

**Quantitative Estimate of the
Air Quality Impacts of Methanol Fuel Use
Executive Summary**

Prepared for the
California Air Resources Board
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by

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As with any study of this type, there are bound to be errors or oversights, which are our responsibility. Feel free to communicate these with the authors. In writing the report, we have attempted to be objective, though personal views and interpretations may lead to certain statements and conclusions. When these are expressed, they are the sole responsibility of the authors. In fact:

The statements and conclusions in this report are those of the contractor and not necessarily those of the State Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products. In addition, they are not necessarily those of the South Coast Air Quality Management District.

Abstract

Methanol fuel use, in both mobile and stationary applications, has been proposed as a strategy to improve air quality in urban areas such as the South Coast Air Basin of California. It is viewed as a potential method to reduce, simultaneously, ozone, NO₂, particulate matter, benzene and other non-criteria pollutants such as peroxyacetyl nitrate and nitric acid. Currently the SoCAB, which encompasses Los Angeles, exceeds the federal and state limits for ozone, NO₂ and particulate matter. This provides the impetus to consider and test the effectiveness of methanol use to improve air quality. In order to assess, quantitatively, the impact that methanol fuel utilization could have in the SoCAB, a three-tiered, photochemical modeling study was designed and executed. The three tiers included chemical kinetics modeling, trajectory model analysis and, Eulerian, airshed modeling of ozone, NO_x, nitric acid, formaldehyde and peroxyacetyl nitrate. The design utilized the strengths of each model formulation to address the issues related to adopting policies for methanol utilization. Particulate matter response to methanol use was calculated from results of photochemical and non-photochemical modeling. Formaldehyde, methanol and benzene buildup under stagnation conditions, and the response to methanol use, was determined using linear modeling. These models were used to study the air quality benefits of methanol use in motor vehicles and stationary sources for the years 2000 and 2010.

One of the most cited potential benefits of switching to methanol fuel is to reduce ozone which is a severe problem in the SoCAB. Over ninety other urban areas also experience ozone levels in excess of the national standard. Chemical kinetics modeling and sensitivity analysis showed that methanol emissions do not add greatly to the formation of ozone, even over multiday episodes. This conclusion was reinforced by trajectory and airshed modeling that showed that the methanol component of the exhaust of methanol fueled vehicles led to little change in the ozone predicted to be formed. A three day period, that was conducive to producing high ozone concentrations, was simulated using the air quality models. The buildup of methanol over the multiday smog episode did not eliminate the ozone reduction potential of utilizing methanol as a motor vehicle fuel. Ozone reductions of up to 17% were predicted for utilizing M100 fueled vehicles. This was 77% of the reduction of removing motor vehicle source emissions completely. The reduction was limited by the relatively small fraction of the total ROG forecast to be attributable to motor vehicles in the year 2000.

Formaldehyde emissions, and the gasoline fraction of methanol fuel blends, proved to be significant contributors to ozone formation. Use of M85, or increased emissions of formaldehyde from motor vehicles (55 mg mi⁻¹ of HCHO vs. 15-18 mg mi⁻¹ as modeled in the base case) led to only half the improvement in the predicted ozone concentrations and exposures. Recent tests, however, indicate that the exhaust and evaporative emissions from M85 may be less reactive than modeled, which would increase the improvements to be expected and decrease the apparent difference between M85 and M100 fuel use.

A concern before this study was that the increased direct emissions of formaldehyde from methanol fueled vehicles would lead to excessive HCHO levels. Calculations by the photochemical models showed that formaldehyde levels during smog episodes should not increase greatly, and may in fact decrease. The reduction in HCHO levels is a result of the low reactivity of methanol leading to lower atmospheric production, offsetting the increased emissions. Formaldehyde exposures, based on methanol fueled light duty vehicles emitting between 15 and 18 mg mi⁻¹ (in use), were 17% less and 13% more than the corresponding base cases for year 2000 and 2010 calculations, respectively.

Concentrations of other pollutants would also decrease if methanol was used. Particulate matter concentrations would decrease because methanol fueled vehicles emit less aerosol carbon than the corresponding conventionally fueled counterparts, especially diesels. Also, emissions of gas phase precursors to aerosol formation, and atmospheric production of particulate matter, is reduced. Particulate matter levels could be reduced up to 19%, based on the annual average at Rubidoux. In particular, aerosol carbon and aerosol nitrate levels would be reduced. Areas heavily impacted by these components would benefit the greatest. Predicted nitric acid, NO_2 and peroxyacetyl nitrate (PAN) were reduced from switching to methanol. Methanol is not a precursor to PAN, and reductions of up to 22% were predicted. Exposures to nitric acid and NO_2 concentrations were predicted to decrease about 28%.

Ambient methanol levels would increase to about 1 ppm under extreme stagnation conditions. HCHO concentrations could approach 90 ppb. This is an order of magnitude less than the OSHA standard. Motor vehicles, powered by conventional fuels, are projected to be the major contributors to ambient benzene in the SoCAB. Switching to methanol would decrease ambient levels of benzene, a carcinogen. Thus, methanol could be used effectively to improve many aspects of air quality in the Los Angeles area.

EXECUTIVE SUMMARY

E1 Methanol as a Clean Fuel

Use of alternative fuels such as methanol is being considered as a strategy to improve air quality in areas like the South Coast Air Basin (SoCAB) of California which experience smog. When used in motor vehicles, methanol is cited as having the potential to substantially reduce the pollution attributable to that source. Methanol can also be used, alone or in conjunction with conventional fuels, to reduce the emissions from stationary sources, including utility boilers, and internal combustion engines. An added benefit of developing the capability of using methanol is that it could reduce our dependence on foreign oil. However, conversion from the conventional fuels now used to methanol would have a significant impact on industry and the consumer, and the environmental benefits must be quantified before adopting a strategy involving methanol.

The SoCAB, which surrounds Los Angeles, experiences ozone levels in excess of three times the national and state standards of 0.12 ppm and 0.09 ppm, respectively. In addition to an ozone problem, PM_{10} levels in the SoCAB have been measured to be about twice the national standards and three times the state standards for both the 24-hour and yearly averaging periods. Methanol, because of its low atmospheric reactivity, low carbon number and clean burning characteristics has the potential to improve air quality, reducing ozone, NO_2 and PM_{10} . The primary component of methanol fuel vehicle emissions is unburned methanol which is less reactive than organics typically emitted from conventionally fueled vehicles. When used in heavy duty vehicles in place of diesel fuel, the commonly observed black cloud is virtually eliminated, and emissions and atmospheric concentrations of nitrogen oxides (NO_x) are reduced. In stationary source applications NO_x reductions can be expected.

In addition to lowering ozone, PM_{10} and NO_x levels, methanol use would decrease atmospheric concentrations of benzene (a carcinogen), peroxyacetyl nitrate (PAN - an eye irritant and phytotoxin), and nitric acid (HNO_3 , a major constituent of acid deposition in the SoCAB). While not being criteria pollutants, these are important constituents of air quality, and their reduction has obvious benefits.

While most of the air quality impacts of utilizing methanol appeared to be positive, a number of questions regarding certain aspects of the impacts were unanswered at the outset of this project. These questions, listed below, were of obvious environmental, economic and regulatory concern:

- Would the use of methanol fueled vehicles (MFVs) lead to increased HCHO levels and, if so, would the concentrations be prohibitive?
- Experiments indicated that methanol use may lose its potential to reduce ozone during multiday smog episodes. Would the buildup of methanol over multiple days severely decrease the effectiveness of methanol use?
- Would methanol build up to levels of concern?
- What would adopting a methanol fuel based strategy do to the atmospheric concentrations of other pollutants, such as NO_2 particulate matter (PM_{10}), PAN, nitric acid and benzene?

- How effective would methanol use be in reducing exposure to ozone and lowering peak ozone concentrations?

Answering these questions is appropriately handled by the use of mathematical models. These models, which include detailed descriptions of the physical and chemical processes involved in pollutant formation and transport, are the most comprehensive and technically defensible means of predicting the impact of emission controls.

E2 Objective and Methodology of This Project

The objective of this study was to quantify to what extent methanol fuel use would improve air quality in the SoCAB. Particular importance was given to addressing the issues identified above. A three-tiered photochemical modeling study, using start-of-the-art tools, was designed and conducted to simulate how atmospheric ozone, HCHO, NO_x, HNO₃, aerosol nitrate and PAN levels would respond to control strategies involving methanol. The three tiers are chemical kinetics modeling, trajectory modeling and Eulerian airshed modeling. Each level involved using progressively more complex representations of the processes involved in the evolution of pollutants in the atmosphere. Each model, as shown in Table 1, has various strengths and limitations. By utilizing the strength of each model, it is possible to develop a more robust view of the impact of methanol on the different pollutants, and the underlying reasons for the observed responses.

Photochemical models, due to their increased computational requirements, are not the most efficient tools to determine how emission changes will affect the concentrations of relatively inert pollutants, such as elemental carbon. Also, if the chemistry of pollutant transformation is relatively linear in emissions of itself, as is the case for benzene and methanol, or in the precursor pollutant, e.g., sulfate, less complex techniques can be used. Where appropriate, photochemical modeling was augmented with linear models to find the impacts of methanol use.

E3 Chemical Kinetic Modeling and Sensitivity Analysis

Chemical kinetics modeling was able to answer one of the major questions outstanding at the start of the project. Previous modeling projects, using single-day trajectories, indicated significant benefits of utilizing methanol in reducing ozone. This was due to methanol's low atmospheric reactivity. However, environmental chamber experiments conducted at the University of California's, Riverside, Statewide Air Pollution Research Center (SAPRC) indicated that over multiday periods the comparative benefit of using methanol diminished markedly. The question arose as to whether the buildup and residence of methanol during multiday smog episodes would negate the benefits of its lower reactivity.

Modeling of the SAPRC experiments showed that the result indicating that methanol loses most of its apparent benefits by the third day is an artifact of the experimental conditions. First, the NO_x present at the beginning of the experiment is almost completely used up by the second and third day of the experiments. Many of the reactive organics, such as alkanes and aromatics, have much longer life times, and persist. At this point, the production of ozone is "NO_x-limited," and is relatively insensitive to changes in the reactivity of the organic. This is characterized by an extremely high ROG/NO_x ratio - far beyond those found in the populated regions of the SoCAB. This is a significant limitation in applying the experimental results to suggest the likely behavior of the atmospheric production of ozone. To first order, continuous injection of NO_x and organics could help alleviate the problem.

Table 1

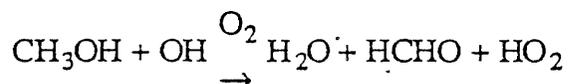
**Three-Tiered Modelling Structure:
Strengths, Weaknesses and Uses of Each Model**

	<u>Strengths</u>	<u>Weaknesses</u>	<u>Uses</u>
Tier 1: Chemical Kinetics Modelling	<p>Fast. Allows for extensive mechanism testing.</p> <p>Good for identifying chemical pathways.</p> <p>Output can be compared to smog chamber mechanisms.</p> <p>Isolates chemistry from atmospheric dynamics</p>	<p>Does not describe atmospheric dynamics of fresh emissions.</p>	<p>Testing chemical mechanisms.</p> <p>Sensitivity analysis.</p> <p>Initial testing of methanol - air quality relationship.</p> <p>Explaining smog chamber results.</p>
Tier 2: Trajectory Modelling	<p>Relatively fast, computationally.</p> <p>Describes important atmospheric processes.</p> <p>Can test importance of emissions, deposition, meteorology and other physical phenomena.</p>	<p>Limitations in model formulation.</p> <p>Only provides information along a single trajectory.</p>	<p>Sensitivity testing of model inputs.</p> <p>Identifying particularly interesting cases for airshed modeling.</p> <p>Initial estimates of emissions - air quality relationships from converting to methanol.</p>
Tier 3: Airshed Modelling	<p>Complete description of atmospheric pollutant dynamics.</p> <p>Provided emissions - air quality relationships across entire basin.</p> <p>Minimal limitations in model formulation.</p>	<p>Computationally intensive.</p>	<p>Develop emissions - air quality relationship for the SoCAB.</p> <p>Primary source of determining expected impact from methanol use.</p>

A second, more fundamental limitation with the experimental results is that on the second and third days of the simulations, heterogeneous reactions due to the walls of the chambers became increasingly more dominant. In particular, modeling showed that the wall source of radicals played a dominating role in driving the oxidation of the reactive organics. This increased the apparent reactivity of methanol. Other limitations include that the chamber experiments do not include the effects of dispersion, turbulence and stratification.

Chemical kinetic modeling, and sensitivity analysis, showed that if a continuous injection of fresh pollutants was used, and if the wall source of radicals is removed, use of methanol would lead to lower ozone levels throughout the experiments. In fact, the sensitivity of ozone formation to methanol emissions is almost negligible over the multiday periods, a conclusion reinforced by trajectory and airshed modeling. On the other hand, emissions of HCHO, which are increased in MFVs, can exacerbate ozone formation.

Chemical kinetics modeling was also used to test the performance of the mechanism used. Tests indicated that, for multiday modeling at low NO_x levels, the peroxy acyl radical reaction with itself was important at night. This reaction was added to the "Extended Caltech" mechanism. The other major extension of the Caltech mechanism was to include the methanol oxidation reaction:



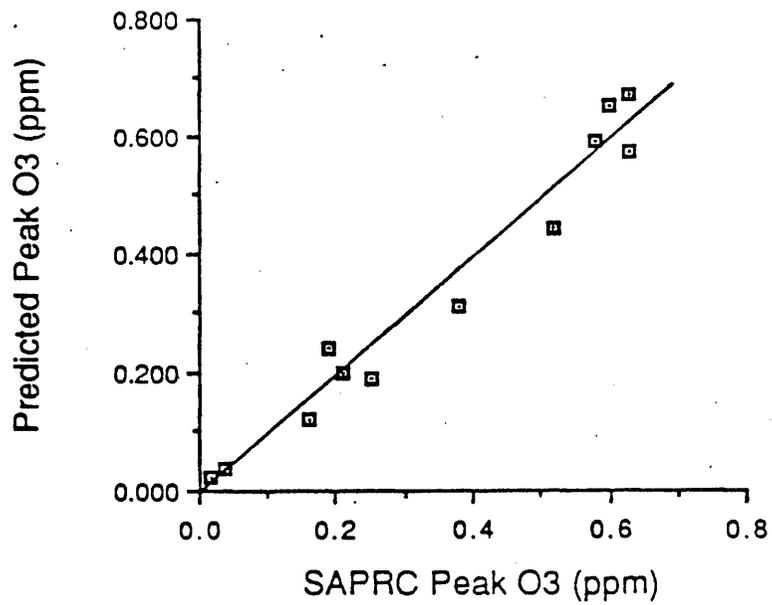
$$k = 1380 \text{ ppm}^{-1} \text{ min}^{-1}$$

After inclusion of these reactions, the extended Caltech mechanism accurately reproduced the ozone concentrations observed during the SAPRC experiments. The extent of agreement is shown in Figures 1 and 2, and Table 2. Performance was comparable to the explicit mechanisms used to model the same experiments. A further test of the mechanism was to compare its predictions to that of a recent, more detailed mechanism. Again the predicted ozone levels were comparable. Good agreement was also found between the predictions of other pollutants and the corresponding pollutant observations. These results strongly supported the conclusion that the Extended Caltech mechanism is suitable for use in studying the atmospheric response to the widespread use of methanol.

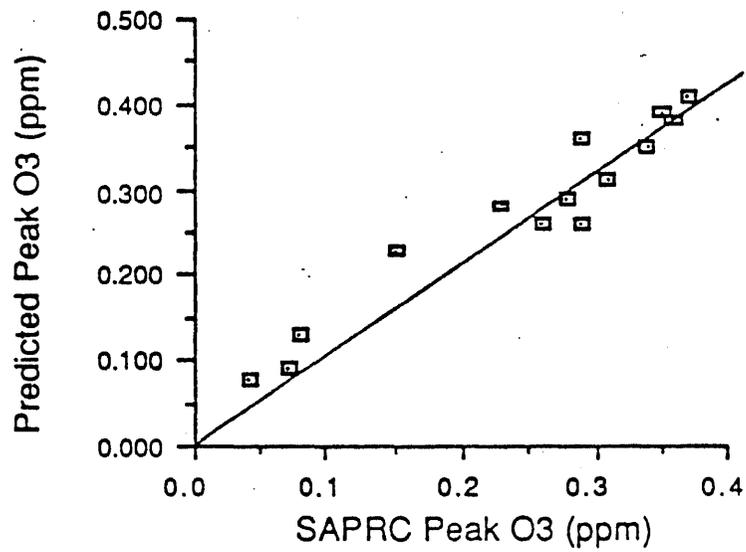
E4 Meteorological and Emissions Inputs for Photochemical Modeling

The CIT¹ trajectory and airshed models were both used to show how pollutants in the Los Angeles area would respond to the use of methanol during a severe ozone episode. Inputs required by those models include meteorological variables and emissions. Meteorological data, including temperature, relative humidity, wind speed and atmospheric thermal structure, corresponding to the August 30 to September 1, 1982 period was chosen for four reasons:

¹ CIT stands for both the Carnegie Institute of Technology, the Engineering College at Carnegie Mellon University, and the California Institute of Technology. Work at both schools has been instrumental in developing and advancing the CIT models.

