquitous occurrence of microorganisms capable of ethanolic fermentation, virtually all sugar-containing foodstuffs are liable to contain a low level of ethanol. This is generally at the ppm level, or less than 1% by weight, except for materials deliberately fermented with an alcohol-tolerant strain of yeast. Ethanol is also a minor product of general metabolism in plants and animals, so a certain amount of endogenous exposure occurs even in the absence of external exposure. Information as to exposure actually occurring or anticipated as a result of the use of ethanol as a fuel additive is limited, in spite of the substantial use of ethanol in fuel in some areas of the U.S. and abroad.

KEY TOXICOLOGIC EFFECTS

Information in this section was primarily extracted from Clayton and Clayton (1994), ACGIH (1991) and Pastino et al. (1997). There is an enormous literature on the health effects of alcoholic beverages, which is of marginal relevance to the question at hand.

Acute Toxicity

At high vapor concentrations, ethanol is irritating to the eyes and the respiratory system. In humans, vapor concentrations above 40 mg/L (20,000 ppm) were considered intolerable. Similar concentrations caused sensory irritation in mice, evidenced by reduction in the breathing rate. Lester and Greenberg (1951) reported transient symptoms of respiratory and eye irritation in volunteers exposed to 10,000-20,000 mg/m^3 (5300 – 10,600 ppm) ethanol vapor. At 30,000 or 40,000 mg/m^3, more severe and continuing irritant responses were reported. They reported “no reaction” to 7500 mg/m^3 (3990 ppm) in patients being treated with tetraethylthiuram disulfide, a drug used to treat alcoholism by precipitating unpleasant symptoms on exposure to ethanol. (However, it is not clear whether the authors meant to include in this description no sensory irritation, or just none of the drug-related reactions to ethanol.) Based on these studies, and on case reports from industrial hygiene studies, OSHA, NIOSH and ACGIH regard 1000 ppm as a no-effect level for irritation (ACGIH, 1991). Ethanol appears to have little irritant effect on the skin.

Large oral or inhaled doses of ethanol cause narcosis, ataxia, and incoordination. These effects are observed in animals after exposure to 4,000 – 10,000 ppm for 8 hours. Humans reported headaches and other signs of incipient intoxication when exposed to levels in excess of about 3000 ppm for 2 hours. Hobbs et al. (1996) reported decreased reaction time, diminished fine motor coordination and impaired judgment after ethanol exposures resulting in blood alcohol concentrations of 4 – 7 mM.

At sufficiently high doses, death results from the effects of central nervous system depression. The oral LD_{50} for adult rats has been reported to range from 11.5 to 17.8 g/kg. Younger animals were more sensitive (LD_{50} = 6.2 g/kg). Inhalation of 10,000 – 30,000 ppm ethanol for extended periods (8 h or more) is lethal to rats. Consumption of large amounts of ethanol has also caused death in humans, but it appears to be difficult to approach the lethal dose level (>400 mg/dL in blood) by inhalation. Pastino et al. (1997) developed a physiologically based pharmacokinetic model for uptake of ethanol by inhalation in rats and mice, and extended this to the human situation by incorporation of appropriate measured parameters. The model was validated against the uptake data measured in humans by Lester and Greenberg (1951). They concluded that after exposure to 600 ppm ethanol, maximum blood ethanol concentrations were less than 10% of the concentration reported by Hobbs et al. (1996) as a threshold for behavioral effects.

Chronic Toxicity

Adverse effects on the liver have been noted in both animals and humans chronically exposed to ethanol. Symptoms initially include fatty infiltration and inflammation, and may progress to focal necrosis and/or fibrosis. Chronic oral doses to animals initiating these effects were typically 8 – 15 g/kg/day (rats, dogs). In humans these symptoms are well known, and are characterized as alcoholic hepatitis and cirrhosis. They are typically seen in abusers of alcoholic beverages. However, it is known that concurrent exposure to some other chemicals (such as carbon tetrachloride), and infection with hepatitis B virus, increase sensitivity to the liver damaging effects of ethanol.

In chronic abusers of alcoholic beverages, neurological and behavioral changes typical of peripheral and central nervous system damage are known. Some of the chronic neurological changes in alcohol abusers may be a result of altered patterns of nutrition.

Carcinogenicity

Ethanol has not been clearly shown to be carcinogenic in laboratory animals, but acts as a promoter or co-carcinogen in animals concurrently exposed to other (carcinogenic) chemicals. For instance, long-term exposure to ethanol in drinking water promotes liver tumors in rats exposed to N-nitrosodiethylamine.

Heavy consumption of alcoholic beverages is known to be associated with increased incidences of some cancers, including those of the oral cavity (especially with concurrent exposure to other carcinogens, e.g., in smokers) and of the liver (in subjects with evidence of advanced alcohol-related liver disease).

Ethanol is not genotoxic in most test systems, although a few equivocal or positive results have been reported, particularly in certain tests examining effects on chromosomes.

Ethanol was was considered by the Proposition 65 Science Advisory Panel (predecessor of the current Carcinogen Identification Committee), who reviewed the evidence as to the carcinogenic and co-carcinogenic effects of ethanol in humans and animals. The listing (in July 1988) of “alcoholic beverages, when associated with alcohol abuse” as carcinogenic was specified by the Panel, and reflects their assessment of the nature of the hazard. OEHHA followed this assessment in concluding that, whereas high levels of chronic exposure to ethanol are carcinogenic to humans, the levels of ethanol predicted to occur in air or water as a result of its use in gasoline were unlikely to result in a cancer risk to the exposed population.

Reproductive and Developmental Toxicity

Rats and mice maintained on liquid diets containing 5 – 10% ethanol for 5 weeks or longer showed some adverse physical and functional effects on the testes. Some indications of toxicity to the fetus, including deaths, growth retardation and increased malformations have been noted in rats and mice given diets in which 15-35% of the calories were derived from ethanol. However in other studies, no effect on the fetuses were seen in mice and rabbits given drinking water containing up to 15% ethanol, or inhaling up to 20,000 ppm ethanol, during pregnancy.

In humans, the “fetal alcohol syndrome” is a well-established consequence of maternal alcohol abuse during pregnancy. This includes retardation of growth and development, certain characteristic physical malformations, and also behavioral and cognitive problems. No reports have appeared of the occurrence of this syndrome after workplace exposures to ethanol by any route. The evidence concerning fetal alcohol syndrome indicates that this effect results from high maternal exposures such as those relating to the consumption of alcoholic beverages. This issue was discussed by the Proposition 65 Science Advisory Panel’s DART Subcommittee, whose conclusions are reflected in the listing of “ethanol in alcoholic beverages” as known to the State of California as causing developmental toxicity.

DOSE-RESPONSE ASSESSMENT

At this time, there are no health assessment values being used by California regulatory programs or by U.S. EPA for estimating potential health impacts from ethanol exposure through air or drinking water. Therefore, OEHHA calculated draft health protective concentrations (HPC) for the purposes of this report. In calculating the HPC for inhalation exposures, OEHHA followed the risk assessment methodology used for developing the acute reference exposure levels (RELs) under the Air Toxics Hot Spots Program risk assessment guidelines process (OEHHA, 1999a). As mandated by state legislation, these guidelines underwent scientific and public peer review, prior to approval by the Scientific Review Panel (Senate Bill 1731, Statutes of 1992, Ch. 1162 of the California Health and Safety Code). Due to the lack of scientific data on effects of extremely low level exposures to ethanol in water (and the probable lack of any such effects), a non-standard approach was taken in estimating a health protective concentration for ethanol in water.

Derivation of Health Protective Concentrations

Inhalation Exposures:

Lester and Greenberg (1951) reported inhalation exposures of volunteers to ethanol vapor, and reported transient (sensory) irritation effects, with a LOAEL of 5300 ppm (10,000 mg/m^3). It is unclear from the experimental account whether a NOAEL for irritant effects was established. The reported LOAEL is consistent with other human studies cited by ACGIH (1991). Since this effect appears from the data to be concentration dependent and does not represent a cumulative damage process, adjustment for duration of exposure is not appropriate. Although other chronic effects result at much higher exposure levels, the short-term LOAEL for irritation is expected to be protective from these also.

draft health protective concentration = LOAEL/UF = 53 ppm (= 100 mg/m^3).

The Uncertainty Factor (UF) used is 100, consisting of an intraspecies factor of 10 (reflecting the fact that the study population was selected to consist of healthy adult volunteers), and a LOAEL to NOAEL extrapolation factor of 10. Other factors are not required since the experimental level is determined in humans, and duration adjustments are not appropriate for the transient sensory response.

Drinking Water Exposures:

Predictions of ethanol dispersion and biodegradation in the environment indicate that ethanol is unlikely to occur in drinking water at levels having any toxicological significance. In particular, many beverages and food products naturally contain small amounts of ethanol, but are not required to report this provided that the content is less than 0.5%. This level is probably not selected for health-protective reasons alone, but nevertheless appears a reasonable basis for identifying a level with no important biological effects in the majority of the population. In setting an upper limit for water, it is necessary to take into account ethanol from other sources like food. It seems unlikely that 100% of the 1.5 kg diet would contain 0.5% ethanol. For the present estimate, it was assumed 0.5 kg of the diet might contain ethanol at 0.5%, and that it is undesirable for water to contribute more than this amount. Furthermore, assuming a direct water consumption of 2 L/d, and a 10% additional contribution by inhalation of ethanol from tap water (e.g., during showering, dish washing, etc.), a draft health protective concentration in water can be calculated as follows:

draft health protective concentration = 0.5% x 0.5 kg/d / 2.2 Leq/d = 0.11% (1,100 mg/L)

Although based on the reporting level for foods and beverages, this allows less ethanol in water than in food products, recognizing that exposure to water can be greater, and involves other routes of exposure, albeit to limited degrees.

FORMALDEHYDE

CAS No: 50-00-0

INTRODUCTION

Formaldehyde is both directly emitted into the atmosphere and formed in the atmosphere as a result of photochemical oxidation of reactive organic gases in polluted atmospheres containing ozone and nitrogen oxides. Photochemical oxidation is the largest source (could be as high as 88%) of formaldehyde concentrations in California ambient air. A primary source of formaldehyde is vehicular exhaust (CARB, 1992; U.S. EPA, 1993). Formaldehyde is a product of incomplete combustion. About 9% of direct formaldehyde emissions are estimated to come from the combustion of fossil fuels from mobile sources (Lawson et al., 1990). Formaldehyde is routinely monitored by the statewide California Air Resources Board (CARB) toxics monitoring network. The mean concentration of formaldehyde from January 1994 through December 1994 monitored by the CARB network was estimated to be 2.66 micrograms per cubic meter ($\mu g/m^3$) or 2.1 ppb (CARB, 1995). When formaldehyde was formally identified as a Toxic Air Contaminant (TAC) the CARB estimated a population-weighted annual concentration of 5.4 $\mu g/m^3$ or 4.4 ppb (CARB, 1992).

KEY TOXICOLOGIC EFFECTS

Acute Toxicity

Exposure to moderate levels of formaldehyde (1-3 ppm) can result in eye and upper respiratory tract irritation (Weber-Tschopp et al., 1977; Kulle et al., 1987). Feinman (1988) states that most people cannot tolerate exposures to more than 5 ppm formaldehyde in air; above 10-20 ppm symptoms become severe and shortness of breath occurs. High concentrations of formaldehyde may result in nasal obstruction, pulmonary edema, choking, dyspnea, and chest tightness (Porter, 1975; Solomons and Cochrane, 1984). Rhinitis and a wide range of asthma-like conditions can result from exposure to formaldehyde. Some studies have reported that workers exposed to low concentrations may develop severe prolonged asthma attacks after prior exposure (Feinman, 1988).

Chronic Toxicity

Formaldehyde primarily affects the mucous membranes of the upper airways and eyes; these effects include potentially precancerous nasal epithelial histological lesions, including keratosis and metaplasia of the nasal epithelium (Edling et al., 1988). Repeated exposure of skin to the liquid also causes irritation and allergic dermatitis.

Dose-dependent increases in health complaints (eye and throat irritation, and headaches) have been noted in residents of mobile and conventional homes at concentrations of 0.1 ppm formaldehyde or above (Ritchie and Lehnen, 1987). Similarly, Liu et al. (1991) found that exposure to 0.09 ppm (0.135 mg/m^3) formaldehyde exacerbated chronic respiratory and allergy problems in residents living in mobile homes. Chronic exposure to formaldehyde has been associated with immunological hypersensitivity and altered immunity (Thrasher et al., 1987). Thrasher et al. (1990) later found that long-term exposure to formaldehyde was associated with autoantibodies, immune activation, and formaldehyde-albumin adducts. The authors suggest that the hypersensitivity induced by formaldehyde may account for a mechanism for asthma and other health complaints associated with formaldehyde exposure.

Carcinogenicity

Epidemiological studies have shown formaldehyde exposure to be significantly associated with cancer at sites in the respiratory tract in workers and in the general population (reviewed in OEHHA, 1992a). Studies of embalmers, who have used formaldehyde, have shown increased rates of brain cancer and of leukemia. Formaldehyde has been demonstrated to cause DNA-protein crosslinks in the nasal mucosa of rodents and non-human primates. Formaldehyde is carcinogenic in rodents, producing squamous cell carcinomas in the nasal passages of male and female rats and male mice (Kerns et al., 1983). Both the International Agency for Research on Cancer and the U.S. EPA have classified formaldehyde as a probable human carcinogen, based on sufficient evidence for carcinogenicity in animals and limited evidence in humans. OEHHA (1992a) developed a cancer unit risk factor for formaldehyde of 6.0×10^{-6} $(\mu g/m^3)^{-1}$ based on rat nasal tumor data (Kerns et al., 1983).

Reproductive and Developmental Toxicity

Exposure of experimental animals to formaldehyde does not appear to result in any significant teratogenic or reproductive effects (CARB, 1992). Formaldehyde is not listed by the State of California as a reproductive or developmental toxicant under Proposition 65, California's Safe Drinking Water and Toxic Enforcement Act of 1986.

DOSE-RESPONSE ASSESSMENT

The following table contains available health assessment values for formaldehyde currently used by California regulatory programs.

Table 4. Health assessment values for formaldehyde

	Health Assessment Value	Reference
Acute reference exposure level (REL)	94 $\mu g/m^3$	OEHHA (1999a)
Proposed chronic reference exposure level (REL)	3 $\mu g/m^3$	OEHHA (1999c)
Cancer potency factor	2.1×10^{-2} $(mg/kg\text{-}day)^{-1}$	OEHHA (1999b)
Unit risk factor	6.0×10^{-6} $(\mu g/m^3)^{-1}$	OEHHA (1999b)
No significant risk level (NSRL)	40 μg/day	OEHHA (1994b)
U.S. EPA reference dose (RfD)	2×10^{-1} (mg/kg-day)	U.S. EPA (1990)
U.S. EPA reference concentration (RfC)	NA	---
Public health goal (PHG)	NA	---
U.S. EPA Lifetime Health Advisory for drinking water	1 mg/L	U.S. EPA (1996)

(based on 70 kg adult)

NA = not available

Since adopted health assessment values suitable for assessing chronic inhalation exposures are not available for formaldehyde, OEHHA has selected the proposed chronic reference exposure level (REL) for use in this report. The proposed chronic REL is currently being developed under the Air Toxics Hot Spots Program risk assessment guidelines process (Senate Bill 1731, Statutes of 1992, Ch. 1162 of the California Health and Safety Code). The methodology used to derived the proposed chronic REL for formaldehyde, as well as the number itself, have undergone an initial round of public and scientific peer review, and is currently being considered by the State's Scientific Review Panel (1999c). The derivation of the proposed chronic REL is summarized below, and explained in detail in OEHHA (1999c).

Derivation of Proposed Chronic Reference Exposure Level

Occupational exposure of 66 workers to formaldehyde for 1 - 36 years (mean = 10 years) resulted in significantly increased symptoms of irritation including nasal and eye irritation, and lower airway discomfort (Wilhelmsson and Holmstrom, 1992). The workers were exposed to a mean concentration of 0.17 ppm while the control group was exposed to a mean concentration of 0.06 ppm. The increase in symptoms of irritation in exposed workers did not correlate with total serum IgE antibody levels. This study is supported by the results of Horvath et al. (1988) which observed significant differences in subjective irritation and pulmonary function in 109 workers exposed to formaldehyde compared to 254 control subjects. The mean formaldehyde concentrations for the exposed and control groups were 0.69 ppm and 0.05 ppm, respectively. Duration of formaldehyde exposure was not stated.

The study by Wilhelmsson and Holmstrom (1992) establishes a NOAEL of 0.06 ppm for long-term irritant effects in humans. Following adjustment of the NOAEL for exposure continuity (10 m^3/day occupational exposure / 20 m^3/day total exposure, 5/7 days per week), the average occupational concentration is 0.02 ppm.

Proposed chronic REL = NOAEL / UF = 0.02 / 10 = 0.002 ppm (= 0.003 mg/m^3)

An uncertainty factor (UF) of 10 was applied, based only upon an intraspecies factor of 10, reflecting the fact that the study population consisted of healthy adult workers. Other factors are not required since the experimental level is determined in humans.

HEXANE

n-Hexane; CAS No.: 110-54-3

INTRODUCTION

Hexane, derived by the distillation and catalytic cracking of crude oil, is an important constituent of gasoline and light petroleum solvents such as petroleum ether. It is also used as a cleaning agent, in glues and paint thinner, and in the solvent extraction of soybean and other food oils. Several different hexane isomers are found in these products; this discussion mainly concerns the unbranched isomer, n-hexane.

The very high volatility, low water solubility, and relatively low soil binding of hexane result in rapid equilibration into the vapor phase after environmental contamination. It does not absorb UV light, so photolysis is expected to be unimportant. Reaction with hydroxyl radical is probably the most important degradation pathway in air (HSDB, 1998). Hexane can also be rapidly degraded by microbes in soil or sewage sludge, but will persist longer in high-concentration hydrocarbon phases in soil. It does not bioconcentrate in sediment, plants, or animals.

Hexane is emitted into the atmosphere from gasoline evaporation and as a constituent of the unburned hydrocarbon fraction in tailpipe emissions. It also is released by evaporation of common solvents and drying of oil-based paints; it is also a product of plant metabolism. Levels of hexane in the low ppb range are commonly detected in both urban and rural atmosphere. Around refineries, manufacturing plants, or hazardous waste sites, concentrations in air approaching 50 ppm have been measured (HSDB, 1998). Hexane is not commonly detected in drinking water, but may be found at trace levels in ground or surface water as a result of natural processes or industrial emissions.

KEY TOXICOLOGIC EFFECTS

Acute Toxicity

Hexane has relatively low acute toxicity. Inhalation, the usual exposure route, may result in some eye, nose, and respiratory tract irritation at concentrations in air above about 1000 ppm. Mild excitation may occur at low doses (disinhibition), followed by sedation and narcosis at higher concentrations and prolonged exposures (usually greater than 5000 ppm). Hepatotoxicity may also occur after acute high doses.

Chronic Toxicity

The primary consideration in chronic exposures to n-hexane is neurotoxicity, which has been observed in animal studies and in human occupational exposures. The toxicity is caused by metabolism of the hexane to 2,5-hexanedione, which apparently crosslinks structural or transport proteins in nerve axons (Lapadula et al., 1986). This results in a peripheral dying-back axonopathy associated with tingling and weakness in the limbs, which may progress to limb paralysis (Sobue et al., 1978; O'Donoghue, 1985; U.S. EPA, 1999c). Branched-chain hexane isomers do not form metabolites that react similarly to 2,5-hexanedione, and these isomers therefore have minimal or no potential to cause the classical hexacarbon neuropathy.

Peripheral neuropathy has been clearly observed in rats with subchronic exposures to about 1000 ppm for 8 hours per day, 5 days per week (Rebert et al., 1982); more subtle changes may be observed in rodents at levels of a few hundred ppm (HSDB, 1998). Human neurotoxic effects are clear at estimated occupational concentrations of 100 ppm or more, and appear likely at chronic exposure levels in excess of 50 ppm (Iida, 1982; Sanagi et al., 1980; Wang et al., 1986).

Carcinogenicity

There are apparently no applicable studies on carcinogenicity of n-hexane. Hexane is not mutagenic in Ames assays nor genotoxic in a variety of short-term tests. However, an increased frequency of chromosomal aberrations was observed in rat bone marrow cells after exposures to concentrations as low as 100 ppm, 6 hours per day for 5 days to 4 weeks (Hazleton, 1980).

Reproductive and Developmental Toxicity

Teratogenicity tests in rats and rabbits show no specific malformations, even at maternally toxic doses. Testicular toxicity is noted in male rats with prolonged exposures to hexane at concentrations of about 1000 ppm or more (Nylen et al., 1989).

DOSE-RESPONSE ASSESSMENT

The following table contains available health assessment values used by California regulatory programs for hexane.

Table 5. Health assessment values for n-hexane.

	Health Assessment Value	Reference
Acute reference exposure level (REL)	NA	---
Cancer potency factor	NA	---
Unit risk factor	NA	---
No significant risk level (NSRL)	NA	---
U.S. EPA reference dose (RfD)	NA	---
U.S. EPA reference concentration (RfC)	0.2 mg/m^3	U.S. EPA (1999c)
Public health goal (PHG)	NA	---

NA = not available

ISOBUTENE

CAS No.: 115-11-7

INTRODUCTION

Isobutene is a chemical intermediate (butyl rubber production, plastics, adhesives), and a component of unleaded gasoline. Only a few isobutene toxicity studies have been reported. However, the studies available indicate that isobutene is probably mutagenic. A long term study demonstrated possible carcinogenic effects, but the data fell short of the criteria for sufficient evidence of carcinogenicity.

KEY TOXICOLOGIC EFFECTS

Acute Toxicity

Shugaev and Yaroslavl (1969) reported a 2-hour LC_{50} (concentration lethal to one-half of the animals exposed) in mice of 178,000 ppm; the same study reported a 4-hour LC_{50} in rats of 266,000 ppm.

Chronic Toxicity

No toxicity was noted in male and female rats exposed to isobutene by gavage for 4 weeks at concentrations of 2, 15 or 149 mg/kg-day (BG Chemie, 1989; reviewed by Cornet and Rogiers, 1997). No significant evidence of toxicity was observed in male and female rats exposed to isobutene by inhalation at concentrations of 250, 1000 or 8000 ppm for 13 weeks (BG Chemie, 1989; reviewed by Cornet and Rogiers, 1997).

Groups of 50 male and 50 female F344/N rats and $B6C3F_1$ mice were exposed to isobutene at concentrations of 0, 500, 2,000, or 8,000 ppm 6 hours per day, 5 days per week, for 105 weeks (NTP, 1998). Survival of exposed male and female rats and mice was similar to that of the chamber controls. Mean body weights of exposed rats were generally similar to those of the chamber controls throughout the study. Mean body weights of exposed mice were generally similar to those of the chamber controls throughout the study except for female mice exposed to 2,000 or 8,000 ppm, which weighed slightly less than chamber controls from about week 52 until week 92. The incidences of hyaline degeneration of the olfactory epithelium were marginally increased in exposed rats; however, the severity of hyaline degeneration increased with increasing exposure concentration in both males and females. The incidences of hyaline degeneration of the respiratory epithelium in all groups of exposed male and female mice were significantly greater than those in the chamber control groups. The incidences of hyaline degeneration of the olfactory epithelium in 2,000 and 8,000 ppm mice were greater than those in the chamber controls.

Carcinogenicity

Isobutene genotoxicity data are mixed. Negative results with isobutene have been reported in several strains of *Salmonella typhimurium* (Staab and Sarginson, 1984; Shimizu et al., 1985; Cornet et al., 1992; NTP, 1998) and in L5178Y mouse lymphoma cells (Staab and Sarginson, 1984), with and without rat liver S9 metabolic activation. Additionally, no induction of micronuclei in human lymphocytes exposed to isobutene *in vitro* were noted by Jorritsma *et al.* (1995). The studies by Cornet *et al.* (1992), Jorritsma *et al.* (1995) and NTP (1998) specifically used testing protocols designed to account for isobutene volatility. However, positive results were reported for gene mutation in S. *typhimurium* (Cornet et al., 1992; Castelain et al., 1993) and *Klebsiella pneumoniae* (Voogd et al., 1981) as well as chromosome damage in lymphocytes (Jorritsma et al., 1995) when the primary metabolite of isobutene, 2-methyl-1,2-epoxypropane, was tested in the absence of metabolic activation enzymes.

Groups of 50 male and 50 female F344/N rats and B6C3F$_1$ mice were exposed to isobutene at concentrations of 0, 500, 2,000, or 8,000 ppm 6 hours per day, 5 days per week, for 105 weeks (NTP, 1998). No increases in tumor incidences were noted in female rats or male and female mice. However, the incidence of thyroid gland follicular cell carcinomas in male rats exposed to 8,000 ppm was increased (although not significantly) compared to the chamber control group and exceeded the historical control range. The thyroid gland follicular cell carcinoma incidences in male rats in the 0, 500, 2,000 and 8,000 ppm exposure groups were 1/48, 0/48, 0/48 and 5/50, respectively.

Reproductive and Developmental Toxicity

No studies on isobutene reproductive or developmental toxicity have been reported in the open literature.

DOSE-RESPONSE ASSESSMENT

At this time, there are no health assessment values being used by California regulatory programs or by U.S. EPA for estimating the potential health impacts from isobutene. Since adopted health assessment values are not available, OEHHA calculated a draft health protective concentration (HPC) for the purpose of this report. In calculating the HPC, OEHHA followed the risk assessment methodology being used to develop the chronic reference exposure levels (RELs) under the Air Toxics Hot Spots Program risk assessment guidelines process. As mandated by state legislation, these guidelines must undergo scientific and public peer review prior to approval by the Scientific Review Panel (Senate Bill 1731, Statutes of 1992, Ch. 1162 of the California Health and Safety Code). While the chronic REL methodology has not been adopted at this time, it has undergone an initial round of public and scientific peer review, and is currently being considered by the Panel. The derivation of the HPC for chronic inhalation exposures is summarized below. Further details on the methodology are provided in OEHHA (1999c). The available toxicity data were insufficient to allow the calculation of an acute HPC or cancer unit risk HPC for isobutene.

