

6.5.3 Diagnostic Calculations

Initial condition effects have been quantified by conducting the **LO IC** and **NO EM** tests for the year 2000, and **LO IC 2010** for 2010. In addition, a number of calculations tested the effects of controls when initial and boundary conditions were greatly reduced, and are described below. **LO IC**, is the same as the base case, except the initial conditions are reduced to background levels. In this case the peak ozone changed very slightly, from 0.261 to 0.255 ppm (2%), though the region over 0.2 ppm showed more variation (see Tables 6.4 and 6.8). Additionally, the peak and average PAN and HCHO agree to within 15%. The **NO EM** test calculation, where emissions are set to zero, and initial conditions are left unchanged from the base case show a peak in the far eastern basin (Fig 6.6a). This is a result of the pollutants present at the beginning of the three day period being transported east and reacting to form ozone. The peak is significantly lower than when emissions are present, and is about 50 km east of the original peak. For the year 2000 calculations, the role of initial conditions, in this case, is to raise the ozone concentrations in the far eastern portions of the basin with little effect on the peak.

In the year 2000 control strategy calculations, initial conditions are left unaltered to remove the possibility of gaming the results. ROG emissions are changing at most about 25% in the calculations below, so initial conditions should not change much between runs. Implementation of a methanol strategy would, most likely, slightly lower the initial conditions. Use of the same initial condition is conservative in favor of conventional controls. However, the bias introduced, as shown, is very small.

When the modeling region was expanded for conducting the 2010 simulations, a much larger portion of the initial condition cloud was contained in the region. Along with the increased emissions in the eastern basin, this led to an ozone peak of 0.32 ppm 50 km east of San Bernardino. In the **LO IC 2010** simulation, where initial conditions were lowered to background levels, the far eastern peak was reduced to 0.24 ppm (Table 6.9, Fig. 6.10c). The predicted ozone levels in the central and western SoCAB remained very similar. For example, the central basin peak near Pomona was 0.31 ppm in both cases. Again, the initial conditions are felt primarily in the far eastern region of the SoCAB, and result in higher ozone in that area.

The presence of the initial pollutant cloud after three days is not a modeling artifact, but is expected due to the long atmospheric lifetimes of the less reactive organics, such as the aromatics and alkanes which can have lifetimes of about four or more days (Pitts and Finlayson-Pitts, 1988, Atkinson, 1987). Because the oxidized nitrogen compounds, such as NO, NO₂ and PAN, have very short lifetimes, the eastern basin is rich in organics, and the local ROG/NO_x ratio is high. The abundance of organics in the eastern SoCAB decreases the sensitivity of the ozone peak to reducing the reactivity of the ROG by switching to methanol. The central basin peak is more sensitive to ROG control. To highlight this sensitivity, three of the control calculations described below were run in two modes. First, initial and boundary conditions were left unaltered, as was the practice in the 2000 simulations. A second set of calculations used the control emissions with low initial and boundary conditions. This reduced the impact of the far eastern peak on the extreme ozone statistics.

Seven calculations show how boundary conditions, or both boundary and initial conditions combined, affect the predictions. **NO EM/LO IC** combines removing emissions and lowering the initial conditions to background values. Figure 6.6d shows that the only significant ozone concentrations occur near the boundaries, and those are much lower than in the base case calculations. The ozone transported in, or formed from pollutants transported in, does not significantly increase the basin-wide ozone levels above background levels. In fact, the basin-wide average is 0.02 ppm, and the peak in Central Los Angeles is only 0.03 ppm. Average formaldehyde and PAN are very low. The peaks are much lower than the base case calculations, and occur on or near the boundaries. The peak ozone value occurs on the downwind boundary, and is due to a combination of nighttime flow reversal and diffusion of the boundary conditions into the boundary grid cells. Exposure to all of the listed pollutants is very low compared to simulations with emissions.