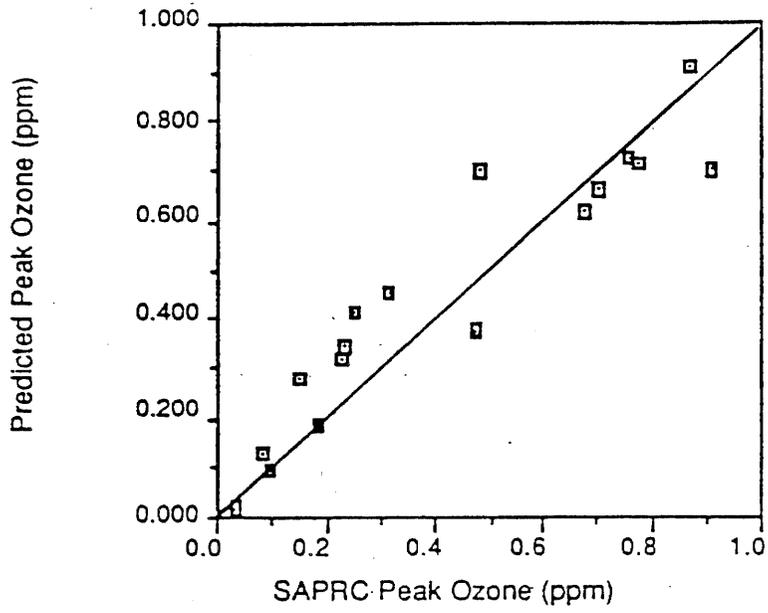


(a)

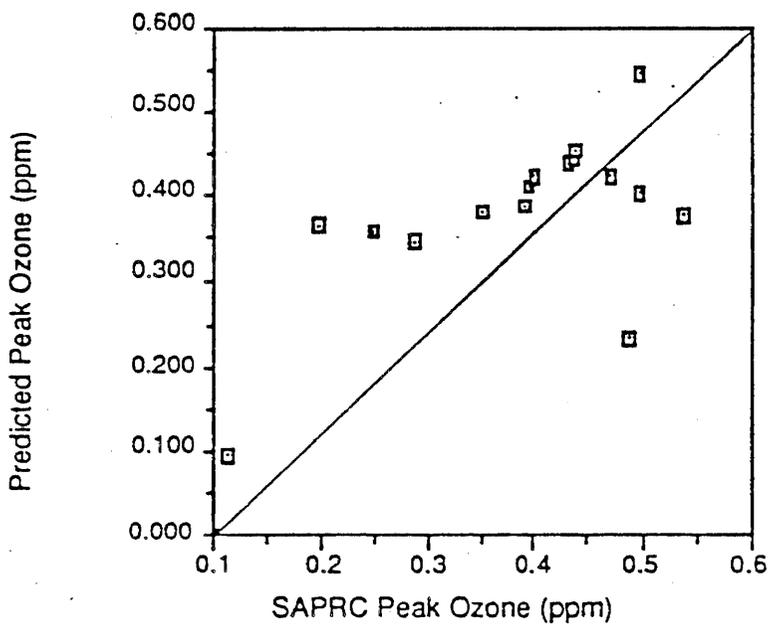


(b)

Figure 1 Plot of predicted peak ozone concentrations vs. measured ozone peaks for the SAPRC Indoor Teflon Chamber smog chamber experiments. The 1:1 correlation line is shown. (a) Day 1 (b) Day 2



(a)



(b)

Figure 2 Plot of predicted peak ozone concentrations vs. measured ozone peaks for the SAPRC Outdoor Teflon Chamber smog chamber experiments. The 1:1 correlation line is shown. (a) Day 1 (b) Day 2

ITC Run Number	SAPRC Experimental Peak Ozone Conc.		Calculated Peak Ozone Conc.	
	(ppm)	time (hrs)	(ppm)	time(hrs)
865	.63	8	.67	8
867	.63	12	.57	12
868	.52	12	.44	12
871	.38	12	.31	12
872	.21	12	.20	12
873	.16	12	.12	12
874	.19	12	.24	12
877	.25	12	.19	12
880	.03	12	.03	12
881	.01	12	.02	12
885	.01	12	.02	12
886	.01	12	.02	12
888	.58	12	.59	12
891	.60	12	.65	9

(a)

ITC Run Number	SAPRC Experimental Peak Ozone Conc.		Calculated Peak Ozone Conc.	
	(ppm)	time (hrs)	(ppm)	time (hrs)
865	.37	24	.41	36
867	.36	36	.38	36
868	.29	36	.36	36
871	.31	36	.31	36
872	.23	36	.28	36
873	.26	36	.26	36
874	.28	35	.29	36
877	.29	36	.26	36
880	.15	36	.23	36
881	.08	36	.13	36
885	.04	36	.08	36
886	.07	36	.09	36
888	.35	36	.39	36
891	.34	36	.35	36

(b)

Table 2 Predicted and Observed Ozone Concentrations
(a) Day 1 (b) Day 2

- 1) The meteorological conditions present during the three-day period, high temperatures, sunlight, and relatively stagnant air, were conducive to forming ozone. By the third day of the 1982 episode, ozone concentrations built up to second stage alert levels (0.35 ppm).
- 2) The atmosphere prior to the start of the episode was relatively unpolluted. This, and the use of three-day modeling periods make predicted pollutant concentrations on the third day relatively independent of the initial conditions chosen.
- 3) Extensive pollutant measurements were made over the first two days of the three-day period. In addition to routine measurements of ozone, NO_x, and CO, trace pollutants like PAN, HNO₃, aerosol nitrate, and ammonia were also measured. This extra data allowed for extremely detailed testing of model performance. The CIT model was able to follow the evolution of not only O₃ and NO₂ (which are more commonly used for model evaluation), but also HNO₃, PAN and aerosol nitrate. No other photochemical model has been tested so closely.
- 4) During this period, the winds were primarily westerly from over the Pacific Ocean. Pollutant concentrations over the Ocean are generally low, and if the boundary of the modeling region is taken sufficiently far out, predicted concentrations in the Basin are relatively independent of the boundary conditions.

In a previous study, this modeling period was used to study the formation and control of aerosol nitrate and nitric acid. Comparison between model predictions and observations were quite good for not only ozone, but also the trace nitrogen containing pollutants such as NO₂, PAN and nitrate. Example comparisons of the predicted and observed ozone, PAN, NO₂, HNO₃ and aerosol nitrate are shown in Figures 3, 4, 5 and 6 for both the trajectory and airshed models.

Figure 7 shows the modeling regions used in this study, and the underlying 80 x 30 grid system used to develop inputs into the model. Meteorological, topographical and emission inputs were generated over the 400 km x 150 km system of 5 km x 5 km grids.

Emission inputs corresponding to two future years, 2000 and 2010, were used in this study. This is because there is an inevitable, and rather large, delay between the adoption of plan to use methanol fuel and the time when a significant fraction of the sources are actually converted. For example, about 10% of the vehicle fleet is replaced each year, and a significant fraction of the mobile source emissions are from vehicles over 10 years old. Years 2000 and 2010 were chosen because inventories for these years were developed for the Air Quality Management Plan (AQMP) process. These inventories should be more accurate than other forecasts, though this necessitated modeling MFV penetration beginning in 1990. While 1990 is too early to see significant numbers of MFVs (or FFVs) being brought into the vehicle fleet, the purpose of this assumption was to estimate the probable air quality impacts after a 10 year period of MFV penetration.

Emission inventories corresponding to the base cases for each year, and those to simulate the changes due to increased use of methanol, were constructed using detailed source emission compositions and levels. Emissions from on-road mobile sources were calculated by vehicle type, age and fuel, and accounted for the fraction of vehicle miles traveled following EMFAC procedures and the emission factors specified in Appendices 4.A through 4.F of the report. Emissions from other sources were, again, treated on a

O₃ AT RUBIDOUX, 31, AUGUST 1982

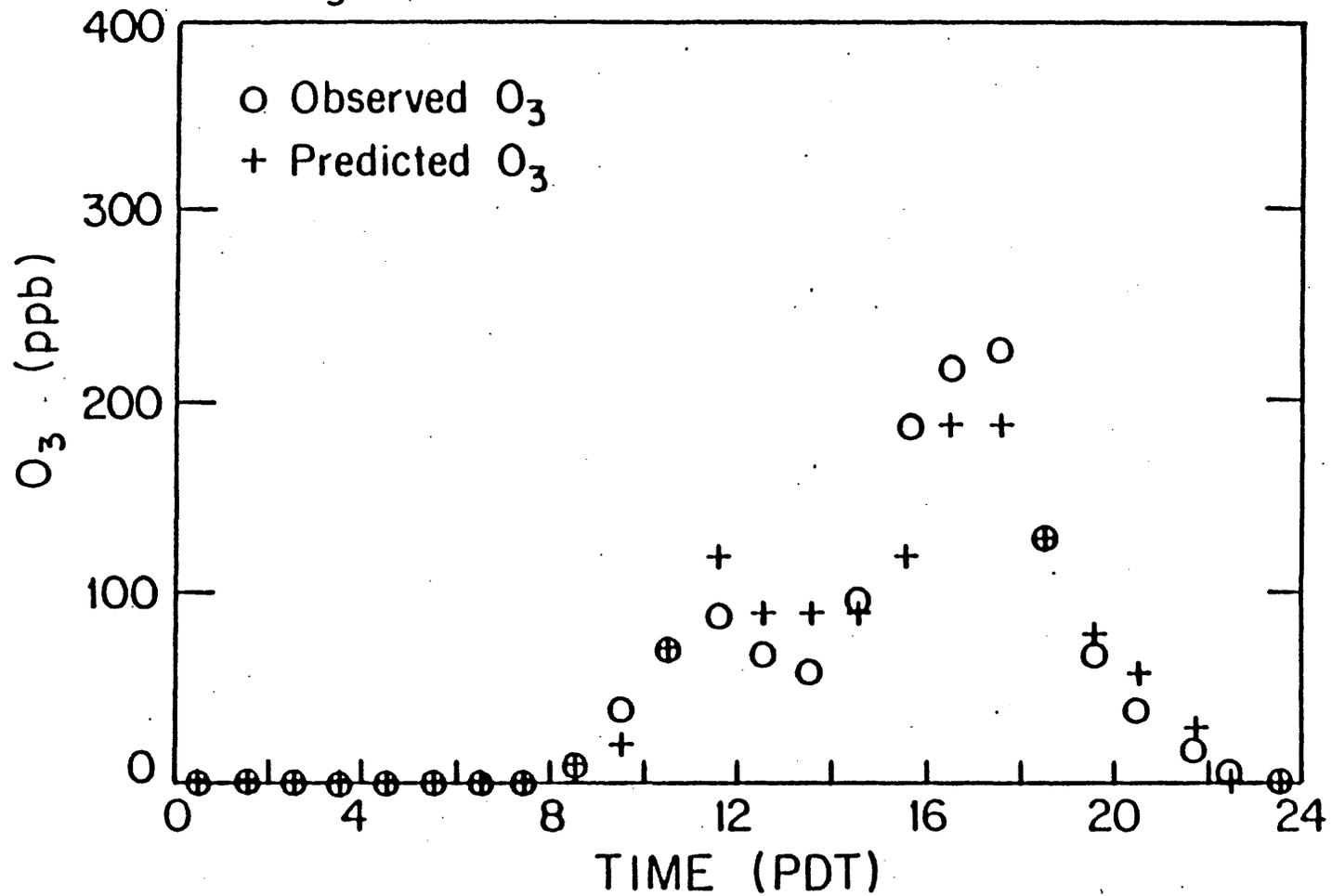


Figure 3 Observed and predicted O₃ at Rubidoux, CA, on 31, August, 1982, using the trajectory model.

TOTAL INORGANIC NITRATE ($\mu\text{g m}^{-3} \text{NO}_3^-$)

TOTAL INORGANIC NITRATE AT RUBIDOUX, 31, AUGUST, 1982

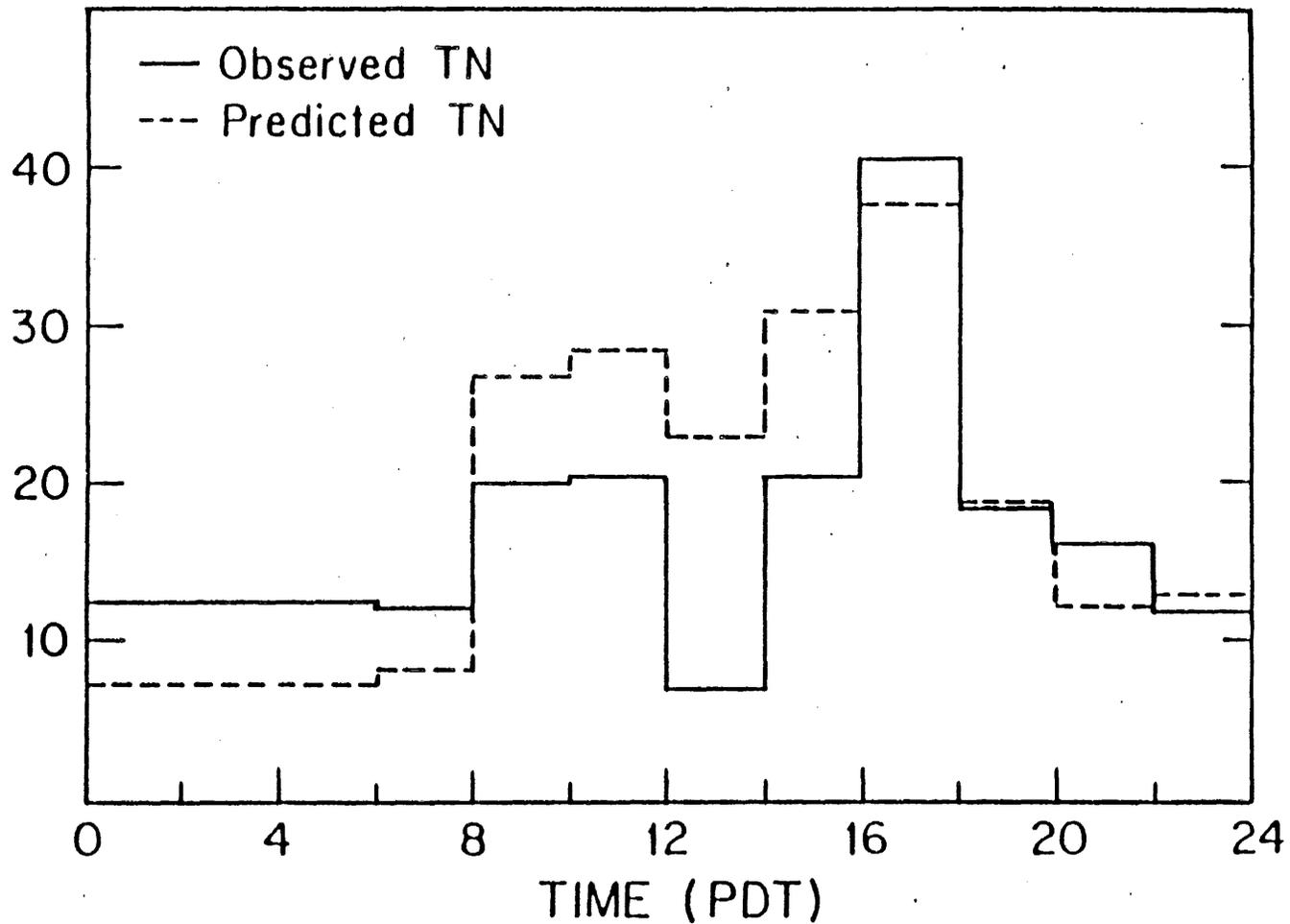


Figure 4 Observed and predicted total inorganic nitrate (TN = aerosol nitrate + nitric acid) at Rubidoux, CA, on 31, August, 1982, using the trajectory model.

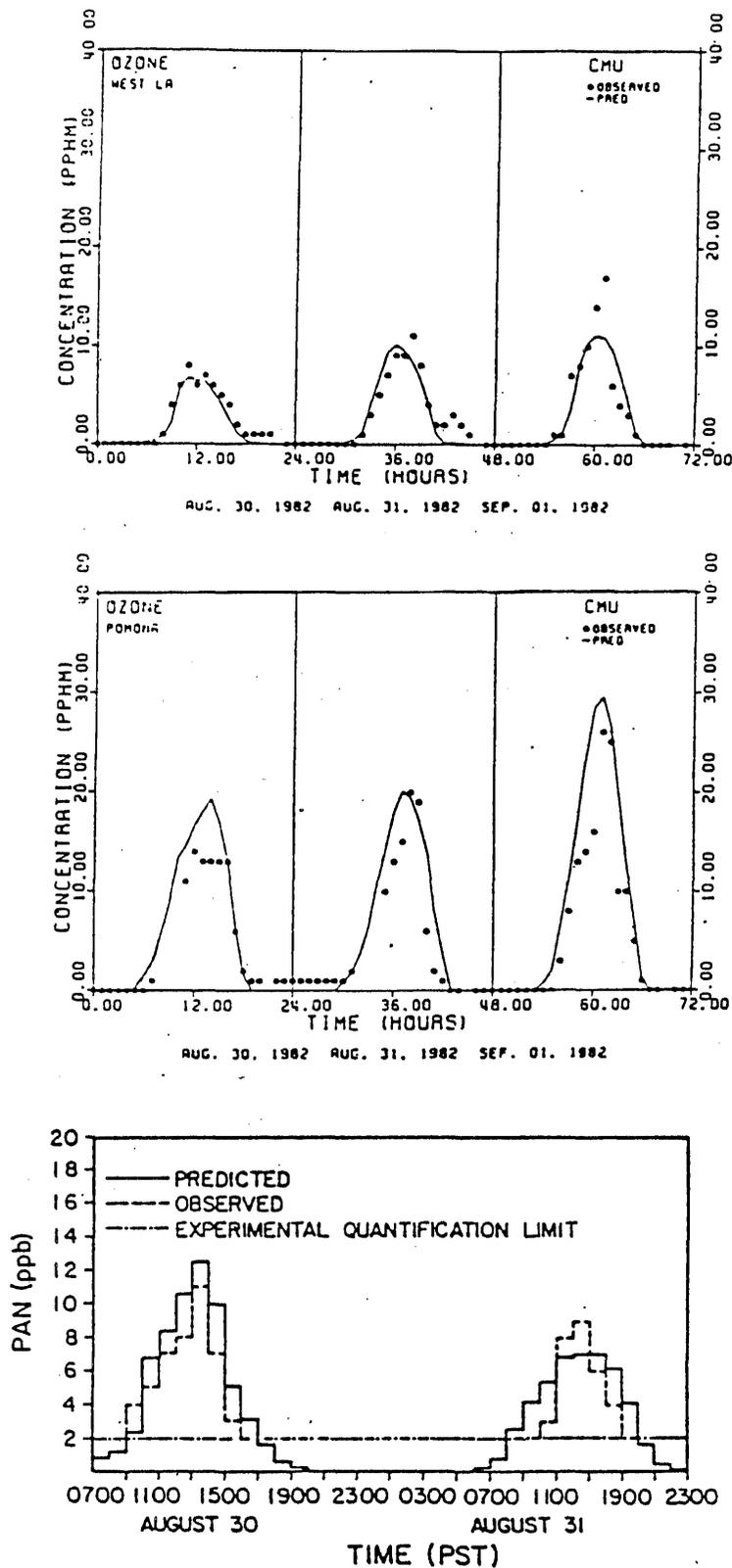


Figure 5 Comparison of predicted and observed ozone (a,b) and PAN (c) concentrations versus time for the 1982 period. (a) Ozone at West Los Angeles (b) Ozone at Pomona (c) PAN at Pasadena (for the first two days only).