Derivation of Health Protective Concentration

NTP (1998) found that isobutene caused significantly increased incidences of respiratory epithelium hyaline degeneration in male and female B6C3F$_1$ mice exposed to 500, 2000 and 8000 ppm when compared to chamber control group animals. A lowest-observed-adverse-effect level (LOAEL) of 500 ppm was observed; a no-observed-adverse-effect level (NOAEL) was not observed in this study. A chronic draft HPC can be calculated for isobutene using the formula:

draft health protective concentration = LOAEL / UF = 2.6 mg/m^3 (1.1 ppm)

The uncertainty factor (UF) for this calculation is 450, which incorporates uncertainty contributions for extrapolation from a “mild effect” LOAEL to a NOAEL (factor of 3), extrapolation from animals to humans using U.S. EPA HEC methodology (U.S. EPA, 1994a) (factor of 15) and for potentially sensitive human subpopulations (10). The animal to human extrapolation factor of 15 was calculated by multiplying a dosimetric adjustment of 5 (using default body weights of 0.0353 and 70 kg for female mice and humans, respectively, and respiratory tract surface area values of 3 and 200 cm^2 for female mice and humans, respectively) by a default uncertainty factor of 3, which is meant to compensate for potential animal-human differences not accounted for by dosimetry.

METHYL TERTIARY BUTYL ETHER (MTBE)

CAS No.: 1634-04-4

INTRODUCTION

Reformulated gasoline containing up to 11% MTBE has been widely used in California since 1996. MTBE is present in ambient air in California, at a statewide average of approximately 2 ppbv, with higher average concentrations in urban areas (e.g., 4 ppbv in the South Coast region), as of March, 1999 (OEHHA, 1999f). Sources of MTBE in ambient air include the manufacture and distribution of oxygenated gasoline, vehicle refueling, and evaporative and tailpipe emissions from motor vehicles.

Due to high water solubility, lack of binding to soil, and persistence in solution, MTBE has become a drinking water contaminant in California. MTBE has been detected in numerous drinking water wells and surface water sources within the state, in addition to multiple detections in groundwater. Sources of MTBE in drinking water include leaking underground storage fuel tanks, recreational power-boating, and refinery wastewater.

Individuals may be exposed to MTBE in contaminated air and water via inhalation, ingestion, and dermal absorption.

KEY TOXICOLOGIC EFFECTS

Acute Toxicity

A number of non-specific acute symptoms have been reported following MTBE exposure, including noticeable odor, headache, nausea or vomiting, burning sensation in the nose or mouth, cough, dizziness, disorientation and eye irritation (University of California, 1998). The existing epidemiological studies of the acute effects of MTBE exposure have reported inconsistent results; however, each of the studies had methodological limitations. There is a need to conduct additional studies specifically designed to identify and characterize the acute human health effects associated with MTBE exposure.

Studies in animals have demonstrated the low toxicity of MTBE, with an acute inhalation NOAEL of 1,440 mg/m3 and an acute oral NOAEL of 40 mg/kg-day (OEHHA, 1999f). Acute effects of MTBE exposure in animals include profound, but reversible general anesthetic effects, decreased breathing rates, and irritation to the nasal mucosa and gastrointestinal tract (OEHHA, 1999f).

Chronic Toxicity

There are presently no human data on the chronic health effects of MTBE exposure. In rats, effects observed include increased relative organ weights for kidney, liver and adrenal gland, increased hyaline droplets in male kidneys, elevated cholesterol, and dysplastic proliferation of lymphoreticular tissues in females (OEHHA, 1999f).

Carcinogenicity

There are no human data on which an evaluation of the carcinogenicity of MTBE can be based. However, there is substantial evidence that MTBE administered by either the oral or inhalation routes is carcinogenic in rats and mice. MTBE causes leukemias and lymphomas in female rats by the oral route, Leydig interstitial cell tumors of the testes in male rats by the oral and inhalation routes, renal tubular tumors in male rats by the inhalation route, and hepatocellular tumors in mice of both sexes by the inhalation route (OEHHA, 1998a). Based on a thorough review of the relevant data, including supporting data on pathology and mechanisms of tumor induction, and carcinogenicity studies of MTBE's primary metabolites TBA and formaldehyde, the UC Report concluded that MTBE is an animal carcinogen with the potential to cause cancer in humans (University of California, 1998). IARC recently classified MTBE as a Group 3 carcinogen (i.e., not classifiable as to carcinogenicity in humans), based on inadequate evidence in humans and limited evidence in experimental animals (IARC, *in press*, cited in OEHHA, 1999f).

Reproductive and Developmental Toxicity

There are no human data on which an evaluation of the developmental or reproductive toxicity of MTBE can be based. Studies in animals suggest that MTBE has the potential to cause developmental toxicity, based on reports of developmental retardation in rats (i.e., postnatal growth retardation) and mice (i.e., lower fetal weights at term, reduced skeletal ossification) (OEHHA, 1998b). MTBE exposure did not result in any observable effects on female fertility in two reproductive toxicity studies in the rat, the only species tested to date. Observations of lower relative uterine and ovarian weights and lengthened estrous cycles in female mice suggest that MTBE may have antiestrogenic effects, however. There are very limited data available from animal studies on the potential for MTBE to cause male reproductive toxicity. No adverse effects on male fertility or reproductive organ weights have been reported, although one study found lower levels of plasma testosterone in rats exposed to MTBE (OEHHA, 1998b).

DOSE-RESPONSE ASSESSMENT

The following table contains available health assessment values used by California regulatory programs for MTBE.

Table 6. Health assessment values for MTBE

	Health Assessment Value	Reference
Acute reference exposure level (REL)	NA	---
Proposed chronic reference exposure level	3 mg/m^3	OEHHA (1999c)
Cancer potency factor	1.8×10^{-3} (mg/kg-day)$^{-1}$	OEHHA (1999f)
Unit risk factor	2.6×10^{-7} (μg/m^3)$^{-1}$	OEHHA (1999f)
No significant risk level (NSRL)	Not listed under P65	---
Drinking Water Advisory	20-40 ppb	U.S. EPA (1997b)
U.S. EPA reference dose (RfD)	NA	---
U.S. EPA reference concentration (RfC)	3 mg/m^3	U.S. EPA (1997c)
Public health goal	13 ppb	OEHHA (1999f)

NA = not available

Since adopted health assessment values suitable for assessing potential health impacts from short-term inhalation exposures to MTBE are not available, OEHHA calculated a draft health protective concentration (HPC) for the purpose of this report. In calculating the HPC, OEHHA followed the risk assessment methodology used for developing the acute reference exposure levels (RELs) under the Air Toxics Hot Spots Program risk assessment guidelines process (1999a). As mandated by state legislation, these guidelines underwent scientific and public peer review, prior to approval by the Scientific Review Panel (Senate Bill 1731, Statutes of 1992, Ch. 1162 of the California Health and Safety Code) and adoption by OEHHA. The derivation of the HPC is summarized below. Further details on the methodology are provided in OEHHA (1999a).

Derivation of Health Protective Concentration

In two-hour chamber studies in which humans were exposed to MTBE during light exercise, Nihlen *et al.* (1998) reported no toxic effects at exposure levels up to 50 ppm MTBE. Endpoints of interest in the study were irritative symptoms, discomfort, and CNS effects. Upon entry into the chamber, subjects reported a 'solvent smell' which gradually declined. Odor detection at this level of exposure is consistent with that reported in other studies (University of California, 1998). This study establishes a NOAEL of 50 ppm for irritative effects in humans for a 2 hour exposure. Applying a modified "Haber's Law" calculation to extrapolate from 2 hours to 1 hour, the equivalent NOAEL is 70 ppm for irritative effects.

$C^nT = K$
$C^n_1T_1 = C^n_2T_2$ where n=2 based on extrapolation from 120 min. to 60 min.
$C^2\,(60) = (50\text{ ppm})^2\,(120\text{ minutes})$
$C = 70\text{ ppm}$

Using the adjusted NOAEL, a draft HPC can be calculated as follows:

draft health protective concentration = NOAEL / UF = 70 / 10 = 7 ppm (25 mg/m^3)

An uncertainty factor (UF) of 10 was applied, based only upon an intraspecies factor of 10, reflecting the fact that the study population consisted of healthy adult volunteers. Other factors are not required since the experimental level is determined in humans and duration adjustments are not appropriate for the transient sensory response.

PEROXYACETYL NITRATE (PAN)

CAS No.: 2278-22-0

INTRODUCTION

Peroxyacetyl nitrate (PAN) is one of a class of common air pollutants, peroxyacyl nitrates, formed by photochemical oxidation from volatile organic hydrocarbons and nitrogen dioxide. PAN acts as a storage reservoir for nitrogen oxides (NO_x) and can accelerate photochemical smog formation. PAN may also contribute to ozone formation downwind of urban areas by transporting NO_x. It is now recognized that PAN is of major importance (along with ozone) when evaluating air quality. PAN concentrations were measured at various ground sites and aloft on three occasions during the summer and fall of 1987 as part of the Southern California Air Quality Study (SCAQS) (CARB, 1989). Urban PAN concentrations in the South Coast Air Basin ranged from 1.1 to 30 ppb. Measurements of PAN in non-air conditioned rooms have shown maximal indoor concentrations of close to 100% of the corresponding outdoor concentrations, with average indoor/outdoor concentration ratios ranging between 0.7 and 0.9 (Jakobi and Fabian, 1997).

KEY TOXICOLOGIC EFFECTS

Acute Toxicity

PAN has been demonstrated to cause eye irritation in humans. A PAN concentration of 4.95 mg/m^3 caused significant eye irritation in 20 human volunteers in 10-15 minutes (Stephens et al., 1961). Drechsler-Parks (1987) found that PAN induced eye irritation in subjects at a concentration of 0.64 mg/m^3 (0.13 ppm).

Human studies examining the effects of PAN on the respiratory system produced varied results. Several studies reported no effect of PAN alone or in the presence of ozone and/or nitrogen dioxide on respiratory functions during exercise of duration ranging from 42 minutes to 2 hours, and at concentrations ranging from 0.64 to 1.49 mg/m^3 (Raven et al., 1974a; Raven et al., 1974b; Drechsler-Parks et al., 1984; Drechsler-Parks, 1987; Drechsler-Parks et al., 1987; Drechsler-Parks et al., 1989; Horvath et al., 1986).

Smith (1965) found that exposure of young men to a PAN concentration of 1.49 mg/m^3 during 5 minutes of light exercise did not result in any change in respiratory rate or expiratory volume compared to exercise in clean air. However, oxygen requirements were increased in the presence of PAN. The authors suggested that this was the result of an increase in respiratory airway tissue resistance. A small but statistically significant reduction (4%) in forced vital capacity (FVC) was observed in men (mean age = 23) performing light exercise while exposed to 1.19 mg/m3 PAN for 4 hours (Raven et al., 1976). However, no changes were noted in mean inspiratory capacity, expiratory reserve volume or forced expiratory volume over 1 second (FEV1.0). Additionally, older subjects (mean age = 48) exposed to PAN under the same conditions did not show changes in FVC.

As part of the Houston area longitudinal epidemiological oxidant study, Javitz et al. (1982) reported a greater incidence of subjective symptoms in 286 subjects with chronic obstructive pulmonary disease (COPD) exposed to ambient concentrations of PAN up to 0.059 mg/m^3. Logistic regressions of a selected set of self-reported health symptoms on oxidants indicated that the incidence of chest discomfort and eye irritation increased by 10.1% and 7.5%, respectively, as PAN increased from 0 to 0.059 mg/m^3.

An LC_{50} (concentration producing mortality in 50% of the animals exposed) for a 2-hour exposure to PAN in strain A male mice for 9 week old and 15 week old animals was reported as being 718-743 mg/m^3 and 495-545 mg/m^3, respectively (Campbell et al., 1967). Kruysse et al. (1977) reported a 4-hour LC_{50} for PAN in 9-week old male and female Wistar rats of 470 mg/m^3 (95 ppm).

A significant increase in mortality due to acute respiratory pneumonia caused by inhalation of *Streptococcus pyogenes* aerosol was seen after a single 3-hour exposure of mice to 14.8-28.4 mg/m^3 PAN (Thomas et al., 1981). The excess mortality ranged from 8 to 39% and the decrease in survival time ranged from 2.4 to 7.9 days.

Chronic Toxicity

Kruysse et al. (1977) exposed male and female Wistar rats to PAN for 6 hours/day, 5 days/week for either 4 or 13 weeks. PAN concentrations used in the 4 week study were 0, 0.9, 4.1, or 11.8 ppm; concentrations used in the 13 week study were 0, 0.2, 1.0 or 4.6 ppm. In the 4 week study, exposure to 11.8 ppm caused elevated mortality, hematocrit values, red blood cell counts and lung weight. In addition, exposure resulted in abnormal behavior, growth retardation, severe inflammation, epithelial metaplasia and hyperplasia in the respiratory tract. Minimal behavioral disturbance, transient growth retardation, slightly increased lung weights and slight histopathological changes in the respiratory tract were noted at 4.1 ppm. No treatment related effects were noted at 0.9 ppm. Exposure to 4.6 ppm in the 13 week study resulted in changes similar to those found at 11.8 ppm in the 4 week study, with the exception that elevated mortality was not observed. No treatment-related effects exhibiting a dose-response were observed at 1.0 ppm.

Male strain A mice were exposed by Dungworth et al. (1969) to 74.3 mg/m^3 (15 ppm) PAN for 6 hours/day, 5 days/week for 6 months. Toxic effects noted included hyperplastic tracheobronchitis, bronchiolitis, pneumonitis, bronchiolectasis, bronchiolarization of alveolar ducts, a focal interstitial fibrotic reaction and patchy centriacinar emphysema. Hyperplasia of the bronchial epithelium was also observed, and foci of squamous metaplasia were observed in the trachea and mainstem bronchi in approximately 50% of the PAN-exposed mice. The authors did not interpret these foci as being neoplastic, but did consider them potentially precancerous.

Carcinogenicity

No human or animal carcinogenicity data exist for PAN. As described above, Dungworth et al. (1969) did note foci of squamous metaplasia in the trachea and mainstem bronchi in PAN-exposed mice, and evaluated those foci as being potentially precancerous but not neoplastic as observed.

Genotoxicity data for PAN is mixed. Kleindienst et al. (1990) found that PAN induced mutations in *Salmonella typhimurium* strain TA100 in the absence of exogenous metabolic activation. Kligerman et al. (1995) reported that an increase in DNA damage was noted in the single cell gel (SCG) in mouse peripheral blood lymphocytes (PBLs) exposed to PAN *in vitro* at concentrations that were cytotoxic (inhibited cell division). However, at lower exposure levels that permitted cell division, no increases in sister chromatid exchanges (SCEs), chromosomal aberrations (CAs), or DNA damage were evident. Male mice were exposed nose-only by inhalation for 1 hour to 0, 15, 39 or 78 ppm PAN, and their lung cells removed and cultured for the scoring of SCEs and CAs. In addition, PBLs and lung cells were analyzed by the SCG assay. No dose-related effects were found in any of the assays. Chinese hamsters exposed to PAN concentrations of approximately 3 ppm for up to 1 month did not show significantly increased frequencies of either gene mutations in lung fibroblasts or increased micronuclei frequency indicating CAs in either lung fibroblasts or red blood cells.

Reproductive and Developmental Toxicity

No reproductive or developmental toxicity studies on PAN have been reported in the open literature.

DOSE-RESPONSE ASSESSMENT

At this time, there are no health assessment values being used by California regulatory programs or by U.S. EPA for estimating potential health impacts from PAN. Since adopted values are not available, OEHHA calculated draft health protective concentrations (HPCs) for the purpose of this report. In calculating the short-term HPCs, OEHHA followed the risk assessment methodology adopted for use in developing acute reference exposure levels (RELs) under the Air Toxics Hot Spots Program risk assessment guidelines process. As mandated by state legislation, these guidelines underwent scientific and public peer review, prior to approval by the Scientific Review Panel (Senate Bill 1731, Statutes of 1992, Ch. 1162 of the California Health and Safety Code) and adoption by OEHHA. A detailed description of the methodology is provided in OEHHA (1999a). In addition, in the absence of an adopted health assessment value suitable for assessing chronic inhalation exposures, OEHHA followed the methodology being used to develop chronic RELs, also legislatively mandated Air Toxics Hot Spots Program risk assessment guidelines process. While the chronic REL methodology has not been adopted at this time, it has undergone an initial round of public and scientific peer review, and is currently being considered by the State's Scientific Review Panel (1999c). The derivation of the draft HPCs are summarized below.

Derivation of Health Protective Concentrations

The short-term HPC is based on Drechsler-Parks (1987) who found that a 2-hour exposure to PAN induced eye irritation in male and female human volunteers at a concentration of 0.64 mg/m^3 (0.13 ppm). This concentration was a lowest-observed-adverse-effect level (LOAEL); a no-observed-adverse-effect level (NOAEL) was not observed in this study. After applying a modification of "Haber's Law" to extrapolate from a 2-hour to a 1-hour exposure duration, the LOAEL is 0.18 ppm.

$$\begin{aligned} C^{n}T &= K \\ C^{n}{}_{1}T_{1} &= C^{n}{}_{2}T_{2} \text{ where n=2 based on extrapolation from 120 min. to 60 min.} \\ (0.13\text{ ppm})^{2}\,(120) &= C^{2}\,(60) \\ C &= 0.18\text{ ppm} \end{aligned}$$

A cumulative uncertainty factor (UF) of 100 is applied based on a factor of 10 to account for extrapolation from a LOAEL to a NOAEL and 10 to account for intraspecies variability. Therefore, an acute 1-hour HPC can be calculated for PAN as follows:

draft health protective concentration = LOAEL / UF = 1.8 ppb (8.8 µg/m^3)

The HPC for chronic exposures is based on Kruysse et al. (1977), who exposed male and female Wistar rats to PAN concentrations of 0, 0.2, 1.0 or 4.6 ppm for 6.5 hours per day, 5 days per week for 13 weeks. Exposure to 4.6 ppm caused elevated hematocrit values, decreased lymphocyte counts, increased lung weights, abnormal behavior, growth retardation, and inflammation, epithelial metaplasia and hyperplasia in the respiratory tract. No treatment-related effects exhibiting a dose-response were observed at 1.0 ppm. The NOAEL identified in this study was 1.0 ppm (4.95 mg/m^3), based on respiratory tract toxicity observed at the next highest dose, 4.6 ppm. An equivalent time-weighted average concentration (C_{AVG}) was calculated from the observed concentration (C_{OBS}) using the relationship:

C_{AVG} = 4.95 mg/m^3 × (6.5 hr/24 hr) × (5 days/7 days) = 0.96 mg/m^3

A draft HPC for chronic exposures can be calculated for PAN using the formula:

draft health protective concentration = NOAEL / UF = 3.2 µg/m^3 (0.6 ppb)

The uncertainty factor (UF) used is 300, and is derived by multiplying a UF of 10 for interspecies variation by a UF of 10 for intraspecies variability and a UF of 3 for subchronic to chronic time extrapolation.

TERTIARY BUTYL ALCOHOL

t-Butanol; CAS No.: 75-65-0

INTRODUCTION

Tertiary butyl alcohol (TBA) has been used as a gasoline octane booster and may be a food contaminant when used in coatings for metallic items that contact food, or as a coating for paperboard food containers. Human exposure can occur via skin contact, inhalation, or ingestion. The Occupational Safety and Health Administration has established a permissible exposure limit of 100 ppm or 300 mg/m^3 for TBA for workplace exposures. TBA is partially metabolized via demethylation in rats to acetone and formaldehyde. TBA is a metabolite of MTBE and exposure may occur through inhalation of MTBE fumes. United States production of TBA in 1991 was estimated at 2,990 billion pounds.

KEY TOXICOLOGIC EFFECTS

Acute Toxicity

The acute toxicity of TBA is low. The oral LD_{50} in the rat is 3500 mg/kg (Schaffarzick and Brown, 1952) and in the rabbit is 3,600 mg/kg (Munch, 1972). In the mouse the LD_{50} by intraperitoneal administration (i.p.) is 441 mg/kg (Maickel and McFadden, 1979). TBA vapors may be irritating to skin, eyes, nose and throat. Inhalation of vapors may cause dizziness, nausea, headache, fatigue, and weakness in the arms and legs. Inhalation of TBA vapors may also cause severe irritation of the respiratory system and narcosis.

Chronic Toxicity

An NTP two-year bioassay was conducted in Fischer 344 rats and $B6C3F_1$ mice exposed to TBA in drinking water (NTP, 1994; Cirvello et al., 1995). Groups of 60 F-344 rats were administered daily doses via drinking water of approximately 0, 85, 195, and 420 mg/kg-d in males and 0, 175, 330, and 650 mg/kg-d in females. Ten animals in each group were sacrificed at 15 months for evaluation; the remaining animals were exposed until the study was terminated at 103 weeks. The high dose groups of both sexes experienced decreased survival. Dose related decrease in body weight gain was also observed. All treated groups of females showed a dose-related increase in kidney weight at the 15-month evaluation. Males exhibited increased kidney weight at the mid and high doses. Nephropathy was seen in all groups of treated females and caused early mortality in high exposure groups. The study did not identify a NOAEL for chronic TBA toxicity in the rat. Groups of 60 B6C3F1 mice of each sex were administered TBA in drinking water at doses of approximately 0, 535, 1035, and 2065 mg/kg-d in males and 0, 510, 1015, and 2105 mg/kg-d in females. Reduced survival was observed in the high dose groups. Thyroid follicular cell hyperplasia was significantly increased in all exposed males and in females at the two higher doses. No NOAEL was identified for chronic TBA toxicity in the mouse.

Carcinogenicity

At the 24 month termination of the NTP rat bioassay, combined adenoma and carcinoma of the renal tubules was found in 8/50, 13/50, 19/50, and 13/50 of the control, low, mid and high dose males, respectively. The two-year survivals were 10/50, 6/50, 4/50, and 1/50, respectively. The increased incidence in the mid dose group was statistically significant (p = 0.01) by Fisher's exact test. The increased mortality in the high dose group may have reduced the observed incidence of renal tumors. Renal tubule hyperplasia was elevated in all treatment groups. Although no renal (or other) tumors were observed in female rats, the incidence of renal hyperplasia was significantly elevated in the high dose group. No renal tubule adenoma or carcinoma was observed in 227 control male rats in the four studies comprising the recent NTP historical control database for drinking water studies indicating the rarity of these neoplasms in male rats. The pathogenesis of proliferative lesions of renal tubule epithelium is thought to proceed from hyperplasia to adenoma to carcinoma (Cirvello et al., 1995). The incidence of renal tubule hyperplasia, adenoma and carcinoma were increased in all treated male groups and in controls compared to historical controls.

In the mouse NTP bioassay incidence of thyroid follicular cell hyperplasia was significantly elevated in all treatment groups of males (5/60, 18/59, 15/59, 18/57) and in the mid and high dose groups of females (19/58, 28/60, 33/59, 47/59). Follicular cell adenomas were significantly higher in high dose females (9/59). Chronic urinary bladder inflammation was seen in both sexes at the high dose, but no urinary bladder neoplasias were observed.

In conclusion, the increased incidence of renal tubule adenoma or carcinoma, combined, in male rats and of thyroid gland follicular cell adenoma in female mice is evidence of a carcinogenic response to TBA.

TBA has been reported as negative in the *Salmonella typhimurium* mutagenicity test, in a chromosome aberrations test in cultured Chinese hamster ovary (CHO) cells, in a sister chromatid exchange test in CHO cells, and in a mutation test in cultured mouse lymphoma cells (Gold et al., 1997).

Reproductive and Developmental Toxicity

No animal studies designed to specifically evaluate reproductive effects of TBA were found. NTP (1994) noted no ovarian histopathology at 20 mg TBA/L in a two year study, however, degeneration of the germinal epithelium of the testes was observed. Anderson et al. (1982) observed that 87 mM TBA did not affect the ability of mouse sperm to fertilize in vitro. No human data were located on the reproductive effects of TBA.

Faulkner et al. (1989) evaluated the developmental toxicity of TBA in two strains of mice exposed orally to 10.5 mmol/kg every 12 hr for days 6-18 of gestation. An increase in resorptions was observed but no malformations, variations, fetal weight effects, or strain differences were seen. In a rat study (Abel and Belitzke, 1992), oral TBA from gestation day eight to parturition at 0, 0.65, 1.3, and 10.9% in diet produced reductions in maternal weight gain, birth weights, and litter sizes (from 11 to 3 pups per litter) as well as reduced weight at weaning and increased perinatal mortality (from 2% to 14%) and postnatal mortality (from 6% to 100%). Malformations were not described and the study was only reported in an abstract. Nelson et al. (1989) exposed rats to TBA by inhalation at 0, 2000, 3500, or 5000 ppm seven hours per day on gestation days 1-19. Decreases in maternal weight gain and fetal weight and increases in narcosis and ataxia were observed, but no effects were seen on resorptions, live litter size, or malformations. An increase in delayed ossification was seen and categorized as a variation.

Daniel and Evans (1982) administered TBA to Swiss Webster mice at up to 1% in the diet and observed decreases in maternal weight gain, fertility, live litter size, and pup weight on postnatal day two, and an increase in stillbirths. At the two highest doses there were significant behavioral effects including cliff avoidance, righting reflex, and open field activity. In an inhalation study where Sprague-Dawley rats were exposed to 6000 or 12,000 mg/m^3 TBA for seven hr per day on gestation days 1-19, no effects were noted on neuromotor coordination, activity, and learning as well as lack of change in neurochemical parameters (Nelson et al., 1991).

DOSE-RESPONSE ASSESSMENT

The following table contains available health assessment values used by California regulatory programs for TBA.

Table 7. Health assessment values for tertiary butyl alcohol

	Health Assessment Value	Reference
Acute reference exposure level	NA	---
Cancer potency factor	3.0×10^{-3} (mg/kg-d)$^{-1}$	OEHHA (1999d)
Unit risk factor	NA	---
No significant risk level (NSRL)	NA	---
U.S. EPA reference dose (RfD)	NA	---
U.S. EPA reference concentration (RfC)	NA	---
Permissible Exposure Limit 8 hr (PEL)	100 ppm, 300 mg/m^3	OSHA (1998)
Short Term Exposure Limit (STEL)	150 ppm, 450 mg/m^3	OSHA (1998)
Threshold Limit Value (TLV/TWA)	100 ppm, 300 mg/m^3	ACGIH (1991)
Action Level for California drinking water (Health & Safety Code Sec. 116445)	0.012 mg/L	OEHHA (1999d)

NA = not available

Toluene

(CAS No. 108-88-3)

INTRODUCTION

Toluene is an aromatic solvent widely used in paint thinners, as a component of gasoline, and as an intermediate in the synthesis of other chemicals. About 6 billion pounds are produced each year (HSDB, 1998). The high volatility of toluene results in rapid evaporation from the liquid phase. Its low water solubility and low soil binding means that it also evaporates relatively rapidly from surface water or soils. Because it is relatively transparent to UV radiation, it is not photodegraded in air; however, it reacts with hydroxyl radicals to yield a half-life of a few hours to a day. It is microbially degraded in soils and groundwater with a half-life of a few days, but can persist much longer under anaerobic conditions and at high concentrations when microbial degradation is inhibited (particularly when liquid phase is present). Toluene is relatively mobile in soil. It does not bioconcentrate in sediment, plants, or animals (HSDB, 1998).