The tests to show the importance of the ROG flux across the boundary, **NO ROG**, **NO ROG/LO IC**, and **NO ROG/LO IC 2010** (Figs. 6.6b, 6.6c, and 6.10d, respectively) can be compared with the base case (**BASE1** and **BASE 2010**) and low initial condition (**LO IC** and **LO IC 2010**) calculations. As seen in Figure 6.10d for **NO ROG/LO IC**, the peak regions are still on the boundary, though one in-basin region downwind of a large NO_x emission area has an ozone peak above 0.10 ppm. This peak is south and east of the peak in the base case calculations, and is due to NO_x emissions reacting with organic gases being advected across the western and southern boundaries. A second peak in the northwest portion of the modeling region is due to pollutants being transported over the northern boundary. When initial conditions are included (**NO ROG**), the peak ozone is very similar in magnitude (3% difference) and location (within 5 km) to **NO EM**. However a much larger portion of the basin is above the 0.12 ppm standard. This is due to the NO_x emitted into the atmosphere when compared to the **NO EM** case. A similar comparison is noted when using the 2010 inventory (**NO ROG 2010**) vs. **BASE 2010** (Fig 6.10d vs. 6.10a).

Lowering the influx pollutant concentrations along the boundaries showed little difference from the base calculations. The peak ozone changed only 0.16% (**CLEAN BC 2010** vs. **BASE 2010**). Spatial and population weighted measures were more sensitive, being reduced about 5-10% when boundary conditions were lowered to very low levels. The difference was mostly in the western basin. It was decided to adopt the levels used in the evaluation as opposed to the lower value. The control measures being studied reduce ROG emissions between 0 and 20%, so the boundaries should not be greatly impacted. The values used in the evaluation correspond to measurements along the coast and out over the ocean (Blumenthal et al. 1984). Using lower boundary conditions would enhance the apparent effectiveness of an ROG control, such as methanol use, though the calculations here indicate that the bias should be small given the relatively small changes being made in the emissions inventory. If much larger changes (50% or more) are made, boundary conditions would increase in importance.

These diagnostic calculations have shown that the results:

- 1) are slightly sensitive to initial conditions, and given that emissions are being changed less than about 25% in the control calculations, the bias introduced should be small.

2) are insensitive to the specification of the boundary conditions over the Pacific Ocean between clean and moderate pollutant levels.

3) respond to the boundary conditions similarly to how the atmosphere responds to the advection of pollutants from outside the modeling region (those emissions being due to biogenic or anthropogenic sources).

and

4) are primarily sensitive to boundary value specification on the boundaries, with relatively little impact on the basin-wide statistical measures used here. The predicted pollutant concentrations are generally a function of in-basin emissions for the base case.

In the control strategy calculations below, boundary and initial conditions are left unaltered between simulations, except for a set of four 2010 calculations, discussed below. This treatment is conservative, but the above calculations show that the bias should be small.

6.5.4 Methanol and Conventional Fuel Scenario Results

A number of issues need to be addressed when evaluating the effectiveness of switching to an alternative fuel such as methanol. In this case, most of the issues deal with using methanol in motor vehicles. These issues are discussed below. It is interesting first to discuss the extent of improvement attainable from any set of controls on mobile sources. This would occur if all mobile source emissions are removed, as is done in the calculation **NO MOBILE** and **NO MOBILE 2010** (Figs. 6.7a and 6.11c). When mobile source emissions are removed from the 2000 inventory, the peak ozone drops from 0.261 to 0.206 ppm, or 0.055 ppm (a 23% reduction). The number of grid-hours with ozone greater than 0.2 ppm is reduced to almost zero, as is the population exposure to stage 1 levels. The peak formaldehyde drops to 11.2 ppb, and the average to 3.9 ppb. Peak PAN is 14 ppb, and the average is 2.0 ppb. In the analysis below, this will be used for comparing the relative benefits of controls. For the year 2010, removing mobile source emissions reduced the peak ozone from 0.32 to 0.28 ppm (12%) in the far eastern basin, and 30% (from 0.31 to 0.22 ppm) in the central basin (Fig 6.9a vs. 6.10c). This trend, that the central basin peak around the Pomona area is more sensitive to controls than the far eastern peak, is prevalent through the 2010 calculations except when initial conditions are greatly reduced (discussed later in this chapter).

An important issue when discussing ozone control, and these results, is whether the reduction is due to lowering NO_x or ROG emissions, or both (or in the case of methanol, the reactivity of the ROG being emitted). Two separate calculations address this question. If only the ROG fraction of mobile sources is removed (**BASE-ROG**), the peak ozone drops to 0.227 ppm. In comparison, if the mobile source NO_x emissions are removed the peak drops to 0.215 ppm (**BASE-NOX**). The number of grids and grid-hours greater than 0.12 ppm are virtually the same in each case, though the number of grids and grid-hours greater than 0.20 ppm O_3 is much less when the NO_x fraction is removed. Conversely, the exposure to ozone above 0.00 ppm increased when NO_x is removed. This is because the ozone in the densely populated region can increase, and the ozone is not precipitated totally at night. This leads to an increased exposure to low concentrations of

ozone. These regions are more sensitive to replacing relatively reactive organic gas emissions with methanol. Removing both the ROG and NO_x led to a greater decrease than either individually, so the benefit can be attributed to controlling both. In this comparison, NO_x is being reduced proportionally more than the ROG (50% vs. 28%).