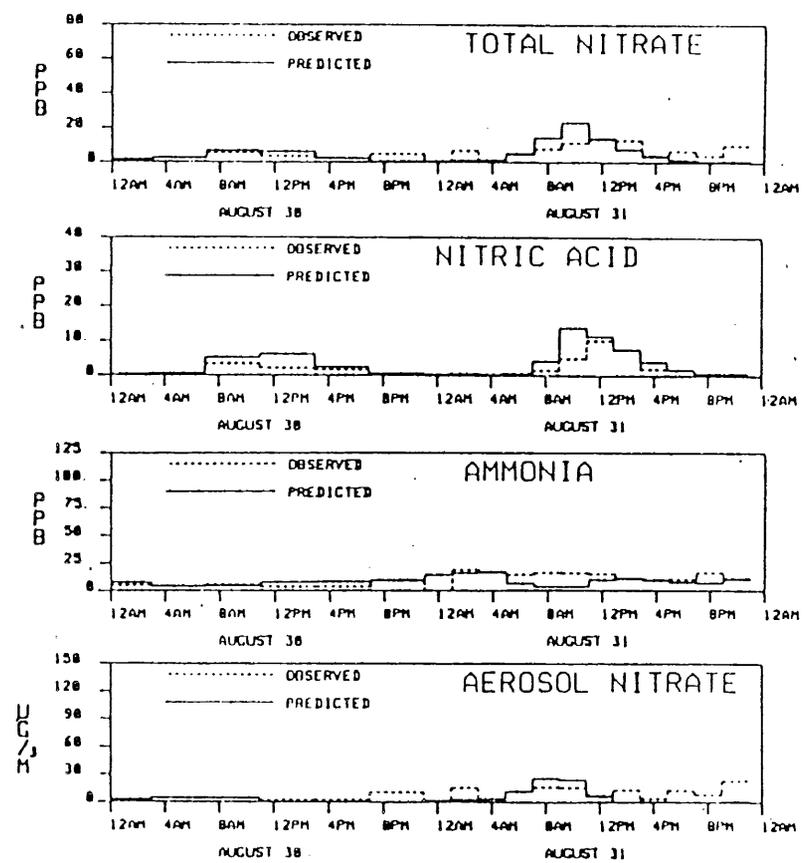
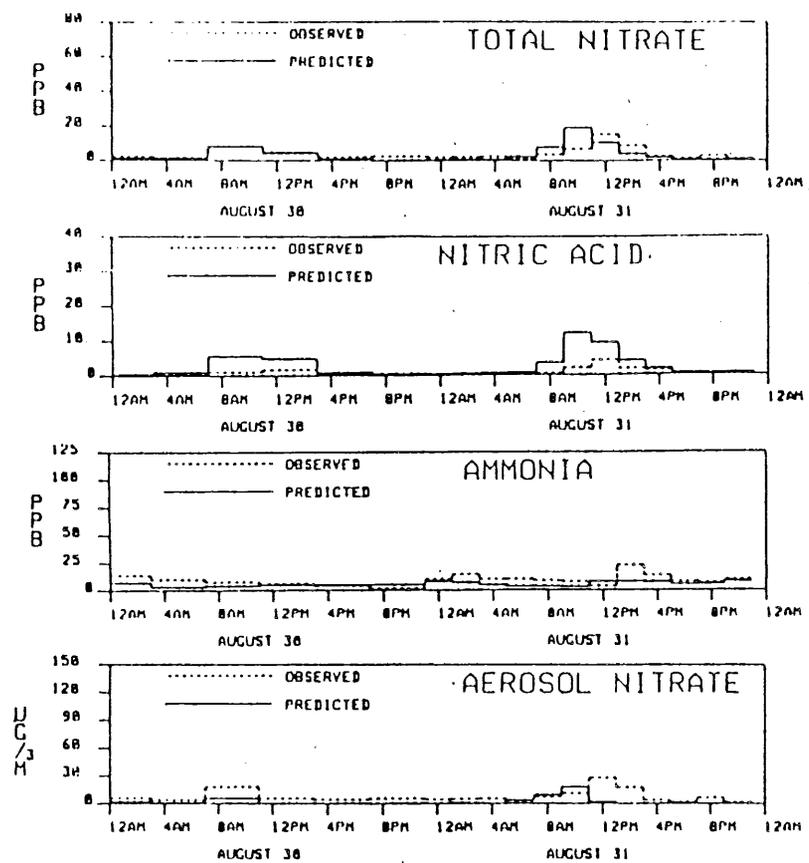


Figure 6 Comparison of predicted and observed concentrations of total nitrate, HNO₃, aerosol nitrate, and NH₃ on 30-31 August 1982. (a) Central Los Angeles (b) Anaheim.

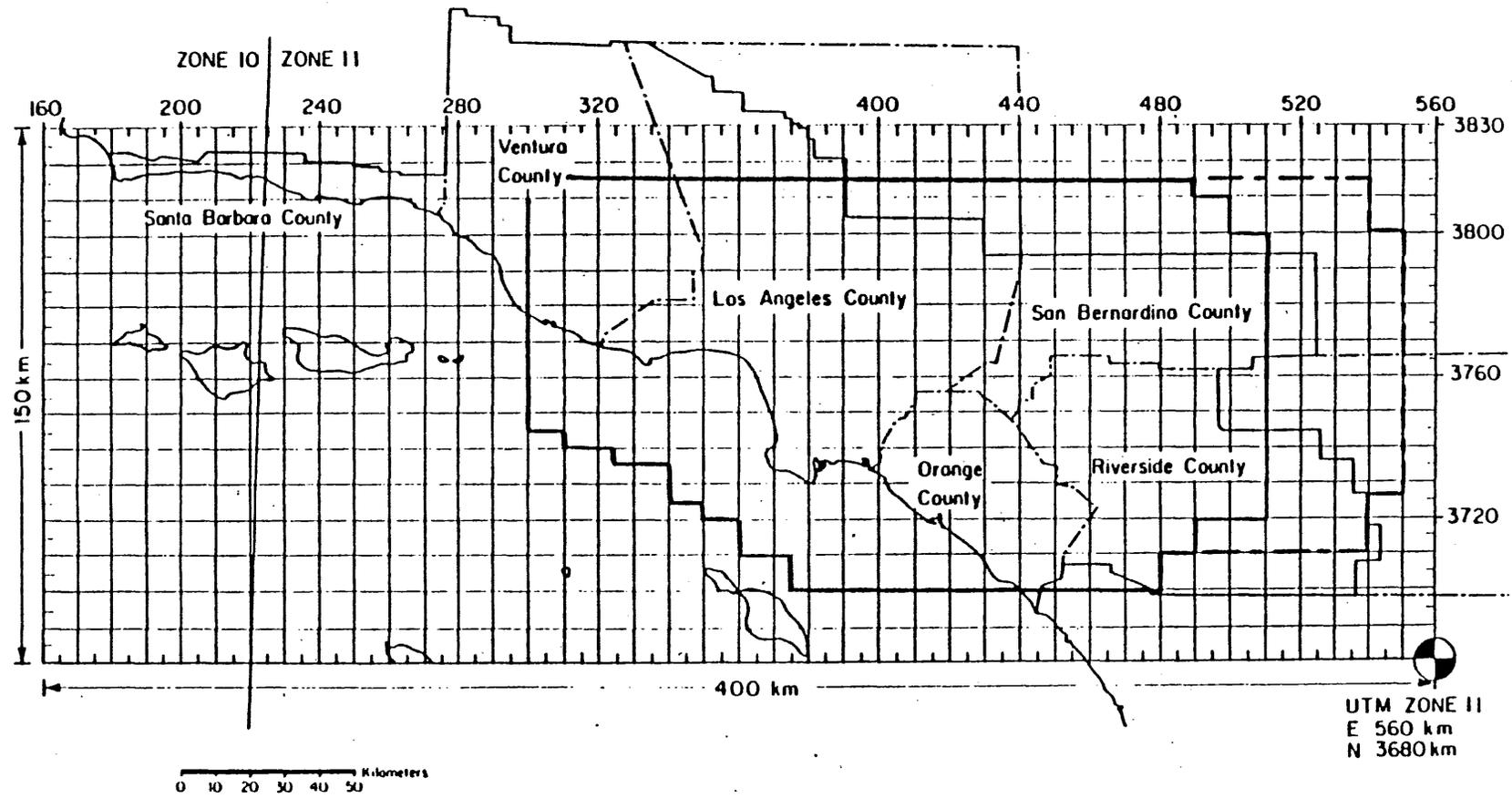


Figure 7 Gridded map of California's South Coast Air Basin (SoCAB), showing the regions used for airshed modeling, and the 5 km by 5 km grid system used for developing the spatially resolved emissions, meteorology and geographic fields. The heavy solid line (—) shows the boundary used for year 2000 air quality calculations, and the heavy dashed line (---) delineates the region used for year 2010 calculations.

detailed basis, accounting for the differences in energy content, vapor pressure, fuel composition and mode of emission (e.g., spillage vs. vapor displacement). This detail was used to insure the integrity and representativeness of the emission inputs.²

E4.1 Motor Vehicle Emission Rates

It was necessary, as part of this study, to estimate future vehicle emission rates for both MFVs and conventionally fueled vehicles (CFVs). This adds uncertainty to the calculations because the effectiveness of future technologies and the role of policy decisions on determining the rates are, themselves, uncertain. For example, EMFAC7C, the emission factors used for calculating on-road motor vehicle emissions from conventionally fueled vehicles in one set of model simulations assumed that light duty vehicles would emit 0.59 g mi^{-1} NMHC (in use) from the year 1990 on. However, CARB is considering tightening standards, reducing the corresponding emission rate to 0.36 g mi^{-1} in 1992 and 0.25 g mi^{-1} NMHC (in use) in 1995. A majority of the trajectory model simulations conducted used the 0.59 g mi^{-1} hydrocarbon (or methanol, in gms C) emission factor and, conversely, a majority of the airshed model simulations used the latter emission rates. While the latter may seem optimistic (for both CFVs and MFVs), this choice was made in response to the expected adoption of new control measures on gasoline and diesel fueled vehicles. Also, this provides a bracket to the expected impact of short term motor vehicle emission control impacts. If these levels are not achieved in practice, the apparent benefits (reduced ozone, aerosol, PAN, nitric acid) and problems (increased methanol) would be greater. The actual emission rates will be further dependent on the ability of industry to meet those standards, the effectiveness of the inspection and maintenance program, etc. In this project, both cases were studied to help estimate the role this change and the uncertainties involved in estimating future emissions would play on judging the effectiveness of utilizing methanol.

Estimating future emissions from MFVs is more problematic than for CFVs because MFVs represent an emerging technology. The decades of research that have gone into optimizing CFVs for fuel efficiency, power and, most importantly in this case, emissions are not present for MFVs. Neither does the detailed history of emission characteristics exist from which to extrapolate future emission rates. The little data that does exist is derived mainly from vehicles converted from those burning gasoline and does not represent the emission characteristics that would be expected from a system optimized for methanol use. Information available for designed systems is promising, though because of their young age it is difficult to extrapolate what the long term emission rates might be, due to factors such as catalyst endurance. Also, CARB is aggressively pursuing developing and testing technologies to clean the exhaust of MFVs which could drastically reduce emissions. This highlights the problems involved with estimating future emissions from a new technology, and the need to consider the uncertainties in those predictions.

Here, the strategy has been to use a broad range of emission rates to cover the range of future emissions. From the variety of simulations, it is then possible to interpolate to estimate the likely air quality resulting from a particular set of emission rates or mix of strategies. In this study, MFVs and gasoline fueled vehicles will achieve the same emission rates of NO_x , CO and NMHC on a year by year basis (See Appendices 4.A

² A recent CARB estimate indicates that the NO_x emission inventory used as part of this study may be 10 to 20% low (K. Wagner, personal communication, 1989). If this is true, the benefits of conversion to methanol would be greater. Likewise, recent tests indicate that the ROG losses from on-road vehicles may be greater than previously believed. If the excess emissions are significant, this would also increase the relative benefits of switching.

through 4.E). This would, for example, be driven by regulatory requirement. Similarly, the organic gas emission rates used for diesel-type MFVs and diesel-fueled vehicles are the same, though the NO_x emissions from methanol-fueled, heavy-duty vehicles are half that of the corresponding diesel-fueled vehicles, and particulate emissions from an MFV are assumed to be negligible.

This study has shown that ozone formation is relatively insensitive to methanol vapor emissions, though it is quite sensitive to HCHO emission. This led to paying particular attention in estimating HCHO emission rates. A range of HCHO emission rates were studied. In the trajectory modeling portion, exhaust HCHO emission rates were varied between 1% and 10%, by mass, of the exhaust NMHC. Most of the simulations corresponded to 4%. (This corresponds to a LDV emission range from 2.5 mg mi^{-1} to 59 mg mi^{-1} , with most using 24 mg mi^{-1} , depending on NMHC emission rate used.) Airshed modeling used HCHO emission rates from light duty vehicles ranging from 3 mg mi^{-1} to 55 mg mi^{-1} , with the default rate for most of the simulations being $15\text{-}27 \text{ mg mi}^{-1}$, depending on model year ($23\text{-}27 \text{ mg mi}^{-1}$ between 1990 and 1993, and $15\text{-}18$ from 1994 on). For comparison, HCHO emissions from a Crown Victoria on M100 were, about, 35 mg mi^{-1} , and $10\text{-}30 \text{ mg mi}^{-1}$ for a Toyota Camry on M85^{3,4}. A Toyota Carina, modified to reduce HCHO emissions, emitted between 9 and 19 mg mi^{-1} . A flexibly fueled Crown Victoria had HCHO emissions between 19 and 35 mg mi^{-1} . Further development of dedicated systems would be expected to decrease the emission rates. Thus, the little data that does exist can support the use of an exhaust emission rate of $15\text{-}27 \text{ mg mi}^{-1}$. Again, it is prudent to cover a spectrum of emission rates, both to assess the range of likely outcomes and to quantify the effect of changes in HCHO emissions. For this reason 55 mg mi^{-1} and 3 mg mi^{-1} HCHO emission rates were simulated. The latter corresponds to emitting slightly more HCHO than a similar calculation for CFVs, and might be realized through engine optimization and catalyst technology development. Furthermore, adoption of the 15 mg mi^{-1} HCHO standard should drive the technology development needed to meet the standard rates modeled.

A similar problem exists for estimating the composition of MFV emissions. Currently, methanol vehicles are being fueled primarily by M85, a blend of 85% (by volume) methanol and 15% premium unleaded gasoline. Pure methanol (M100) is not used as frequently because of technological and safety problems. It is not clear what the long term choice of fuel will be, so simulations were conducted studying both fuels. Emissions from M100 vehicles were modeled as being primarily methanol with formaldehyde levels discussed above. It is expected that some additive is necessary. The additive may be organic, in which case it would contribute to reactive organic gas (ROG) emissions at a rate depending on the concentration and composition. EPA³ and CARB⁴ results show that the non-methane hydrocarbon emissions from M100 fueled vehicles would be small. CARB found the NMHC exhaust fraction of an M100 vehicle to be 3% of the non-methane organic gas emissions. Thus, the actual exhaust of an M100 may be very slightly more reactive than as modeled.

The future composition of the non-methanol component of M85 is also undecided, and varies between the U.S. and Europe. The exhaust composition would be affected by the choice of additive. In this study, the exhaust from an M85 was set to be 50% methanol by mass, and 50% non-methanol reactive organics similar in composition to a light-duty, catalyst-equipped vehicle. If either the mass emission rate of non-methanol organic gases

³ Snow, et al. (1989) *J. Air Pollut. Control Assoc.*, 39, 48-54.

⁴ CARB (1989) Response to Sierra Research Report entitled Potential Emissions and Air Quality Effects of Alternative Fuels, El Monte, CA.

is less than 50%, or the additives and exhaust products are less reactive than CFVs, the reactivity of the exhaust would be less than as modeled. For example, in a recent study,³ emissions from an M85 Ford Escort had consistently less total hydrocarbon (THC) than methanol, usually with THC about one third of the methanol. Thus, using an exhaust composition of 50% methanol, 50% other organic, by mass, may overstate the reactivity of M85 exhaust. It was decided that this choice, and the choice of no non-methanol, non-formaldehyde organic in M100 exhaust bracketed the range of likely compositions. The future composition of the exhaust is likely in between, making the expected benefits from M85 greater than as modeled and benefits from M100 very slightly less.

In analyzing the results of the modeling, it is necessary to consider the outcome of the various simulations, and to avoid looking solely at any single simulation. For example, the 3 mg mi⁻¹ HCHO scenario represents how the use of MFVs would impact air quality in the long term after considerable technological advancement, similar to the advances resulting in emission controls on current vehicles. It is fully realized that this is not currently achieved, though, this represents one end of the spectrum. On the other hand, 55 mg mi⁻¹ HCHO is viewed as an upper bound, representing the other end. These extremes, along with the intermediate choices, allow for a greater understanding of the possible outcomes and the ability to interpolate between the cases studied. This is done in the summary. It would be imprudent to base any decision, or review, on an extreme case or any single case. Again, because of the uncertainties in estimating future emissions, this project has studied a spectrum of possible emission levels and compositions, bracketing the likely outcomes.