Toluene reaches the environment by vapor emission from chemical manufacturing, including fuel production, by evaporation from motor vehicles and tail-pipe emissions, from leaking fuel storage tanks, and from drying of oil-based paints and solvents. It is commonly detected in both rural and urban ambient air. Median concentrations in air of about 1 ppb in rural or remote areas, and 5 to 10 ppb in urban areas are common. Maximum urban air concentrations can reach more than 1,000 ppb (Singh et al., 1981). The time course of the toluene variations and the toluene/benzene ratios indicate that automobiles are the most common source of atmospheric toluene (HSDB, 1998; citing Termonia, 1982; Sexton and Westberg, 1980; Tsani-Bazaca, 1982). Toluene is also detected in drinking water supplies, usually at concentrations below 1 ppb. In a survey of finished drinking water from groundwater sources, toluene was detected in <5% of the samples, while it was detected in 19% of the samples of drinking water derived from surface water (Dyksen and Hess, 1982; Coniglio, 1980).

KEY TOXICOLOGIC EFFECTS

Acute Toxicity

Inhalation exposure to high levels of toluene causes headaches and eye and respiratory irritation. Excitability followed by sedation is observed in animal exposure studies. With prolonged high exposures (>10,000 mg/m^3, or 2500 ppm), narcosis, then death can occur. Drinking pure toluene can cause the same systemic toxic effects. Toluene also has been purposely inhaled as an intoxicant, which has resulted in neurotoxicity and kidney damage. Severe acute toxicity from exposure to toluene in drinking water is unlikely because of the solubility limit mentioned above (0.067%).

Chronic Toxicity

Prolonged exposures to toluene result in decreased body weight and increased liver weight (NTP, 1990), the parameters used by U.S. EPA for risk assessment (U.S. EPA, 1999b). Decreased thymus weight in a subchronic study (Hsieh et al., 1989) represents a more sensitive index of toxicity than observed in chronic studies. Alterations of immune parameters were also observed. Therefore the latest OEHHA assessment of chronic hazard (OEHHA, 1999g) is based on the Hsieh subchronic study in mice, with a lowest observed adverse effect level of 105 mg/kg-day, and a no observed adverse effect level of 22 mg/kg-day for toluene supplied in drinking water.

Carcinogenicity

In several animal studies, no evidence of carcinogenicity of toluene has been observed in either mice or rats. Most genotoxicity analyses are negative. There is also no evidence in humans to suggest carcinogenicity. Toluene is not considered to be a carcinogen.

Reproductive and Developmental Toxicity

Animal studies provide clear evidence of developmental toxicity of toluene (Donald et al., 1991), including fetal growth inhibition and retardation of skeletal development. Deleterious effects occur with higher doses than the effects above, so health-protective levels are not based on these effects (OEHHA, 1999g). There is some evidence of possible adverse reproductive effects of toluene in humans (Arnold et al., 1994; Taskinen et al., 1994), but the data are not suitable for deriving safe exposure levels for risk assessment. Toluene is listed as a developmental toxicant by the State of California under Proposition 65, the Safe Drinking Water and Toxic Enforcement Act of 1986.

DOSE-RESPONSE ASSESSMENT

Toxicity of toluene is lower than that of many other organic solvents. The rapid metabolism to hippuric acid and excretion avoids the pathways for formation of reactive metabolites that occur with benzene, its close structural relative. The following table contains available health assessment values used by California regulatory programs for toluene.

Table 8. Health assessment values for toluene.

	Health Assessment Value	Reference
Acute reference exposure level (REL)	37 mg/m^3	OEHHA (1999a)
Proposed chronic reference exposure level	0.4 mg/m^3	OEHHA (1997a)
Cancer potency factor	NA	---
Unit risk factor	NA	---
Acceptable intake level (Prop. 65)	7 mg/day oral 13 mg/day inhalation	OEHHA (1994b)
No significant risk level (NSRL; Prop. 65)	NA	---
U.S. EPA reference dose (RfD)	0.2 mg/kg-day	U.S. EPA (1999b)
U.S. EPA reference concentration (RfC)	0.4 mg/m^3	U.S. EPA (1999b)

Public health goal (PHG)	**150 ppb**	**OEHHA (1999g)**

NA = not available

XYLENES

CAS No.: 1330-20-7 (technical grade; a mixture of o-, m-, and p-xylene)
95-47-6 (ortho-xylene, o-xylene)
106-42-3 (para-xylene, p-xylene)
108-38-3 (meta-xylene, m-xylene)

INTRODUCTION

Mixtures of o-, p- and m-xylenes are extensively used in both the chemical and petroleum industries. In the chemical industry, xylenes are used as solvents for products including paints, inks, dyes, adhesives, pharmaceuticals, and detergents. In the petroleum industry, xylenes are used as antiknock agents in gasoline and as intermediates in synthetic reactions. Exposures to xylenes from use in gasoline come from tailpipe emissions (i.e., emissions of unburned fuel), as well as from fugitive emissions.

Xylenes (isomers and mixtures) are regulated as toxic air contaminants in California under AB 1807 and are monitored by the statewide CARB toxics monitoring network.

KEY TOXICOLOGIC EFFECTS

Acute Toxicity

Despite its structural similarity to benzene, xylene does not influence hematopoiesis. In humans, the principal systemic effects of acute xylene exposure are on the central nervous system, but it is also a respiratory and eye irritant. A no-observed-adverse-effect level (NOAEL) for humans based on eye irritation has been estimated to be approximately 100 ppm for at least a 30-minute exposure (OEHHA, 1999a; based on data from the following sources: Nelson et al., 1943; Carpenter et al., 1975; Hastings et al., 1984).

From studies of experimental animals, LC_{50} values (i.e., the air concentrations lethal to 50% of a test population) have been reported for rats and mice. Six-hour LC_{50} values in mice for each xylene isomer are: 4,595 ppm (19,942 mg/m^3), 5,267 ppm (22,859 mg/m^3) and 3,907 ppm (16,956 mg/m^3) for o-, m-, and p-xylene, respectively (Bonnet et al., 1979). A four-hour LC_{50} for mixed xylenes was estimated as 6,700 ppm (29,078 mg/m^3) in rats (Carpenter et al., 1975). In rats, acute xylene exposure has been noted to cause changes in liver (i.e., increased liver weight, changes in cytochrome P450 content and activity, decreased liver glutathione concentrations), as well as changes in lung (i.e., microsomal membrane damage, decreased P450 content, inhibition of aryl hydrocarbon hydroxylase and CYP2B1 activities) (OEHHA, 1999a).

Chronic Toxicity

Information on the chronic toxicity of xylenes to humans is almost exclusively limited to studies of occupational exposures in which persons usually inhaled a mixture of hydrocarbon solvents. However, chronic xylene exposure has been associated with effects in a number of organs and organ systems, including: lungs (e.g., labored breathing, impaired pulmonary function), skin and eyes (irritation), neurological system (headache, dizziness, irritability, weakness, slowed reaction time, decreased muscle coordination, confusion, impaired short-term memory, anxiety); heart (abnormal electrocardiogram, palpitations), gastrointestinal system (nausea, vomiting, gastric discomfort), and possibly the reproductive system (discussed below). Of the few available chronic studies in animals, none comprehensively examined systemic effects (OEHHA, 1999c). An inhalation study by Tatrai et al. (1981) provides a lowest-observed-adverse-effect level (LOAEL) for body weight gain in male rats of 1096 ppm o-xylene.

Carcinogenicity

No exposure studies were located that specifically examined the carcinogenic effects of xylene in humans. No inhalation exposure studies were located that examined the carcinogenic effects of xylene in experimental animals. In an oral carcinogenicity study, rats and mice were administered mixed xylenes by gavage in corn oil 5 days/week for 103 weeks (NTP, 1986). Mice received daily doses of 500 or 1000 mg/kg, and rats received daily doses of 250 or 500 mg/kg. There was no evidence for treatment-related carcinogenicity.

Reproductive and Developmental Toxicity

Reproductive effects were documented by Taskinen et al. (1994) who found increased incidence of spontaneous abortions in 37 pathology and histology workers exposed to both xylene and formaldehyde in the work place. The multiple chemical exposures and the small number of subjects in this study limit the conclusions that can be drawn as to reproductive effects of xylene in humans (OEHHA, 1999c).

Developmental effects, including reduced fetal weights and ossification defects in bones of the skull, have been documented in offspring of animals exposed to xylenes while pregnant. It appears that all three isomers of xylene are fetotoxic and that many of the fetotoxic responses are secondary to maternal toxicity. However, there is inconsistency among the various studies as to the concentrations of xylene producing developmental effects and of those producing no developmental effects (OEHHA, 1999a and 1999c; ATSDR, 1995).

Xylenes are not listed as reproductive or developmental toxicants by the State of California under Proposition 65, the Safe Drinking Water and Toxic Enforcement Act of 1986.

DOSE-RESPONSE ASSESSMENT

The following table contains available health assessment values used by California regulatory programs for xylenes.

Since adopted health assessment values suitable for assessing chronic environmental exposures to xylenes are not available, OEHHA used the proposed chronic reference exposure level (REL) for the purpose of this report. The proposed chronic REL is currently being developed under the Air Toxics Hot Spots Program risk assessment guidelines process (Senate Bill 1731, Statutes of 1992, Ch. 1162 of the California Health and Safety Code). The methodology used to derived the proposed chronic REL for xylenes, as well as the number itself, have undergone an initial round of public and scientific peer review, and are currently being considered by the State's Scientific Review Panel. The derivation of the chronic REL is summarized below, and detailed in OEHHA (1999c).

Table 9. Health assessment values for xylenes

	Health Assessment Value	Reference
Acute reference exposure level (REL)	22000 m/m^3	OEHHA (1999a)
Proposed chronic reference exposure level	700 m/m^3	OEHHA (1999c)
Cancer potency factor	NA	---
Unit risk factor	NA	---
No significant risk level (NSRL)	NA	---
U.S. EPA reference dose (RfD)	2 mg/kg-day	U.S. EPA (1987)
U.S. EPA reference concentration (RfC)	NA	---
Public health goal	1.8 mg/L	OEHHA (1997c)

NA = not available

Derivation of the Proposed Chronic Reference Exposure Level

The proposed chronic REL is based on an epidemiologic investigation of workers exposed to xylene solvents (Uchida et al., 1993). The study population consisted of 175 men and women exposed to 14.2 ± 2.6 ppm mixed xylenes (geometric mean) for an average 7 years. The control population consisted of 241 men and women. A dose-related increase in the prevalence of eye irritation, sore throat, floating sensation, and poor appetite was reported. A lowest-observed-adverse-effect level (LOAEL) of 14.2 ppm was identified. A no-observed-adverse-effect level (NOAEL) was not obtained from this study.

While the Uchida et al. (1993) study was based on occupational exposures, the chronic REL is intended to protect the general public who could be exposed continuously. Therefore, an equivalent time-weighted average concentration (C_{AVE}) was estimated from the observed concentration (C_{OBS}) as follows:

$$C_{AVE} = C_{OBS} \times (10\ \text{m}^3\text{/day occupational exposure} / 20\ \text{m}^3\text{/day total exposure}) \times (5\ \text{days} / 7\ \text{days})$$

In addition, a cumulative uncertainty factor of 30 was applied, 3 for LOAEL to NOAEL extrapolation and 10 for sensitive persons within the population. Therefore:

$$\text{Proposed chronic REL} = C_{AVE} / \text{UF} = 0.17\ \text{ppm}\ (170\ \text{ppb};\ 0.7\ \text{mg/m}^3;\ 700\ \mu\text{g/m}^3)$$

The same study (Uchida et al., 1993) was used to derive the public health goal (PHG) of 1.75 mg/L for xylenes in drinking water (OEHHA, 1997c).

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Appendix B. Response to Comments

B.1. Peer Review

Peer review was invited from the following individuals:

Dr. Joseph R. Landolph
USC/Norris Comprehesive Cancer Center
University of Southern California

Dr. Alvin Greenberg
Risk Science Associates
San Rafael, CA

Dr. Catherine VandeVoort
California Regional Primate Research Center
University of California, Davis.

In this Appendix, the comments of the peer reviewers (with the exception of Dr. VandVoort - see page B-24) are provided followed by OEHHA's responses to those comments.

B.1.1. Comments of Dr. Landolph

Peer review comments from Prof. J.R. Landolph primarily address the risk characterization of the pollutants of concern that will be emitted under various fuel scenarios. These fuel scenarios include MTBE-containing fuel based on the 1997 emission inventory, and MTBE-containing fuel, ethanol-containing fuel (both 2% and 3.5% ethanol fuel scenarios), and non-oxygenated fuel based on predicted 2003 emissions. The comments also address the methodology used for quantifying cancer and noncancer risks, research needs, conclusions, and toxicity summaries in Appendix A. Responses will be made to the 'specific comments', which address in greater detail all the 'general comments' made

General Comments

The stated objective of this report is to evaluate the public health impacts of utilizing ethanol as an oxygenate in gasoline. This report therefore quantitates and summarizes the health risks to humans when various formulations of gasoline are utilized in California, including methyl tertiary butyl ether (MTBE)-based California Phase 2 Reformulated gasoline (CARFG), nonoxygenated gasoline, gasoline containing ethanol with an overall oxygen content of 2%, and gasoline containing ethanol with an oxygen content of 3.5%. Health risks quantified included toxicity to the ocular and respiratory systems of humans exposed to these fuels, and the lifetime risk of incurring cancer that would occur in humans exposed to these fuels. The authors evaluated evaporative emissions, tailpipe (exhaust) emissions, and atmospheric transformation products that arise from the use of ethanol in gasoline. The authors utilized data generated by the model from the California Air Resources Board, which included estimates of total air concentrations of various pollutants, identified chemicals of potential concern, and generated a quantitative risk assessment of the health effects that these concentrations of these pollutants could induce in humans. Specifically, the authors generated lifetime cancer risk estimates and also acute and chronic hazard indices associated with exposure to the separate and total fuel components.

The Chemicals of Potential Concern (COPC) identified included the oxygenates MTBE and ethanol; the combustion products butadiene, formaldehyde, acetaldehyde, and carbon monoxide; the evaporative emittents benzene, hexane, and toluene; and the atmospheric transformation products peroxyacetyl nitrate(PAN) and ozone. These are appropriate choices for the Chemicals of Potential Concern. Perhaps heptane, which is very neurotoxic, should be included in this section as well. They then used health assessment values to determine toxic or carcinogenic risk due to the separate chemicals and to the chemicals in the aggregate, assuming additivity of the risks. They found firstly that for most COPC, the non-cancer hazard Quotients (HQs) were below one, except that the chronic HQ for formaldehyde varied from 1.8 to 2.4, the HQ for acute exposure to PAN varied from 2.3 - 2.4, the HQ for acute exposure to carbon monoxide varied from 1.0 to 1.6, and the HQ for acute ozone exposure varied from 2.5 to 2.7.(Tables 5a and 5b). Clearly, attention needs to be focussed on these values, and they need to be lowered if possible in the future by encouraging more public transportation, use of electric-powered cars, and use of solar-powered cars.

The lifetime cancer risk values for exposure to these fuels and their components varied considerably. For the 1997 MTBE-gasoline formulation, the greatest risks came from benzene (upper risk, 110/million), butadiene (upper risk, 130/million), and formaldehyde (upper risk, 33/million). All these lifetime cancer risks decrease with all four fuel formulations considered (Table 5c). A conclusion that can be drawn is that the lifetime cancer risks are similar with all four fuel formulations, and lower than those that occur with use of the 1997 MTBE fuel formulation. The authors further found that the cumulative cancer risks for each of the four new fuel scenarios decreased from the 1997 MTBE-containing gasoline scenario, and were similar(Table 7). Hence, removing MTBE from the gasoline would certainly improve the environmental situation as regards pollution of the ground water with this chemical, and would lead to cancer risks similar to those induced by the other three fuel scenarios for 2003 (Table 7). The cumulative lifetime risks for cancer from fuel exposure decreased from 280/million in the 1997 MTBE-containing gasoline scenario, to 170 - 190/million for the scenarios using the four types of gasoline in 2003. This is an improvement in the lifetime cancer risk and again indicates that MTBE can likely be removed from the gasoline, and replaced with ethanol, and that the lifetime cancer risk of Californians will not be changed significantly. However, what worries the reviewer is that the lifetime cancer risks still remain too high, and would lead to approximately 190 cancers/million, which would lead to 190 x 30 or 5,700 excess cancers in California due to the use of these fuels. Clearly, some thought should be given to gradually moving to electric-powered automobiles and trucks, to solar-powered automobiles and trucks, and to increased use of public transportation to lower both the HI and lifetime cancer risk values.

Again, for toxicity considerations, Tables 8-10 are very instructive. They indicate that the HQ values for fuel constituents either remain the same or decrease slightly when one considers the 1997 MTBE-gasoline values compared to the 2003 values for the four fuels considered. This again suggests that the MTBE-containing gasoline can likely be replaced with the four fuel scenarios in the year 2003, and the individual and cumulative

HI values will either stay the same or decrease slightly. What is again worrisome is that the cumulative acute HI values range from 6.3 to 6.7 for eye irritation and from 3.6 to 3.8 for acute respiratory irritation, which is too high(Tables 8 and 9). It is further worrisome that the maximum cumulative chronic hazard indices range from 4.8 - 5.0 for respiratory irritation(Table 10). This data indicates that one can replace the 1997 MTBE-gasoline scenario with the four fuel scenarios proposed for 2003 with either the same or slightly decreased cumulative HI values, and one can remove the MTBE from the gasoline and have about the same cumulative HI value in 2003, benefiting from same HI value and eliminating the threat of pollution of water supplies by MTBE. However, it still appears that further reduction in pollution is necessary to lower the cumulative HI values.

I very much enjoyed reading this report. It is clearly written, well-written overall, and comes to firm conclusions. I was very impressed with the Appendix. I actually suggest placing the Appendix under the Section, Chemicals of Potential Concern, Section 2.0. Otherwise, the reader is constantly looking to determine which citations have been made to document the scientific statements that are made in section on Chemicals of Potential Concern, and this is distracting. The conclusions that the authors came to are very reasonable and consistent with the data and calculations they presented.

I agree that the health risks, both for toxicity and for carcinogenesis, are not significantly different between the 2003 formulations of gasoline, whether it contains MTBE, 2% ethanol, 3.5% ethanol, or non-oxygenated gasoline. Hence, from the standpoints of toxicity and carcinogenicity, any of these four formulations should work well. There are slight differences, and I would recommend choosing those formulations that show the lowest human health risk possible, in the interests of the people of the State of California. I also recommend some discussion as to why the 2003 risks are significantly below the 1997 risks in terms of toxicity and carcinogenicity. This was ascribed to lower fuel consumption in 2003. Watching the traffic increase in Los Angeles over time, and knowing the projected population increase in California with time, I am very skeptical about this forecast. Please summarize this consideration, making concise references to the relevant OEHHA documents on this issue, to fortify the conclusions cited about less use of gasoline in 2003, by adding one extra paragraph or so.

Passing from the conclusions in the document on the relative hazards of the four formulations of gasoline, this reviewer is concerned that the cumulative (additive) Hazard Indices are significantly above 1.0 for the chemicals studied, some reaching as high as 6.9 for the 1997 MTBE gasoline acute eye irritation HI value (Table 8, upper bound value). Even for the 2003 values, with the four gasoline formulations, the values range from 6.3 to 6.7, which in my opinion is far too high and erodes the safety margin built into the HI index. Some effort should in my opinion be made to address this situation by lowering the levels of toxic fuel components in the air even further. In Table 9, the cumulative acute HI values for respiratory irritation are also too high, ranging from 3.9-4.0 in 1997 to 3.6 to 3.8 projected in the year 2003. This might present a significant problem for children, athletes who exercise strenuously, and young children. Some attempt should also be made to address this situation in the future.

In addition, the cumulative lifetime cancer risks can be used to show that in California, with 30 million people, there could be as many as 5,100 extra cancers incurred. In my opinion, these risks are too high, even though I am aware that 32% of the population of the U. S. will eventually contract cancer. This should be more strongly emphasized in the text. This data suggests to me that further efforts should be made to encourage motorists and truck drivers (particularly with the risk from diesel fuel) to convert to electric-powered or solar-powered vehicles, gradually so this does not disrupt the economy, and to convince the people of California to use more public transportation, to reduce the risks of toxicity and carcinogenicity from air-borne gasoline constituents, and to reduce pollution of the water with gasoline constituents, including not only MTBE but also benzene, toluene, xylenes, ethylbenzene, butadienes, and hydrocarbons. This clearly is the wave of the future.

I have made a number of specific suggestions, criticisms, and comments in the following pages that refer to specific sections of the text., which are intended to be constructive and to help improve the quality of the document. This is already a very good document, and my suggestions and comments are intended to help improve it slightly to ensure that it is excellent. Please feel to contact me for any clarifications that you many need. My specific comments follow.

Response: OEHHA thanks Dr. Landolph for his general comments on the “Potential Health Risks of Ethanol in Gasoline” document. All general comments are also addressed in the specific comments, often with greater detail. Responses will therefore be addressed to all to the specific comments.

Specific Comments

Comment 1: Section 2.0 Hazard Identification: Chemicals of Concern. The chemicals of potential concern appear to have been chosen appropriately. Page 3, paragraph 3, line 6: Heptane should also be considered in this analysis, since it is more neurotoxic than hexane, pentane, and octane. "Heptane is considerably toxic to the human nervous system(neurotoxic)." Encyclopedia of Toxicology, Philip S. Wexler, Ed., Volume 2, pages 77-78.

Response: It is assumed that the reviewer is referring to n-heptane, which has a similar chemical structure to n-hexane, a known neurotoxic agent in laboratory animals and humans. n-Heptane is present in the various fuel scenario compositions at levels roughly equal to that of n-hexane. A review of current literature exploring the toxicology of n-heptane in rats did not find any evidence for neurological disturbances at concentrations as high as 3000 ppm for 26 weeks, or 1500 ppm for 30 weeks (Snyder, 1987). Examination of the formation of the neurotoxic metabolites following n-hexane or n-heptane exposure was conducted in both rats and humans (Filser et al., 1996). In both species, urinary excretion of the n-heptane neurotoxic metabolite (2,5-heptanedione) was significantly less compared to the urinary excretion of the n-hexane neurotoxic metabolite (2,5-hexanedione). Also, the neurotoxic potency of the n-heptane metabolite was found to be considerably less than that of the n-hexane metabolite. The authors concluded that for both humans and rats, the neurotoxic potency of n-heptane is significantly lower than that of n-hexane. In addition, two comparative studies observed neurotoxicity in rats following n-hexane exposure, but not following n-heptane exposure

(Frontali et al., 1981; Takeuchi et al., 1980). No human studies on the neurotoxic effects of n-heptane exposure could be located. However, anecdotal evidence in a shoemaker suggests n-heptane may have been involved in the development of peripheral neuropathy (Valentini et al., 1994). However, this case study was confounded by the presence of several other solvents in the workroom air. Based on the lack of evidence for noncancer effects, including neurotoxicity, and the evidence that maximum levels of n-hexane are predicted to be nearly two orders of magnitude below the level of concern, n-heptane was not considered for analysis in this report.

Comment 2: Section 5.1. Estimating Cancer Risk: This section is very well-written and very clearly written. The reviewer suggests a definitive literature citation under section 5. 1, Estimating Cancer Risk, to follow the statement that, "Typically carcinogenesis is treated as a "non-threshold" toxicological phenomenon." Citation of the latest U. S. E.P.A. document on this issue would be helpful here. The reviewer agrees that a non-threshold approach is correct for cancer induction for this section.

Response: OEHHA thanks Dr. Landolph for his comments and agrees that clarification is needed to lead the readers to more information regarding non-threshold carcinogenesis, if they wish to do so. Appendix A contains a detailed toxicity summary of each of the chemicals of concern for this document and includes citations and detailed information on the development of each cancer risk value. A sentence will be added to section 5.0 to direct readers to Appendix A for more information on individual chemicals.

Comment 3: Section 5.1. Estimating Non Cancer Risk: This section is also very well-written and also very clearly written.

Response: OEHHA thanks Dr. Landolph for his comments.

Comment 4: Section 6.1.1: Acetaldehyde: Page 10, para. 2: The authors should take into consideration the sensitivity of asthmatics to acetaldehyde, since asthmatics are likely the sensitive receptors in the population in California, as regards toxicity of acetaldehyde to humans, and since acetaldehyde is very toxic to the pulmonary system.

Response: The acute and chronic Health Protective Values (HPCs) are intended to protect identifiable sensitive individuals, including asthmatics, from harm due to chemical exposure. The application of a 10-fold intraspecies uncertainty factor to the NOAEL is used to account for the known variability within the human population, unless the NOAEL is based on a sensitive subpopulation (i.e. asthmatics) of humans. However, HPCs may not necessarily protect hypersensitive individuals who may develop an idiosyncratic response (including allergic hypersensitivity). Development of the HPCs, including application of uncertainty factors, is contained in Appendix A for each chemical. However, OEHHA agrees this information should be more apparent to the readers of the risk characterization section. Dr. Landolph also expressed similar concern about the irritant effects of ethanol, formaldehyde, MTBE, and PAN in sensitive humans.

Therefore, a sentence will be added to Section 6.1 direct readers to the Appendix for detailed information on the basis and development of the HPCs.

Comment 5: Section 6.1.2. Benzene: Page 19, line 3: The authors should state here, "Acute Myelogenous Leukemia," rather than simply "leukemia," since AML is the type of leukemia that the epidemiological studies definitively indicate is increased in humans upon exposure to benzene.

Response: The sentence “The primary endpoint in human is leukemia.” has been modified to read: “The primary toxic endpoint in humans is acute myelogenous leukemia, but strong evidence exists to suggest that benzene causes other forms of leukemia as well (OEHHA, 1999e).” Also, in response the following sentence has been changed to indicate that the current cancer unit risk value for California is based on total leukemia (i.e., all forms of leukemia as a related class of diseases). (Federal potency values are also based on total leukemia).