In the calculations below, methanol is primarily being considered as an ROG control on motor vehicles, with some NO_x reduction from stationary source use and in diesel vehicles. When interpreting the results, the benefits are relative to only perturbing 28% of the inventory. From the above calculations, in the absence of NO_x controls, ROG controls, alone, on motor vehicles would lead to only a 0.034 ppm drop (13%) in peak ozone in the year 2000 and 0.041 ppm (13%) in 2010. The less-than-proportional response to controls is what makes ozone difficult to control. In previous calculations (Tesche et al. 1984, Whitten et al., 1987) even less response was noticed for greater control levels. An obvious conclusion from these calculations is that mobile source controls alone will not bring the SoCAB into compliance, and concurrent controls on stationary sources are needed. This also suggests looking into further NO_x controls. In this case, the impact on other pollutants should be considered.

6.5.4.1 Control of Conventionally Fueled Vehicles

One issue to address before adopting a strategy involving methanol fueled vehicles is to determine the ability of stringent controls on conventionally fueled vehicles to improve air quality. This can then be weighed against improvements from switching to MFVs. Comparison of **BASE1** and **ADV CONV** shows that use of advanced technology on-road vehicles (e.g., LDVs emitting 0.25 g/mi ROG, 0.2 g/mi NO_x) will reduce peak ozone by 6%. The number of grid-hours greater than 0.2 ppm O₃ is lowered 42%. Peak PAN is reduced by only 1% and average PAN by 4%. Ambient formaldehyde levels would decrease appreciably. Peak formaldehyde at Downtown Los Angeles would decrease 15% and the basin-wide average formaldehyde level would decrease 17%. Total exposure to ozone increased 0.4 % due to NO_x emission reductions in the central basin, raising lower O₃ concentrations. Exposure above 0.20 ppm decreased 36%. Year 2010 results are similar. Peak ozone was reduced 6% and exposure above 0.20 ppm was reduced 26%. Exposure above 0.30 ppm was reduced 99%. Average formaldehyde, PAN, NO₂ and HNO₃ levels dropped between 10% (PAN) and 23% (NO₂).

Another calculation, **ADV LMD 2010**, looked at the effectiveness of just the light and medium duty vehicles meeting the emissions outlined in Appendix 4.C for advanced conventionally fueled vehicles (Fig 6.12c). The peak ozone was reduced 7%, and the exposure to ozone over 0.20 ppm was reduced 26%. A similar calculation, **ADV LMD/NO ROG 2010**, is used to elucidate the role of the reactive organic fraction of those emissions (Fig. 6.12d). Peak ozone was reduced 4% from **ADV LMD 2010**, and exposure to ozone above 0.20 ppm was reduced 37%.

6.5.4.2 Effectiveness of Fuel Types

Two different methanol-based fuels have been studied here, referred to as M100 (or neat) and M85. In this study, the difference between the two fuels is that the exhaust of the M100 fueled vehicle is composed of methanol and formaldehyde only, and the exhaust of the M85 vehicle contains components of conventionally fueled vehicles in about a fifty-fifty ratio to the methanol (see Appendix 4.E). Thus the exhaust of the M85 is more reactive.

(Recent findings suggest that the difference in reactivity may be small, see the discussion below.) Comparing the **STD M85** and the **STD M100** calculations (Figs. 6.9a and 6.8c), shows the effect of the assumed difference in the reactivity. NO_x emissions are the same in both calculations. Peak ozone decreases from the base of 0.261, to 0.245 for the M85 case and to 0.223 for the M100 simulation. In this case, the M85 calculation is midway in between, or about 50% of the improvement is derived from going to M85 vs M100. The number of grid-hours greater than 0.2 ppm O_3 goes from 510 to 286 to 140 for the same three cases, respectively. When compared to M100, using M85 raises PAN levels slightly (0.2 ppb on average), while average formaldehyde concentrations are nearly unaltered, though the Downtown peak is slightly lower. Population exposure is about the same for both the M100 and M85 cases, about 7% from the base case. Year 2010 results show a reduction in population exposure to stage 1 ozone levels of 16% from the base case if M85 fuel is used, and 24% if M100 fuel use is simulated. Exposure to high ozone levels, above 0.30 ppm, is lowered considerably more: 92% for both M85 and M100.