As an example of the use of multiple scenarios across a range of compositions, it is possible that the conversion to using methanol fuel would be facilitated by first introducing flexible-fueled vehicles (FFVs). Depending on the mode of operation and the technological optimization for reducing emissions, the air quality impact can be estimated by interpolating between the base cases and the M85 case. If the emissions are low in hydrocarbon, the M100 calculations can be used. In essence, the cases chosen can be viewed as a parametric analysis of the sensitivity of air quality to the formaldehyde and non-methane hydrocarbon content of the emissions. The detail in treating MFV and CFV emissions has been used to achieve as accurate a projection of emissions from affected individual sources as possible, and to facilitate further analysis.

E5 Trajectory Model Simulation of Methanol Fuel Use

Trajectory modeling of the impact of methanol fuel, the second tier of the photochemical modeling program, was conducted for three reasons (see, also, Table 1). Because the trajectory model is relatively fast computationally, a large number of simulations can be conducted to test the sensitivity of model components to inputs. A second reason was to further test the ability of the Extended Caltech Mechanism to describe atmospheric chemistry by simulating pollutant dynamics under actual atmospheric conditions, and comparing those results with observations and a second mechanism. Finally, a large number of methanol fuel use scenarios can be run to develop preliminary methanol use - air quality relationships, suggesting particularly insightful calculations for further study using the more computationally intensive airshed model. An added benefit of these calculations is to allow more direct interpolation of the results of the limited number of airshed simulations.

Trajectory models, however, suffer from inherent limitations in their formulation. First, since they computationally track the formation of pollutants in a single air parcel, they cannot show the basinwide impacts of changing emissions. A tremendous number of

simulations would be required, negating their computational speed advantage. Two other limitations are that they neglect horizontal wind shear and horizontal diffusion. Neglecting these two processes limits the duration over which trajectory models may be applied. During the period modeled, vertical wind velocity measurements indicated limited shear at night, allowing for multiday simulations.

Three trajectories were identified to test the impact of methanol use in the SoCAB. The trajectories were chosen to terminate in San Bernardino, Norco and Pasadena. Trajectory paths were calculated backwards in time to a starting location over the Pacific Ocean. Emissions in the trajectory modeling calculations corresponded to the Year 2000, and perturbations of that inventory simulated the use of methanol or other controls. Over 150 calculations, covering over 50 scenarios, were conducted to explore how pollutant levels in the SoCAB would be affected by, among other issues, varying levels of methanol fuel use in mobile sources, different exhaust and fuel compositions, and higher deterioration rates and deposition rates. These tests included a parametric comparison of the impacts of emission changes, both individually and by combinations of control levels on mobile and stationary sources. Calculations showed that conversion to methanol would lower ozone and PAN at all three sites, and that HCHO concentrations may increase or decrease slightly. The extent of the ozone reduction was highly dependent on the location in the Basin.

In the Eastern Basin, i.e., at the termination of the Norco and San Bernardino trajectories, ozone formation was found to be NO_x -limited. In this case ozone formation was more sensitive to the availability of NO_x , and was less sensitive to ROG emissions. Methanol substitution still lowered ozone almost as effectively as removing the fraction of ROG being replaced. Tests showed that even over three-day simulations, methanol emissions led to little increase in ozone formation, as compared to removing mobile source ROG emissions. PAN was also lower in the methanol cases. Ambient formaldehyde levels stayed within a few ppb of the Base calculation, and were decreased if methanol fueled vehicles emit 4% HCHO (as a percent of ROG) or less. The reason for the decrease in ambient HCHO levels in contrast to increased HCHO emission is because atmospheric production from other organic gases is less when methanol is used.

Ozone at Pasadena responds very differently to emission changes than ozone at the Eastern Basin sites. In this case Pasadena, like most central basin sites, is not NO_x limited, and is more sensitive to ROG controls and the use of methanol. Predicted ozone decreased 19% (4% HCHO in exhaust) when the use of M100 fueled vehicles was simulated. HCHO dropped 10%, and PAN was decreased 37%. Increasing the fraction of HCHO in the exhaust from 4% to 10% (by mass) decreased the ozone reduction by 2%.

In all three trajectories, use of M100 fuel was predicted to be substantially better than M85. At Pasadena, the ozone reduction calculated for M85 was 45% of that for M100 use.

If the entire fleet met an 0.25 g mi^{-1} ROG and 0.20 g mi^{-1} NO_x in-use standard (called here, advanced technology), ozone was predicted to drop between 6% and 13%. The use of comparable MFVs resulted in further decreases of up to 30%.

A series of sensitivity calculations were performed with the trajectory model to determine how the results depend on inputs and the chemical mechanism used. Of interest, ozone levels were reduced slightly when emissions were delayed two hours. Ozone levels were insensitive to initial conditions and the assumed HCHO deposition rate.

Ozone levels in the Eastern SoCAB increased as the O_3 deposition rate was decreased. Switching chemical mechanisms changed the predicted peak just over 10%, but showed the same general response to emission controls.

Results from the trajectory modeling gave preliminary evidence that methanol use would be beneficial during multiday smog episodes. Ozone and PAN were both reduced, and predicted HCHO levels increased or decreased a few ppb. These calculations suggested a number of issues to be investigated further using the grid-based airshed model, including the difference in the effectiveness of M100 vs M85 fuel, the comparative benefits of low emitting methanol and conventional vehicles and the impact of varying levels of formaldehyde in the exhaust of MFVs.

E6 Airshed Modeling

The final step of the three-tiered photochemical modeling program involved using the grid-based, Eulerian airshed model to examine the basinwide impacts of methanol use on photochemical pollutants. While computationally intensive, the CIT airshed model contains detailed descriptions of the atmospheric chemistry and physics and enjoys few limitations. In previous evaluations, and those conducted as part of this project, the CIT model was shown to accurately follow the evolution of photochemical pollutants, including trace nitrogenous pollutants as is shown in Figures 4 through 6.

After evaluation, a series of emission control and sensitivity calculations were performed using emissions corresponding to the Years 2000 and 2010. Thirty five calculations, described in Table 3, were designed to address the issues identified during the course of the project and to document the sensitivity of the model to boundary and initial conditions, and emissions. Choice of emission characteristics is explained in E4.A, above, and detailed in appendices 4.a through 4.F of the main report. Each scenario followed the evolution of the pollutants over the three-day period. Predicted pollutant concentrations and exposures are listed in Tables 4 through 7, and shown graphically in Figures 8 through 16.

Tables 4 through 7 characterize the predicted pollutant concentrations using a variety of metrics, giving a more complete view of the air quality changes. First, the peak concentrations of O_3 , NO_2 , HCHO, PAN and HNO_3 , predicted within the Basin, are given. This is the extreme value, and may occur anywhere in the modeling region, even in relatively unpopulated regions. In many of the Year 2010 simulations the peak ozone occurs in the Far Eastern Basin, where the population density is low. Two other parameters are used to show the basinwide responses. First, the average concentration, \bar{c} is the average of the predicted concentrations over time and space:

$$\bar{c} = \frac{1}{AT} \int_T \int_A c(\bar{x}, t) d\bar{x} dt$$

where T corresponds to the 24 hour period encompassing the third day of the simulation, and A is the area of the modeling region.

A second measure is related to the co-occurrence of high pollutant concentration and people. In this study it is termed the "exposure" and is found by multiplying the predicted concentration by the population residing in that area. The exposure in each grid of the modeling region is summed to get the basinwide exposure. In this case, the exposures, E, were found as:

Table 3a List of Emissions Scenarios, Year 2000

Scenario Name	Scenario Description*
BASE1A	Original projected year 2000 emissions inventory. (4.A-1)
BASE1	Base case emissions. Mobile emissions reduced from those in EMFAC7C Appendices. (4.A)
NO MOBILE	Base case emissions (BASE1) minus emissions from: petroleum refining operations, retail gasoline and diesel distribution, all on-road sources except motorcycles as well as mobile off-road farm equipment, construction equipment, locomotives, utility vehicles, and recreational vehicles except motorcycles.
ADV CONV	Full penetration of low emitting CFVs into on-road mobile sources. All others as per BASE1. These vehicles have emissions matching in-use for year 2000.(4.C)
ADV METH	Full penetration of low emitting MFVs into on-road mobile sources. Convertible off-road mobile sources (NO MOBILE) also switched to methanol fuel. Gasoline retailing converted to methanol. (4.D)
STD M100	100% penetration of MFVs into on road mobile sources from 1990 to 2000. Similar conversion for off-road mobile sources and retail gasoline operations as described in ADV METH. HCHO emissions from LDVs 15-27 mg/mi
FULL METH	Same as ADV METH plus conversion to methanol of utility boilers, stationary industrial IC Engines, and non-refinery industrial boilers.
BASE-ROG	Same as BASE1 minus ROG emissions of all sources listed in NO MOBILE.
BASE-NOx	Same as BASE1 minus NOx emissions of all sources listed in NO MOBILE. (4.A)
STD M85	Same as STD M100 except fuel used is M85 instead of M100.
METH 50	Same as STD M100 except only 50% penetration of on-road mobile sources from 1990 to 2000.
HIGH FORM	Same as STD M100 except nominal HCHO emissions are increased from 15 mg/mi to 55 mg/mi. (4.B)
ADV METH/NO ROG	Same as ADV METH minus methanol and HCHO emissions of all sources converted to methanol. (4.D)
*Letters in parentheses refer to Appendices describing emissions factors or emissions reductions.	

Table 3b List of Emissions Scenarios, Year 2010

Scenario Name	Scenario Description
BASE 2010	Original projected year 2010 inventory.
ADV CONV 2010	Full penetration of low emitting CFVs into on-road mobile source's. See Appendix 4.C for emissions. (e. g. LDA 0.25 g/mi ROG, 0.2 g/mi NOx.) Other sources unperturbed.
ADV METH 2010	Full penetration of low emitting M100 MFVs into vehicle fleet. MFVs meet proposed year 2000 standard. Other sources unperturbed.(4.D)
STD M100 2010	100% penetration of standard technology M100 vehicles into light and medium duty vehicle fleet from 1990 on. Methanol emissions, on a carbon mass, set to same rate as used for CFVs in the base case. HCHO emissions from LDAs set to 15-23 mg/mi. Service station emissions adjusted: refinery, heavy, and medium duty vehicle emissions unaltered. (4.C)
STD M85 2010	Same as STD M100 2010, except that M85 vehicles are used. Exhaust emissions assumed to be 50% methanol, 50% gasoline components, with HCHO emissions at 15-23 mg/mi. (4.E)
NO MOBILE 2010	On-road mobile source emissions removed from base 2010 inventory.
NO MOBILE ROG 2010	BASE 2010 calculation with the ROG fraction of on-road emissions removed.
ADV LMD 2010	Advanced conventionally fueled vehicles, except heavy duty vehicle emissions are unaltered. (4.C)
ADV LMD NO ROG 2010	Similar as above, except ROG component of light and medium duty vehicles is removed. All other sources unaffected.
ADV CONV/LO IC 2010	Similar to ADV CONV 2010, except that initial and boundary conditions were lowered to clean background levels.
ADV METH/LO IC 2010	Similar to ADV METH 2010, except that initial and boundary conditions were set to clean, background levels.
M85 LO IC 2010	Similar to STD M85 2010, except that initial conditions and boundary conditions were set to clean, background levels.

Table 3c Evaluative and Diagnostic Calculations	
Scenario Name	Scenario Description
1982	Simulation using base 1982 emissions used for performance evaluation.
Year 2000	
LO IC	
NO EM	
NO EM/LO IC	
NO ROG	
NO ROG/LO IC	
2000X	BASE1 calculation with expanded modeling region.
Year 2010	
NO ROG/LO IC 2010	Same as NO ROG/LO IC above, except that the 2010 inventory is used at the base.
LO IC 2010	Same as LO IC above, except that the base inventory is for 2010.
CLEAN BC 2010	Boundary conditions over Pacific Ocean set to very clean conditions. All other inputs unaltered.
LO BC/LO IC 2010	BASE 2010 conditions with initial conditions and western boundaries set to clean levels.

Table 4 Ozone Concentrations and Exposures in the Year 2000

SCENARIO	CONCENTRATIONS		EXPOSURES						
	MAX. ¹ (ppm)	AVG. ² (ppm)	Person ppm hours ³ ([O3] > x)				Person hours ⁴ ([O3] > x)		
			x = 0.00 (1000s)	x = 0.12 (1000s)	x = 0.20 (1000s)	x = 0.30 (1000s)	x = 0.12 (1000s)	x = 0.20 (1000s)	x = 0.30 (1000s)
BASE1A	0.26979	0.04504	12,568	7,314	2,586	0	41,348	11,690	0
BASE1	0.26114	0.04444	12,459	7,080	2,171	0	40,683	9,902	0
NO MOBILE	0.20631	0.04081	12,486	5,384	58	0	35,391	284	0
ADV CONV	0.24565	0.04346	12,506	6,655	1,392	0	39,647	6,509	0
ADV METH	0.22317	0.04053	11,707	5,655	352	0	35,769	1,688	0
STD M100	0.22343	0.04055	11,725	5,673	364	0	35,848	1,747	0
FULL METH	0.21907	0.04042	11,805	5,626	241	0	35,948	1,163	0
BASE-ROG	0.22760	0.03833	9,819	4,449	462	0	27,878	2,236	0
BASE-NOx	0.21532	0.04234	14,432	6,837	131	0	44,598	636	0
METH 50	0.25025	0.04280	12,015	6,530	1,483	0	38,935	6,902	0
STD M85	0.24479	0.04174	11,649	6,167	1,260	0	37,007	5,909	0
HIGH FORM	0.24199	0.04149	11,579	6,070	1,108	0	36,660	5,202	0
ADV METH/NO ROG	0.21501	0.03962	11,192	5,153	217	0	33,091	1,047	0
SC1982	0.32709	0.05713	14,615	9,520	4,545	175	50,757	19,328	575
DIAGNOSTIC SCENARIOS									
NOEM	0.18483	0.02552	7,836	368	0	0	2,621	0	0
NO ROG	0.19081	0.02694	6,295	1,140	0	0	7,955	0	0
NO ROG/LO IC	0.16609	0.02106	4,990	244	0	0	1,843	0	0
LO IC	0.25428	0.04129	12,582	6,680	697	0	41,135	3,266	0
NO EM/LO IC	0.13919	0.02186	6,955	17	0	0	129	0	0

1 Maximum species concentration predicted within the modeling region.
 2 Average species concentration throughout the modeling region for the day.
 3 Exposure above cutoff, see Eqn. 1 (population x concentration x hours)
 4 Exposure above cutoff, see Eqn. 2 (population x hours)

Table 5 Concentrations and Exposures of Pollutant Species in the Year 2000

SCENARIO	NO2			HCHO			PAN			HNO3		
	MAX. ¹ (ppm)	AVG. ² (ppm)	EXP. ³ (1000s)	MAX. (ppb)	AVG. (ppb)	EXP. (1000s)	MAX. (ppb)	AVG. (ppb)	EXP. (1000s)	MAX. (ppb)	AVG. (ppb)	EXP. (1000s)
BASE1A	0.206	0.021	13,959	27.6	5.5	2,439	16.8	2.6	748	26.4	3.3	1,370
BASE1	0.192	0.020	13,201	29.7	5.8	2,779	15.2	2.5	722	24.5	3.1	1,317
NO MOBILE	0.090	0.010	7,005	23.7	3.9	1,578	14.0	2.0	689	16.9	2.0	895
ADV CONV	0.153	0.016	11,124	27.1	4.8	2,073	15.0	2.4	736	21.5	2.7	1,168
ADV METH	0.114	0.014	9,684	29.2	4.9	2,320	11.1	1.8	559	18.5	2.3	938
STD M100	0.125	0.014	9,687	28.9	5.0	2,326	11.1	1.8	562	18.5	2.3	938
FULL METH	0.111	0.014	9,239	28.7	4.9	2,257	11.5	1.8	565	18.1	2.2	896
BASE-ROG	0.155	0.019	11,964	30.9	4.3	1,752	11.2	1.7	447	23.3	2.9	1,117
BASE-NOx	0.092	0.009	6,828	29.5	5.1	2,550	15.9	2.0	863	15.9	1.7	715
METH 50	0.152	0.019	12,753	26.7	5.6	2,656	12.0	2.1	632	22.8	2.9	1,156
STD M85	0.164	0.019	12,411	27.7	5.4	2,551	11.8	2.0	590	22.6	2.9	1,134
HIGH FORM	0.170	0.018	12,142	35.0	6.1	3,203	11.5	1.9	564	22.3	2.8	1,118
ADV METH/NO ROG	0.107	0.014	9,588	30.4	4.1	1,750	10.3	1.7	530	18.2	2.3	928
SC1982	0.338	0.031	20,175	50.6	8.4	4,062	28.4	3.9	1,033	69.5	5.0	2,045
DIAGNOSTIC SCENARIOS												
NOEM	0.013	0.001	140	8.0	1.9	537	8.7	0.6	146	7.3	0.6	185
NOROG	0.087	0.017	9,103	10.7	2.6	824	8.5	0.9	173	25.2	2.7	933
NO ROG/LO IC	0.088	0.017	8,888	10.6	2.3	747	8.5	0.6	123	25.9	2.6	905
LO IC	0.181	0.021	11,630	38.0	6.0	2,490	16.9	2.2	728	31.5	3.0	1,137
NO EM/LO IC	0.013	0.001	124	6.8	1.6	475	8.5	0.4	107	4.3	0.5	161