Comment 6: The reviewer also suggests citing literature references for induction of AML in humans upon benzene exposure, particularly that from the shoe factory workers in Turkey and other countries. On line 6, the reviewer suggests citing the work of C. Maltoni showing that benzene is a multi-site carcinogen in animals, and also the IARC and U. S. E. P. A. classifications of carcinogenicity for benzene. Page 20, para. 3: Please cite the reference for reduced birth weights in newborns as the most sensitive toxicological end-point for benzene exposure. Also, I suggest indicating that even though this is the most sensitive endpoint, there is no evidence to suggest that this endpoint is of toxicological concern under these scenarios, if this is the case. Otherwise, the sentence is somewhat misleading and tends to imply that there may be a problem with induction of this endpoint under the exposure scenarios, which I do not believe the authors mean to imply. Similarly, in the next sentence, the authors should also cite a literature reference to benzene-induced hematoxicity, including aplastic anemia. They should also state directly that at the exposure levels considered, this is not expected to be a problem, unless they believe otherwise.

Response: OEHHA believes that these comments were adequately discussed in Appendix A, Page A-5. In response to the reviewer’s comments, a reference to Appendix A has been added to “Section 6.1.2 Benzene”. Since there are over 20 epidemiological studies of leukemia among benzene exposure populations as well as numerous animal bioassays, OEHHA has chosen to cite secondary review documents (e.g., ATSDR, 1997; OEHHA, 1999e) to support the points discussed above.

The sentence regarding the noncancer issue will be modified so that it is clear that at the resulting exposure levels, no acute and chronic noncancer effects are expected to occur.

Comment 7: Last two sentences on page 19, and first two sentences on page 20, the reviewer suggests citing the literature on whether benzene carcinogenesis has a threshold, and also citing the official U. S. E. P. A. position on this and the IARC position on this.

Response: Following the sentence describing the threshold issue (first line, page 20), the following citation is added "(reviewed in OEHHA, 1999c)". (Again, a review citation was chosen instead of adding numerous necessary primary citations).

In response to the suggestion for a citation on U.S. EPA and IARC's position on low dose linearity, we have added (after the sentence on line 2 of page 20) the following citations "(OEHHA, 1999c; U.S. EPA, 1999)" to indicate that OEHHA and U.S. EPA treat benzene as a substance that does not function through a threshold mechanism for cancer. IARC does not routinely conduct dose-response evaluations of carcinogens and to our knowledge has not taken a position on the issue.

Comment 8: I suggest adding a few other reference values into the table on cancer slope factors, such as those for strong carcinogens like aflatoxin B 1 and benzo(a)pyrene, and a few weak ones as well, in order to allow the reader to calibrate himself/herself as to the strength of the benzene, butadiene, etc. cancer slope factors, and a small amount of discussion as to how strong the slope factors are for the compounds considered in this document. One or two sentences on this is sufficient).

Response: OEHHA believes that an additional table containing unrelated cancer risk values is not necessary for this document. Table 5c, maximum lifetime cancer risks, and Table 7, lifetime cancer risk and cumulative cancer risks, should allow a more appropriate comparison of cancer risks for the chemicals of concern that will impact the entire South Coast Air Basin.

Comment 9: <u>Section 6.1.3. Butadiene</u> The reviewer suggests citing a literature review on the carcinogenicity of butadiene, on page 20, para 4, line 4. Line 8 should also include a literature reference to the epidemiological studies of butadiene-induced human cancer in epidemiological studies. Many of these comments could be addressed by placing the Appendix section into section 2, if this is consistent with the form this document must take in final form. Similarly, page 21, para. 1, line 1, should also include a reference to the studies of lymphoma induction in mice upon exposure to butadiene. Similarly, lines 5-7 should have a reference or two to the original scientific literature, and also the positions of the IARC and the U. S. E. P. A. on the question of no threshold for this compound should also be mentioned here.

Response: OEHHA thanks Dr. Landolph for pointing out the seemingly disconnect between the listed unit risk values, as well as the noncancer HQs, in the risk characterization section and their basis in the Appendix. Lack of citations for the cancer and noncancer effects for many of the other chemicals are also listed as a concern by Dr. Landolph. As indicated in the previous response, the basis and the development of the unit risk factors and HQs, including a full list of citations, is included in Appendix A. OEHHA believes that for simplicity and ease of reading, the basis and development of

HPCs for individual chemicals should remain separate from the risk characterization. However, this fact will be emphasized in section 6.1 by adding language that will direct the reader to Appendix A for further information on individual chemicals. This should clarify Dr. Landolph's individual concerns regarding citations of critical studies involved in the development of the HPC for each chemical.

Comment 10: Page 21, para. 3, lines 5-7 should indicate that although the most sensitive endpoint for acute exposure is reduced birth weights in newborns and under chronic exposure is ovarian atrophy, there is not expected to be any such induction under the exposure scenarios, if indeed this is the position of OEHHA.

Response: OEHHA agrees that clarification is needed to indicate that the noncancer endpoints will not be reached under the estimated exposure scenarios. Dr. Landolph also expressed a similar concern for the language used in describing the most sensitive noncancer endpoint for some of the other chemicals. OEHHA will modify the discussion of the noncancer endpoints for each chemical, where appropriate, to indicate that under the expected exposure conditions the most sensitive indicator of toxicity will not be reached.

Comment 11: Section 6.1.4. Ethanol, This section is appropriately concise. However, some short discussion regarding the possible effects of ethanol upon the respiratory tracts of the most sensitive receptors, i. e., likely asthmatics, should be briefly mentioned here.

Response: OEHHA thanks Dr. Landolph for his comments. As discussed in a previous response, an intraspecies uncertainty factor is applied to the NOAEL to protect sensitive humans such as asthmatics. Details on the development of the HPC for ethanol can be found in Appendix A.

Comment 12: Section 6.1.5. Formaldehyde, In this section, page 22, para. 2, some mention should be made that formaldehyde and other aldehydes are very irritating and toxic to the respiratory tract. Some concise discussion should be made as to whether levels of formaldehyde would be reached that could be irritating or toxic to the respiratory tracts of humans under the forecast exposure scenarios. On lines 5-7, the original animal studies on the carcinogenicity of formaldehyde to the nasal passages of rats should be cited. Page 23, paragraph 2, lines 4-5 should have a citation to the scientific papers in which these effects were found, and also to data of Henry d'A Heck of CIIT that formaldehyde causes DNA cross-links in cells from nasal passages of rats exposed to formaldehyde. This reviewer is worried about the HQ being 2.4 for formaldehyde at present. This reviewer also agrees that acetaldehyde and other aldehydes likely cause additive effects in terms of respiratory toxicity and ocular toxicity. These respiratory effects could be dangerous in asthmatics, who should be considered the sensitive receptors in the population of humans in California that could be exposed to gasoline. Some modification to the sentences on page 23, para. 2, lines 9 and 10 should be made. An HQ of 2.4 is too high when the entire population of California would be exposed to acetaldehyde.

Response: OEHHA thanks Dr. Landolph for his comments on the formaldehyde risk characterization. As indicated in section 5.2, the exceedance of an HQ of one does not necessarily mean that a health impact will in fact occur. It is impossible to calculate the lowest concentration at which any one individual in a diverse population would respond. The interpretation of the HQ for formaldehyde currently present in the risk characterization is the most concise analysis that OEHHA can reliably report, given the wide interindividual differences in response and generally limited information. The citations that Dr. Landolph requests can be found in the Appendix A toxicity summary for formaldehyde. However, a sentence will be added to the summary to include the DNA cross-link findings as Dr. Landolph suggests. As discussed in an earlier response, the application of a 10-fold intraspecies uncertainty factor to the NOAEL is used to account for the known variability within the human population, unless the NOAEL is based on a sensitive subpopulation (i.e. asthmatics) of humans. The application of uncertainty factors for individual chemicals can be found in Appendix A. OEHHA thanks Dr. Landolph for revealing that OEHHA did not adequately explain that the annual average exposures for formaldehyde (and the other chemicals) are actually based on South Coast Air Basin (SCAB) scenario estimates. A statement clarifying this point has been added to Section 4.0 of the report.

Comment 13: There is some inconsistency between lines 1-3 and lines 11- 12, in terms of formaldehyde concentrations being two-fold above the REL (lines 1-3) and again being two-fold below the acute REL (lines 11- 12). Please be consistent here.

Response: OEHHA thanks Dr. Landolph for pointing out this apparent inconsistency. As explained in the formaldehyde risk characterization, the proposed chronic REL is currently going under review and may change. If the value for the chronic REL is increased, the disparity between the acute and chronic REL will become smaller. However, animal studies have indicated that near the chronic LOAEL, acute and subchronic exposures to formaldehyde may not result in any microscopic histopathological inflammatory changes to the nasal epithelium. With longer, near lifetime exposures at the same concentrations, inflammatory changes will indeed develop in the nasal cavity. This same sort of scenario may be a contributor to the disparity between the acute and chronic REL.

Comment 14: Section 6.1.6. Methyl t-Butyl Ether(MTBE). Page 24, para. 1, lines 2-4: Please cite the original scientific literature from which these data are derived to strengthen this document.

Response: The citations for MTBE may be found in Appendix A.

Comment 15: Line 10: Please state directly that you are utilizing a linear, no-threshold model for MTBE carcinogenesis.

Response: Upon review of the risk characterization for MTBE, OEHHA agrees that the type of cancer potency model used for unit risk factor development was not clearly stated. Language will be included to show that a non-threshold model was used.

Comment 16: Para. 2, lines 3-5: Why is the 2003 scenario showing a 30% lower cancer risk? Please explain this.

Response: The paragraph in question shows that the 1997 cancer risk from MTBE in MTBE-containing fuel is 3.6 excess cancer cases per million people exposed. The MTBE risk based on 2003 MTBE-containing fuel is shown in parenthesis as 2.5 excess cancer cases (per million people exposed). 2.5 / 3.6 equals a 30% reduction in cancer risk. OEHHA will clarify this paragraph so the 30% reduction in cancer risk is more apparent.

Comment 17: Further, the authors should point out that with a population of thirty million, 3.6 excess cancers per million becomes 102 excess cancers per 30 million. This is getting to be too high an excess cancer risk, in my opinion.

Response: OEHHA thanks Dr. Landolph for revealing that OEHHA did not adequately explain that the annual average exposures for MTBE (and the other chemicals) are actually based on South Coast Air Basin (SCAB) scenario estimates. Dr. Landolph also expressed this same concern regarding the cumulative excess cancer cases as presented in section 6.3. The SCAB is known to have the worst air quality in the State. When Dr. Landolph states “102 excess cancers per 30 million”, he appears to be estimating the excess cancer risk for the entire State of California based on the estimated annual average MTBE exposure in the SCAB. Therefore, using the MTBE cancer risk values for the entire State overestimates the MTBE cancer risk for the population of California. OEHHA will incorporate language into section 4.0 to clarify this misunderstanding.

Comment 18: Page 24, paragraph 3: Please state whether or not these toxicological endpoints would occur in sensitive receptors, i. e., asthmatics, in MTBE-gasoline exposed populations at ambient concentrations. MTBE is a very irritating substance for humans. Scientific studies on the human toxicity of MTBE should also be cited here. What is the projected increased effect of MTBE-containing gasoline upon asthmatics and cigarette smokers in regards to pulmonary toxicity?

Response: As discussed in earlier responses, similar concerns were expressed by Dr. Landolph for other chemicals. Regarding MTBE, as well as the other chemicals, please refer to the Appendix A toxicity summaries.

Comment 19: Section 6.1.7. Peroxyacetyl Nitrate (PAN). Page 25, para. 2: The authors should cite the scientific papers dealing with the toxicity of PAN, particularly review articles. Secondly, these acute noncancer HQ values for PAN at 2.4 are too high.

Page 25, last sentence, and 26, top line: Do the authors feel that any of these endpoints may at any time be induced in humans being exposed to PAN in ambient air due to PAN in gasoline? Please state this one way or the other definitively, or indicate the uncertainty.

Response: Citations for PAN are located in Appendix A. OEHHA acknowledges that the potential for sensory irritation from PAN, as explained in the document, was somewhat vague. To rectify this problem, OEHHA will incorporate language similar to that found in section 6.1.5. (formaldehyde): “It is possible that some sensitive individuals may develop acute adverse effects at the maximal predicted exposure. Simultaneous exposure to other sensory irritants, such as formaldehyde, may exacerbate the eye irritation caused by PAN”.

Comment 20: Re Table 5a: This reviewer is concerned about the HQ values for formaldehyde and PAN. Please give us HQ values for all the other HQ's added together, and also lifetime cancer risk values when all the lifetime cancer risk values for each compound are added together. This reviewer is concerned about the cumulative, additive HQ values for formaldehyde, PAN, and the other values added together for sensitive receptors, i. e., asthmatics. Please comment on this.

Response: Tables addressing the combining of HQs, known as Hazard Indexes (HIs), can be found in section 6.4, Cumulative Noncancer Impact of Multiple Chemical Exposures. This section also discusses how to interpret these results, and their limitations. Tables that address the combining of lifetime cancer risk values can be found in section 6.3, Cumulative Cancer Impact of Multiple Chemical Exposures.

Comment 21: It is also noteworthy that the benzene cancer risks decrease under the 2% ethanol/2003 and the 2003 NonOxy/2003 scenarios compared to the 1997 values. Similarly, the formaldehyde cancer risks decrease from the 1997 values under all four 2003 scenarios. This seems to indicate that eliminating MTBE would eliminate MTBE pollution and its carcinogenicity and toxicity, without significantly altering the concentrations of the other toxic and carcinogenic pollutants. This is good. However, the cumulative HI and lifetime cancer risk values may still be too high to adequately protect public health. More thought needs to be given to this issue.

Response: OEHHA agrees that the lifetime cancer risk and some cumulative HIs appear to be excessive. However, OEHHA noted in the report that for both the individual chemicals and their cumulative effects, there are numerous uncertainties to take into account when interpreting these numbers. Given this, it is the risk managers for the air management districts (e.g., the South Coast Air Quality Management District) and CARB that would use the hazard estimates determined by OEHHA and decide if appropriate measures are be taken to protect public health.

Comment 22: Section 6.2. Risk Characterization for Other Compounds of Concern: - Page 29, paragraph 1: The authors should give a one paragraph, concise discussion on the toxicity and carcinogenicity of toluene, xylenes, isobutene, and n-hexane, particularly with regard to their neurotoxicity to humans.

Response: The potential for carcinogenicity and toxicity for each of the chemicals listed above is summarized in Appendix A. OEHHA will include a sentence in section 6.2, Risk Characterization for Other Compounds of Concern: Toluene, Xylenes, Isobutene, n-Hexane to inform readers of the presence of these summaries in the Appendix.

Comment 23: The reviewer suggests mentioning that although there are large uncertainty values associated with lifetime cancer prediction, nevertheless, there is firstly good news that all aggregate lifetime cancer risk values are lower in 2003 than in 1997, and secondly, that the 2% ethanol and 3.5% ethanol formulations are the lowest among these, and decrease from 290 to 190, which is a 34% decrease of the upper values, and from 270 to 170, which is a 37% decrease in the lower bound values. This is very good news, and it should be emphasized. It suggests that the State of California may be able to eliminate the MTBE in the gasoline, and get even lower lifetime cancer risks for its population, plus eliminate the problem of MTBE from leaking gasoline storage tanks fouling the water supplies from wells.

Response: OEHHA agrees that the reduction of cancer risk under the 2003 scenarios compared to the 1997 fuel scenario is an encouraging result. However, we feel it is important to maintain a technical presentation of the results. As discussed in our report, given the uncertainties in the individual chemical estimates and the inherent uncertainty in addition of multiple cancer risk estimates, OEHHA believes the differences in cumulative cancer risk between the four 2003 formulations are not significant.

Comment 24: Another consideration that should be mentioned is that even at a lifetime cancer risk of 170/million(2003 lower bound scenarios), this would translate to 170 x 30 or 5, 100. extra cancers in the State of California due to the carcinogens in gasoline. OEHHA should consider recommending to the Governor of California that California move slowly and gradually away from gasoline-powered vehicles(to minimize economic disruption) and continue to move toward solar-powered vehicles, electric-powered vehicles, and more public transportation. These calculations are very illuminating. It should also be stated that any change in gasoline formulation is an experiment on the people of California. It should be done very carefully, perhaps in one part of the State at a time, to ensure we are not causing any harm by this change in gasoline formulation. It appears from the data in this table 8 that if the State of California shifted from MTBE-containing gasoline to 2% or 3.5% ethanol-containing gasoline, that the HQ value would be similar to or the same as that for MTBE gasoline, and one could eliminate the water-fouling, toxic, and carcinogenic properties of MTBE that arise when gasoline tanks leak MTBE-containing gasoline. However, these HI values are still too high, and again it should be pointed out that a gradual shift away from gasoline-powered vehicles and toward solar-powered and/or electric-powered vehicles, and also toward more use of public transportation should be serious goals for California in the future.

Response: OEHHA shares Dr. Landolph's concern that the cumulative cancer risks and HI's presented in our report may indeed result in important public health issues, particularly for the people living in the South Coast Air Basin where these emission estimates were modeled. OEHHA's current mandate with regard to the ethanol fuel report is to present Californians with the cancer and noncancer risks scenarios associated with the various fuel formulations. It is conceivable that OEHHA will be asked in the future to develop airborne hazard risk estimates based on alternative transportation means and alternative fuel vehicles. However, it is primarily the purview of the California Air Resources Board (CARB) to address these issues. OEHHA will strive to present to the public the most up-to-date health hazard assessments associated with fuel combustion emissions.

Comment 25: Section 6.4. Cumulative Noncancer Impact of Multiple Chemical Exposure**.** This section is written well and in a clear fashion. At the end of paragraph 3, page 34, the authors should discuss that the cumulative (added) HI values firstly are considerably in excess of 1.0, and in fact are as high as 6.9(1997 MTBE value). It seems to this reviewer that this is simply too high a cumulative HI value. This should be discussed in terms of its impact on human health. All attempts should be made to lower this value. It appears from the data in this table 8 that if the State of California shifted from MTBE-containing gasoline to 2% or 3.5% ethanol-containing gasoline, that the HQ value would be similar to or the same as that for MTBE gasoline, and one could eliminate the water-fouling, toxic, and carcinogenic properties of MTBE that arise when gasoline tanks leak MTBE-containing gasoline. However, these HI values are still too high, and again it should be pointed out that a gradual shift away from gasoline-powered vehicles and toward solar-powered and/or electric-powered vehicles, and also toward more use of public transportation should be serious goals for California in the future.

Response: OEHHA thanks Dr. Landolph for his comments. With regard to the cumulative HI values, as indicated in section 5.2, the exceedance of an HQ (or an HI) of one does not necessarily mean that a health impact will in fact occur. It is impossible to calculate the lowest concentration at which any one individual in a diverse population would respond. The interpretation of the cumulative HIs is the best analysis that OEHHA can reliably report, given the wide interindividual differences in response, the generally limited information, and the uncertainties that go into combining HQs for a given endpoint. With regard to encouraging the public to use alternative methods of transportation, OEHHA's mandate is to present Californians with the cancer and noncancer risks assessments associated with the various fuel formulations. It is conceivable that OEHHA will be asked in the future to develop airborne hazard risk estimates based on alternative transportation means and alternative fuel vehicles. However, it is primarily the purview of the California Air Resources Board (CARB) to address these issues.

Comment 26: In addition, for Table 9, regarding respiratory toxicity, this reviewer was again surprised that the HI values were as high as 3.9 - 4.0 for the 1997 MTBE-containing gasolines. It is gratifying that no matter which of the four formulations of gasoline is used in 2003, the HI values decrease to as low as 3.7(upper bound) or 3.6 (lower bound), which represent decreases of 7.5% and 7.7%, respectively. This is very good news, and it should be stated this bluntly in this section and is cause for optimism. It should also be stated that it looks like the State of California can move to 2% ethanol-containing or 3.5% ethanol-containing gasoline, not cause any significant increase in respiratory HI values, and eliminate any further increases in the MTBE pollution of the water sources in California due to leaking underground storage tanks. This should be stated precisely in the discussion to this section. Similar statements apply to Tables 9 and 10, and these statements should be made more boldly in the discussion of these two tables.

Response: OEHHA shares Dr. Landolph's optimism concerning the reduction in HI values resulting with the 2003 fuel scenarios. However, given the limitations in the estimates, as described in section 6.4, the reductions in HI values can be considered only modest at best. Also, it should be emphasized that these reductions, according to CARB's companion document to this report, result from an overall reduction in fuel emissions. All in all, OEHHA agrees that including additional statements emphasizing the modest reductions in HI values will enhance the interpretation of the noncancer results. OEHHA believes that MTBE's air quality impact is relatively small in comparison to its impact on water quality. The greatest impact of removing MTBE from gasoline is detailed in section 6.5, Health Impacts of Drinking Water Contamination by Gasoline Components.

Comment 27: Page 35, para. 2, lines 3-5: What the authors say is factually correct. However, the reviewer is more worried about the HI for these two substances exceeding 1.0 individually, and that the cumulative HI is as high as 5 for table 10. This should be mentioned more strongly.

Response: OEHHA thanks Dr. Landolph for his comment. A sentence will be added to the paragraph to emphasize that, individually, these substances (formaldehyde and PM10) may result in chronic respiratory irritation in sensitive people.

Comment 28: Page 38, para. 3, lines 2-3: Values for tertiary butyl alcohol are not listed in Table 4. Please list them or correct this sentence.

Response: OEHHA thanks Dr. Landolph for alerting OEHHA to an error in this paragraph. The correct table referring to the health protective concentrations for drinking water is actually Table 3, not Table 4 as indicated. The CARB could not detect measurable air levels of tertiary butyl alcohol in the South Coast Air Basin. Therefore, it is not listed in Table 4.

Comment 29: Page 38, para. 4, line 5: "organoleptic" is a sophisticated but not a commonly used scientific word. Please substitute another word, such as toxic and/or noxious. Also, in this paragraph, please reference the appendix or the original scientific literature on the toxicity and carcinogenicity of MTBE.

Response: OEHHA agrees that “organoleptic” is not a commonly used word in general toxicology circles. However, its use is much more common in reference to water pollution issues and is appropriate in the discussion of drinking water contamination by gasoline components. OEHHA will include, in parentheses, the one word definition (i.e. noxious) provided by Dr. Landolph.

Comment 30: Section 6.5. Health Impacts of Drinking Water Contamination by Gasoline Components: This section is very well-written, and it suggests that ethanol contamination of the water due to use of ethanol in gasoline should present very minimal toxic and carcinogenic risk and no objectionable taste or smell problems for public drinking water. A concluding sentence such as this should be placed at the end of this section to wrap this section up well. The fact that ethanol is biodegraded rapidly is also cause for cautious optimism. However, the reviewer recommends being cautious in the area of ethanol, since there is little or no data on the pulmonary effects of ethanol or ethanol-containing gasoline.

Response: OEHHA agrees that a concluding statement as offered by Dr. Landolph will enhance the interpretation of the water contamination issues and will be added to section 6.5.

Comment 31: Section 6.6.2. Uncertainties in Exposure Assessment, Page 43, para. 3: The authors should indicate some of the data that went into the assessment of lesser gasoline use in 2003 compared to 1997, particularly since the number of people living in the State of California is increasing dramatically with time.

Response: OEHHA agrees that the primary reasons for the year 2003 reduction in emissions are not clearly explained. OEHHA will add a sentence to Section 6.6.2 to clarify that the ARB assumptions of reduced air emissions for 2003 are based on a total reduction of overall fuel emissions. It is expected that at least a portion of these emission reductions will result from an increased proportion of cleaner fuel-burning, vehicles on California roads.

Comment 32: This report could also use an Executive Summary of no more than 250 words at the front.

Response: OEHHA agrees that an executive summary would enhance the document. One is being prepared that will include the analysis by OEHHA, as well as the analysis of the California Air Resources Board and the State Water Resources Control Board.

Comment 33: Section 7.0. Research Needs, This section is appropriately written, but is somewhat dry. The authors should add some more enthusiasm to this section, since it will be widely read. In particular, this section should emphasize the need for more research on the pulmonary toxicity of ethanol alone and of ethanol-containing gasoline.

Response: While this section may be somewhat dry, it should be stressed that this section is a work-in-progress and will be modified in future drafts. OEHHA will modify this section to include Dr. Landolph's timely comments on the need for research on the pulmonary toxicity of ethanol and ethanol-containing gasoline.

Comment 34: Section 8.0 Summary/Conclusions.- On page 52, either at the end of para. 1, or as a separate para., I recommend inserting: "Further efforts to encourage Californians to utilize electric-powered cars or solar-powered cars, or public transportation, to reduce the cumulative HI values even farther, and preferably to 1.0 or below, should be made. This is particularly important to protect the health of sensitive receptors, such as asthmatics, athletes, and children."

Response: OEHHA commends Dr. Landolph on his encouragement of Californians to use cleaner transportation options. However, it is not the mandate of OEHHA to begin a conversation about other fuel alternatives in this document. Laying out the airborne health risks associated with the various fuel scenarios will generate such discussion.

Comment 35: Appendix A: Toxicity Summaries: This section is excellent. The authors should make better use of it, by stating in the earlier sections, "summarized in the Appendix." This would also strengthen the earlier sections.

Response: This helpful comment was addressed in an earlier response. The statement "summarized in the Appendix" or similar language will be included in the main document where appropriate.

Comment 36: Editorial Comment: This reviewer really likes the comprehensive reviews of the toxicity of the various gasoline components in the Appendix. This reviewer recommends that the Appendix be placed at the front of the report, on page 2, Chemicals of Potential Concern. It helps a scientist understand how these COPC were identified, and to appreciate the toxic and carcinogenic risks that these substances can pose in the air.

Response: OEHHA appreciates Dr. Landolph's comment. However, for the sake of simplicity and ease of reading by a general audience, the toxicity summaries in Appendix A will be kept out in the main body of the text.

Comment 37: The country of Brazil has used ethanol as a fuel in automobiles for many years. Some attempts should be made to capture in this document the health effects if any in humans that use of ethanol as a fuel has caused. The Brazilian experience, if it has been documented, would be invaluable to capture for California in this document before any final decisions on gasoline reformulations are made.

Response: OEHHA thanks Dr. Landolph for highlighting the presence of these data in the literature. In fact, the CARB cites this Brazilian study in the companion document to this report. As part of their evaluation of the potential air quality impacts of substituting ethanol-blended gasoline for MTBE-blended gasoline, the Air Resources Board conducted a literature review of related programs implemented elsewhere. The studies of the impact of the use of ethanol fuel on air quality conducted in Denver, Albuquerque, and Brazil provided the most useful insights.

References

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B.1.2. Comments of Dr. Greenberg

Peer review comments on the document “Potential Health Risks of Ethanol in Gasoline” were received from Dr. Alvin Greenberg.