It should be noted that the future compositions of M100 and M85 fuels are not yet finalized and the exhaust composition is still uncertain. The M100 and M85 organic gas compositions chosen for this study were to bound the likely exhaust composition. As the data becomes available, the two cases can be used to bound the likely impacts. Of note, recent measurements indicate that a large fraction of the non-methanol, non-formaldehyde organic fraction of the exhaust of an M85 vehicle may be from the lubricating oil. This has two ramifications. First, the lubricating oil will also be present in the M100 exhaust, so the reactivity of the two mixtures may be very similar. Secondly, the products of the lubricating oil being emitted may not be photochemically as reactive as that assumed in the calculations above. The data is not yet available to determine if this is the case. This information is of critical importance in determining the relative benefits of M85 and M100 fuels. Also, the need for cold start and luminosity additives to M100 could add some reactivity to the exhaust. This would bring the reactivities of the exhaust and evaporative emissions from the two differently fueled vehicles closer together.

Switching the light and medium duty vehicles to methanol starting in 1990 to either M100 (**STD M100 2010**) or M85 (**STD M85 2010**) showed reduced ozone exposure compared to the base case (**BASE 2010**). The M100 calculation predicted ozone exposures very similar to having no ROG emissions from advanced light and medium duty CFVs (**ADV LMD-ROG 2010**). These results are very suggestive of the ability of methanol utilization to reduce ozone levels, especially considering that some of the emissions in the standard methanol cases are coming from older, degraded, MFVs and CFVs. This also leads to the conclusion that if mobile sources were responsible for a larger fraction of the emissions that there would be more apparent change between conventional and methanol fuel use scenarios, and the air quality benefits would be greater.

6.5.4.3 Advanced Technology Vehicles

Four runs (two each for 2000 and 2010) show the comparative advantage of using low-emission (advanced technology) MFVs vs. low-emission CFVs. For the year 2000, calculations show the peak ozone for the MFV case (**ADV METH**) was 0.223 ppm (Fig 6.8b), as compared to 0.246 ppm for the low emission CFVs (**ADV CONV**). For comparison, recall that the peak for the base case was 0.261, and the **NO MOBILE** case led to 0.206 ppm. Using the difference between the **BASE1** and **NO MOBILE**

predictions (0.055 ppm) as the maximum attainable improvement, the **ADV METH** gives 69% of that, and the **ADV CONV** would result in 27% of the attainable improvement. As with other comparisons between scenarios, the area and time weighted measures show a greater percentage variation. In this case, the **ADV METH** has 86% fewer grid-hours greater than 0.20 ppm O₃, while the **ADV CONV** has 42% less than the base case.

In the 2010 calculations, switching from an advanced conventionally fueled vehicle fleet (**ADV CONV 2010**) to an equivalent methanol fueled fleet (**ADV METH 2010**) reduced the total exposure 7%, and the exposure to ozone above 0.20 ppm was reduced 33% (Fig 6.11b vs. 6.11a). Peak ozone in the eastern basin was reduced 6%.

Peak PAN for the **ADV METH** calculation is 26% less than the **ADV CONV**, and the average is 26% less. Peak formaldehyde increases 3.2 ppb (20%) when the methanol fueled vehicles are used, though the average levels are virtually the same (within 3%). NO₂ levels, both peak and average, drop when methanol is used as the primary fuel.

As a measure of the reactivity of the ROG component of the exhaust in these two cases, the **ADV METH/NO ROG** (Fig. 6.9c) uses the same NO_x emissions as in **ADV METH** (which are about the same as **ADV CONV**), but no mobile source methanol or formaldehyde emissions. This would be similar to a fleet of automobiles that emit no organic gases, and low levels of NO_x. Peak ozone is lowered to 0.215 ppm, and the grid-hours greater than 0.20 ppm is 51. Thus, the organic fraction of the exhaust of an advanced M100 would be responsible for about 0.01 ppm of ozone (at this level of emissions). In comparison, the organic fraction of an advanced CFV is responsible for 0.031 ppm in the peak ozone (again, at this level of emissions). In fact, for all of the air quality measures shown in Tables 6.4 and 6.5, except for ambient formaldehyde levels, **ADV METH/NO ROG** is just slightly better than **ADV METH**. This shows the low reactivity of MFV exhaust as compared to conventionally fueled vehicles.