1 Maximum species concentration predicted within the modeling region.

2 Average species concentration throughout the modeling region for the day.

3 Population exposure within the SoCAB as defined in Eqn. 1 (population x concentration x hours)

Table 6 Ozone concentrations and Exposures in the Year 2010

SCENARIO	CONCENTRATIONS		EXPOSURES						
	MAX. ¹ (ppm)	AVG. ² (ppm)	Person ppm hours ³ ([O3] > x)				Person hours ⁴ ([O3] > x)		
			x = 0.00 (1000s)	x = 0.12 (1000s)	x = 0.20 (1000s)	x = 0.30 (1000s)	x = 0.12 (1000s)	x = 0.20 (1000s)	x = 0.30 (1000s)
BASE 2010	0.32149	0.05159	15,264	9,840	5,159	108	50,989	21,473	353
NO MOBILE 2010	0.28045	0.04644	15,154	7,804	1,950	0	46,412	8,860	0
NO MOBILE ROG 2010	0.32188	0.04804	13,082	7,782	3,609	83	42,043	15,242	272
ADV CONV 2010	0.30265	0.04927	15,111	8,906	3,668	1	48,650	15,884	4
ADV METH 2010	0.28506	0.04611	14,019	7,651	2,365	0	43,947	10,568	0
STD M100 2010	0.30788	0.04799	13,470	7,976	3,823	9	43,101	16,389	29
STD M85 2010	0.30853	0.04928	14,266	8,700	4,234	9	46,482	17,964	29
ADV LMD 2010	0.29846	0.04891	14,703	8,656	3,807	0	47,176	16,481	0
ADV LMD NO ROG 2010	0.30849	0.04676	12,770	7,303	3,259	9	40,356	14,086	29
ADV CFV/LO IC 2010	0.26578	0.04267	13,014	6,985	1,202	0	41,970	5,485	0
ADV MFV/LO IC 2010	0.25600	0.04133	12,924	6,683	844	0	40,920	3,888	0
M85 LO IC 2010	0.28312	0.04223	12,176	6,613	1,653	0	38,795	7,495	0
DIAGNOSTIC SCENARIOS									
CLEAN BC 2010	0.32201	0.04925	13,885	8,373	4,392	78	43,513	18,091	257
LO BC/LO IC 2010	0.30553	0.04785	13,604	8,093	4,040	9	42,834	16,991	29
NO ROG/LO IC 2010	0.19049	0.01527	2,498	14	0	0	107	0	0
LO IC 2010	0.31258	0.04617	14,051	8,836	3,471	37	48,757	15,331	120

1 Maximum species concentration predicted within the modeling region.

2 Average species concentration throughout the modeling region for the day.

3 Exposure above cutoff, see Eqn. 1 (population x concentration x hours)

4 Exposure above cutoff, see Eqn. 2 (population x hours)

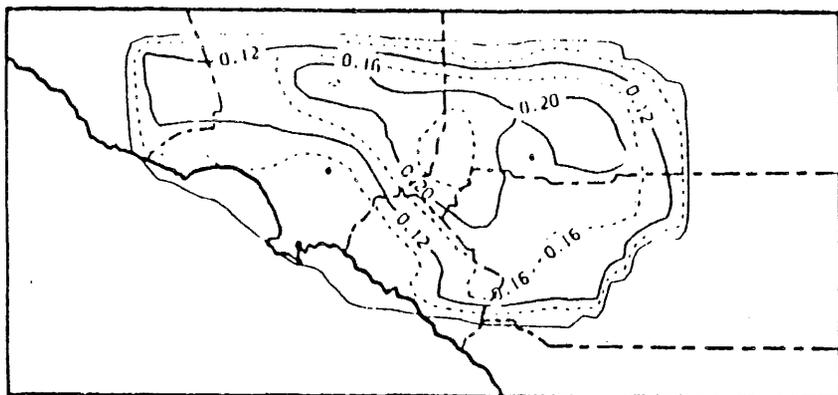
Table 7 Concentrations and Exposures of Pollutants Species in the Year 2010

SCENARIO	NO2			HCHO			PAN			HNO3		
	MAX. ¹ (ppm)	AVG. ² (ppm)	EXP. ³ (1000s)	MAX. (ppb)	AVG. (ppb)	EXP. (1000s)	MAX. (ppb)	AVG. (ppb)	EXP. (1000s)	MAX. (ppb)	AVG. (ppb)	EXP. (1000s)
BASE 2010	0.222	0.022	17,485	27.2	6.0	3,071	21.1	3.1	952	31.3	3.7	1,747
NO MOBILE 2010	0.122	0.011	9,511	23.0	4.5	2,082	18.7	2.4	898	18.1	2.3	1,163
NO MOBILE ROG 2010	0.191	0.021	16,461	40.0	4.9	2,232	19.9	2.6	688	31.5	3.7	1,691
ADV CONV 2010	0.177	0.017	13,828	24.0	5.3	2,582	19.6	2.8	924	23.8	3.0	1,467
ADV METH 2010	0.158	0.015	12,476	25.4	5.3	2,588	15.8	2.2	713	21.0	2.7	1,219
STD M100 2010	0.180	0.021	16,338	29.5	6.6	3,478	16.4	2.3	643	30.0	3.6	1,557
STD M85 2010	0.184	0.021	16,775	28.8	6.4	3,328	17.0	2.5	755	29.5	3.6	1,572
ADV LMD 2010	0.193	0.019	15,096	24.8	5.5	2,726	16.3	2.5	802	25.6	3.2	1,419
ADV LMD NO ROG 2010	0.199	0.021	16,171	41.3	5.1	2,322	16.7	2.3	617	29.9	3.6	1,530
ADV CFV/LO IC 2010	0.146	0.016	13,240	23.8	4.5	2,274	15.7	2.0	670	24.4	3.0	1,460
ADV MFV/LO IC 2010	0.157	0.015	12,209	27.8	4.7	2,441	13.7	1.7	607	20.9	2.6	1,204
M85 LO IC 2010	0.174	0.021	15,971	29.0	5.5	2,982	13.8	1.8	539	29.9	3.6	1,545
DIAGNOSTIC SCENARIOS												
CLEAN BC 2010	0.197	0.021	16,623	27.1	5.6	2,770	20.6	2.8	787	31.0	3.7	1,727
LO BC/LO IC 2010	0.185	0.021	16,561	27.1	5.5	2,747	18.5	2.6	753	30.7	3.7	1,721
NO ROG/LO IC 2010	0.088	0.017	11,117	8.0	1.4	467	8.5	0.4	36	24.0	2.4	896
LO IC 2010	0.225	0.022	17,147	27.8	5.4	2,903	19.4	2.4	805	30.8	3.7	1,737

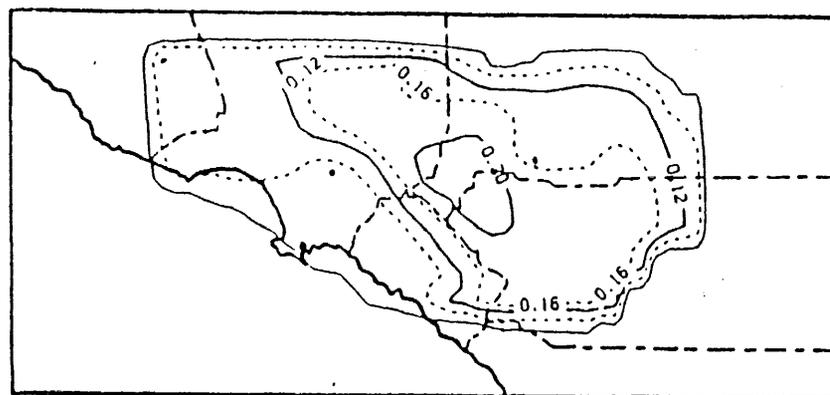
1 Maximum species concentration predicted within the modeling region.

2 Average species concentration throughout the modeling region for the day.

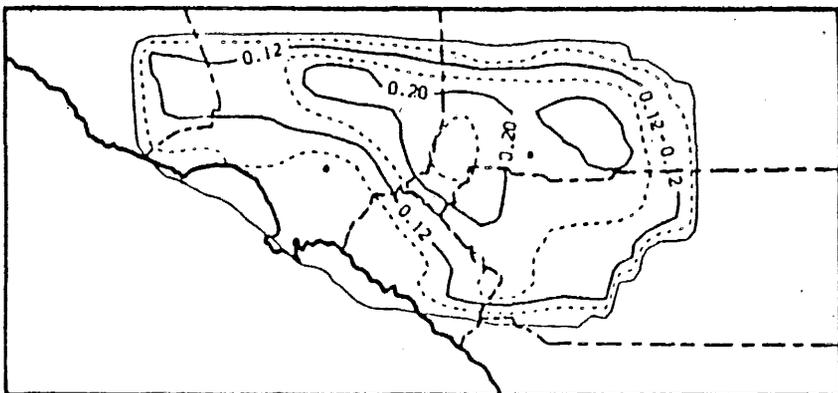
3 Population exposure within the SoCAB as defined in Eqn. 1 (population x concentration x hours).



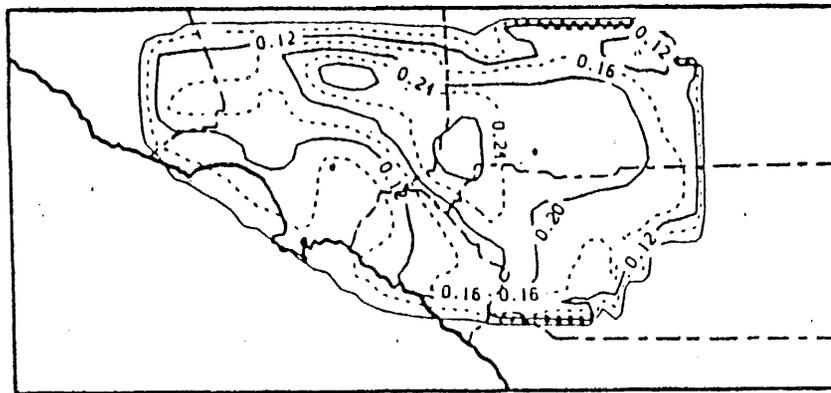
a) BASE1A



c) LO IC

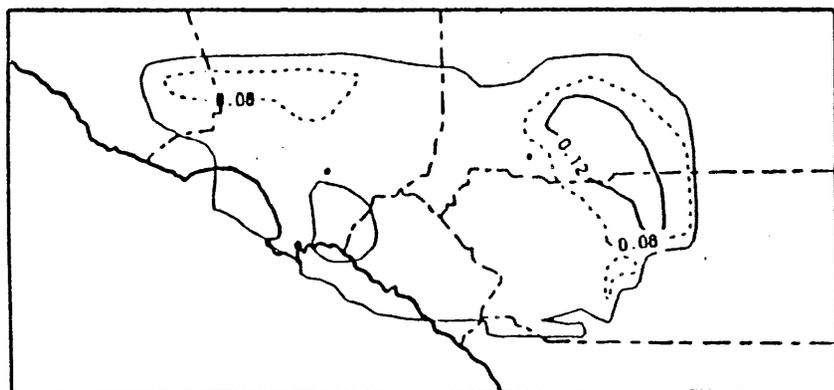


b) BASE1

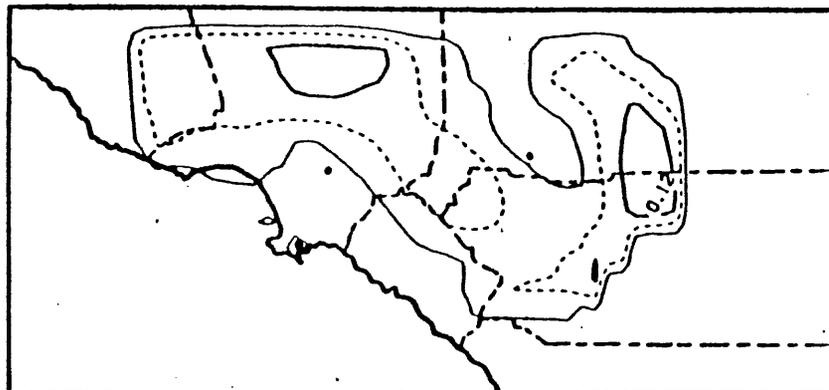


d) 1982

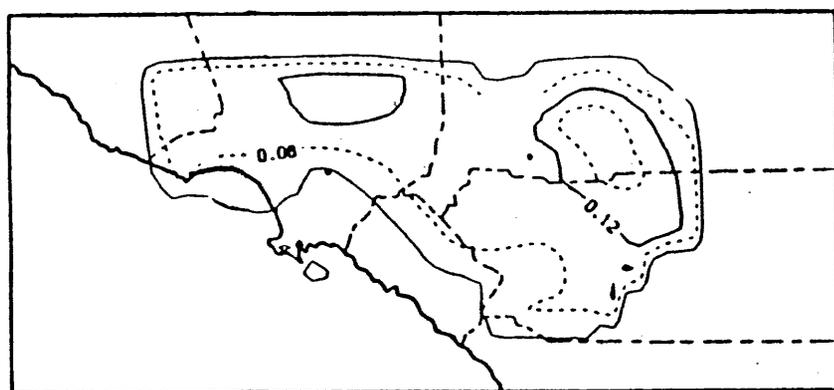
Figure 8 Spatial Distribution of Ozone at 1:00 pm on the Third Day of the Simulation. Ozone isopleths are shown at 4 ppbm intervals. a) BASE1A; b) BASE1; c) LO IC; d) 1982.



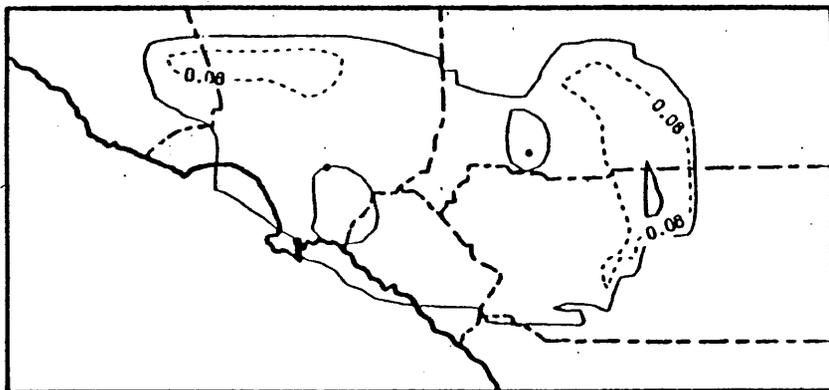
(a)



(c)

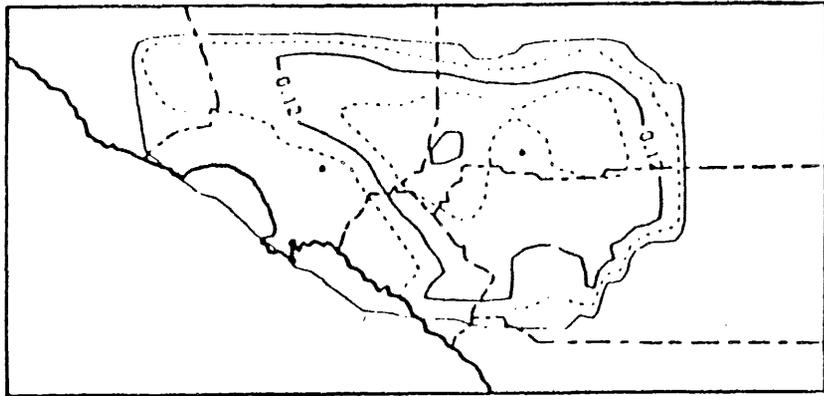


(b)

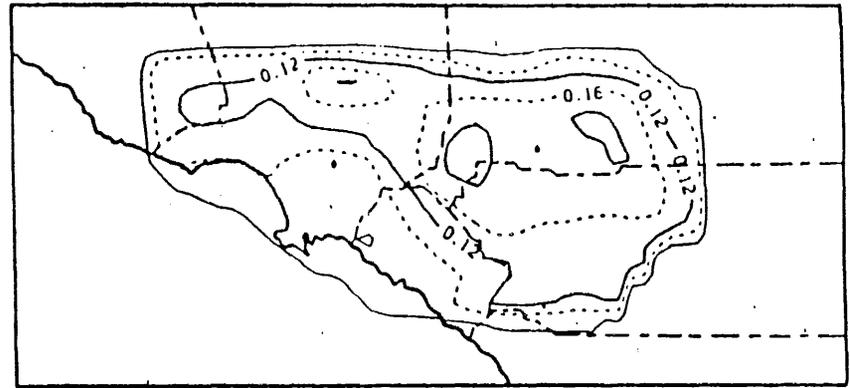


(d)

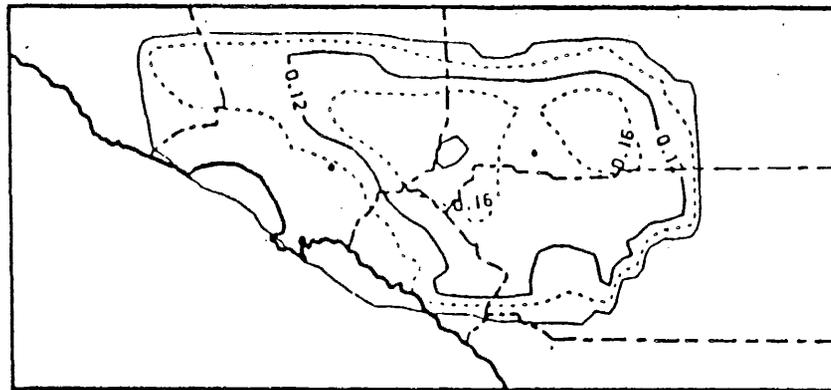
Figure 9 Spatial Distribution of Ozone at 1:00 pm on the Third Day of the Simulation. Ozone isopleths are shown at 4 pphm intervals. a) NO EM; b) NO ROG; c) NO ROG/LO IC; d) NO EM/LO IC.