General Comments

Comment 1: Any risk assessment is usually written for a specific audience. For this document, it is unclear who the intended reader is and the level of scientific sophistication of that reader. As a result, I found some sections to be very remedial in nature while others were in need of additional explanation and/or clarification.

Response: Thank you for the comment. The body of the text is intended for a more general audience, as opposed to the appendix which is intended to provide a more detailed scientific description of chemical toxicity. OEHHA staff will work to make the language in body of the text more consistent for a general audience.

Comment 2: The document also lacks an Executive Summary with accompanying summary tables, a tool I have found very useful in risk communication. As I read the document, I found myself constructing such a table from the information presented in various sections. This table could prove very useful in describing in "pictorial" format (as opposed to narrative format) the overall conclusion of the document. Thus, I suggest the inclusion of a brief Executive Summary with a table which depicts each chemical assessed, the unit risk value and noncancer REL (or appropriate health-protective Level), the degree of 'uncertainty about that value in relative terms (high degree of uncertainty, medium, low and very low), and the net effect on ambient levels in three future scenarios (2% EtOH, 3.5% EtOH, and non-oxy fuel) as compared to the present scenario (1997 w/MTBE) and expressed as decreased levels, slightly decreased levels, slightly increased, increased, or little change (remains about the same). The final line of this table could represent the cumulative impacts showing a slight decrease in risks and hazards.

Response: OEHHA agrees that an executive summary would enhance the document. Thank you for your specific suggestions regarding a table. An executive summary is currently being compiled that will include the analyses of OEHHA, the California Air Resources Board (CARB) and the State Water Resources Control Board (SWRCB). OEHHA will incorporate an overall health assessment table in the executive summary that will present the total picture of the air impact of the ethanol fuel alternatives.

Comment 3: I was pleased to find a section on research needs in this document. I found the tables in §7 to be most informative. The toxicity profiles found in Appendix A are particularly well written and consistent.

Response: Thank you for the comment.

Specific Comments:

Comment 4: §2.0 Hazard Identification: Chemicals of Concern. It is unclear from reading this section and section 4.0 Exposure Assessment how (and even if) *"the impacts from evaporative emissions, exhaust emissions, as well as secondary transformation products"* were assessed in this document. I understand that CARB provided the modeling for these three emissions sources but §4 lacks even the mention of these sources. A brief qualitative description of the modeling results (perhaps describing the relative contribution of each to airborne levels) would be helpful.

Response: OEHHA thanks Dr. Greenberg for his comment. OEHHA has added the following language to section 4 to clarify the sources of emissions modeled by CARB:

"The CARB conducted modeling analyses of the air quality impacts of use of one fuel versus another. The South Coast airshed was selected as the basis of their modeling efforts since the South Coast is a severely impacted area of the State and one which has been extensively studied. The CARB analysis includes consideration of the changes in ambient air concentrations of specific toxic components of exhaust, evaporative components, and subsequent reaction products that would result from substituting ethanol-blended gasoline for gasoline blended with MTBE. The modeled air concentrations incorporate all sources of emissions within the South Coast airshed, including stationary source emissions, mobile source emissions and background emissions. However, stationary source and background emissions are not expected to change between the various fuel scenarios…"

We feel this adequately summarizes CARB's work. Readers are referred to CARB's document for further details.

Comment 5: It is also unclear how the *"chemicals determined to be the most important in terms of public health risk"* were selected. Was this an "intuitive" process or a more formal process using screening information or toxicity scores. I don't disagree with the chemicals selected; I feel that the document should be clear in the process and identify any chemical which was initially considered but dropped from the list for whatever reason. This becomes an important issue when reading §6.6 (see below).

Response: The selection relied on identification of fuel constituents and atmospheric products by CARB, and initial screening of available toxicological data. An informal process was used. The document will be amended as follows (Sec 2, para 2.):

"CARB provided the speciation profiles for the air emissions and modeling to determine concentrations of key chemicals from the four fuels. OEHHA focused this analysis on key chemicals associated with fuel use and potential changes in air concentration of those chemicals. Selection of chemicals of concern initially relied on the identification of representative fuel constituents and atmospheric contaminants by CARB, and a preliminary assessment of toxicological data available from secondary sources in the literature. The chemicals determined to be the most important in terms of public health risks, which were selected for more detailed evaluation for this report, are: ... "

Comment 6: §3.1.1 Carcinogenic Endpoints. The document states that the unit risk values are *"usually a 95% upper confidence limit of the slope of the dose-response curve"*. If values other than the 95% UCL were used, they should be identified. If none, than drop the term "usually" for this report.

Response: For clarification, the word 'usually' has been dropped. OEHHA intended to indicate that not all unit risk or cancer potency factors that have been developed by other U.S. agencies used the 95% upper confidence limit in representing the upper bound estimate of the risk. However, with regards to the chemicals presented in this document that have unit risk factors or cancer potency factors, all were calculated with a 95% upper confidence limit of the slope of the dose-response curve, representing an upper bound estimate of the risk.

Comment 7: §3 Table 3. Health Assessment Values. Ethanol is considered to be non-carcinogenic in this document. Yet, the human data show increased incidence of esophageal cancer in persons who drink and smoke heavily. This fact should be discussed and either dismissed as a "high-end dose" effect or included and assessed.

Response: Thank you for the suggestion. OEHHA is adding language to the ethanol summary in Appendix A to reflect this comment, as well as suggestions from other commenters.

Comment 8: § 4 Exposure Assessment. Table 4. The health effects tables in §3 list the relevant health levels in both ppb and the more appropriate $\mu g/m^3$. Table 4 lists predicted airborne concentrations in ppb only. Please add the values in $\mu g/m^3$.

Response: OEHHA thanks Dr. Greenberg for his suggestion that presenting the values in $\mu g/m^3$ would be more appropriate. However, OEHHA believes that for the purpose of consistency, the values in Table 4 should be presented in the same units as that provided by CARB. OEHHA also feels that units expressed as ppm or ppb is more suitable for a general audience. OEHHA does agree with Dr. Greenberg that $\mu g/m^3$ is a more appropriate scientific notation and is therefore used in the toxicity summaries, in addition to the ppm or ppb notation in the Appendix.

Comment 9: It is my understanding that the 1997 MTBE, the 2003 MTBE, and the 2003 Non-Oxy scenarios lack ethanol in the fuel supply. Why then is an airborne concentration for ethanol listed for these three scenarios? MTBE is listed as "zero" for the three "no MTBE" scenarios. Shouldn't it be the same for the three "no Ethanol" scenarios? Please explain.

Response: OEHHA thanks Dr. Greenberg for pointing out this apparent inconsistency. In CARB's report, other sources of emissions, including stationary sources, were included in the emission analysis. Therefore, CARB's predicted atmospheric concentrations for the South Coast Air Basin as presented in Table 4 represents all sources of atmospheric emissions, including both mobile and stationary sources. The ethanol emissions shown in the non-ethanol-containing fuel scenarios are primarily from stationary sources, such as consumer products. There are no detectable MTBE levels in the atmosphere under non-MTBE-containing fuel scenarios because stationary sources of MTBE are negligible. OEHHA will incorporate language in section 4 to clarify this issue.

Comment 10: § 6.1.6 Risk Characterization of MTBE. The document states that, *"In the 2003 scenario with the same MTBE-containing fuel, the predicted concentration of MTBE in air … is approximately 30% lower."* This statement is supported by the modeling results found in Table 4 yet there is no explanation for this finding in this section. This decrease is shown for all chemicals of concern and again, no explanation is provided. Perhaps the explanation resides in §6.3, page 32, where the reduction is explained as being due to "expected reductions in overall emissions". Or, perhaps the explanation resides in the CARB report on modeling but it would be useful to provide one here. The fact that this document estimates a decreased risk in the year 2003 under the "do nothing" scenario might be cause for scrutiny.

Response: OEHHA thanks Dr. Greenberg for pointing out the vagueness of this statement. OEHHA intended to simply state that the estimated cancer risk for MTBE is reduced by 30% under the 2003 scenario, as compared to the 1997 scenario. The paragraph in question shows that the 1997 cancer risk from MTBE in MTBE-containing fuel is 3.6 excess cancer cases per million people exposed. The MTBE risk based on 2003 MTBE-containing fuel is shown in parenthesis as 2.5 excess cancer cases (per million people exposed). 2.5 / 3.6 equals a 30% reduction in cancer risk. OEHHA will clarify this paragraph so the 30% reduction in cancer risk is more apparent.

Comment 11: §6.3 Cumulative Risk. The discussion on page 33 regarding a potential for increased exposure and risk in areas located near freeways or fuel depots warrants further assessment. While I realize that this is not an easy task, CARB is developing and using models to address a similar scenario as part of the risk characterization of diesel exhaust. Because the document readily admits that the risk assessment results were dependent upon *"population-weighted annual averages* a typical exposure along a freeway may very well be underestimated. And while it is true that this assessment is undoubtedly more precise in describing the relative differences between the different fuel scenarios, some of these differences now identified as small (or insignificant) may in fact be larger for a more heavily exposed populations. Further assessment is needed to answer that question.

Response: OEHHA agrees that further exposure assessment is needed to fully answer this question, and that this information would enhance the document. CARB is continuing to study various exposure scenarios. As more exposure data specifically addressing “hot spots” (e.g. exposures near freeway and fuel depots) become available from CARB, this report will be updated to reflect any possible new findings and conclusions.

Comment 12: §6.4 Cumulative Noncancer Impact of Multiple Chemical Exposures.

While it is clear that document seeks to assess the relative differences in risk/hazard posed by the various fuels and does not lay claim to present absolute risks/hazards of each formulation with great accuracy, the reader of this document will nevertheless focus some attention on the absolute risk/hazard of each fuel. This may be particularly true when it comes to the review and evaluation of the hazard index due to the release of respiratory irritants, including the criteria pollutants. Therefore, it may be useful to include background levels of the criteria pollutants in the South Coast Air Basin, an act consistent with the AB2588 risk assessment guidelines. This could be presented in a separate table distinct from Tables 9 and 10 and with a suitable narrative description.

Response: The exposure estimates for 1997 and 2003-MTBE fuel scenarios include background levels, as well as all stationary sources, of the criteria pollutants. OEHHA believes that presenting background levels of the criteria pollutants in the South Coast Air Basin would not provide a useful purpose to the intended audience and may detract from the focus of the report (i.e. differences in overall airborne levels of pollutants under various fuel alternatives).

Comment 13: §6.6 Uncertainties and Data Gaps. Other chemicals of concern are discussed in section 6.6.1. It appears that many of these chemicals, although emitted or formed as a result of atmospheric transformation, were not included in the risk assessment due to lack of suitable toxicological data. It is my view that all potential chemicals of interest should be listed in sections 2 and 6 along with all known and relevant toxicological data. If it is then determined that they would not influence the risk assessment significantly, they could be removed from consideration. For some, surrogates could be used and hence an "upper-bound" of risk and hazard could be calculated. A summary of this effort could be depicted in tabular form.

Response: OEHHA prefers to limit the chemicals listed in section 2 to those included in the quantitative analysis. OEHHA believes this will provide a more concise and straightforward presentation of those chemicals of concern. We were unable to find any useful data on the other chemicals of concern discussed in section 6.6.1 to estimate their potential public health risk. We prefer to leave those chemicals for discussions of uncertainty, data gaps, and research needs.

B.1.3. Comments of Dr. VandeVoort

Peer review comments on the document “Potential Health Risks of Ethanol in Gasoline” were received from Dr. VandeVoort (University of California at Davis).

General Comments

Comment 1: This report carefully details the source of data that was used to calculate risk assessment of potential health impacts for four options of future fuel composition.

The report also emphasizes that because most of the available data in the literature is based on exposure to one chemical at a time, and that gasoline is a complex mixture of chemicals and subsequently reacted or partially-reacted compounds, that the conclusions of the relative risks from gasoline exposure are probably inaccurate.

Response: OEHHA would like to clarify that we do not consider the relative risks from the gasoline fuel scenarios as ‘probably inaccurate’. Rather, one of the primary conclusions that OEHHA established from the risk analysis is that there is more confidence in the relative differences between fuels than the absolute magnitude of the risk faced by the exposed population under the various scenarios considered. Comparison of the aggregate cancer and noncancer risks among the five fuel scenarios gives a reasonably good indicator of the relative impact of each fuel on the cancer and noncancer risk from airborne pollutants in the South Coast Air Basin.

Comment 2: The appendix A summarizes the various toxicities of the chemicals found in gasoline or their transformed by-products. These summaries appear to be accurate, but of course these statements are only as complete as current research in the literature. I happen to feel strongly that the mouse and rat are not adequate models for the studies of human female reproductive and developmental effects of these compounds. Tables 11 and 12 carefully detail where the need for further research is the greatest and the report clearly states how this lack of information can affect the accuracy of the predicted potential health effects of the four fuel options.

Response: OEHHA thanks Dr. VandeVoort for her general comments on the “Potential Health Risks of Ethanol in Gasoline” document. OEHHA has been careful to identify uncertainties and data gaps in the information presently available, and is undertaking further risk assessment of fuel-related pollutants, particularly in response to new data as these become available.

Major Points of Concern:

Comment 3: Although ethanol is a common dietary component for many people, it is not without risk. As this report states, there is little information available on the risk of inhaled ethanol. Also, ethanol is both water and fat soluble and can be used to emulsify or solubilize many compounds that would otherwise be water insoluble. Therefore, care must be taken in evaluating the long-term effects because of the potential of ethanol to change the interaction of chemical mixtures.

Response: OEHHA agrees that research is needed to investigate the potential of ethanol to change the interaction of chemical mixtures. As stated in section 6.5, research is currently being conducted to determine whether any secondary effects of ethanol, such as enhancement of migration through soil, or acceleration or inhibition of biodegradation, would alter the concentrations of compounds of concern (such as benzene) in impacted wells. Preliminary screening model results by the Lawrence Livermore National Laboratory indicate that the cosolvency effect of ethanol is not likely to play a significant role in influencing groundwater transport of benzene. It is expected that the cosolvency effect of ethanol will be at least partially offset by the rapid biodegradation of ethanol in soil, particularly in comparison to MTBE.

Comment 4: One major omission from the report is any evidence that an attempt was made to get data from the midwest where gasohol (gasoline with ethanol) has been in use for decades.

Response: Dr. VanderVoort's concern is addressed in the California Air Resources Boards' (CARB) companion document to this report. The CARB presents the results of a literature review conducted to find studies that measure the direct impact of the use of ethanol in gasoline on air pollution. All these studies addressed the effects on atmospheric concentrations of compounds of concern: direct, systematic comparisons of health effects in comparable areas using fuels with and without ethanol do not appear to have been undertaken. Two of the three most useful studies identified by the CARB were conducted in Denver and Albuquerque.

Comment 5: One of the major problems with this report is that the atmospheric concentration estimates are not derived by the OEHHA, but rather are furnished by the CARB, and therefore there is no explanation of how the levels of chemicals are rationalized. An example of this is formaldehyde. Table 4 presents the CARB data on atmospheric concentrations of pollutant levels for various scenarios. Formaldehyde levels are the same regardless of scenario. Although MTBE is transformed into formaldehyde and ethanol is not, the levels of atmospheric formaldehyde are equivalent. This would seem to defy common sense. Another problem with the CARB data is which chemicals were included and which were not. Atmospheric levels of xylenes are not included, despite the fact that they are included in Appendix 1 and they are identified as having adverse health effects. Other chemicals not included are listed on page 29.

Response: The predicted change in air concentrations of pollutants due to the use of ethanol-based fuels is discussed in the CARB's companion document to this report. In brief, CARB used the best available information on the emission characteristics of fuels that will be available in 2003, along with a comprehensive analysis of current air quality concentrations and a state-of-the-science photochemical model to estimate air quality in the future under the various fuel scenarios. The final report delivered to the Environmental Policy Council will include the full reports from OEHHA, CARB and SWRCB, and also an Executive Summary which OEHHA believes will make the relationship between the different phases of the risk assessment process clear.

CARB estimates that for all three MTBE-free gasolines, there will only be a modest overall reduction of 2 to 4% for formaldehyde compared to the 2003 MTBE-fuel gasoline (as reflected in Table 4). The formaldehyde emissions resulting from the combustion of the non-oxygenated fuel components is partly the reason for this modest reduction in formaldehyde. However, the atmospheric concentration estimates presented in Table 4 also include total emissions (mobile, area, stationary, and natural sources) of formaldehyde in the South Coast Air Basin. Thus, the reductions in formaldehyde due to use of ethanol-based fuels are 'diluted' when all primary and secondary sources of formaldehyde are included. Because Dr. VandeVoort and other reviewers had somewhat similar concerns about Table 4 and section 4, OEHHA has incorporated language to section 4 to emphasize that our risk analysis is based on total emissions of chemicals of concern in the South Coast Air Basin.

OEHHA thanks Dr. VandeVoort, as well as other reviewers, for concern about OEHHA's decision-making process for chemicals of concern. OEHHA has incorporated language into section 2 to define how a chemical of concern was chosen. As stated in Section 6.2, xylenes were not regarded as a chemical of concern because xylenes are not a suspected human carcinogen and the annual average concentrations found or estimated were substantially below health protective concentration. Therefore, detailed atmospheric levels for xylenes are not presented in Table 4. Nonetheless, a risk characterization for xylenes and some other compounds not considered chemicals of concern are included in Section 6.2 because they are substantial fuel components.

Comment 6: The report states that the evaluation focuses on the key differences resulting from the use of four different fuels (page 43). It is difficult to determine what these key differences are. In fact, the report itself, in the summary/conclusions states "It appears that there are no substantial differences in the public heath impacts of the different non-MTBE fuel formulations considered in the scenarios for year 2003." At this point, someone must be asking why there is a proposal to add ethanol to gasoline when the outcome appears to be the same as that for the non-oxygenated fuel in 2003? Why consider taking an action which may increase risk to public health due to unknown effects of ethanol in chemical mixtures when there appears to be no gain?

Response: This comment is also addressed in CARB's part of the ethanol fuels report. Currently, federal law requires gasoline to include an oxygenate for regions in California designated as non-attainment areas. Under an MTBE ban, ethanol would be the only possible oxygenate. 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. In the event that the federal law for oxygenates is partially or fully rescinded, use of the non-oxygenate fuel may increase in California. However, there is arguably a greater lack of health effects data for some of the alkylates in the non-oxygenated fuel compared to ethanol. The need for more health effects data on the alkylates is noted in section 6.6, Uncertainties and Data Gaps, and section 6.7, Research Needs.

The summary statement quoted refers to the health impacts of air pollution changes expected due to the replacement of MTBE with ethanol as the oxygenate in gasoline. The replacement of MTBE by ethanol was initiated because of the expectation that it would result in substantial water quality improvements. A key requirement of the Executive Order was to determine that the substitution (proposed to improve water quality) would not result in worse public health risks from air pollution. OEHHA considers that the present report addresses this requirement, within the limitations of the data available.

Comment 7: The report mentions in several places that data is not available, such as data on the toxicity of alkylates (page 42). It also states that the report focuses on the key primary and secondary pollutants, but there is a possibility that a significant chemical has been omitted (page 43). Further confusion arises on page 38 where it is stated that Table 4 shows the health protective concentrations for drinking water for various gasoline components, however Table 4 is the atmospheric concentration data. I found this data in Table 3, however, TBA was not included (as stated in same paragraph). However, there appears to be no data available on what the actual levels of these compounds are in drinking water. Also in the same paragraph, TBA is identified as one of the breakdown products of MTBE. However, it is not listed as one of the “key” pollutants on any of the tables. TBA is known to have adverse effects in male rats (just one example, Acharya et al., Exp Toxicol Pathol 1997 Dec; 49(5):369-73). These statements do not leave the reader with a high degree of confidence in the list of chemicals which have been selected as key chemicals and emphasize the possibility of the omission of something important.

Response: The lack of toxicity data for some alkylates and the possibility that a significant chemical has been omitted are included in the uncertainties and data gaps listed in Section 6.6. As with any risk assessment, some uncertainties and assumptions exist when developing health protective values. This process becomes increasingly challenging when evaluating health risks involving complex mixtures (such as the fuel scenarios) for an entire air basin. OEHHA would be remiss if all the uncertainties, however minor, resulting from these fuel scenarios were not included in the risk assessment. The inclusion of uncertainties is meant to encourage scientific debate concerning the degree of confidence in a health protective value. Just as important, risk assessment is a dynamic process undergoing constant refinement as more toxicity and exposure data is generated. OEHHA and CARB have ongoing research programs to address data gaps, and to evaluate new data as they become available. Laying out the uncertainties and data gaps in a risk assessment is meant to encourage research to increase the degree of confidence in a health protective value and minimize the uncertainties and data gaps.

OEHHA thanks Dr. VandeVoort and other reviewers for alerting OEHHA to the incorrect Table reference in the draft version of Section 6.5. The correct table reference (Table 3) will be inserted in the final version. Tertiary butyl alcohol (TBA) is not listed in Table 4 because the CARB could not detect measurable air levels of TBA in the South Coast Air Basin. OEHHA will also remove the erroneous sentence that indicates health protective values for formaldehyde and TBA are found in Table 3. Regarding the lack of actual levels of key compounds in drinking water, the State Water Resources Control Board did not supply OEHHA with chemical exposure data that would allow quantitative risk estimates for drinking water.

Comment 8: Another unknown factor is what compound will be used to denature the ethanol. Denaturation of the ethanol is apparently required by law. Although gasoline would seem to be an adequate denaturant, perhaps the ethanol must be denatured at the time of manufacture, especially if it is to be transported prior to blending with gasoline. The report states on page 45 that naphtha or another gasoline-like compound may be used. Again, the additions of such compounds increases the complexity of the chemical mixture with unknown effects. Furthermore, the potential for increased public health risk due to manufacturing and transporting ethanol that could be denatured with a toxic compound does not seem to have been considered.

Response: OEHHA agrees that the type of denaturant that will be used does result in an uncertainty for the exposure assessment. However, as stated in Section 6.6, Uncertainties and Data Gaps, the denaturant is likely to be a gasoline-like material with a similar chemical profile to the hydrocarbon component of the blended fuel. It is therefore unlikely to have a substantial effect on the health impacts of the combined fuel. Its presence as a fraction of a percent in ethanol is unlikely to increase public health risk due to manufacturing and transporting of ethanol.

Comment 9: Finally, the most serious concern is that the data to evaluate the movement of the various gasoline options through the soil and into groundwater are not available. Apparently, the SWRCB has contracted with Lawrence Livermore Laboratories to model a variety of scenarios related to the release of these various gasolines into soil and water.

Response: SWRCB has contracted with Lawrence Livermore Laboratories to more clearly address these water contamination issues. As stated in one of the preceding responses, preliminary screening model results indicate that the cosolvency effect of ethanol is not likely to play a significant role in influencing groundwater transport of benzene or other gasoline components. Also, it should be emphasized that qualitatively, removal of MTBE, which is already a problem with groundwater users, would be an unqualified benefit. Direct effects of ethanol would appear to be minimal even in cases of severe contamination, although the potentially adverse consequences of contamination by the hydrocarbon fraction of the gasoline would remain.

Comment 10: The lack of data in the area of drinking water contamination makes it virtually impossible to review the health risk of ethanol in gasoline. The report acknowledges (page 40) that research has been undertaken to determine if there is a risk of a secondary effect of ethanol, however the report is not specific at this point as to who is doing this research. Is it the same research mentioned above regarding models at Lawrence Livermore Labs? If so, how can they model the effect of a mixture of chemicals when they do not know how those chemicals affect one another? Furthermore, the report appears to suggest that because ethanol is rapidly biodegradable and that it is ingested routinely as a part of the diet that the potential for health effects is low. While this conclusion is likely true, this state will be using millions of gallons of this gasoline each year and because of the potentially severe consequences if adverse effects are not recognized, I feel that ethanol in gasoline should not be approved until the commissioned studies are complete. It seems that MTBE was given approval before studies were performed to determine health risks of the chemical at the level of MTBE that was approved for use. We are now trying to compensate for the results of that decision.

Response: The current OEHHA report presents only a limited evaluation of potential water impacts. Any risk assessment activity is limited by the extent of currently available data, and the conclusions must identify areas of uncertainty as well as areas where predictions can be made. As stated in an earlier response, these impacts (including determination of any risks of a secondary effect of ethanol) are the subject of research currently being conducted by Lawrence Livermore National Laboratory for the State Water Resources Control Board. OEHHA agrees that these issues are complex and difficult to model. When the results are available, OEHHA will be examining them to determine whether there are any noteworthy public health consequences.

OEHHA’s role is to assess the health impact of the alternative fuel formulations, not to make recommendations. Our report, along with the reports of CARB and SWRCB will be presented to the Governor's Environmental Policy Council for consideration. The reviewer's comments regarding the potential use of ethanol in gasoline will be part of the OEHHA report and will also be considered by the Environmental Policy Council.

Comment 11: Overall conclusion: Whenever complex chemical mixtures must be evaluated, there will be problems in data interpretation. However, in this report there are large sections of data that have not been obtained, namely the data on the health effects of soil and groundwater contamination. It is impossible to reasonably assess the potential health risks of ethanol in gasoline if only the atmospheric data is available.

Response: OEHHA thanks Dr. VandeVoort for her comments and agrees that the potential water contamination issues will require further research. As with any risk assessment activity, in order for any evaluation to be undertaken in response to the Governor’s Executive Order, it was necessary to do what could be done with the data available. OEHHA feels that both the areas of knowledge and the areas of uncertainty have been fairly presented, thus providing a basis for the Environmental Policy Council’s deliberations. As stated above, OEHHA looks forward to obtaining more data, and will provide updated risk assessments as these data are received.

B.2. Public Comments.

The following responses address the comments from the public on the draft Office of Environmental Health Hazard Assessment (OEHHA) document, Volume 5, "Potential Health Risks of Ethanol in Gasoline", which is part of the report to the California Environmental Policy Council titled, "Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate". The following organizations and individuals have submitted comments:

Oxygenated Fuels Association	- comments dated November 30, 1999
Methanex Corporation	- comments dated November 26, 1999
Professor Richard Wilson, Harvard University, on behalf of American Methanol Institute	- comments dated November 30, 1999
Western States Petroleum Association (WSPA)	- comments dated November 30, 1999

The following responses address their comments.

B.2.1. Comments from the Oxygenated Fuels Association, Inc.

Comments on the document “Potential Health Risks of Ethanol in Gasoline” were received from John Kneiss on behalf of the Oxygenated Fuels Association, Inc. (OFA) on November 30, 1999.