6.5.4.4 Formaldehyde Exhaust Fraction

Formaldehyde is a suspected carcinogen, and much of the reactivity of MFV exhaust is from the formaldehyde fraction. Two questions must be addressed. First, how sensitive is ozone formation to the amount of HCHO in the exhaust. Second, to what extent do as the direct emission of HCHO lead to increased ambient levels of formaldehyde. The answers to these two questions could be crucial in determining whether to set a formaldehyde emission standard, and at what level.

One calculation involved simulating a fleet of MFVs emitting 55 mg HCHO/mi (**HIGH FORM**), as compared to the assumed default of 15-18 mg/mi (**STD M100**). Comparing **HIGH FORM** to **STD M100** shows an increase in peak ozone of 0.015 ppm, though the number of grid-hours greater than 0.2 ppm almost doubles.

The formaldehyde levels downtown, which are sensitive to direct emissions, increase 4.9 ppb (25%) when the emission level is increased. However, the average HCHO increases only 13%. Even in the high formaldehyde case, predicted HCHO levels are significantly less than those in 1982, and the average is only 5% more than the year 2000 base case (BASE1).

6.5.4.5 Partial Penetration of Methanol Fueled Vehicles

METH 50 (Fig. 6.9a) is used to check if the benefits of utilizing methanol are proportional to their penetration into the vehicle fleet. From this calculation, and the full and no use cases, it is possible to determine what the air quality improvement would be if only a fraction of the fleet were methanol. In this intermediate case, the peak ozone drops to 0.25 ppm, not quite half way between the **BASE1** peak and the **STD M100** peak. Exposure to high ozone levels (above 0.20 ppm) is more than midway between the two cases. This is an indication of the non-linearity of the response, and that the benefits will increase as a larger fraction of the fleet is converted to methanol.

6.5.4.6 Stationary Source Use of Methanol

If maximum methanol fuel utilization were to occur on stationary sources to reduce NO_x emissions, both ozone and PAN levels would decrease compared to the use on mobile sources alone. Comparison of **ADV METH** and **FULL METH** shows that peak ozone concentration is decreased an additional 4 ppb (2 %) in the full methanol use scenario. The spatial and temporal measures also improve slightly. While the improvements are small, so is the change in the emissions. This calculation does show the impacts of NO_x control on stationary sources. Peak and average PAN levels decrease 23 and 25% respectively. Maximum formaldehyde at Downtown Los Angeles increases by 5% and basin-wide average formaldehyde increases by 2%.

6.5.4.7 Clean Initial and Boundary Condition Control Simulations

Four of the 2010 calculations were run a second time, lowering the initial conditions to clean levels, and lowering the boundary conditions to match (Fig 6.13). This decreased the far eastern peak, and makes the effect of emission controls on the air quality in the most populated portions of the SoCAB more apparent. Rerunning the 2010 base case with low emissions, as described in the diagnostic section, reduced the peak ozone only 0.01 ppm to 0.31, but more importantly this peak was in the central basin. The reduction in exposure, especially to high ozone levels (above 0.20 and 0.30 ppm) is greatly reduced from the base case, though the total exposure is only reduced 11% (**LO BC/LO IC 2010** vs. **BASE 2010**).

Stringent controls on conventionally fueled vehicles resulted in a predicted drop in peak ozone of 14% to 0.266 ppm, and the exposure above 0.20 ppm dropped 70% (**ADV CONV/LO IC 2010** vs. **LO BC/LO IC 2010**). Switching to advanced methanol fueled vehicles reduced the peak ozone to 0.256 ppm (18 % from the base), and the exposure to ozone above 0.20 ppm was decreased by 79%. Formaldehyde exposure declined 12%. NO_2 and nitric acid exposure also dropped. If standard technology M85 vehicles are introduced starting in 1990 (**STD M85/LO IC 2010**), the peak predicted ozone is 0.28 ppm and the exposure is 12,176 ppm-person-hours, or 14% less than the base case. Exposure to ozone over 0.20 ppm decreased 59%. Formaldehyde exposure increased by 8%. In each of the methanol utilization scenarios, PAN exposure, and the peak PAN were reduced.