(a)

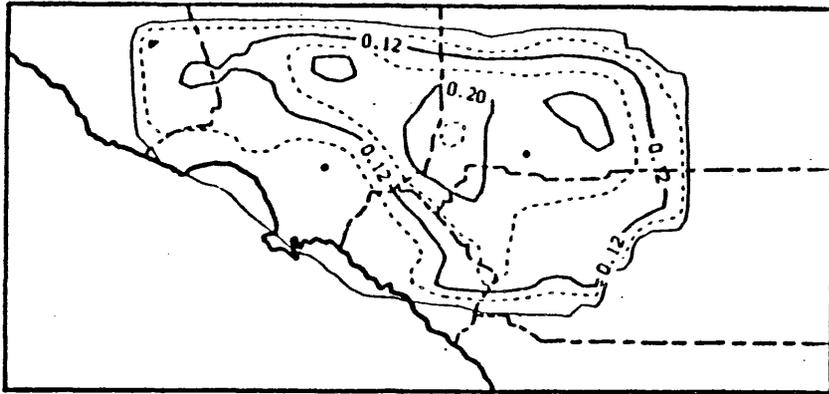


(b)

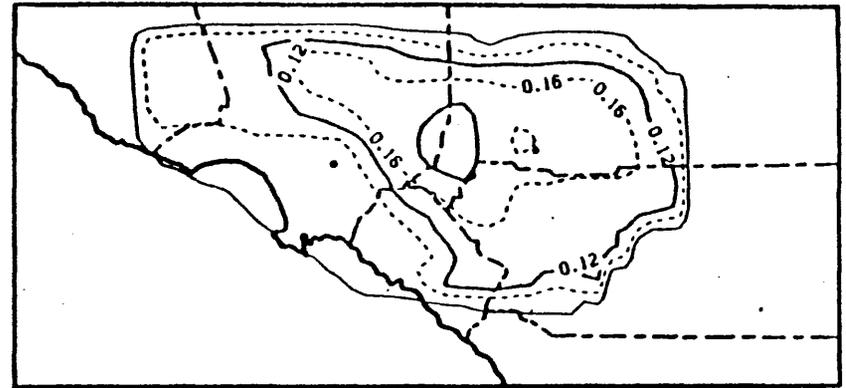


(c)

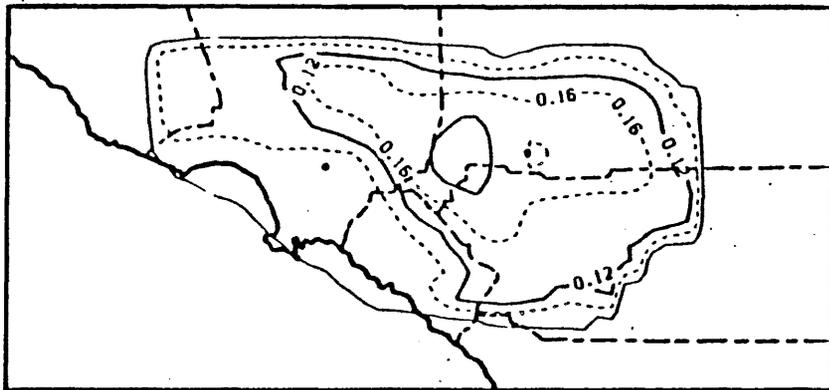
Figure 10 Spatial Distribution of Ozone at 1:00 pm on the Third Day of the Simulation. Ozone isopleths are shown at 4 pphm intervals. a) NO MOBILE; b) BASE-ROG; c) BASE-NOX.



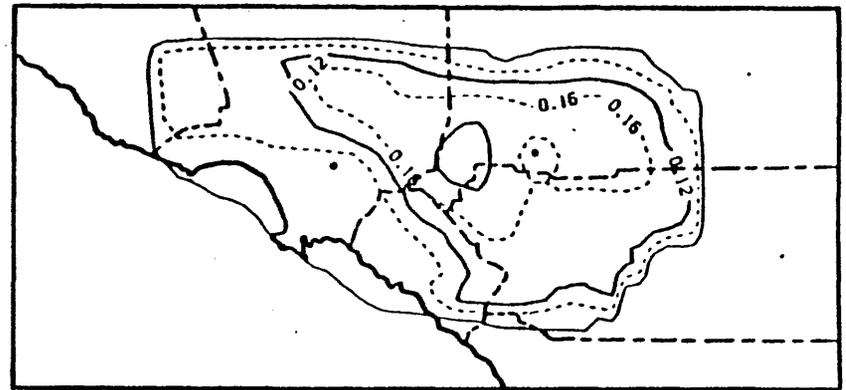
(a)



(c)

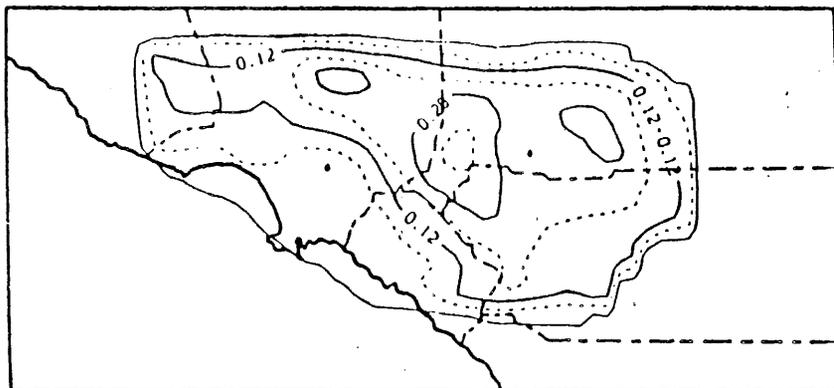


(b)

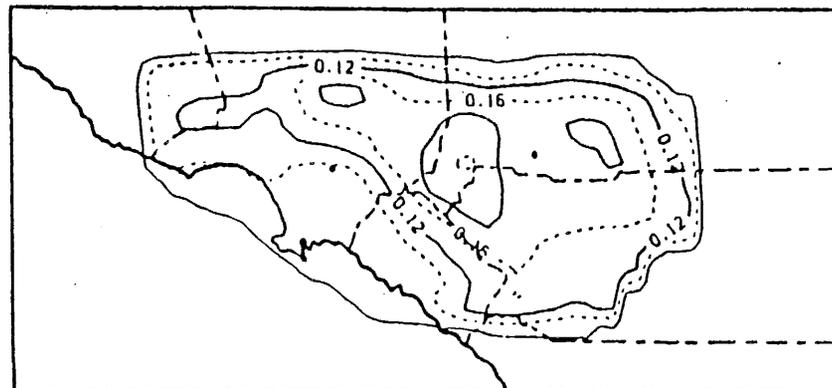


(d)

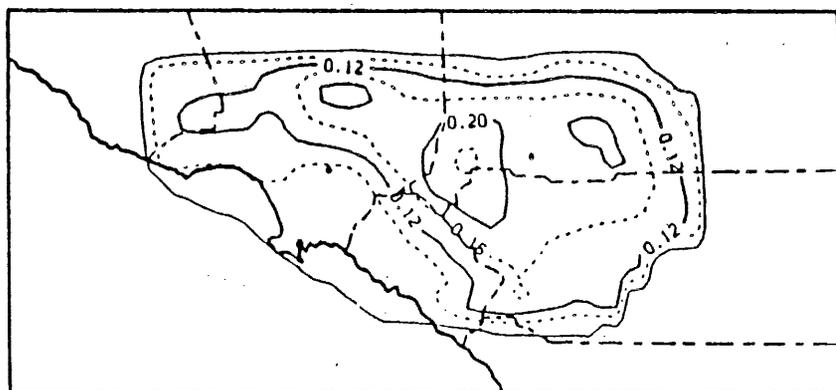
Figure 11 Spatial Distribution of Ozone at 1:00 pm on the Third Day of the Simulation. Ozone isopleths are shown at 4 pphm intervals. a) ADV CONV; b) ADV METH; c) STD M100; d) FULL METH.



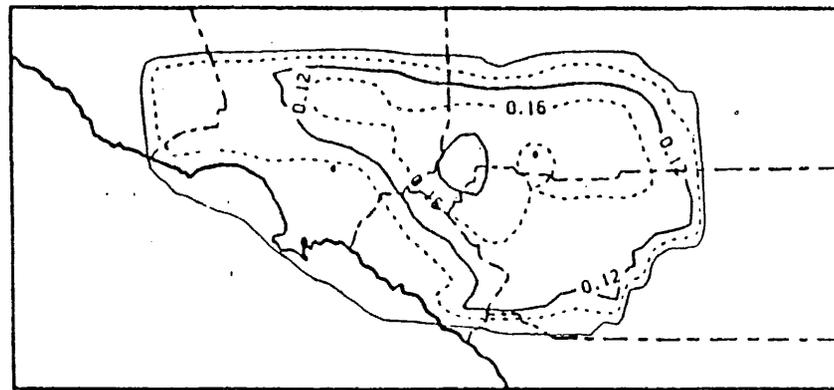
(a)



(c)

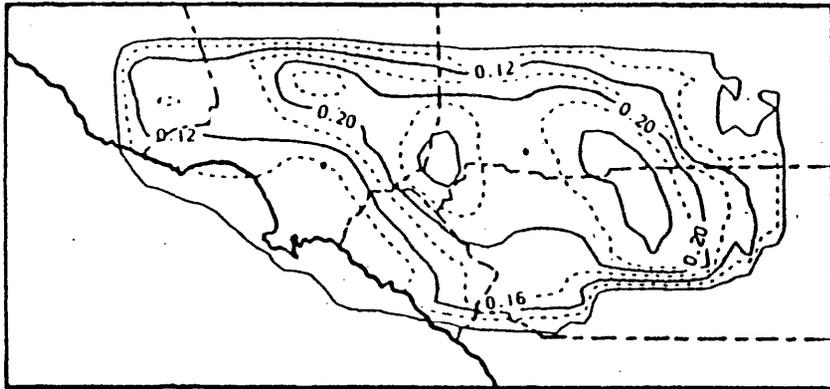


(b)

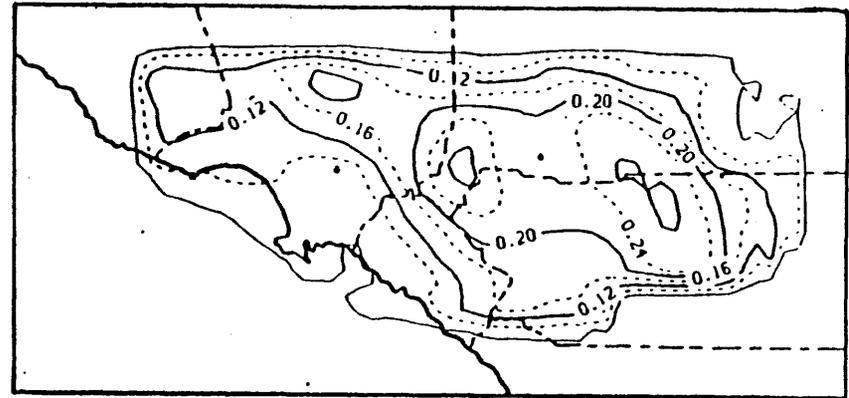


(d)

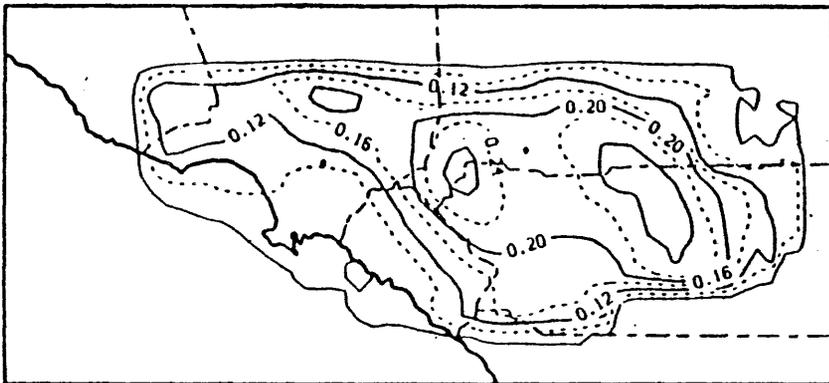
Figure 12 Spatial Distribution of Ozone at 1:00 pm on the Third Day of the Simulation. Ozone isopleths are shown at 4 pphm intervals. a) METH 50; b) STD M85; c) HIGH FORM; d) ADV METH/NO ROG.



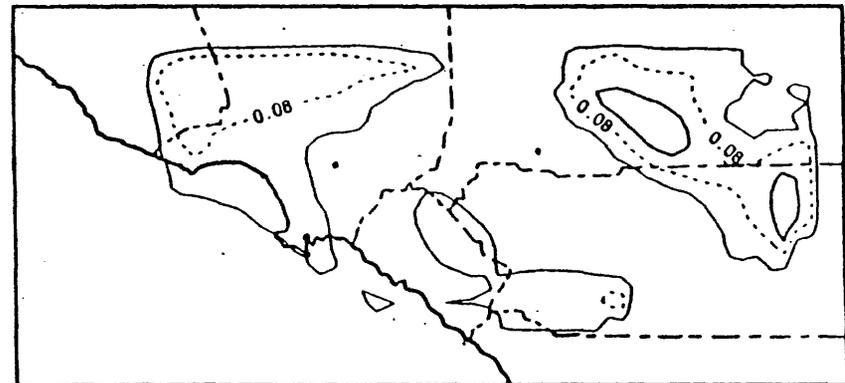
(a)



(c)

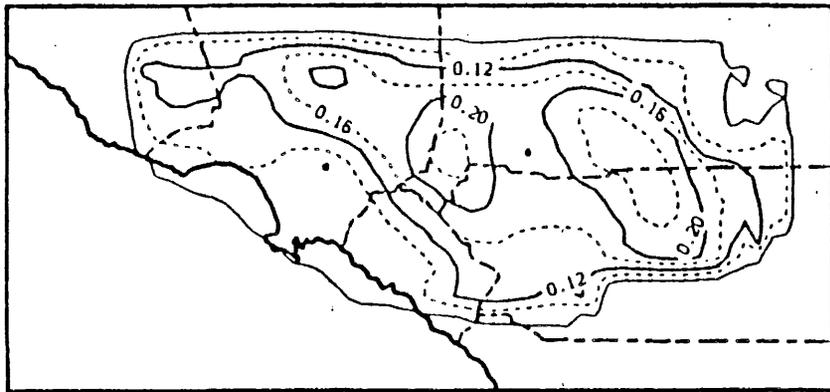


(b)

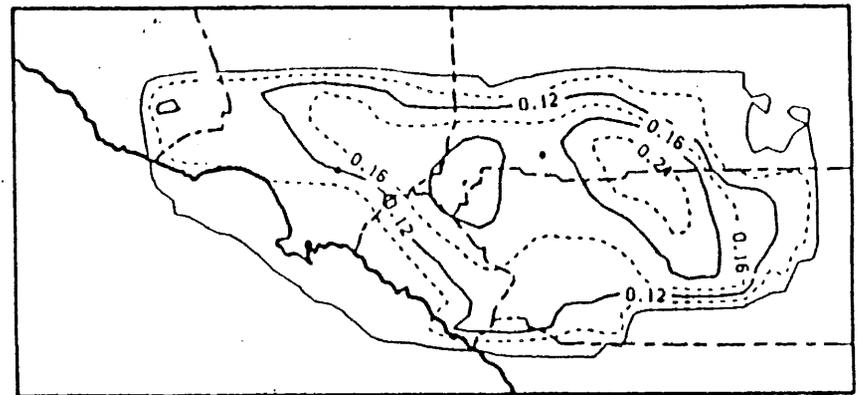


(d)

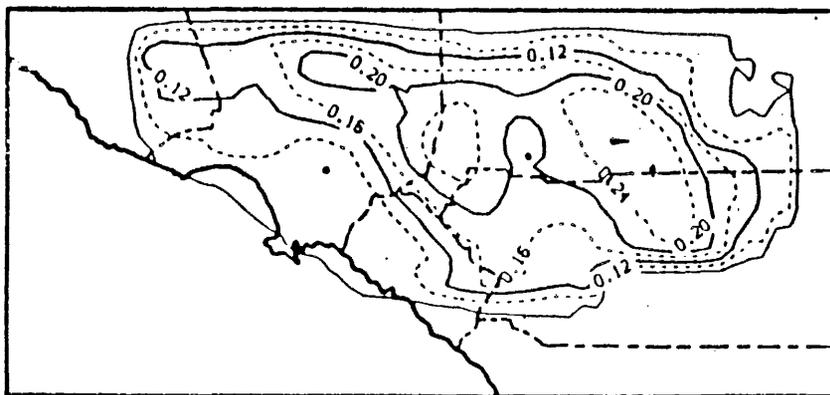
Figure 13 Spatial Distribution of Ozone at 1:00 pm on the Third Day of the Simulation. Ozone isopleths are shown at 4 pphm intervals. a) BASE 2010; b) CLEAN BC 2010; c) LO BC/LO IC 2010; d) NO ROG/LO IC 2010.