Comment 1: In general, OFA believes that the OEHHA assessment of ethanol in gasoline is incomplete because it fails to fully examine the available data on the health effects of ethanol. For example, OEHHA's reliance on secondary reviews of the ethanol database, rather than conducting evaluations of primary scientific literature on ethanol health effects studies, results in understatement of the potential risks associated with increased exposure from expanded use of ethanol in gasoline. As an example, OEHHA has not incorporated into the assessment research showing that exposure to ethanol increases the hematotoxicity of inhaled benzene (Baarson, Snyder, Green, et al. 1982. Toxicol. Appl, Pharmcol. 64(3): 393-404). Such an important potential interaction should be fully considered in the OEHHA assessment, in light of the anticipated increased use of ethanol blending to gasoline in the state.

Response: Due to the short timeframe for this report, OEHHA relied primarily on existing risk assessments for ethanol. OEHHA does not consider that any important interactions have been ignored, taking into account likely concentrations and routes of exposure. However, this is an area of continuing research and OEHHA will continue to be alert for such possible effects.

Comment 2: In several places (first seen on the last line of page 4, and later in Table 1 and Table 7) OEHHA's draft describes the "probability of extra cancer cases occurring in an exposed population..." [emphasis added]. This statement is incorrect. The process used by OEHHA not only estimates the dose-response curves but selects the upper-95% confidence level (95%-UCL) rather than the most likely estimate of risk. The correct interpretation of the 95%-UCL is that it is a limit below which the true risk is likely to be present 95% of the time; and the true risk may be zero. As an estimate, neither the 95%-UCL nor the most-likely-estimate of risk indicate that an increase will occur, only that the chance of a compound-related tumor is increased. OFA recommends changing the language in the report to clarify the conclusions.

Response: OEHHA has been careful to characterize measures such as cancer risk estimates appropriately, following established standard risk assessment methodology. The draft document explains the uncertainties and limitations of these estimates.

Comment 3: The entries under "ethanol" in Table 1 indicate no evidence of carcinogenicity by inhalation. While that statement may be technically accurate, it omits consideration of a substantial body of pertinent information, and runs contrary to some principles of data interpretation. First scientific information indicates that ethanol is known to be absorbed from both the lungs and the gastro-intestinal tract. Furthermore, the organs on which ethanol produces its major toxicity (liver and nervous system) are distal from the portals of entry into the body. Based on the kinetics of ethanol, similar target tissue concentrations are likely to be present for the same doses of ethanol, regardless of route. Thus, toxicity (qualitative and quantitative) observed by ingestion of ethanol should also be similar by inhalation, provided that there is dose equivalency. As noted in the Appendix to the OEHHA draft report (pp 12ff.), human evidence indicates that consumption of large amounts of alcoholic beverages in which ethanol is the major constituent produced cancer in humans - a fact that led URC, and more recently the NTP, to find that alcoholic beverage(s) is a known human carcinogen. Thus, ethanol should be considered a possible human carcinogen by inhalation, and a unit risk should be estimated by inhalation, relying on toxicokinetic information.

Response: Data on the carcinogenicity of ethanol was reviewed in depth under Proposition 65, the State’s Safe Drinking Water and Toxics Enforcement Act. Under Proposition 65, the Science Advisory Panel (predecessor of the current Carcinogen Identification Committee) carefully reviewed a large amount of evidence on the carcinogenic effects of ethanol in humans and animals. Their conclusion was that ethanol is a human carcinogen under specific circumstances, namely at high doses and only by the oral route. Therefore, the panel listed “alcoholic beverages, when associated with alcohol abuse” as carcinogenic under Proposition 65. OEHHA followed this assessment in concluding that levels of ethanol predicted to occur in the air or water as a result of its use in gasoline were unlikely to result in a cancer risk to the exposed population.

In comments submitted by Dr. Richard Wilson of Harvard University (letter dated November 30, 1999), Dr. Wilson presents a carcinogenic potency (or unit risk factor) for ethanol that he derived from the rat studies of Holberg and Ekstrom (1995). The potency he presents, 2.0×10^{-4} (mg/kg-day)$^{-1}$, is generally consistent with similar evaluations conducted for comparative purposes but not used in regulatory assessments. The following conclusions may be drawn from this potency. First, it is one order of magnitude lower than the potency of 1.8×10^{-3} $(\text{mg/kg-day})^{-1}$ calculated by OEHHA for MTBE. The most recent atmospheric concentration estimates provided by CARB indicate that the “best baseline” prediction of population-weighted annual average exposure in the South Coast airshed for 2003 is 8.8 ppb ethanol (in the exposure scenario with ethanol-based fuel containing 3.5% oxygen), and 5.1 ppb ethanol for the continued use of MTBE fuel in 2003. In other words, according to CARB’s estimates, the replacement of MTBE by ethanol will result in an increase of 3.7 ppb (6.96 $\mu g/m^3$) in the average exposure to ethanol. Using Dr. Wilson’s potency to calculate risk, along with the usual assumptions of 70 kg body weight and 20 m^3 inhaled air per day, a lifetime cancer risk of 4×10^{-7} is derived. This risk estimate is below the 10^{-6} risk level usually regarded as *de minimis*. The total ethanol concentrations in air predicted by CARB, which include some non-fuel related ethanol contributions such as those from stationary sources are also associated with risks less than 10^{-6}. In other words, even if one accepts that ethanol should be regarded as a human carcinogen by the inhalation route, with a linear low-dose response, the risks predicted on this basis from ethanol are negligible. If the *de minimis* criterion is not used to completely discount cancer risks from ethanol, the predicted risk from expected concentrations of MTBE is about fivefold greater than for ethanol. Although MTBE is a weak carcinogen compared to some other fuel-related pollutants such as benzene or butadiene, its predicted contribution to the overall cancer risk is not negligible.

Comment 4: The entries under "MTBE" in Tables 1 and 7 (and also pp 22 and 24, and in the Appendix, pp A-24 ff) indicate that MTBE is treated as a "possible human carcinogen." OFA objects, to this designation, and to the application of the methodology on which OEHHA's position is predicated, since it fails to take full and objective account of the scientific evidence. On numerous other occasions, OFA has provided ample data and justification to support the conclusion that the cancer data are either not applicable to humans based on known modes of action or the result of flawed experimentation or are indeterminate by virtue of study design limitations. Expert groups around the world (including IARC, NTP, Prop 65 CIC have concluded that the evidence is inadequate to characterize MTBE as to its cancer potential for humans. OFA recommends that MTBE be treated not as a carcinogen but should be evaluated for non-carcinogenic chronic toxicity endpoints.

Response: The scientific evidence regarding MTBE toxicity is extensively discussed in OEHHA’s Public Health Goal (PHG) risk assessment that was prepared under the California Safe Drinking Water Act, which is referenced in the draft ethanol report. The MTBE risk assessment and the conclusions as to its carcinogenicity went through an open public and scientific peer review process, and have been endorsed by the State’s Scientific Review Panel for the purposes of the Toxic Air Contaminant program. The conclusions are also in agreement with the 1998 UC Report (Health and Environmental Assessment of MTBE: Report to the Governor and Legislature of the State of California as Sponsored by SB 521). The Proposition 65 Carcinogen Identification Committee (CIC) was divided on the issue of whether MTBE had been clearly shown to be a carcinogen. However, the CIC declined to add MTBE to the Proposition 65 list of chemicals known to the state to cause cancer.

Comment 5: OEHHA's draft report (Table 4) provides estimates of air concentration ranges for the compounds selected for this comparison. It is our understanding that the figures for the 1997 baseline scenario (population-weighted annual average) are also modeled despite having empirical data which are more realistic and more reliable than those modeled. We note that, assuming that the correctness of relative concentrations, ethanol increases appreciably in the atmosphere - a situation that was not taken into account in estimating the risks of ethanol in gasoline.

Response: This comment pertains to the work by CARB, which is discussed in detail in their report. However, it is important to note here that the 1997 measured data was used by CARB to calibrate the model for that year.

Comment 6: Table 10 of the draft report fails to include chronic hazard quotients for MTBE for pulmonary irritation. OFA recommends that this be included to complete the comparison. We believe that it will demonstrate that the concentrations of MTBE presently in breathing zone air are unlikely to cause respiratory irritation.

Response: The chronic hazard quotient is based on the most sensitive toxicological endpoints. As described in appendix A of the report, respiratory irritation is known to be associated with acute exposures to MTBE; however, based on the very limited available data on chronic exposures, pulmonary irritation does not appear to be a critical endpoint. The most important constraint on acceptable long-term exposures to MTBE derives from the potential for carcinogenicity.

Comment 7: In Section 6.5 (pp 38), ethanol should be added as a compound of concern. Under the proposed administrative action, ethanol would be present in very large amounts in California, and exposures to ethanol by the general population through air and water over and above that found in food and consumed as alcoholic beverages could be significantly increased.

Response: After careful consideration of the available scientific information, it appears that ethanol is only toxic at very high doses, and under specific circumstances, such as by the oral route. Consideration of the likely fuel-related exposures via contamination of air or drinking water suggest that these would make an insignificant contribution to the general population exposure to ethanol. However, in Table 11 of the report (“Research Needs for More Complete Understanding of the Potential Health Effects of Ethanol in Gasoline”), OEHHA does include ethanol (at low concentrations) in the list of compounds for which basic toxicology information is needed.

Comment 8: The OEHHA draft (pp 39) incorrectly states that health protective goals have been set for ethanol. We are unaware of any such goals being set for ethanol, despite the presence of "gasohol" over more than two decades of use. At this time, we understand that water utilities have no cost-effective way to monitor the presence of ethanol in ground or surface water.

Response: The report states that there is no regulatory value for ethanol for either air or water (page 42 and appendix A). It is for this reason that OEHHA developed draft health protective concentrations (HPCs) for the purposes of this report. Both measurement and theoretical studies of ethanol in ground and surface water are presently ongoing, and OEHHA is following the results of these studies with interest.

Comment 9: OEHHA incorrectly concludes that the presence of MTBE must be called a "problem." We believe that a balanced view should point out that a very large fraction of MTBE detections are below levels that would present a health risk or that would produce detectable tastes or odors. OFA recommends that OEHHA places the detections of MTBE in groundwater into proper perspective. Examination of California's Department of Health Services monitoring data for drinking water sources (ground water supplies) shows a dramatic decrease in the rate of detections for MTBE, and that only a few isolated instances found levels that exceeded state health protective levels.

Response: It is clear from the Executive Order (D-5-99) that the Governor regards MTBE contamination of the environment as a problem. OEHHA refers the commenter to the California Department of Health Services and the State Water Resources Control Board for data on MTBE monitoring and their evaluation of the impact on water resources.

Comment 10: OEHHA's treatment of the uncertainties in its comparative evaluation was certainly an extensive list. However, it lacked a critical ingredient: namely the impact on the estimates made for each compound selected. Since the uncertainties are likely to vary considerably from one data type (toxicity, exposure) to another among the compounds, the degree of confidence in each conclusion may prove considerable and not be captured by the two point estimates (low and high) given in OEHHA's draft report. OFA recommends that OEHHA estimate the impact of the designated uncertainties in their reported values, and describe the degree of overlap among the values.

Response: For the carcinogens of interest, OEHHA has included a discussion of the degree of confidence in each of the risk estimates based on the uncertainties inherent in the individual potency values. OEHHA agrees that this is important, especially for carcinogens since they drive the overall risk estimates. In addition, further discussion of uncertainties and confidence can be found in the original documentation cited for each of the health assessment values. Very often it is not possible to quantify uncertainty since uncertainty is defined as that which one does not know. Most “uncertainty analyses” in risk assessment actually evaluate variability in measured parameters. The uncertainties noted are due to a lack of data making quantification of uncertainty itself very uncertain.

Comment 11: OEHHA's characterization of ethanol's toxicity (Appendix, ppA.13ff) raises major considerations about its health consequences, and is essential to obtain a fair comparison of risks.

First, OEHHA dues not take into account uniquely susceptible individuals in deriving health protective concentrations, although mention is made that a few such groups exist (other factors such as prescription and over the counter drugs should have been considered yet were not). At a minimum, OEHHA should have included an additional uncertainty factor of 10 to take into account this consideration.

Second, OEHHA makes no mention of infants whose developing nervous systems may be particularly vulnerable to the toxic properties of ethanol. Under the proposed scenario of expanded use of ethanol, these infants might receive doses that pose risks of diminished learning capacity or altered liver function because of added doses of ethanol via the air they breathe and possible ingestion of impacted water resources.

Third, OEHHA makes no mention of a group of individuals whose exposure to ethanol poses a threat to themselves as well themselves, namely recovering alcoholics whose inhalation exposure to ethanol (e.g., during refueling a vehicle) would very likely increase above the background in foods. The exposure levels to ethanol which increase risks to such individuals is uncertain, and OEHHA has not adequately incorporated uncertainty (safety) factors to protect against such risk.

Fourth, OEHHA mentions fetal alcohol syndrome, only to dismiss its significance without data or justification being cited to support this conclusion.

In summary, the draft health protection concentration for ethanol cited in OEHHA's draft report is not substantiated by the scientific evidence and does not represent sound policy of health protection. OFA recommends major revisions to the ethanol discussion and assessment in the Appendix to reflect the full measure of scientific knowledge.

Response: (There appear to be some grammatical peculiarities in the original text of this comment, but OEHHA has endeavored to respond to the intended meaning.)

The draft health protective concentration (HPC) for ethanol includes an uncertainty factor of 10 to account for interindividual variability within the human population, including potentially sensitive human subpopulations (e.g., infants). This standard methodology was also used for MTBE to account for sensitive subpopulations.

Our review of the literature on ethanol uptake shows that very extreme exposures by inhalation are required to achieve absorption of sufficient ethanol to produce a significant impact relative to intake from foods and beverages, or to have any impact on central nervous system function. Such exposures would be extremely irritating and individuals would not stay in the environment long enough to absorb sufficient quantities of ethanol. It is unclear what end-point of concern the comment refers to in relation to recovering alcoholics, although as noted elsewhere such individuals were included among the study populations on which the HPC was based. Similarly, all the evidence concerning fetal alcohol syndrome indicates that this effect results from high maternal exposures such as those relating to the consumption of alcoholic beverages. This issue was discussed by the Proposition 65 Science Advisory Panel’s DART Subcommittee, whose conclusions are reflected in the exact wording of the listing of “ethanol in alcoholic beverages” as known to the State of California as causing developmental toxicity.

OEHHA notes the commenter’s dissatisfaction with the review of ethanol toxicity. In response to these and other comments received on the possible hazards of ethanol exposure, OEHHA has expanded the review of ethanol toxicity in the report to further explain the basis for the conclusions reached.

B.2.2. Comments from Methanex Corporation

Comments on the document “Public Health Risks of Ethanol in Gasoline” were received from Michael Macdonald, Vice President with Methanex Corporation, in a letter dated November 26, 1999.

Comment 1: Co-solvency and plume length issues detract from improved gasoline containment.

The view of the draft supporting LLNL report, that ethanol can increase gasoline plume lengths, is consistent with the Federal EPA's Blue Ribbon Panel conclusions and with submissions made by Malcolm Pirinie to the UC Davis study public hearings earlier this year. Likewise, the conclusion that ethanol acts as a co-solvent for BTEX in water has also been demonstrated by others (see Journal of Chemical and Engineering Data, Volume 40, No. 1, 1995, pages 315-320, attached).

We believe it is important to note and understand these effects, but we urge you to avoid the trap of making them the issue, when the real issue is gasoline release to the environment. We advocate a strong regulatory and enforcement approach to ensure a reliable, environmentally sustainable fuels infrastructure.

Response 1: Comment noted; State Water Resources Control Board is evaluating co-solvency and plume length.

Comment 2: Don't perpetuate mis-information.

Inclusion of MTBE cancer risk estimates on page 8 of your draft would give any layperson the impression that MTBE is a carcinogen, whereas the approximately 290 scientific papers we have reviewed do not support that assertion.

In appendix A to your draft you referenced just the IARC study, but we suggest that (by itself) the IARC determination that MTBE is "not classifiable" as a carcinogen could also easily be prone to misinterpretation. We request you also include reference to the NTP and Proposition 65 determinations to "not list" MTBE as a carcinogen.

We urge you to fairly represent the body of science available and to not perpetuate the mis-information that has so far clearly characterized the MTBE debate.

Response 2: These issues were extensively discussed in OEHHA's risk assessment of MTBE that was prepared under the California Safe Drinking Water Act (amended Health and Safety Code, Section 116365), which is referenced in the present document. The risk assessment of MTBE and the conclusions as to its carcinogenicity went through an open public and scientific peer review process. It has been endorsed by the State's Scientific Review Panel for the purposes of the Toxic Air Contaminants program. (The conclusions are also in agreement with the UC Report, also referenced in the present Ethanol Report). The Proposition 65 Carcinogen Identification Committee (CIC) was divided on the issue of whether MTBE had been clearly shown to be a carcinogen. However, the CIC declined to add MTBE to the Proposition 65 list of chemicals known to the state to cause cancer.

Comment 3: Aerial benzene may be understated

We have reviewed data from a European oil company showing that ethanol forms azeotropes in gasoline, significantly increasing the total volume and fraction of benzene and olefins in the lower boiling range cuts. Directionally, this would be expected to result in an increase in aerial benzene and olefin emissions. We note on page 31 of your draft report that aerial benzene is a key cancer concern, and separately, that VOC's in general, and olefins in particular, are ozone precursors. Our interpretation of pages 7-8 of CARB's draft supporting report is that aerial benzene concentrations were estimated from actual 1997 field data. As ethanol was not widely used in California at that time, we must assume that the field data did not include any impact from ethanol's azeotropic effects, meaning that ambient levels or emissions of benzene, olefin and total VOC for ethanol-blended gasoline would be understated in CARB's analysis.

Please provide us your understanding of ethanol's effects on aerial benzene, olefin and VOC emissions, and confirm that our understanding of CARB's analysis is correct.

Response 3: Governor Gray Davis's Executive Order D-5-99 requires the California Air Resources Board (CARB) and the State Water Resources Control Board (SWRCB) to conduct an environmental fate and transport analysis of ethanol in air, surface water, and ground water. It requires OEHHA to 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. Since this comment relates directly to CARB's work, we are forwarding your letter to CARB for their consideration. OEHHA is not in a position to speak for CARB. We respectfully defer to them for their expertise in this area.

Comment 4: Co-mingling effect

Ethanol exhibits "non ideal" behavior - one result of this is that a mixture of ethanol - blended gasoline of a given RVP and non-ethanol-blended gasoline of the same RVP will have a higher RVP than the individual gasolines. This is what is known as the "co-mingling" issue with ethanol-blended gasoline, and we could find no reference to it in

CARB's draft supporting report. The obvious expected effect of co-mingling would be further increased VOC emissions.

Please provide us with your understanding of the co-mingling effect and confirm that CARB did not consider it in their analysis.

Response 4: Again, this comment relates directly to CARB's work. We are therefore forwarding your letter to CARB for their consideration. OEHHA is not in a position to speak for CARB. We respectfully defer to them for their expertise in this area.

B.2.3. Comments of Prof. Richard Wilson

Comments on the document "Potential Health Risks of Ethanol in Gasoline" were received from Prof. Richard Wilson (Harvard University), on behalf of the American Methanol Institute on Nov 30th, 1999. The comments address the cancer risk assessment methodology used by OEHHA for ethanol (contrasted to that used for methyl tertiary-butyl ether) and for combustion products such as formaldehyde and butadiene.

Comment 1: In making a comparative risk assessment it is not adequate to take risk assessments for ethanol and MTBE, done at different epochs and by different people. It is necessary to go over the assumptions of the risk assessments and repeat the assessments on a comparable basis. It is here that I find that the OEHHA report is inadequate. In particular, OEHHA uses an old procedure for consideration of the carcinogenicity of ethanol and a more modern and more conservative procedure for estimating the carcinogenicity of MTBE.

In Table 1 page 8 the draft report compares Health Assessment values and Draft Health Protective Concentrations for several chemicals including MTBE and ethanol. In a report sent to OEHHA I commented upon the draft cancer potency assessment for MTBE. I agreed with the Office of Environmental and Health Hazard Analysis (OEHHA) that the potency is not large but came up with a potency (often called a unit risk factor) of $(0.0006\ \mathrm{mg/kg.day})^{-1}$ which is slightly smaller than that selected by OEHHA - the difference being primarily the degree of conservatism. When calculating the unit risk OEHHA assumes a linear dose response relationship at low doses, accepted the somewhat scientifically weak data for inhalation, and ignored (as is usual) the evidence that MTBE reduces the risk of some tumors and may well be a net anticarcinogen. This is what is called a "conservative" approach, which is designed not to understate the risk- I used similar assumptions, but noted that they may not be true.

But the draft report fails to give ethanol an equally pessimistic treatment. First and foremost ethanol is definitely an unequivocally a human carcinogen in the ordinary sense of the word. There is ample evidence that in a significant group of people (cigarette smokers) consumption of ethyl alcohol increases the occurrence of lip cancer. Indeed the synergism between smoking and alcohol is one of the few known examples of a multiplicative synergism that is expected on most multistage cancer models.

Response: The scope and timetable for OEHHA's report on ethanol in gasoline require the use, wherever possible, of existing State risk assessments (which have often taken substantial time to prepare, and have been subject to extensive peer review and public comment). Failing the availability of State assessments, other authoritative sources such as US EPA regulatory assessments were used when available. The current report relies on assessments of MTBE for the State's Drinking Water and Toxic Air Contaminants (TAC) programs. OEHHA previously responded to Prof. Wilson's comments on the public review draft of the assessment for the TAC program, and was pleased to note that his conclusions were broadly similar to OEHHA's, in spite of minor differences in emphasis and choice of default assumptions. The version of OEHHA's risk assessment of MTBE for the TAC program, which incorporated responses to comments from Dr. Wilson and others, was recently approved by the State's Scientific Review Panel on Toxic Air contaminants. OEHHA's assessment also relies on existing State assessments of ethanol carcinogenicity, in particular the listing as a carcinogen under Proposition 65 of "Alcoholic beverages, when associated with alcohol abuse". This listing reflects agreement with Dr. Wilson's identification of ethanol as a human carcinogen under specified circumstances, and the well-known synergism with smoking. Our reliance on existing risk assessments of ethanol also includes taking note of the listing under Proposition 65 of "Ethyl alcohol in alcoholic beverages" as a developmental toxicant.

Comment 2: Estimates of risk of ingestion of ethanol have been made for at least 30 years. The most important fact about the carcinogenicity of ethanol is that it is unequivocally a human carcinogen - in the simple sense that it has been shown (albeit at a high dose) to cause cancer in people. Ethanol has sometimes been called a co-carcinogen because the evidence that it increased cancers (in humans) was in situations where other chemicals (nicotine) are present. Also the first experiments that showed that alcohol caused an increase in cancer in laboratory animals was an increase in liver cancers (angiosarcoma) when another chemical was present. There is a similar discussion on page A13 of an experiment where N-nitrodiethylamine was present. This led to a model - unverified - that ethanol only causes cancer when these other chemicals present. This model was introduced before the present cancer assessment guidelines and enabled regulators to exclude ethanol from such mandates as Proposition 65. But a careful consideration of possible mechanisms shows that there is just as much reason to accept low dose linearity for ethanol as for most other chemicals.

Response: Ethanol was not "excluded from … (the) mandate (of) … Proposition 65". It was considered by the Science Advisory Panel (predecessor of the current Carcinogen Identification Committee), who carefully reviewed a large amount of evidence as to the carcinogenic and co-carcinogenic effects of ethanol in humans and animals. Their conclusion was that it was inappropriate to recommend a listing implying that ethanol was carcinogenic at low doses or by routes other than oral. The exact wording of the listing (in July 1988) was specified by the Panel, and reflects their assessment of the nature of the hazard. OEHHA followed this assessment in concluding that levels of ethanol predicted to occur in air or water as a result of its use in gasoline were unlikely to result in a cancer risk to the exposed population.

Comment 3: The third line of argument comes from the observation that there is a statistical correlation between carcinogenic potency in rodents and acute toxicity in rodents. Although there exist chemicals for which acute toxicity has been measured and a carcinogenic potency has not been measured or established, there exist no data to disprove the idea that such chemicals are carcinogenic with a potency given by the approximate correlation which is too weak to be measured. Ethanol is toxic - but weakly so. Indeed the recent tragic history of fraternity parties out of control shows that people have been killed by toxic doses of ethanol. (No one to my knowledge has ever been killed by a toxic dose of MTBE). The weak measured carcinogenicity in male rats is consistent with the Zeise correlation.

Response: OEHHA is familiar with this argument, and has debated the significance of the Zeise correlation in several contexts over the last decade. Various explanations have been proposed for the apparent correlation between carcinogenic potency and quantitative measures of acute toxicity. Some of these relate to proposed mechanisms of carcinogenesis, whereas others point to a purely practical or mathematical reason for the effect. It is not usually accepted as a justification for identifying a particular mechanism (such as increased cell turnover resulting from cytotoxicity) for a carcinogenic effect unless there is additional, independently derived evidence to support such a mechanism. However, in the specific case of ethanol extensive evidence on the nature, occurrence and dose response for hepatotoxicity and other responses after substantial oral doses is available. It may be that this toxicity is an important contributor to the observed carcinogenic and co-carcinogenic effects. Such a mechanistic role for cytotoxicity is usually advanced as a justification for adopting a threshold model for dose-response assessment, rather than the linear approach advocated by Dr. Wilson in his comments. The Science Advisory Panel considered such mechanistic explanations in their conclusions as to the appropriate form of listing for Proposition 65.

Comment 4: … at high doses ethanol given to female rats with no other specific carcinogen present increases the rate of cancers both of the pancreas and pituitary and that in male rats it increases cancer of the liver[4]. An analysis of these data shows that the increase is significant at the level of $P < 0.05$ by the Fisher exact test and by the MSTAGE maximum likelihood program for each of these. Nonetheless ethanol is a very weak carcinogen with a potency of 0.00004, 0.0005 and 0.00003 $(\text{mg/kg body weight})^{-1}$ for each of these outcomes respectively. I take a mean of 0.0002 $(\text{mg/kg body weight})^{-1}$.