This sequence of simulations reinforces the results of similar comparisons above. The benefit of these calculations is that they highlight the impacts in the most heavily

populated regions. Converting to methanol has the potential of reducing the peak ozone, and greatly reducing the exposure to high ozone levels (above 0.20 ppm). Formaldehyde exposure was relatively unimpacted, and could decrease. Predicted PAN, NO₂ and nitric acid levels, and hence exposure, decrease if methanol was used.

6.6 Summary and Conclusions

Airshed modeling has led to a number of points to be considered when viewing the effectiveness of utilizing methanol. First, no set of mobile source controls alone will bring the SoCAB into compliance with the NAAQS. In fact, removing mobile sources altogether will still result in Stage 1 ozone levels. However, the emission controls considered here would result in reducing peak ozone by up to 0.11 ppm from 1982 levels to the year 2000. Part of this improvement is from the expected conventional controls that will become effective between now and the year 2000, and then further benefits from utilizing methanol in mobile and stationary sources. Much of the improvement will be lost as increased activity between 2000 and 2010 leads to an increase in emissions basin-wide. There will also be a shift in the location of the peak pollutant concentrations to the east. The peak ozone in the 2010 calculations is 40 km east of Riverside instead of in the Pomona area. The pollutants within the urbanized core of the SoCAB will not increase as greatly as those downwind.

Methanol can have a role in reducing levels of photochemical pollutants. In each comparison, methanol fuel use reduced ozone, PAN and NO₂ in relationship to a similar case using CFVs. In head-to-head comparisons, the reduction in ozone is due to both reducing the reactivity of the organic exhaust and lowering NO_x emissions. PAN levels are reduced significantly when CFVs are replaced.

The amount of ozone reduced is sensitive to fuel type and exhaust composition. M85 vehicles have greater evaporative emissions, and the exhaust (as modeled here) is more reactive. These two effects lead to reducing ozone only about half as much as in the M100 cases. When the formaldehyde emissions are increased from 15 mg/mi to 55 mg/mi, the ozone increases by about 0.02 ppm (10%). Tests showed that the ROG emissions from an advanced MFV emitting 3 mg/mi HCHO, contribute to the formation of only about 5% of the ozone.

These calculations show that using methanol would lead to decreases in high ozone concentrations in the peak regions in the central portion of the SoCAB, and, to a lesser extent, in the far eastern basin. In the far eastern basin, the atmosphere is ROG rich, and the predicted decrease in ozone is derived from a reduction in NO_x emissions. The central basin peak is sensitive to replacing the ROG emissions by a much less reactive gas (methanol), and to reducing the NO_x emissions. In the western, urban area, the atmosphere is NO_x rich, and reducing the reactivity of the ROG and decreasing NO_x emissions compete, resulting in little change in ozone concentrations.

Concern over the possible increases in ambient formaldehyde during photochemical episodes was addressed. The above calculations show that while the morning peak formaldehyde at sites heavily impacted by direct emissions from MFVs may increase a few ppb, average levels will remain about the same and may possibly decrease. In either case, the change is not substantial, and the levels are much lower than those found for 1982.

The three tiered photochemical modeling portion of this study, concluding with the airshed modeling, has shown the low reactivity of methanol in the atmosphere. Even over three day episodes, methanol emissions don't produce significant amounts of ozone and considerably less than CFV exhaust. Ozone was reduced when methanol was used in both stationary and mobile sources. Reduction in ozone was not spatially uniform. More improvement is noted over the central, populated regions. Further downwind (east), the peak ozone is more sensitive to reducing NO_x . This is especially evident in the trajectory and 2010 calculations. A combined strategy of reducing the reactivity of the ROG and reducing NO_x would be beneficial basin-wide.

7.0 Aerosol Modeling of the Impact of Methanol Fuel Use

7.1 Introduction

Atmospheric aerosols have come under increased scrutiny as evidence of their environmental and health effects has risen. A potential benefit derived from using methanol is a reduction in the formation of airborne particles, or aerosols due to decreased direct emissions of particulate matter, and lower emissions of aerosol precursors. Small particles scatter light efficiently, leading to greatly reduced visibility. Carbonaceous particles can also absorb light, further decreasing visibility. Health concerns about fine particulate matter arise because near-micron size particles penetrate the lung more deeply than larger particles. Deposition of particulate matter is also of concern due to the possibility of corrosion and of increased soiling.