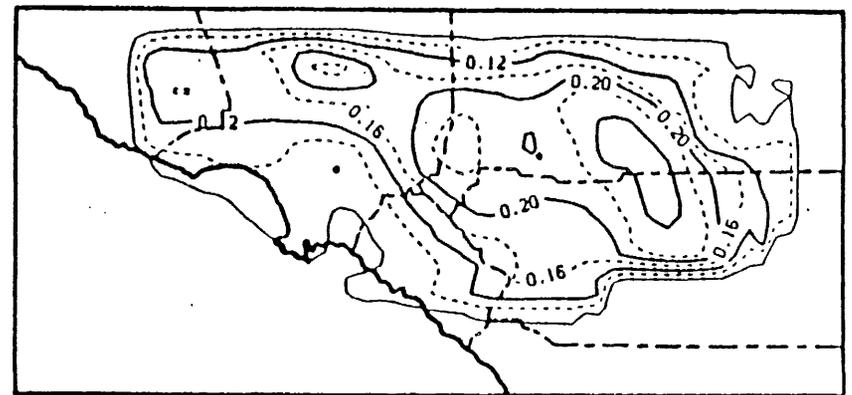
(a)



(c)

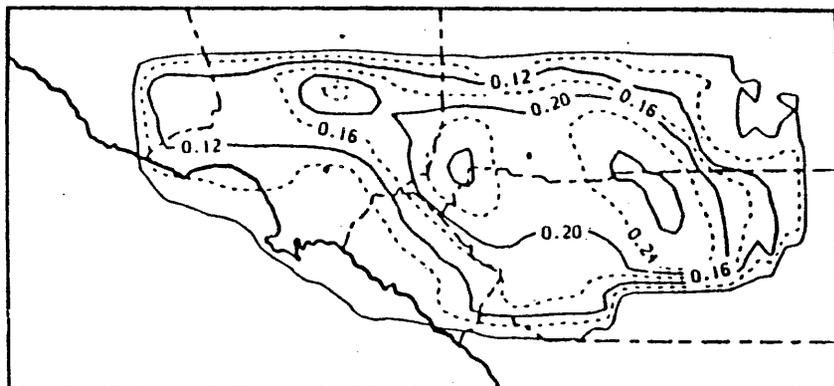


(b)

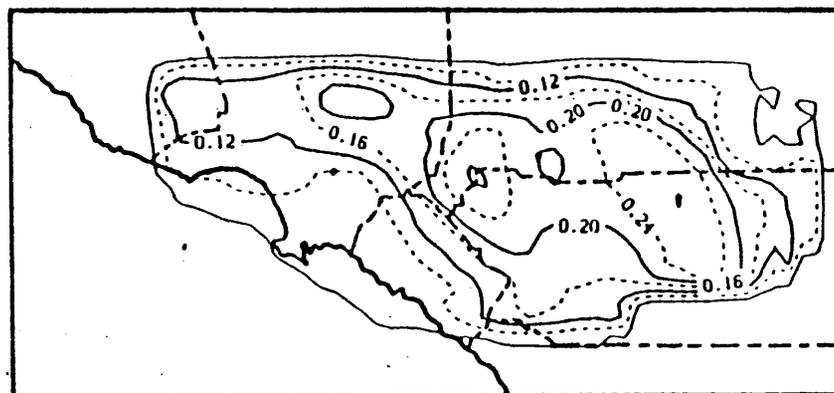


(d)

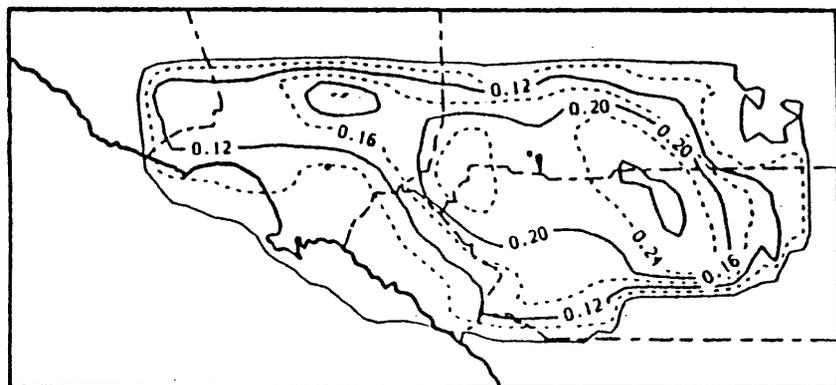
Figure 14 Spatial Distribution of Ozone at 1:00 pm on the Third Day of the Simulation. Ozone isopleths are shown at 4 ppb intervals. a) ADV METH 2010; b) ADV CONV 2010; c) NO MOBILE 2010; d) NO MOBILE ROG 2010.



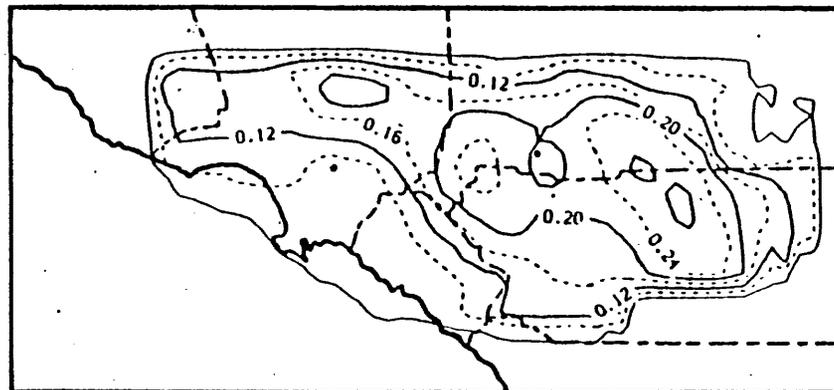
(a)



(c)

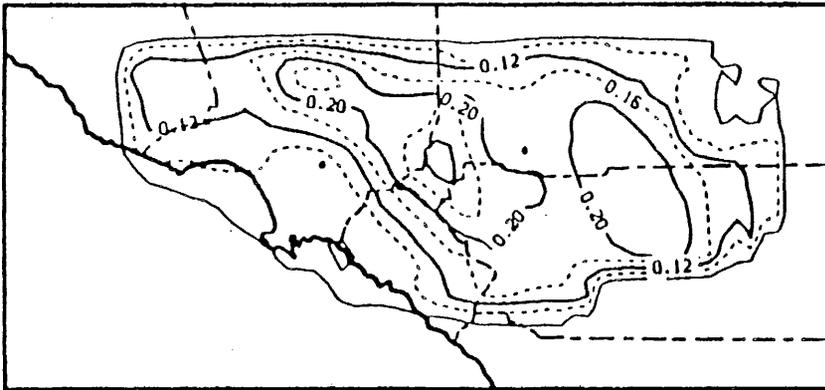


(b)

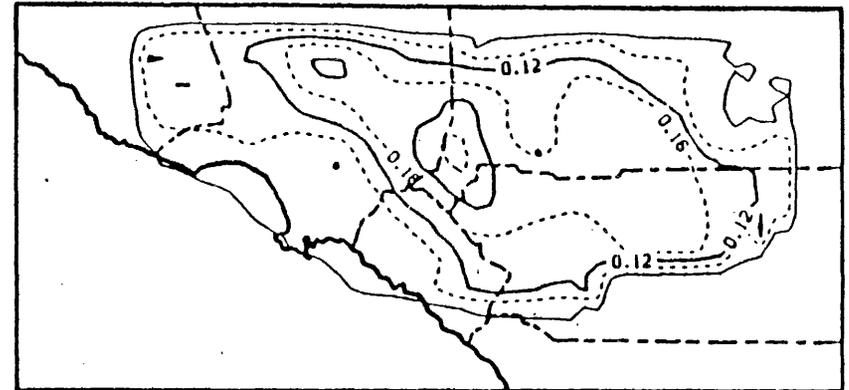


(d)

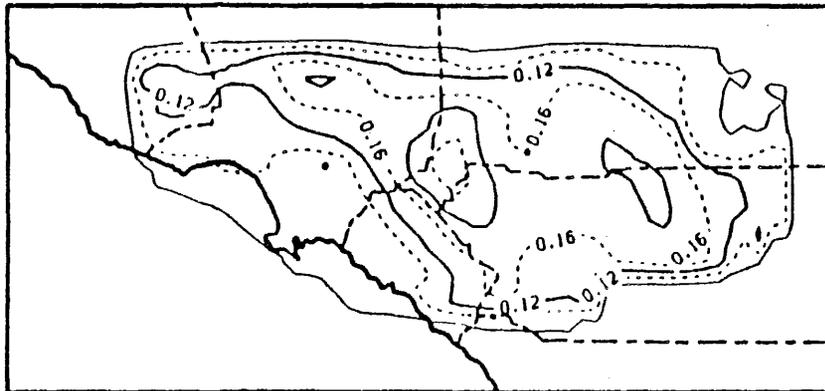
Figure 15 Spatial Distribution of Ozone at 1:00 pm on the Third Day of the Simulation. Ozone isopleths are shown at 4 pphm intervals. a) STD M85 2010; b) STD M100 2010; c) ADV LMD 2010; d) ADV LMD/NO ROG 2010.



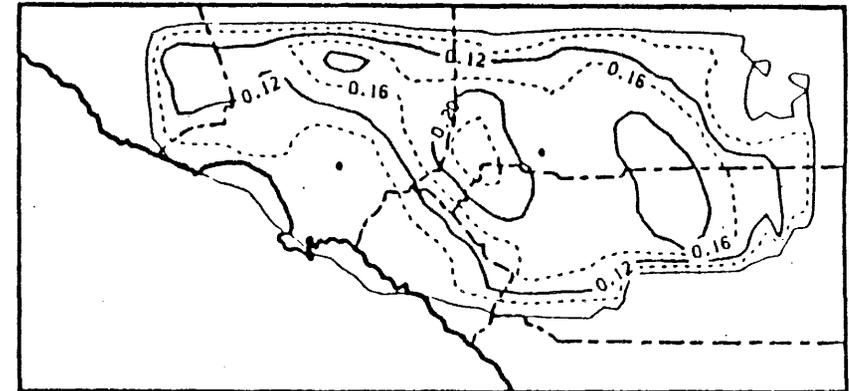
(a)



(c)



(b)



(d)

Figure 16 Spatial Distribution of Ozone at 1:00 pm on the Third Day of the Simulation. Ozone isopleths are shown at 4 pphm intervals. a) LO IC 2010; b) ADV CONV/LO IC 2010; c) ADV METH/LO IC 2010; d) STD M85/LO IC 2010.

$$E_1 = \int_T \int_A c(\bar{x}, t) P(\bar{x}) H(c - c_0) d\bar{x} dt \quad (1)$$

and

$$E_2 = \int_T \int_A P(\bar{x}) H(c - c_0) d\bar{x} dt \quad (2)$$

where $P(\bar{x})$ is the population at location \bar{x} , and $H(c - c_0)$ is a cut-off (Heaviside step function) that is 1 if c is greater than some minimum value c_0 , and 0 if it is less. E_1 is concentration weighted and has units of person per hours and E_2 , which does not include concentration weighting, has units of ppm-hours. The reason for including a cut-off level is because researchers have found that adverse health and environmental effects from ozone become most notable above certain levels, and regulations are formulated to limit exposure to higher concentrations. The use of a cut-off allows quantification of exposure solely to high levels. In this study, levels were chosen corresponding to the NAAQS of 0.12 ppm ozone, the first stage alert level of 0.20 ppm, and 0.30 ppm, as well as 0.0 ppm. For the other pollutants listed, PAN, NO₂, HCHO and HNO₃, the cut-off chosen was 0.0 ppm, and $H=1$ (so it could be neglected). By comparing the exposures for different cut-off levels, it is possible to identify how well a strategy controls high ozone concentrations vs. average levels. The peaks, averages and exposures are given for simulations of the future years' air quality and for 1982.

Diagnostic calculations showed that, over the range of emissions changes involved in these calculations, that boundary conditions have little effect. By the third day, the impact of changing initial conditions is felt almost solely in the Far Eastern Basin. (The change in that part of the Basin is small - only about a 10% change in the ozone levels in the Far Eastern portion, and only a 3% change in the predicted peak.) Lowering boundary conditions to clean levels had a very small impact on the predicted peak (0.1%). On the other hand, removing all, or part of the emissions, greatly affected predicted concentrations. For example, removing emissions lowered the predicted ozone to background levels over most of the modeling region, showing that boundary and initial condition impacts were limited. These diagnostic calculations showed that the emission control simulations would represent the actual response of the atmosphere, with little bias from presumed initial and boundary calculations.

As shown in Tables 4 and 6, switching to methanol is predicted to result in lower peak ozone concentrations and exposures. For example, switching to comparable M100 vehicles is predicted to lower the ozone in the Year 2000 from 0.26 ppm to 0.22 ppm (14%). Totally removing mobile source emissions only reduced the peak ozone to 0.21 ppm. Switching to methanol, in this case, was 69% as effective as totally removing mobile source related emissions. Exposures to Stage 1 ozone levels decreased by 83%, or 86% of the decrease noted if mobile source emissions were removed.

Less improvement is noted for the M85 simulation. The ozone reductions for both the peak and the exposure calculations are only about half as great for M85 as compared to the equivalent M100 scenarios. This is due to the more reactive hydrocarbons, that compose about half the exhaust and 80% of the evaporative emissions, and the increase in evaporative emissions. However, recent measurements indicate that the exhaust and evaporative ROG emissions from an M85 vehicle would contain less gasoline-type components than modeled. (Integral in the design of this study was to bracket the likely

emission levels.) This would increase the benefits of M85, approaching the benefits found for M100 use.

If the formaldehyde fraction of the exhaust is increased (e.g., Year 2000 light duty automobiles emit 55 mg mi^{-1} as opposed to 15 mg mi^{-1} in the standard case), the predicted reduction in the ozone is cut from 4 pphm to 2 pphm - or about 50%. The exposure is not as adversely affected, for example the reduction in exposure to ozone levels above 0.12 ppm is only 29% less in the high formaldehyde case versus the Base Case calculations.

Ambient formaldehyde concentrations and exposures did not increase significantly when the use of methanol was simulated and decreased in any of the methanol simulations. This is due to the drastically reduced atmospheric formation of HCHO when methanol replaces the more reactive ROG associated with gasoline use.

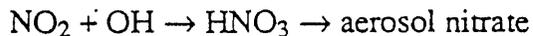
Predicted PAN, nitric acid and NO_2 concentrations generally decreased in the simulations involving methanol use. This is due to the lower reactivity of the hydrocarbon, reducing the oxidation rate of NO to NO_2 (and then to HNO_3), and the reduction of NO_x emissions from diesel vehicles. PAN levels decreased by about 25%. NO_2 levels were reduced about 30%, and HNO_3 was reduced, on average, about 25%.

Airshed modeling indicated that ozone levels could be effectively reduced by switching to methanol. The actual reduction is moderated by the limited ROG emissions expected to be derived from on-road sources in future years. For example, in the Year 2000 inventory, only 23% of the total ROG emissions are from mobile sources. Totally removing the ROG component of mobile source related emissions reduced the ozone exposure above 0.12 ppm by 37%. This is slightly greater than the calculation simulating conversion to M100 which dropped the exposure by 21%. A similar comparison of exposures above 0.20 shows that switching to methanol gives a greater benefit. This is because of the reduction in NO_x emissions from diesel vehicles. If mobile source emissions were a larger fraction of the ROG inventory, or NO_x emissions were greater, the apparent benefits of methanol conversion would be even greater. This would result from further controls on stationary sources, such as those proposed in the AQMP, or failure of motor vehicles to meet the emission levels used in this study.

E7 Response of Aerosol Concentrations to Methanol Use

Atmospheric aerosols have come under increased scrutiny as evidence of their environmental and health effects has been found. Small particles are of particular concern because they can penetrate the lung more efficiently than the larger particles, and also scatter light effectively. For this reason, both the State of California and EPA have promulgated standards for small particulate matter, known as PM_{10} (particulate matter less than $10 \text{ }\mu\text{m}$ s in diameter). The SoCAB experiences PM_{10} levels of about $300 \text{ }\mu\text{g m}^{-3}$ (24-hr average), twice the national standard of $150 \text{ }\mu\text{g m}^{-3}$ and 6 times the state standard of $50 \text{ }\mu\text{g m}^{-3}$. Annual average PM_{10} levels are similarly in excess of the applicable federal and state standards of $50 \text{ }\mu\text{g m}^{-3}$ (arithmetic mean), and $30 \text{ }\mu\text{g m}^{-3}$ (geometric mean), respectively. Primary constituents of aerosol in the SoCAB are nitrate, sulfate, diesel particulate, secondary organic and road dust.

Methanol use would reduce fine particulate matter in a variety of ways. Used in diesels, methanol virtually eliminates the soot commonly seen emanating from heavy duty trucks and buses. Also, by reducing NO_x emissions, the secondary formation of aerosol nitrate via NO_x oxidation:



is reduced. Methanol contains no sulfur; so, oxidized sulfur emissions, the precursor to aerosol sulfate, are reduced. Finally, the secondary formation of organic aerosols by gas phase oxidation would decrease because methanol oxidation products will not condense at atmospheric concentrations.

The airshed and trajectory models were used to calculate the impact that methanol use would have on the formation of secondary nitrate and organic carbon aerosol. Dispersion modeling results were used to determine the expected changes in sulfate and diesel particulate levels. Together, the two approaches were used to calculate how methanol would affect total PM_{10} concentrations at Rubidoux, the site experiencing the highest measured PM_{10} levels in the SoCAB. Both peak 24-hr and yearly average levels were predicted.

Predicted PM_{10} concentrations at Rubidoux, without methanol use, were $98.35 \mu\text{g m}^{-3}$ (annual average) and $324 \mu\text{g m}^{-3}$ (peak, 24-hr average), and as shown in Figures 17 and 18, methanol use could drop that substantially. Predicted levels given full methanol use are $79 \mu\text{g m}^{-3}$ (annual average) and $210 \mu\text{g m}^{-3}$. At this point road dust is the largest contributor to PM_{10} .

The calculated PM_{10} levels were then used to estimate visibility by a correlation between particulate loading and light extinction.⁵ Visibility was then found from the light extinction factor. For the Base Case, the annual average visibility was calculated to be 6 miles. Extensive methanol use could almost double that to 11 miles.

E8 Wintertime Formaldehyde, Methanol and Benzene Levels

Buildup of formaldehyde and methanol during low ventilation, low mixing height conditions, such as might be expected to occur during the winter, was investigated using linear roll back techniques. If MFVs become the dominant transportation mode, they will most likely be the principle source of both HCHO and methanol. Currently, motor vehicles are the dominant source of CO. Using this common trait, future, ambient, HCHO (or methanol) concentrations were calculated by scaling historic peak CO concentrations in the SoCAB by the ratio of the forecast HCHO (or methanol) emissions to the CO emissions corresponding to the historic peaks. This calculation led to a predicted peak HCHO concentration in the SoCAB of 89 ppb under extreme meteorological conditions, and assumed that the MFVs emit 55 mg mi^{-1} of HCHO. This value, 89 ppb, is less than historical levels in the SoCAB, and is near the level that eye irritation occurs in sensitive individuals. If the nominal, expected, HCHO emission rate is used ($15\text{-}27 \text{ mg HCHO mi}^{-1}$, in use), the predicted peak HCHO level is 40 ppb, which is very near the predicted summertime peaks, and significantly less than historic peak levels.

Methanol concentrations would build up to about 0.93 ppm. This is significantly less than the threshold limit value of 200 ppm, and "it is unlikely that a normal human being could ever be exposed to enough of it (methanol) to experience acute toxicity" (Marnett,⁶ 1988). Formaldehyde exposure, discussed above, is cited as being of more concern.

⁵ Groblicki, et al. (1981) *Atmospheric Environment*, 15, 2473-2484.

⁶ Marnett, L.J. (1988), "Health Effects of Aldehydes and Alcohols in Mobile Source Emissions." In: *Air Pollution, The Automobile and Public Health*, National Academy Press, Washington, DC, pp. 579-603.