Response: OEHHA thanks Dr. Wilson for sharing his analysis, which is generally consistent with similar evaluations conducted for comparative purposes but not used in regulatory risk assessments. The following conclusions may be drawn from Dr. Wilson's calculation. The potency he presents, 2.0×10^{-4} $(\text{mg/kg-day})^{-1}$, is one order of magnitude lower than the potency of 1.8×10^{-3} $(\text{mg/kg-day})^{-1}$ calculated by OEHHA for MTBE. Examination of the CARB tables for levels in the South Coast airshed for 2003 reveals a prediction of 8.8 ppb for the population-weighted annual ethanol exposure in the scenario with ethanol-based fuel containing 3.5% oxygen, as opposed to 5.1 ppb for the continued use of MTBE fuel in 2003. In other words, the replacement of MTBE by ethanol results in an increase of 3.7 ppb (6.96 $\mu g/m^3$) in the average exposure to ethanol. If Dr. Wilson's potency is used, with the usual assumptions of 70 kg body weight and 20 m^3 inhaled air per day, this implies an increased lifetime cancer risk of 4×10^{-7}, below the 10^{-6} level usually regarded as *de minimis.* The total levels of ethanol predicted by ARB are also associated with risks less than 10^{-6}. These total levels include some non-fuel related ethanol contributions such as those from stationary sources. In other words, even if Dr. Wilson's argument is accepted, that ethanol should be regarded as a human carcinogen by the inhalation route, with a linear low-dose response, the risks predicted on this basis from ethanol are negligible. If the *de minimis* criterion is not used to completely discount cancer risks from ethanol, the predicted risk from expected total air levels of MTBE is about fivefold greater than for ethanol. Although MTBE is a weak carcinogen compared to some other fuel-related pollutants such as benzene or butadiene, its predicted contribution to the overall cancer risk is not negligible.

At the time of preparation of this report, we lack quantitative predictions of possible levels of ethanol in drinking water as a result of fuel contamination of aquifers. However, the qualitative predictions available indicate that any such contamination to a significant degree is very unlikely to occur, due to the rapid biodegradation of ethanol in surface waters and aquifers. Unfortunately MTBE is not subject to such rapid biodegradation, and its potential to contaminate drinking water sources is a matter of record. This therefore leads us to confirm our earlier conclusions that substitution of ethanol for MTBE in fuel would not result in adverse public health consequences, either in regard to the predicted changes in air pollution or based on our current information on the potential for water contamination.

Comment 5: It can be considered a judgement call on whether there is a linear dose response for ethanol and/or MTBE. For MTBE, OEHHA follow the US EPA in claiming to use a linear dose response as a default. It is important to understand one of the main arguments used by the US EPA in 1975 when they assumed default linearity. This was the argument by Crump et al. This is based upon the well known fact that cancers caused by environmental agents are indistinguishable (at present and maybe forever) from cancers that occur naturally. Even though "defense mechanisms" may act to prevent the cancerous effect at low doses, the existence of the naturally occurring cancers (30% of the US population) shows that some natural process has already exceeded the threshold below which the defense mechanism is postulated to occur. Under these circumstances, Taylor's theorem suggests that there should be linearity of response with the environmental dose (which is a dose added above the natural one). Crawford and Wilson[8] showed that this simple argument should apply for other lesions and biological endpoints and is in fact very common.

However OEHHA fails to use the linear dose response default for ethanol, and no good scientific reason is adduced for not using the linear response - only the unsupported statement that it is a "co-carcinogen". Moreover there is no statement of what "co-carcinogen" means or might mean in practice.

Response: OEHHA thanks Dr. Wilson for his restatement of the general principles underlying the use of linear low-dose extrapolation as a default in carcinogen risk assessment. As he observes, these are accepted and used by US EPA and OEHHA, both generally and in the specific case of OEHHA’s MTBE risk assessments. However, OEHHA considers that these arguments in favor of the linear default are inapplicable to ethanol, and relies to a substantial degree on the arguments which were considered by the Science Advisory Panel in preparing their recommendation for listing under Proposition 65. Since it was not the purpose of our document on ethanol in gasoline to review or revisit current State risk assessment policy or conclusions, we did not attempt to restate these deliberations. However, it may be of interest to consider Dr. Wilson’s potency calculation as applied to non-fuel sources of ethanol exposure. Ethanol occurs commonly as an ingredient of foods and drinks (other than items usually classified as "alcoholic beverages"), at levels which may be as high as 0.1% (reference). Plausible exposures to ethanol from such sources (which vastly exceed the predictions for atmospheric ethanol pollution) result, using Dr. Wilson's potency, in predictions of substantial cancer incidences of ethanol-related tumors which should be readily observable in the many diet-oriented epidemiology studies of cancer incidence. To the contrary, there are no studies indicating associations between cancer and consumption of fruit juices or other sugar-containing dietary elements, or of the many manufactured foods which contain ethanol as a minor additive or accidental component. Furthermore, the liver and oral cancers to which Dr. Wilson refers as ethanol-related are in fact relatively rare findings in the general population, outside of identified risk groups such as those subject to certain viral infections, or known to ingest enormous quantities of ethanol. If there were a substantial additive contribution (following Crump, Taylor, Wilson and others) to the background cancer incidence from incidental consumption of lower levels of ethanol, one would expect a much more general incidence of ethanol-related cancers, a noticeable clustering of ethanol-related tumors in several easily identifiable dietary classifications, and the appearance of common tumors as well as or instead of rare tumors in the extreme-exposure sub-populations. Since none of these phenomena are observed, it is not unreasonable to characterize Dr. Wilson's prediction as being inconsistent with the available evidence.

Comment 6: The Direct Risk from Either Ethanol or MTBE is Small. (and further explanation)

Response: OEHHA agrees, and states in the document, that the cancer risk from atmospheric MTBE is substantially less than that from certain other pollutants associated with fuel use. It is not clear that this is true in all situations for contamination of water which may be used as a drinking water source, but we lack the quantitative information to evaluate this issue further. OEHHA also calculated and characterized the risk associated with ethanol exposures predicted by the CARB model. Using CARB figures (slightly revised following review) and OEHHA's unit risk for MTBE, the risk from ethanol (using Dr. Wilson's unit risk factor) was found to be approximately one fifth of that predicted from MTBE. Furthermore, the risk predicted was less than the *de minimis* level of 10^{-6}. Finally, OEHHA does not agree with Dr. Wilson's proposal to assume low dose linearity for predicting a cancer risk associated with low inhalation exposures to ethanol. Calculations using his unit risk factor for common dietary exposures to ethanol yield unrealistic predictions. In summary, OEHHA agrees that the direct risk from MTBE as an air pollutant is small, but considers that the direct risk from ethanol as an air pollutant is even lower, and probably negligible.

Comment 7: OEHHA should Discuss the Carcinogenicity of Ethanol. Since the existence or otherwise of a threshold, and the meaning of the work co-carcinogen" is a debatable matter on which reasonable people may differ, the above argument may not be generally accepted. BUT it is sufficiently reasonable that it is grossly improper for OEHHA to issue a document claiming, as it does, to make a comparison between use of MTBE and use of ethanol, without even a discussion of reasonable ranges of opinion.

Response: OEHHA remains very interested in the scientific debates which surround many of these issues, in particular those relating to ethanol, and thanks Dr. Wilson for his contribution to this debate.

Comment 8: The combustion products such as formaldehyde and butadiene. It has long been known that the combustion products from burning of fuels can be much more hazardous than the direct ingestion or inhalation of the fuels themselves. Indeed the purpose of adding MTBE is to reduce some of there combustion products - carbon monoxide and particulates. Moreover the only strong complaint about public health about MTBE is a suggested effect of combustion products. Discussion of combustion products is hard, and inherently uncertain. It is not therefore surprising that this is a weak part of the draft report. But it should be emphasized that the combustion products all of which listed -acetaldehyde, benzene, butadiene, formaldehyde and PAN - are both more toxic and more carcinogenic than either ethanol or MTBE. Although the argument in the earlier pages that the difference in risk from direct exposure to ethanol or MTBE should be insignificantly different from zero, that may not be said of the combustion products for which the risk is 100 times as big (see page 5c of the draft report). The only important differences listed are between the first column and the second and other columns - a calculated difference in risk as shown on page 5c of about 0.00007 (7 X 10^{-5}) per lifetime. Both the first two columns are for reformulated gasoline with MTBE, but the distinction is an assumed total reduction in emissions between 1997 and 2003. No difference is stated between the risk of combustion products of reformulated gasoline with MTBE than of gasoline with 3.5% ethanol.

The choice between MTBE and ethanol must be based upon other factors. Are the particulates and toxic combustion products reduced more by ethanol than by MTBE? Are there products not considered? It is also necessary when risks are this low to consider the whole life cycle in a Life Cycle Analysis. What is the risk in the chemical plant making MBTE? What is the risk of pesticides in growing the corn to produce the ethanol? Nonetheless the calculated cancer risk from the combustion products is only of the order of 0.0001 (10^{-4}) per lifetime which is the risk level below which most risk assessors would believe the risk is unimportant.

Response: OEHHA agrees with Dr. Wilson that the most important toxic impacts are those of combustion products and atmospheric reaction products derived from fuel use, rather than from effects of either MTBE or ethanol themselves. OEHHA relied on CARB’s model to determine what changes would occur if ethanol were substituted for MTBE by 2003. Although there are some changes in the relative contributions of different pollutants, the overall impact of that substitution on public health risk from air pollution is not large. This conclusion is based on those toxic chemicals, particulates, and criteria air pollutants for which we have both model atmospheric data and toxicological information. As noted by Dr. Wilson, and detailed in OEHHA’s analysis of uncertainties and research needs, there are still some aspects where we lack sufficient information to reach a conclusion. Some of these (including life cycle analyses) are currently the subject of ongoing research sponsored by various Cal/EPA Boards and Departments. OEHHA notes that the risk level regarded as unimportant for regulatory risk assessment purposes is usually 10^{-6}, not 10^{-4}. On this basis, the risk contribution from certain fuel-related air pollutants in the South Coast airshed is by no means trivial, and is currently the target of regulatory efforts by CARB to ameliorate these conditions.

B.2.4. Comments from WSPA

Comments on the document “Public Health Risks of Ethanol in Gasoline” were received from Gina Grey of WSPA. Comments are dated November 30, 1999.

Comment 1: The public health impact analysis is incomplete. WSPA believes that OEHHA, by using a standard, default health risk assessment approach focusing on modeled ambient air exposures to ethanol fuel emissions, has neglected to consider potential impacts associated with unexpected circumstances. The analysis needs in depth analysis and evaluation to look beyond the easily quantified, expected exposures. Several examples of potential, unevaluated problem areas are provided in our comments, but, obviously, others exist and should be considered.

Response: Lifecycle analysis and consequences of accidental releases of various types are the subject of research by Lawrence Livermore National Laboratory for the State Water Resources Control Board (SWRCB). At the time of preparation of this report, these analyses were incomplete; however, when the results are available OEHHA will be examining them to determine whether there are any noteworthy public health consequences.

Comment 2: OEHHA's analysis fails to uniformly apply current public health policies. OEHHA has defined MTBE as a human carcinogen, while ignoring the known potential for ethanol to cause cancer in humans. WSPA believes that neither of these chemicals should be considered to cause cancer in humans at low environmental levels. Nevertheless, OEHHA should not rely on a major shift in California's cancer policy paradigm when evaluating ethanol and should evaluate both chemicals, ethanol and MTBE, using the same criteria. Applying a less rigorous carcinogenicity analysis to ethanol results in an apple and orange comparison that skews the overall risk assessment results.

Response: In preparing this report OEHHA used, wherever possible, existing risk assessments for specific chemicals that have been developed under other California regulatory programs. These assessments have been subject to extensive peer review and public comment.

In the case of MTBE, OEHHA relied on risk assessments that were developed under California’s Safe Drinking Water Act (amended California Health and Safety Code, Section 116365) and the Toxic Air Contaminant Program (California Health and Safety Code 39660 et seq.). These risk assessments conclude that MTBE is a potential human carcinogen.

OEHHA has not ignored the known potential for ethanol to cause cancer in humans. This issue is discussed at greater length in the response to comments by Dr. Richard Wilson of Harvard University. OEHHA relied on the existing State assessments of ethanol carcinogenicity, in particular the listing as a carcinogen under Proposition 65, the

State's Safe Drinking Water and Toxics Enforcement Act. Ethanol was considered by the Science Advisory Panel (predecessor of the current Carcinogen Identification Committee), who carefully reviewed a large amount of evidence as to the carcinogenic effects of ethanol in humans and animals. Their conclusion was that ethanol is a human carcinogen under specified circumstances, namely at high doses and only by the oral route. Therefore, the panel listed "alcoholic beverages, when associated with alcohol abuse" as carcinogenic under Proposition 65. OEHHA followed this assessment in concluding that levels of ethanol predicted to occur in the air or water as a result of its use in gasoline were unlikely to result in a cancer risk to the exposed population.

In comments submitted by Dr. Richard Wilson of Harvard University (letter dated November 30, 1999), Dr. Wilson presents a carcinogenic potency (or unit risk factor) for ethanol that he derived from the rat studies of Holberg and Ekstrom (1995). The potency he presents, 2.0×10^{-4} $(mg/kg\text{-}day)^{-1}$, is generally consistent with similar evaluations conducted for comparative purposes but not used in regulatory assessments. The following conclusions may be drawn from this potency. First, it is one order of magnitude lower than the potency of 1.8×10^{-3} $(mg/kg\text{-}day)^{-1}$ calculated by OEHHA for MTBE. The most recent atmospheric concentration estimates provided by CARB indicate that the "best baseline" prediction of population-weighted annual average exposure in the South Coast airshed for 2003 is 8.8 ppb ethanol (in the exposure scenario with ethanol-based fuel containing 3.5% oxygen), and 5.1 ppb ethanol for the continued use of MTBE fuel in 2003. In other words, according to CARB's estimates, the replacement of MTBE by ethanol will result in an increase of 3.7 ppb (6.96 $\mu g/m^3$) in the average exposure to ethanol. Using Dr. Wilson's potency to calculate risk, along with the usual assumptions of 70 kg body weight and 20 m^3 inhaled air per day, a lifetime cancer risk of 4×10^{-7} is derived. This risk estimate is below the 10^{-6} risk level usually regarded as *de minimis*. The total ethanol concentrations in air predicted by CARB, which include some non-fuel related ethanol contributions such as those from stationary sources are also associated with risks less than 10^{-6}. In other words, even if one accepts that ethanol should be regarded as a human carcinogen by the inhalation route, with a linear low-dose response, the risks predicted on this basis from ethanol are negligible. If the *de minimis* criterion is not used to completely discount cancer risks from ethanol, the predicted risk from expected concentrations of MTBE is about fivefold greater than for ethanol. Although MTBE is a weak carcinogen compared to some other fuel-related pollutants such as benzene or butadiene, its predicted contribution to the overall cancer risk is not negligible.

Comment 3: OEHHA's analysis fails to quantify potential water impacts. The introduction of large amounts of ethanol into California's gasoline supply could have a number of direct and indirect impacts on water quality. OEHHA has not completed the analysis and a large number of questions must be answered. Several of the missing portions of the analysis have been highlighted by OEHHA as areas requiring additional data or study. WSPA concurs, but believes that the data should be collected and evaluated before a risk assessment is generated.

Response: The present analysis is based on available information, and therefore can only provide qualitative evaluation of potential water impacts. These impacts are the subject of research currently being conducted by Lawrence Livermore National Laboratory for the State Water Resources Control Board (SWRCB). At the time of preparation of this report these analyses were incomplete, but when the results are available OEHHA will be examining them to determine whether there are any noteworthy public health consequences.

Comment 4: OEHHA's analysis does not quantify uncertainty. The input data and assumptions used in OEHHAs analysis have a high uncertainty associated with them. Everything from estimates of concentrations of chemicals in the environment, to the toxicological endpoints used to characterize potential public health risks, has varying degrees of uncertainty. While some inputs may have low uncertainty, others are likely to have very high levels. The level of uncertainty could very well be a more important metric for evaluating the potential impacts of ethanol in gasoline than the absolute values themselves and OEHHA needs to provide some quantification of these uncertainties.

Response: The uncertainty in exposure estimates is discussed in greater detail in the accompanying report by CARB, and OEHHA cites the plausible range of values from their predicitions, and quotes their descriptive notes where appropriate. Source documents for toxicological standards from California or U.S. EPA describe uncertainty and variability issues in detail. OEHHA has been careful to characterize measures such as cancer estimates appropriately, following established practice in deriving 95% upper confidence limits. Where health protective levels were derived for this document, the size and nature of uncertainty factors used are described. As more information becomes available and measured emissions data are obtained, OEHHA will be continuing to review these and may reach additional conclusions as a result.

Comment 5: Resolution of research needs and outstanding issues. As part of its analysis, OEHHA has identified a number of data needs and issues requiring resolution. WSPA believes that many of these data needs or issues are of sufficient import that the analysis of the potential public health and environmental impacts of ethanol in gasoline can not be completed until this information is available.

Response: The present assessment is not intended to be a final assessment, but rather the best analysis possible with currently available data. As further information becomes available, OEHHA will be continuing to examine the health impacts of fuel-related toxics in air and water. Any additional information on the toxic effects or environmental occurrence of fuel-related pollutants which the commenter (or others) currently possess, or obtain in the future, will be welcomed as a contribution to this ongoing review.

Comment 6: In extensive written comments, WSPA requested the development of key information that has still not received the appropriate attention. For example, WSPA requested a clear description of the risk management process that will be used by the agencies and the EPC for the evaluation of ethanol as a replacement for MTBE. This information has still not been developed to the detriment of the analyses conducted by the individual agencies. There does not seem to be a clear picture of how the information developed will be utilized. Worse, the tone of the most recent workshop suggested that the completed analyses were a proforma exercise.

Response: The OEHHA report was produced at the direction of Cal/EPA responding to the Governor’s executive order. The report was produced using an independent and objective approach with no preconceptions or direction as to its conclusions. In regards to the request for a description of the risk management process that will be used by Cal/EPA and the EPC, that is beyond the scope of the present health effects assessment.

Comment 7: A complete conceptual life-cycle model of the manufacture, distribution and use of ethanol in the blending of fuels and the storage, distribution and use of those blended fuels. The OEHHA analysis presents a regulatory-style analysis of public health impacts that is limited to exposures of evaporative and tailpipe emissions in ambient air. Although the agency's workplan suggested it would also evaluate compounds present in drinking water, the draft document approaches drinking water in a limited, qualitative manner only. There is no analysis of any number of potential other sources of exposure that could change depending upon the specific use of an oxygenate. These include, for example, manufacturing facility emissions, blending emissions, and storage facility emissions. Without this type of analysis it will not be possible to form any supportable conclusions concerning potential public health impacts.

Response: According to CARB’s accompanying chapter regarding the exposure scenarios and data, the comment’s assertion that only tailpipe and evaporative emissions were considered is inaccurate. Fugitive emissions from fueling activities are included in the CARB analysis.

A full life-cycle analysis could not be done by the deadline. However, the report by the SWRCB evaluates a number of scenarios representing storage and distribution. OEHHA will be evaluating this type of information in the future.

Comment 8: The sources and degree of uncertainty as well as recommendations for resolving uncertainty need to be provided. The OEHHA analysis presents estimates of risk without quantification of potential uncertainty. The document explains that this is acceptable because the estimates of risk are relative and it is the relative difference between the fuels that is important. This is unacceptable from a risk management perspective. Not only is it likely that the uncertainty in the exposure estimates is high (and also the relative uncertainty between various fuel types), but also that the uncertainty in estimates of potential risk due to uncertainty in the health criteria is extremely high. The latter is, of course, purposefully biased in the risk assessment process in a health conservative manner so that the actual value may be substantially less, but not higher. Without an analysis of uncertainty there is no indication by which the validity of the results for comparison between scenarios can be ascertained.

Response: As noted above, the uncertainty in exposure estimates is discussed in greater detail in the accompanying report by CARB, and OEHHA cites the plausible range of values from their predicitions, and quotes their descriptive notes where appropriate. Source documents for toxicological standards from California or U.S. EPA describe uncertainty and variability issues in detail. OEHHA has been careful to characterize measures such as cancer estimates appropriately, following established practice in deriving 95% upper confidence limits. Where health protective levels were derived for this document, the size and nature of uncertainty factors used are described. As more information becomes available and measured emissions data are obtained, OEHHA will be continuing to review these and may reach additional conclusions as a result.

In addition, it is important to note that not all sources of uncertainty result in risk estimates higher than the actual risk. As noted in OEHHA’s report, many of the acknowledged uncertainties affect risk estimates to the same extent for the different fuel scenarios. It is for this reason that our confidence in relative predictions is greater than our confidence in the absolute predictions.

Comment 9: OEHHA should evaluate taste and odor effects on groundwater. OEHHA did not analyze potential taste and odor effects on groundwater due to the presence of ethanol breakdown products or the potential for ethanol to alter the effect of gasoline components on the taste and odor of water. This in turn is directly tied to water based criteria that could lead to unacceptable water quality. This information is critical for any risk management decision. The simple question of "'How much ethanol (or breakdown products) in drinking water would be considered unacceptable?" must be answered in order to evaluate the significance of environmental contamination.

Response: At present, OEHHA has received no indication from the SWRCB that contamination of drinking water by ethanol at any level detectable by chemical analysis, let alone taste and odor, is likely. However, if and when more detailed information is available on this point OEHHA will determine whether any further evaluation of toxicological or sensory (organoleptic) properties is needed.

Comment 10: The public health impact analysis is incomplete. OEHHA's analysis applies standard health risk assessment policy/methods to modeled ambient air concentrations of a select list of chemicals of concern. Yet, simple inspection of the modeled concentrations without the health risk assessment provides the same conclusions: there are no differences between the fuel types. This type of approach does not do justice to the potential ramifications, if an unforeseen problem develops.

The OEHHA analysis appears to assume that the key (if not sole) impacts from ethanol-based oxygenated fuels will occur in ambient air from normal use. Other potential problem areas do not appear to have been explored and are not quantified?

A complete analysis is needed. For example, could hot soak emissions plus tailpipe emissions at low speed from ethanol-based fuels lead to higher concentrations of irritants (or carbon monoxide) inside parking structures? Or, will the consumer refueling with ethanol-based fuel notice a different smell or a minor nasal irritation that would lead to perceptions of health concerns similar to what happened with MTBE in several states? It is common knowledge that there is the potential for toxic interactions with very low levels of ethanol for individuals taking the prescription drug disulfiram (Antabuse). Could these individuals be a sensitive population for ethanol exposure and, if they are, what restriction on levels of ethanol in drinking water would be required to provide adequate health protection? Numerous questions such as these should have been posed and answered in a quantitative manner within the assessment. The basis for eliminating a potential problem from consideration should be clearly stated. Without this type of analysis, the potential for a currently unrecognized significant public health problem (or perceived problem) is high.

Response: CARB has examined different scenarios with various vehicle types and use patterns, and is continuing to research these issues as part of their long-standing programs for study and regulation of mobile and stationary sources of air pollutants. OEHHA will be continuing to work with CARB to examine possible public health consequences of any such situations.

The ethanol irritation data examined in developing a draft health protective concentration (HPC) for the purposes of this report specifically included a group of subjects receiving disulfiram treatment for alcoholism. OEHHA risk assessment policy includes application of an uncertainty factor (default value of 10) for inter-individual variation in the human population, which is designed to allow for the possibility of sensitive sub-populations among those exposed to general environmental contaminants. Low levels of ethanol are common in many natural and manufactured food products without causing apparent problems to the general population, and these may involve considerably higher exposures to ethanol than are anticipated as a result of its incorporation in fuel.

Comment 11: OEHHA's analysis fails to uniformly apply current public health policies. Over the last twenty years, California EPA and its predecessor agencies have firmly established a carcinogen assessment policy. This policy has dictated in a highly inflexible manner that chemicals with data suggestive of a potential cancer risk be evaluated as if they do, in fact, represent a cancer risk. In quantitative analyses (i.e., health risk assessments), no allowance is made for the weight of evidence and there is no established mechanism for incorporating alternatives to the default linear extrapolation and use of the statistical upper-bound of cancer potency estimates. Exceptions, if any, to this are rare. This policy dictates that there is no dose (exposure) other than zero that is without risk.

The evaluation of MTBE exposures in the OEHHA analysis aggressively follows this policy; California leads the world in ascribing human carcinogenic risk to MTBE exposures. For example, the International Agency for Research in Cancer (IARC) recently described the carcinogenic potential for MTBE as "inadequate evidence in humans", "limited evidence" in experimental animals" and "not classifiable as to its carcinogenicity to humans" (IARC, September 30, 1999). Nevertheless, OEHHA, consistent with the California policy (although at odds with the failure to list under Proposition 65), evaluates MTBE at low levels in ambient air as if it is a human carcinogen.

Although we strongly believe that the available data does not support the regulatory conclusion that exposures to environmental levels of MTBE represents a cancer risk, the decision to so treat MTBE is consistent with the state's ultra-conservative approach. However, and although we agree with OEHHA's assessment of the lack of cancer risk associated with low environmental exposures to ethanol, its failure to incorporate the potential carcinogenicity of ethanol into the analysis by development of a cancer potency slope using the consistently applied methodology is an entirely inappropriate regulatory paradigm shift. Ethanol is a known human carcinogen; IARC identifies ethanol as a known human carcinogen and ethanol (in alcohol beverages) is listed under California's Proposition 65. Under these circumstances, OEHHA should either apply the same rigorous and ultra-conservative cancer risk assessment methodology it uses to evaluate MTBE, or provide a solid scientific rationale for not doing so. OEHHA's apparent reliance on the fact that ethanol is commonly found in the environment, that regulatory bodies do not seem to be concerned over low ethanol exposures and that the carcinogenic effects are seen only at high exposure levels consistent with the induction of other toxicity is not sufficient. Consider the recent development and application of a cancer potency slope for exposure to crystalline silica by OEHHA for a Safe Use Determination under Proposition 65. Crystalline silica is another agent that is ubiquitous in the environment and appears to only cause cancer at high exposure levels associated with silicosis. OEHHA has previously even noted that the carcinogenic effect of crystalline silica appears to operate under a threshold mechanism. Nevertheless, OEHHA applied the standard multi-stage extrapolation to generate a cancer potency slope for the Safe Use Determination. Why has it not done so in the case of ethanol?

Response: As stated in the response to comment 2, it was necessary for OEHHA to rely on existing risk assessments for specific chemicals that have been developed under other California regulatory programs. OEHHA has not ignored the known potential for ethanol to cause cancer in humans. OEHHA relied on existing State assessments of ethanol carcinogenicity, in particular the listing as a carcinogen under Proposition 65, the State’s Safe Drinking Water and Toxics Enforcement Act. Ethanol was considered by the Science Advisory Panel (predecessor of the current Carcinogen Identification Committee), who carefully reviewed a large amount of evidence as to the carcinogenic effects of ethanol in humans and animals. Their conclusion was that ethanol is a human carcinogen under specific circumstances, namely at high doses and only by the oral route. Therefore, the panel listed “alcoholic beverages, when associated with alcohol abuse” as carcinogenic under Proposition 65. OEHHA followed this assessment in concluding that levels of ethanol predicted to occur in the air or water as a result of its use in gasoline were unlikely to result in a cancer risk to the exposed population.