In response to the problems that fine particulate matter may pose, the national standard was set at $150 \mu\text{g m}^{-3}$ of particulate matter less than $10 \mu\text{ms}$ in diameter (PM_{10}) during a 24 hr period. The annual average standard (arithmetic mean) is $50 \mu\text{g m}^{-3}$. The state standards are stricter: $50 \mu\text{g m}^{-3}$ 24 hr average, and $30 \mu\text{g m}^{-3}$ annual geometric mean. Concentrations of PM_{10} in the SoCAB have been measured up to $299 \mu\text{g m}^{-3}$, almost twice the EPA standard (Solomon et al. 1988), and the annual average surpasses the $50 \mu\text{g m}^{-3}$ standard across the basin (SCAQMD, 1988).

Fine particulate matter is due primarily to gas-to-particle conversion following chemical reaction and also to road dust. Major components of PM_{10} include nitrate, sulfate, organic carbon, and elemental carbon. Ammonium is associated with the sulfate and nitrate. This chapter investigates the effects of methanol fuel substitution on atmospheric levels of fine aerosols and how these effects would impact visibility.

Sources that could be converted to methanol contribute to elemental carbon, organic carbon, sulfate and nitrate aerosol formation. Converting these sources would lower atmospheric aerosol concentrations. Methanol use in diesel engines will decrease elemental carbon emissions and will reduce the emissions of precursors to sulfate, nitrate, and organic aerosols. Methanol use in gasoline fueled engines would decrease the precursor emissions of secondary organic aerosols and sulfate. Stationary source use reduces NO_x emissions and the resulting nitrate.

Fine carbon aerosols are relatively unreactive, being directly emitted from fuel combustion. Their concentrations at a receptor site are functions of emissions, transport, diffusion, and deposition. In areas such as Downtown Los Angeles, which is heavily impacted by motor vehicle emissions, up to 40% of the total particulate can be fine carbon aerosols (Gray, 1986). There are two groups of fine carbon aerosols that are of primary concern. The first is organic carbon aerosols and the second is elemental carbon aerosols. Certain organic carbon particulates, such as polynuclear aromatic hydrocarbons (PAH), are suspected carcinogens (Finlayson-Pitts and Pitts, 1986). Elemental carbon (sometimes referred to as graphitic carbon) is an efficient light absorber, and, in areas such as downtown Los Angeles and Denver, can be the primary source of visibility degradation.

By contrast, aerosol nitrates are formed in the atmosphere, from reactions of NO_x , ROG, and their products. Their concentrations depend not only on emissions and transport phenomena, but also on reactions with other atmospheric pollutants. Because of this nonlinear photochemical behavior, the response of aerosol nitrate concentrations to

methanol utilization were determined by analysis with the airshed model. Aerosol nitrates have possible health effects and can reduce visibility by scattering light. In areas of the eastern SoCAB, up to 40% of the fine particulate, by mass, can be aerosol nitrates (Solomon et al., 1988).

Aerosol sulfates are also secondary pollutants, formed by reaction of SO_x and photochemical oxidants. Up to 35% of the particulate matter mass, depending on location in the SoCAB, can be made up of aerosol sulfates. Aerosol sulfates have possible health effects, cause materials damage, reduce visibility, and can be acidic.

Finally, secondary organic aerosols are primarily formed by gas-phase reactions of cyclic olefins, diolefins, and aromatics. The trajectory model was used to determine concentrations of organic aerosols along specific trajectories within the basin. Organic aerosols soil surfaces, scatter light, and may have health effects (Finlayson-Pitts and Pitts, 1988).

The following sections discuss each of the four aerosol groups, and how methanol utilization would impact concentrations in the SoCAB. Because their formation and behavior in the atmosphere are different, four procedures are used to estimate the impact that utilizing methanol would have on small particle concentration and speciation in the year 2000. To calculate the change in primary organic and elemental carbon concentrations, the particle-in-cell model results of Gray (1986) are used. Secondary organic aerosol formation is studied using the trajectory model of Bouvier (1986), updated to reflect the findings of Stern et al. (1987). Sulfate concentration changes are predicted using the dispersion modeling results in the recent AQMP (SCAQMD, 1988). The formation of aerosol nitrate is an integral part of the photochemical cycle, and is dependent on the dynamics of the hydrocarbons and NO_x , as is the formation and evolution of O_3 and HCHO. For this reason, the airshed modeling calculations described in Chapter 6 are used to address how aerosol nitrate concentrations will change if MFVs penetrate significantly into the vehicle fleet. Each of these sets of calculations is described in detail below, along with analysis of the results. The results from studying the individual components are then collected to determine how total atmospheric PM_{10} levels at a heavily impacted receptor site would be affected if methanol was used. Finally, these results are used to model the expected changes in visibility.