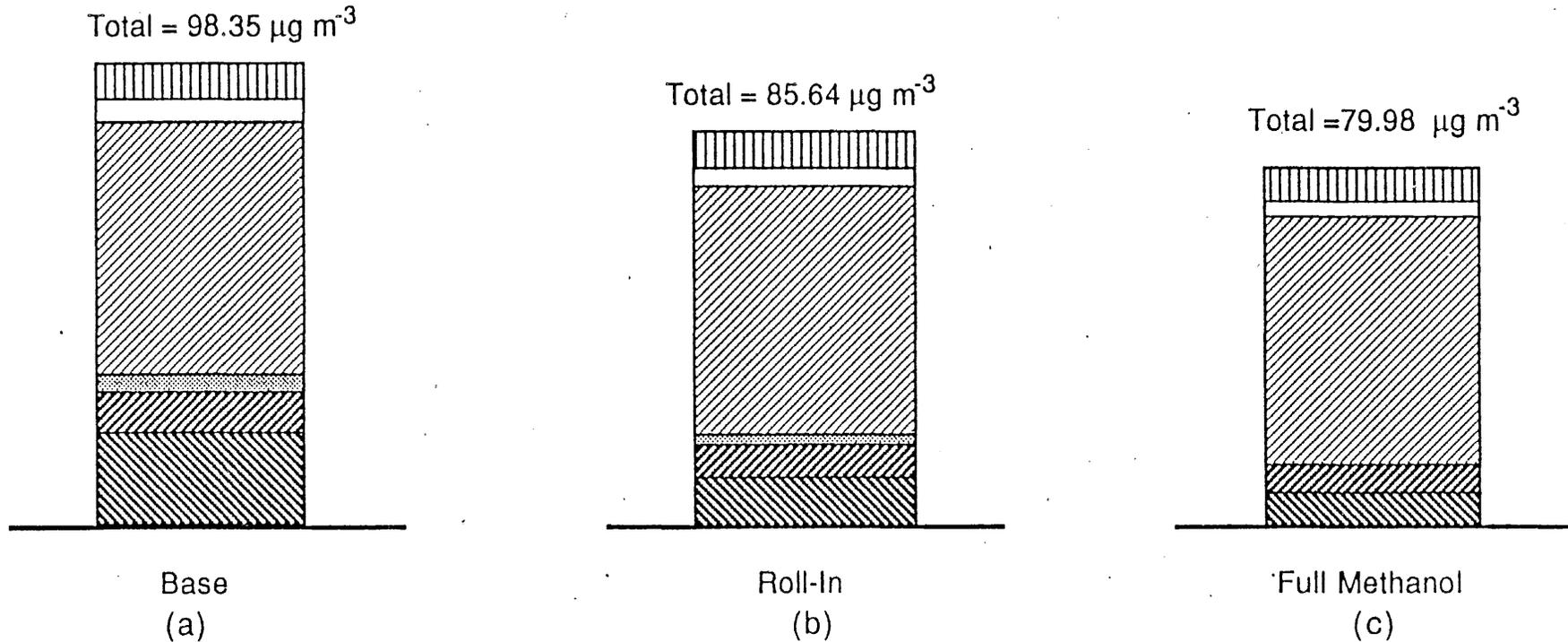
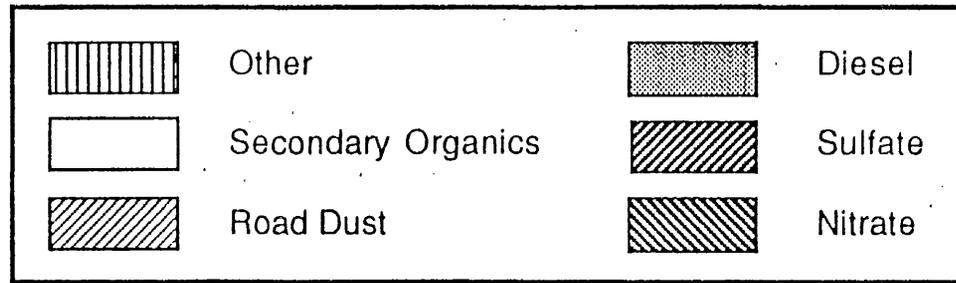


Figure 17 Source contributions to annual average PM₁₀ levels at Rubidoux for the year 2000 for a) Conventional (BASE case) fuel use, b) Roll in from 1990 on of M100 MFVs, and c) Full use of methanol fuels in applicable sources.

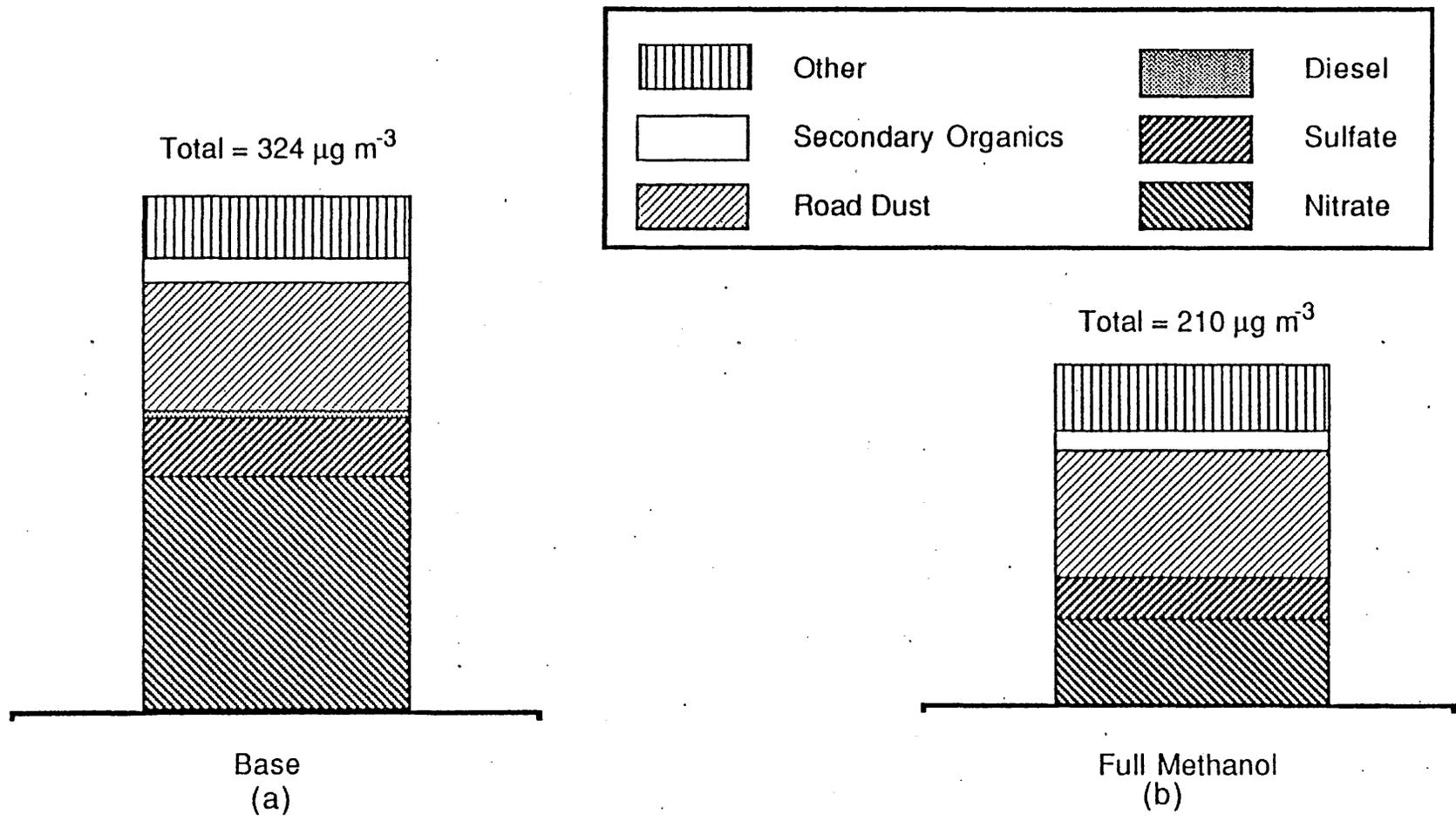


Figure 18 Source contributions to peak, 24-hr average PM10 at Rubidoux for a) BASE, year 2000, and b) Full methanol utilization case

Methanol fueled vehicles emit little or no benzene, a carcinogen. Currently, motor vehicles are the largest source of benzene, so switching to MFVs would drastically lower benzene levels in the SoCAB. Using a rollback calculation, the maximum predicted benzene using conventionally fueled vehicles would be 29 ppb. This would drop towards zero as the percentage of M100 MFVs increase to complete penetration of the vehicle fleet. M85 vehicles would, if benzene is included in the blending mixture, still result in non-negligible levels of benzene due to evaporative emissions.

E9 Future Studies

In accomplishing this project, as is the case of any project this size, a number of areas for future work were identified that would decrease uncertainties in a future study of this type. The three-tiered design and multiple simulations were used to locate, quantify and minimize uncertainties as the project progressed. One of the key uncertainties, and area for further study, is the composition of the emissions from both M85 and M100 fueled vehicles. The composition of the exhaust and evaporative emissions from future MFVs will dramatically affect their impact on photochemical air pollution. This study showed the nearly negligible reactivity of methanol over multiple day periods. However, HCHO is very reactive. More concrete test data is needed for dedicated MFVs, as well as FFVs using advanced engine and catalyst systems. These programs, which are currently being undertaken by both governmental agencies and industrial organizations, will be critical. Realizing that this data is not currently available, this project used a variety of exhaust compositions to bracket that which is likely in the future. From the results here, the air quality impact can be assessed by interpolation.

A second concern is whether similar results would be found if different meteorological conditions were modeled. While previous studies have generally relied on using a single period, primarily due to expense, it would be instructive to model more than one period. Two other periods, such as one of the South Coast Air Quality Study (SCAQS)-three-day intensive measurement period and the June 5-7, 1985 period used in the Air Quality Management Plan (AQMP) process would be viable and cost effective choices. The use of multiple periods would be a unique addition to the foundation of photochemical modeling studies in support of policy decisions.

Other future projects include the use of alternative chemical mechanisms, looking at non-methanol, "clean" alternative fuels, and studying the impact on aqueous phase chemistry.

E10 Summary

This study was undertaken to address the issues critical to assessing to air quality benefits and concern of utilizing methanol fuel. These issues were listed in the first part of this summary, and the findings relevant to each issue are recapped, below.

- **Would the use of MFVs lead to increases in ambient HCHO levels and, if so, would the concentrations be prohibitive?**

Photochemical modeling showed that the use of MFVs would not increase summertime HCHO levels markedly, and could lead to a decrease. Non-photochemical calculations (roll back), led to the result that peak, 1-hr levels would be less than historical levels, and less than the suggested ambient standard under the most severe conditions.

- Experiments indicated that methanol use may lose its potential to reduce ozone during multiday smog episodes. Would the buildup of methanol over multiple days severely decrease the effectiveness of methanol use?

Results showed that a major reason for the experimental findings was due to limitations in interpreting results from the experiments conducted. In particular, the very low NO_x levels on Days 2 and 3 of the experiments, leading to an unrealistically high ROG/ NO_x ratio, and the wall effects impede direct use of the results and mask the benefits of methanol substitution. Extensive modeling showed that under realistic atmospheric conditions the buildup of methanol does not erase the ozone reduction potential.

- Would methanol build up to levels of concern?

Peak 1-hour methanol concentrations are expected to reach about 1 ppm. This is orders of magnitude less than the threshold limit value. Multiple studies have concluded that, at this level, exposure to ambient methanol should not lead to toxicity.

- What would adopting a methanol fuel based strategy do to the atmospheric concentrations of other pollutants such as NO_2 , PM_{10} , PAN, nitric acid and benzene?

Besides reducing ozone, methanol would reduce NO_2 , PAN, PM_{10} , HNO_3 and benzene. Airshed calculations predicted up to a 49% decrease in peak NO_2 , 27% decrease in peak PAN, and 24% decrease in peak HNO_3 . Exposures dropped by a similar or smaller margin. Calculated PM_{10} levels decreased up to 19% for an annual average, or 35% for the peak 24 hour average. The major remaining PM_{10} source became road dust in both cases. Benzene levels would decrease markedly if methanol were used. These results highlight some of the co-occurring benefits of methanol fuel use.

- How effective would methanol use be for reducing exposure to ozone and lowering peak ozone concentrations?

A variety of metrics, including population based exposure calculations, exposures to high ozone, and peak ozone concentrations, were included in the analysis. It was found that switching to methanol would significantly lower peak ozone and exposure to high ozone concentrations. In the airshed calculations, replacing the on-road mobile source vehicle emissions by emissions from neat MFVs led to nearly the same O_3 reduction as totally removing on-road mobile source emissions. Using M85 led to about half the reduction as the calculation based on M100 fuel use. Exposure to Stage 1 levels decreased up to 83% for MFVs as compared to a calculation using CFVs with similar emission rates. Ozone reduction was limited by the relatively small percentage (~ 25%) of ROG that is forecast to be emitted by on-road motor vehicles compared to other sources in the years 2000 and 2010. If motor vehicles make up a greater fraction of the total emissions than that assumed, the apparent benefits of converting will become greater.

- How can the results be used for determining the impact of intermediate cases?

It was realized at the outset of this project that the emission characteristics of future MFVs is uncertain, and that there is little data even for current vehicles. Thus, multiple scenarios were conducted, bracketing the likely emission characteristics. For example, one calculation examined the impact of a fleet of vehicles emitting large amounts of

formaldehyde (LDVs emitting 55 mg mi⁻¹), and another looked at the result if a fleet of M85 vehicles emitted 50% NMOG and 50% methanol. The total reactivity of the ROG emissions in these two cases is higher than is planned. On the other hand, an optimal case looked at a fleet of M100 vehicles emitting no NMHC and 3 mg mi⁻¹ HCHO. The default MFV had HCHO emissions of 15 - 27 mg mi⁻¹ (LDVs). These calculations can be used as bounds for interpolating to intermediate cases.

As an example, tests⁴ show that the average NMHC exhaust emission rate from three FFV Crown Victorias (mileage between 6700 and 15,000 miles) operating on M85 is 0.09 g mi⁻¹. This is below that assumed for the M85 case (0.295 g mi⁻¹ in 1990-1991). If this value were to be achieved in-use, the expected benefit would be greater than that for the M85 calculation, approaching that for M100. (The HCHO emission rate is 20 - 30 mg mi⁻¹, near the 23 mg mi⁻¹ rate used for both M100 and M85 calculations.) Linear interpolation between those two calculations can be used to estimate the expected air quality benefits. In the M100 calculation, the exposure above 0.20 was 364 person ppm hours, and the corresponding exposure for the M85 case was 1260 person ppm hours. The expected exposure in this example is:

$$[364] \left(\frac{0.295 \text{ g/mi} - 0.09 \text{ g/mi}}{0.295 \text{ g/mi}} \right) + [1260] \left(\frac{0.09 \text{ g/mi}}{0.295 \text{ g/mi}} \right) = 637 \text{ person ppm hours}$$

A similar interpolation would show the expected peak to be about 0.23 ppm. This can be compared to a base case exposure of 2586 person ppm hours. The reduction in exposure is 72% of that found for totally removing mobile source emissions. If the HCHO emissions were significantly different than 23 mg mi⁻¹, the two bounding cases (55 mg mi⁻¹ and 3 mg mi⁻¹) would be used for interpolation.

E10.1 Conclusion

Methanol fuel use could lead to improvements in a number of facets of air quality. Shown here, conversion to methanol would lead to lower ozone, NO₂, PAN, nitric acid, benzene, and PM₁₀ levels. The degree to which conversion will improve air quality is integrally tied to the level of emissions, especially HCHO and NO_x, achieved. MFVs with HCHO emissions corresponding to the near-term target of 15-27 mg mi⁻¹ gives substantially lower ozone than a fleet emitting 55 mg mi⁻¹. This could argue for a separate standard on HCHO emissions.

Use of M100 fuel led to twice the ozone reduction of M85 fuel use. This is because, as modeled, the exhaust emissions from an M85 vehicle contained about equal portions of methanol and gasoline-derived products by mass, and the evaporative emissions were modeled as being rich in gasoline products. In practice, the difference between M100 and M85 use may prove to be less pronounced. First, M100 fuel will likely require an additive for safety and technological reasons (luminosity and cold-start). Also, measurements indicate that M100 exhaust contains some (~3%) non-methane hydrocarbon, possibly due to lubricating oil. These two factors would tend to make M100 exhaust slightly more reactive than modeled. Secondly, recent tests indicate that the exhaust from an M85 vehicle is only about one third hydrocarbon (by mass) and hot soak emissions are only 18% hydrocarbon. As discussed in the example above, this would result in a less reactive emission composition than modeled. Also, the blending component of M85 could be optimized to reduce the reactivity of the emissions. If explicitly modeled after development of the detailed emission characteristics, these factors would lead to M100 showing slightly less benefit than modeled, and M85 use would show greater benefit. The emission parameters used in the modeling

were chosen using preliminary data and to bracket the probable future characteristics. As better data becomes available for emissions from MFVs, it is possible to use the results, interpolating to find the expected air quality impacts.

If emissions from motor vehicles are greater than forecast, the benefits fo switching to methanol would be more pronounced. For example, recent tests indicate that there are excess running emissions from motor vehicles. The projected inventories do not incorporate these emissions. If they do persist, switching to a lower reactivity organic mixture would decrease ozone more than was found in this study. The same is true if the technology is not installed to meet the relatively stringent levels used here. An increase in either ROG or NO_x emissions would amplify the ozone reduction benefits resulting from methanol use, either as M85 or M100.

These results, derived using a series of advanced photochemical air quality models substantiate previous modeling and experimental studies showing the effectiveness of methanol substitution on reducing ozone. This study extends those findings to showing the basinwide dynamics of ozone using more realistic future conditions, and also shows the benefits of simultaneously lowering concentrations of other air pollutants.