Comment 12: OEHHA's analysis fails to quantify potential water impacts. OEHHA's justification for not analyzing water impacts is meretricious in that it presumes that because the Regional Boards will eliminate the use of groundwater impacted by chemicals, then there are no chronic exposures and no potential impacts. The same would, of course, be true of MTBE.

OEHHA further discounts groundwater impacts from ethanol because it degrades. However, as indicated in Volume 4, Chapter 3 of the report entitled "The Effect of Ethanol on BTEX Biodegradation and Natural Attenuation", ethanol degrades to volatile fatty acids (e.g., acetic acid). These acids would likely have secondary effects, e.g., changes in taste and odor. Even under OEHHA's presumption that water districts would close wells to eliminate exposures, there is still the larger issue of "What levels of ethanol and/or degradation products will require well closure?" Without health and/or organoleptic criteria by which modeled concentrations can be evaluated, it will not be possible to determine potential impacts to groundwater. To assert that there will be none, absent an evaluation, is not supportable.

Nor does OEHHA consider mutual solvency and how it might impact groundwater. For example, the presence of ethanol would increase solubility of chlorinated solvents already present in soil and groundwater. The presence of ethanol also appears to alter biodegradation dynamics for BTEX by decreasing degradation (See Volume 4, Chapter 2 - A Critical Review: The Effect of Ethanol in Gasoline on the Fate and Transport of BTEX in the Subsurface). This in turn could impact the influence of other chemicals, as well as petroleum hydrocarbons, at currently impacted sites (i.e., increase plume size). It should be noted that the absence of this type of evaluation in the report is an example of what is lacking, as discussed in the first comment.

Response: As noted above (see response to comment 3), our report presents only a preliminary, qualitative evaluation of potential water impacts. The potential water impact issues raised here by the commenter are the subject of research currently being conducted by Lawrence Livermore National Laboratory for the State Water Resources Control Board (SWRCB). At the time of preparation of this report these analyses were incomplete, but when the results are available OEHHA will be examining them to determine whether there are any public health consequences.

Comment 13: OEHHA's analysis does not quantify uncertainty. While OEHHA discusses sources of uncertainty (e.g., extrapolation from animal data to humans), the analysis does not attempt to quantify uncertainty. Yet, it is critical for the risk manager to understand both the sources of uncertainty as well as the potential magnitude and direction of that uncertainty. By relying upon standard, default health risk assessment techniques, OEHHA has excluded valuable risk management information. For example, OEHHA uses the statistical upper-bound in describing the potential carcinogenicity of chemical emissions (except for ethanol). This is standard policy. Missing, however, is information on the most likely estimate of cancer risk both from a statistical standpoint as well as a "weight of evidence" perspective. While OEHHA does mention that actual risks could be substantially lower, they provide no basis for evaluating, for example, whether equivalent theoretical risks due to exposure to benzene and butadiene represent an equivalent potential for actual risks. Other uncertainties arise from the emission estimates, the estimates of ambient air concentrations, the worst-case exposure scenarios rather than likely exposure scenarios, and the exclusion of variations in exposures through OEHHA's use of standardized population-weighted exposures. The need to include quantification of uncertainty in the analysis is also important because of the relative nature of the analysis performed by OEHHA. Currently, the health risk assessment shows no difference between the various fuel scenarios. However, if one scenario has greater uncertainty than other scenarios, then that may be the information most critical to the risk management decision.

For some time, health risk assessment methodology has been utilizing stochastic techniques for quantifying risk in which the uncertainty or variability of assumptions are explicitly incorporated into the analysis. These techniques work equally well for toxicity endpoints as well as exposure assumptions, and California EPA has expended extensive effort to develop models utilizing stochastic techniques and has promoted their use. OEHHA should use these existing techniques to quantify uncertainties and incorporate considerably more information into the analysis.

Response: As noted in a previous response, additional details on cancer risk assessments are available in the existing chemical-specific risk assessment documents to which OEHHA referred in developing the assessment for ethanol in fuel. CARB’s accompanying report deals with selection of scenarios (which in the case of the cancer predictions are estimated annual averages, not worst-case scenarios), and model uncertainties in the prediction of exposures. OEHHA’s cancer risk assessment policy includes consideration of uncertainties, and the use of a weight of evidence approach. The properties of various statistical measures available for expressing cancer risk estimates (including the unsuitability of the “maximum likelihood estimate” due to its statistical instability in the standard linearized multistage model) have also been the subject of very extensive discussion in the scientific literature. These considerations are incorporated in U.S. EPA and California risk assessment guidelines. OEHHA refers the commenter to these sources for clarification.

OEHHA is in the process of developing guidance for utilizing stochastic techniques in exposure assessment, and may consider using this methodology more extensively in future assessments of fuel-related health risks. However, the stochastic techniques for quantifying exposure are not, as implied by the comment, readily applicable to “toxicity endpoints”. The stochastic analysis requires extensive data on specific data on specific parameters in a model, and as developed by Cal/EPA, only defines variablity. The uncertainties in “toxicity endpoints” and health criteria are far less amenable to a credible stochastic assessment.

Comment 14: Resolution of research needs and outstanding issues. OEHHA identified a number of data needs, which have been separated into areas of research and issues. Many of these components have previously been identified by WSPA. While WSPA does not believe all of the identified areas are of equal merit or even useful for differentiating between potential public health impacts of fuels (e.g., toxicology of alkylates), several are critical. For example, OEHHA identified:

- Development of health assessment values for ethanol,
- Identification of breakdown products in water,
- Impacts of transportation accidents,

- Impacts of watercraft,
- Information on localized "hot spots", and
- Life-cycle analysis to determine overall exposure from production, use and disposal of motor fuels.

WSPA concurs that these are key unknowns. However, we want to emphasize the agency should provide recommendations such as: what data/studies are needed, how long they would likely take, and what expertise is needed to accomplish their acquisition. Until the information is available to either answer these key questions or incorporate the results into the analysis, any conclusion regarding the potential public health impacts of ethanol in gasoline relative to the other potential fuel scenarios will not be accurate or complete.

Response: OEHHA believes its analysis is accurate, based on the currently available data. As more data become available, the assessment of public health impacts of fuel components will be extended to reflect any new findings and conclusions. OEHHA would be pleased to discuss the need for additional studies and their possible scope with any interested parties. However, such discussions are outside the scope and timescale determined by the Governor’s Executive Order for this document.

ADDENDUM

Estimating atmospheric concentrations and the resulting risks posed by the chemicals of concern for the South Coast Air Basin is a very complex and dynamic process. As more information is obtained on atmospheric chemistry fate and health effects of these chemicals, there is the expectation that the modeled atmospheric concentrations and health risk values will change. Ultimately, the goal is to provide a more accurate analysis and lower the uncertainty involved in the process. Thus, CARB performed a supplementary "upper-bound model" simulation on the five fuel scenarios that formed the original basis of the health impacts assessment. The additional model inputs included the effects of emission uncertainty and chlorine chemistry, uses updated MTBE and ethanol rate constants, and corrects boundary conditions for several substances.

The resulting atmospheric concentration estimates are shown in Table A-1, and our conclusions are as follows:

- The "upper-bound model atmospheric concentrations" presented here are generally lower than the original atmospheric concentrations presented in Table 4. Thus, the cumulative hazard indices and cumulative cancer risks are predicted to be lower under this modified model simulation.
- The only increased atmospheric levels under the modified model simulation were for ethanol. In some cases these were nearly double the original predicted atmospheric concentrations. However, the increased ethanol concentrations are expected to have no impact on health due to ethanol's low anticipated health risk relative to other fuel-related chemicals.
- Comparing the atmospheric concentrations among the year 2003 fuel scenarios under the modified model, there are higher concentrations of acetaldehyde in the scenario with ethanol (3.5% oxygen) fuel. This difference was less marked in the predictions of the previous version of the model. However, the health impact of the higher acetaldehyde concentrations is negligible due to its relatively low health risk compared to other chemicals of concern.
- Under the modified model, the upper range estimates of PAN concentrations are higher in the scenario with ethanol (3.5% oxygen) fuel. This difference also was less marked with the previous version of the model. If the atmospheric concentrations of PAN were in fact to be substantially increased, this would be of concern since PAN has a relatively high health impact for acute eye irritation. However, given the total range of the predicted PAN concentrations and the uncertainty in the model prediction, it is unclear whether PAN results in a greater health risk under the ethanol (3.5% oxygen) fuel scenario.
- It appears that the modified model simulations are more sensitive to fuel composition in the predictions of ethanol, acetaldehyde, and PAN concentrations (and therefore of the associated health impacts) compared to the other chemicals of concern.

- There are no indications of substantial differences between the 2003 fuel types in cancer or noncancer health impacts of airborne exposures, whether the original or modified model is used. Therefore, there are no grounds to recommend one fuel over another based on health impacts of air pollution. Similarly, there is no indication that any of those fuel choices would result in worse health impacts than the current situation.

In addition to predicted values for PM_{10}, CARB also included in their latest report predicted values for $PM_{2.5}$. As with PM_{10}, CARB states that they expect no difference among 2003 scenarios, and therefore only provided a maximum daily average (81 $\mu g/m^3$) and a maximum annual average (25.9 $\mu g/m^3$) for the 1997 MTBE fuel scenario for $PM_{2.5}$. Currently, although U. S. EPA has proposed standards for $PM_{2.5}$, there are no state or federal standards in place for this material. However, it is commonly assumed that the ratio of $PM_{2.5}/PM_{10}$ is 0.5. Use of the California PM_{10} standards (30 $\mu g/m^3$ for the annual average; 50 $\mu g/m^3$ for the 24-hr average standard) results in values of 15 and 25 $\mu g/m^3$, respectively, as guidance for interpreting the significance of the predicted $PM_{2.5}$ concentrations. While it is known that these guidance values for particulates are frequently exceeded in California, according to CARB's report, there is no difference expected among the 2003 scenarios.

Further discussion and analysis of the atmospheric concentration estimates based on the modified model simulations can be found in section 4.2.2 of CARB’s “Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline. Final Report to the California Environmental Policy Council. December, 1999”.

Table A-1. Atmospheric Concentration Estimates: Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin Using “Upper-Bound Model Simulations” [a]

		1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 Non-Oxy
Acetaldehyde (ppb)						
Population-Weighted Annual Exposure						
	Upper	1.8	1.5	1.5	1.8	1.5
	Lower	1.8	1.4	1.5	1.7	1.4
Maximum Daily Average						
	Upper	11.0	7.9	8.1	8.5	8.0
	Lower	5.1	3.7	3.8	4.0	3.7
Maximum 1 Hour Average						
	Upper	17.7	12.4	12.7	13.6	12.3
	Lower	13.8	9.7	9.9	10.6	9.6
Benzene (ppb)						
Population-Weighted Annual Average						
	Upper	1.19	0.68	0.67	0.69	0.63
	Lower	1.07	0.61	0.60	0.62	0.57
Maximum Daily Average						
	Upper	9.5	5.6	5.6	5.7	5.2
	Lower	7.4	4.4	4.3	4.4	4.1
Maximum 1 Hour Average						
	Upper	22.4	13.1	13.1	13.1	12.1
	Lower	11.6	6.8	6.8	6.8	6.3
Butadiene (ppb)						
Population-Weighted Annual Average						
	Upper	0.36	0.20	0.19	0.20	0.20
	Lower	0.34	0.19	0.18	0.19	0.18
Maximum Daily Average						
	Upper	2.9	1.5	1.5	1.5	1.5
	Lower	2.0	1.1	1.1	1.1	1.1
Maximum 1 Hour Average						
	Upper	6.7	4.0	4.0	4.0	4.0
	Lower	3.1	1.9	1.9	1.9	1.9
Ethanol (ppb)						
Population-Weighted Annual Average						
	Upper	5.4	5.1	10.9	14.2	5.1
Maximum Daily Average						
	Upper	51	48	98	125	48
	Lower	47	45	93	121	44
Maximum 1 Hour Average						
	Upper	108	101	213	268	101
	Lower	78	74	191	267	74

Table A-1 (continued). Atmospheric Concentration Estimates: Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin Using "Upper-Bound Model Simulations"[a]

		1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 Non-Oxy
Formaldehyde (ppb)						
Population-Weighted Annual Average						
	Upper	4.7	3.7	3.4	3.5	3.4
	Lower	4.7	3.6	3.4	3.5	3.4
Maximum Daily Average						
	Best	14.0	9.8	9.2	9.6	9.1
Maximum 1 Hour Average						
	Upper	37.8	26.5	25.1	25.9	24.9
	Lower	20.3	14.2	13.5	13.9	13.4
MTBE (ppb)						
Population-Weighted Annual Average						
	Upper	3.9	2.4	0	0	0
	Lower	3.6	2.2	0	0	0
Maximum Daily Average						
	Upper	29	18	0	0	0
	Lower	13	8	0	0	0
Maximum 1 Hour Average						
	Upper	67	41	0	0	0
	Lower	19	12	0	0	0
PAN (ppb)[b]						
Maximum Daily Average						
	Upper	5.0	3.3	3.2	3.4	3.1
	Lower	2.5	1.7	1.6	1.7	1.6
Maximum 1 Hour Average						
	Upper	10.0	6.3	6.0	6.5	5.7
	Lower	5.0	3.1	3.0	3.2	2.9

Table A-1 (continued). Atmospheric Concentration Estimates: Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin Using "Upper-Bound Model Simulations"[a]

	1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 Non-Oxy
Carbon Monoxide (ppm)					
Maximum 8 Hour Average					
Best	**17.5**	**12.7**	**12.7**	**12.1**	**13.1**[c]
Maximum 1 Hour Average					
Best	**22.5**	**16.1**	**16.1**	**15.3**	**16.6**[c]
Nitrogen Dioxide (ppm)					
Maximum Annual Average					
Best	**0.043**	CARB reported, "No difference expected among 2003 scenarios" [d]			
Maximum Daily Average					
Best	**0.117**	**0.095**	**0.095**	**0.095**	**0.095**
Maximum 1 Hour Average					
Best	**0.255**	**0.207**	**0.207**	**0.207**	**0.207**
Ozone (ppm)					
Maximum 8 Hour Average					
Best	**0.206**	**0.165**	**0.159**	**0.162**	**0.159**
Maximum 1 Hour Average					
Best	**0.244**	**0.190**	**0.182**	**0.186**	**0.182**
Particulate Matter (10 microns or less) (mg/m^3)					
Maximum Annual Geometric Mean					
Best	**56**	CARB reported, "No difference expected among 2003 scenarios" [d]			
Maximum Daily Average					
Best	**227**	CARB reported, "No difference expected among 2003 scenarios" [d]			

[a] Source: Table 4.9 of "Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline. Final Report to the California Environmental Policy Council. December, 1999. California Air Resources Board, Cal/EPA"

[b] A population-weighted annual average for PAN was not determined because consistent long-term measurements of atmospheric PAN have not been performed. See CARB report for details.

[c] This 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.

[d] No significant change compared to 1997 MTBE-fuel scenario. See CARB report for details.

Tables A-2 and A-3 display the non-cancer Hazard Quotients (HQs) generated from the modeled atmospheric concentrations in Table A-1. The relatively marginal increase in the acute atmospheric acetaldehyde concentrations under the 3.5% ethanol fuel scenario relative to the other fuel scenarios did not translate into a proportionally higher HQ. This was primarily due to acetaldehyde’s relatively low HQ. In contrast, the upper range atmospheric PAN concentrations under the 3.5% fuel scenario exhibited a proportionally increased HQ compared to the other fuel scenarios. Although the proportional increases in upper range PAN and acetaldehyde concentrations were similar under this fuel scenario, there is likely greater concern for PAN’s acute effects because of its relatively high HQ. However, it is not clear how real this difference is because the lower range PAN HQ is proportionally similar to the lower range PAN HQs in the other fuel scenarios. Given the total range of the PAN HQs and the uncertainty in the model prediction, it is unclear whether PAN results in a greater health risk under the 3.5% ethanol fuel scenario.

Table A-2. Range of Estimated Maximum Noncancer Hazard Quotients (HQ) for Various Scenarios in the South Coast Air Basin Based on ARB's "Upper-Bound Model Simulations"

		1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 NonOxy
Acetaldehyde						
Chronic HQ	Upper	0.4	0.3	0.3	0.4	0.3
	Lower	0.4	0.3	0.3	0.3	0.3
Acute HQ	Upper	0.3	0.2	0.2	0.2	0.2
	Lower	0.2	0.1	0.2	0.2	0.1
Benzene						
Chronic HQ	Upper	0.06	0.03	0.03	0.03	0.03
	Lower	0.05	0.03	0.03	0.03	0.03
Acute HQ	Upper	0.06	0.03	0.03	0.03	0.03
	Lower	0.03	0.02	0.02	0.02	0.02
Butadiene						
Chronic HQ	Upper	0.09	0.05	0.05	0.05	0.05
	Lower	0.09	0.05	0.05	0.05	0.05
Acute HQ	Upper	0.05	0.03	0.03	0.03	0.03
	Lower	0.02	0.01	0.01	0.01	0.01
Ethanol						
Chronic HQ	Best	0.0001	0.0001	0.0002	0.0003	0.0001
Acute HQ	Upper	0.002	0.002	0.004	0.005	0.002
	Lower	0.001	0.001	0.004	0.005	0.001
Formaldehyde						
Chronic HQ	Upper	2.4	1.9	1.7	1.8	1.7
	Lower	2.4	1.8	1.7	1.8	1.7
Acute HQ	Upper	0.5	0.3	0.3	0.3	0.3
	Lower	0.3	0.2	0.2	0.2	0.2
MTBE						
Chronic HQ	Upper	0.005	0.003	0.0	0.0	0.0
	Lower	0.005	0.003	0.0	0.0	0.0
Acute HQ	Upper	0.01	0.006	0.0	0.0	0.0
	Lower	0.003	0.002	0.0	0.0	0.0
PAN*						
Acute HQ	Upper	5.5	3.5	3.3	3.6	3.2
	Lower	2.7	1.7	1.7	1.8	1.6

* A population-weighted annual average for PAN was not determined because consistent long-term measurements of atmospheric PAN have not been performed. See CARB report for details.

Table A-3. Range of Estimated Maximum Noncancer Hazard Quotients (HQ) for Various Scenarios in the South Coast Air Basin Based on ARB's "Upper-Bound Model Simulations" – Criteria Air Pollutants

	1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 NonOxy
Carbon Monoxide					
Acute 8 hour HQ	1.9	1.4	1.4	1.3	1.5
Acute 1 hour HQ	1.1	0.8	0.8	0.8	0.8
Nitrogen Dioxide					
Chronic HQ	0.8	concentrations not estimated by CARB since no significant change in Maximum 1-Hour*			
Acute 1 hour HQ	1.0	0.8	0.8	0.8	0.8
Ozone					
Acute 8 hour HQ	2.6	2.1	2.0	2.0	2.0
Acute 1 hour HQ	2.7	2.1	2.0	2.1	2.0
Particulate Matter (PM10)					
Chronic HQ	1.9	CARB reported, "No significant change expected among			
Acute 24 hour HQ	4.5	2003 scenarios" for both annual and daily concentrations*			

* compared to exposure estimates for the 1997 MTBE-fuel scenario (see CARB report for details)

With regard to the chemicals that are predicted to pose a cancer risk (Table A-4), the modified model simulation does not change the existing conclusions that, (1) we have more confidence in the relative risks estimates than the absolute values of concentrations and risk, and (2) there are no substantial differences between the 2003 fuel types with regard to the cumulative lifetime cancer risk estimates. As expected, the marginal increase in atmospheric acetaldehyde concentrations under the 3.5% ethanol fuel scenario relative to the other fuel scenarios did not result in a significant increase in cumulative cancer risk. This is primarily due to acetaldehyde's considerably lower cancer risk relative to other carcinogens such as benzene.

Table A-4. Lifetime Cancer Risk from Individual Chemicals and Cumulative Lifetime Cancer Risk for Each of the Five Fuel Scenarios Based on ARB's "Upper-Bound Model Simulations"

Chemical		1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 NonOxy
Acetaldehyde	Upper	8.6 E-6	7.2 E-6	7.2 E-6	8.6 E-6	7.2 E-6
	Lower	8.6 E-6	6.7 E-6	7.2 E-6	8.1 E-6	6.7 E-6
Benzene	Upper	1.1 E-4	6.3 E-5	6.2 E-5	6.4 E-5	5.9 E-5
	Lower	1.0 E-4	5.7 E-5	5.6 E-5	5.8 E-5	5.3 E-5
Butadiene	Upper	1.3 E-4	7.4 E-5	7.0 E-5	7.4 E-5	7.4 E-5
	Lower	1.3 E-4	7.0 E-5	6.7 E-5	7.0 E-5	6.7 E-5
Formaldehyde	Upper	3.3 E-5	2.6 E-5	2.4 E-5	2.5 E-5	2.4 E-5
	Lower	3.3 E-5	2.5 E-5	2.4 E-5	2.5 E-5	2.4 E-5
MTBE	Upper	3.6 E-6	2.2 E-6	0	0	0
	Lower	3.3 E-6	2.0 E-6	0	0	0
Cumulative Lifetime Risk	Upper	2.9 E-4	1.7 E-4	1.6 E-4	1.7 E-4	1.6 E-4
	Lower	2.7 E-4	1.6 E-4	1.5 E-4	1.6 E-4	1.5 E-4
Excess Cancer Cases Per Million Individuals	Upper	290	170	160	170	160
	Lower	270	160	150	160	150

For non-cancer cumulative impacts, the toxicological endpoints of concern, acute eye irritation (Table A-5), acute respiratory irritation (Table A-6), and chronic respiratory irritation (Table A-7), remained the same under the modified model simulations. The only noticeable difference among the fuel scenarios was that for acute eye irritation, the 2003 MTBE and 3.5% ethanol fuels had slightly higher upper range acute HIs relative to the other year 2003 fuels. The secondary pollutant PAN was primarily responsible for the increased disparity, due to the higher upper range estimate of its HQ under these two fuel scenarios. However, the lower range of the cumulative HIs does not show as great a disparity among the fuel scenarios. There is considerable uncertainty involved in the model predictions, including both the range of estimates with this "upper bound model" and the differences between this model and the earlier one. It cannot therefore be definitely concluded that the 3.5% ethanol fuel will result in greater eye irritation relative to the other fuels. Improvement in atmospheric modeling and measurement may eventually resolve this uncertainty.

Table A-5. Maximum Acute Hazard Quotients (HQ) and Cumulative Acute Hazard Indices (HI) for Eye Irritation for Each of the Five Fuel Scenarios Based on ARB's "Upper-Bound Model Simulations"

Chemical		1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 NonOxy
Acetaldehyde	Upper	0.3	0.2	0.2	0.2	0.2
	Lower	0.2	0.1	0.2	0.2	0.1
Ethanol	Upper	0.002	0.002	0.004	0.005	0.002
	Lower	0.001	0.001	0.004	0.005	0.001
Formaldehyde	Upper	0.5	0.3	0.3	0.3	0.3
	Lower	0.3	0.2	0.2	0.2	0.2
MTBE	Upper	0.01	0.006	0	0	0
	Lower	0.003	0.002	0	0	0
PAN	Upper	5.5	3.5	3.3	3.6	3.2
	Lower	2.7	1.7	1.7	1.8	1.6
Nitrogen dioxide	Best	1.0	0.8	0.8	0.8	0.8
Ozone	Best	2.7	2.1	2.0	2.1	2.0
Cumulative HI	Upper	10.0	6.9	6.6	7.0	6.5
	Lower	6.9	4.9	4.9	5.1	4.7

Table A-6. Maximum Acute Hazard Quotients (HQ) and Cumulative Acute Hazard Indices (HI) for Respiratory Irritation For Each of the Five Fuel Scenarios Based on ARB's "Upper-Bound Model Simulations"

Chemical		1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 NonOxy
Acetaldehyde	Upper	0.3	0.2	0.2	0.2	0.2
	Lower	0.2	0.1	0.2	0.2	0.1
Ethanol	Upper	0.002	0.002	0.004	0.005	0.002
	Lower	0.001	0.001	0.004	0.005	0.001
MTBE	Upper	0.01	0.006	0	0	0
	Lower	0.003	0.002	0	0	0
Nitrogen dioxide	Best	1.0	0.8	0.8	0.8	0.8
Ozone	Best	2.7	2.1	2.0	2.1	2.0
Cumulative HI	Upper	4.0	3.1	3.0	3.1	3.0
	Lower	3.9	3.0	3.0	3.1	2.9

Table A-7. Maximum Chronic Hazard Quotients (HQ) and Cumulative Chronic Hazard Indices (HI) for Respiratory Irritation for Each of the Five Fuel Scenarios Based on ARB's "Upper-Bound Model Simulations"

Chemical		1997 MTBE	2003 MTBE	2003 Et2%	2003 Et3.5%	2003 NonOxy
Acetaldehyde	Upper	0.4	0.3	0.3	0.4	0.3
	Lower	0.4	0.3	0.3	0.3	0.3
Ethanol	Best	0.0001	0.0001	0.0002	0.0003	0.0001
Formaldehyde	Upper	2.4	1.9	1.7	1.8	1.7
	Lower	2.4	1.8	1.7	1.8	1.7
Nitrogen dioxide	Best	0.8	0.8	0.8	0.8	0.8
PM_{10}	Best	1.9	1.9	1.9	1.9	1.9
Cumulative HI	Upper	5.5	4.9	4.7	4.9	4.7
	Lower	5.5	4.8	4.7	4.8	4.7

In conclusion, the modified model simulation did not change the original finding that the different fuel types are substantially the same with regard to airborne cancer and noncancer health risks. However, given that we have more confidence in the relative risk estimates than the absolute values of the risks, the slight increase in atmospheric PAN concentration resulting with the new model input should be further explored.

While the modified model simulation resulted in lower cancer risks and noncancer health effects under all 2003 fuel scenarios relative to the original model simulation, it should be emphasized that these changes are modest and do not diminish the need for the existing regulatory action on automobiles. With the complexities involved in predicting atmospheric concentrations, it is uncertain whether further refinements of the atmospheric modeling will increase or decrease the overall health risks. Ultimately, the differences for cancer and noncancer health risks are not substantial enough between the 2003 fuel types to recommend one fuel over another based on airborne exposure, nor is there any indication that any of those fuel choices would result in worse health impacts than the current situation.