7.2 Primary Carbon Aerosols

This section identifies the source of primary carbon aerosols in the urban atmosphere, and then presents a methodology for determining their concentration as a function of emissions. The model used as the basis of this methodology comes from Gray (1986). Effects of various scenarios on fine carbon emissions are reviewed, and these emissions are input to the model. The resulting fine carbon levels are then presented along with a discussion as to the significance of methanol fuel usage on atmospheric fine carbon levels.

7.2.1 Fine Carbon and Fine Elemental Carbon

Aerosol carbon species that are of primary concern in the urban atmosphere are fine organic and elemental carbon. Fine particle carbon can be emitted directly into the atmosphere, or it can be formed in the atmosphere from reactions of other emissions. Most of the experimental data has been collected at or near ground level. Because the majority of the fine particle carbon in the SoCAB is from direct emissions into the atmosphere (Gray,

1986), a source-receptor analysis can be used to determine the relationships between emissions and the bulk of the aerosol carbon concentrations.

7.2.2 Source Receptor Analysis of Carbon Aerosol Concentrations

A source-receptor analysis of pollutant concentration assumes that emissions of m sources combine linearly at the receptor site. If c is a vector of all pollutant species measured at the receptor site, s is a vector of emissions of all significant sources (in this case all significant sources in the modeling region) then the relationship between c and s is given by

$$\begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & \cdots & a_{m1} \\ a_{21} & a_{22} & \cdots & a_{2m} \\ \cdot & \cdot & \cdot & \cdot \\ a_{n1} & a_{n2} & \cdots & a_{nm} \end{bmatrix} \begin{bmatrix} s_1 \\ s_2 \\ \cdot \\ s_m \end{bmatrix} \quad (7.1)$$

where c_i is the concentration of pollutant species i , as measured at the receptor site (measured in units of mass/volume), s_j is the total emissions of source j (measured in units of mass/time), and a_{ij} is the fraction of species i emitted by source j that traveled to the receptor site. In compact form, this is shown as:

$$\bar{C} = A \bar{s} \quad (7.2)$$

where \bar{C} is the concentration vector, \bar{s} is the source emission rate vector, and A is the transfer matrix. A can be thought of as a mathematical description of the transport of particulate matter.

The values of a_{ij} are determined in two steps. First, the emissions of each source are broken up by species and fraction. For example, if a source had total particulate emissions of 200 kg/day, 150 kg/day of fine carbon, of which 80 kg/day is elemental carbon, then the fractional distributions for fine and elemental carbon are 0.75 and 0.4, respectively. (Elemental carbon is a component of total carbon.) Next, a Lagrangian trajectory analysis is used to determine what fraction of the emissions from a particular source reach a particular receptor site. In this case, the particle-in-cell model by Cass (1982), and refined by Gray (1986), is used. This depends on the respective locations of the source and site, and on the meteorological conditions. This transport fraction is multiplied by the species emission fraction to get the specific a_{ij} . Once the a_{ij} are known, future changes in pollutant concentrations at the receptor site can be determined as a function of changes in source emissions.

This section investigates the effects of fuel substitution and emissions controls on atmospheric fine carbon and atmospheric fine elemental carbon. Therefore the number of species, n , in the above equation is two. The number of sources, m , and their total emissions are s_1 through s_m . The values of s_1 through s_m for the base case come from the 1982 CARB carbon particulate matter emissions inventory (Allen, 1986; Avlani, 1986), and are then updated to reflect changes in emissions between 1982 and 2000. The data used for the updating comes from the SCAQMD projections of changes in source

emissions (SCAQMD and SCAG, 1982). This methodology was selected because the Gray study performed a Lagrangian analysis and determined A matrices for specific locations within the basin, and the entire basin, at different time periods in 1982. If one assumes that emissions sources will have a similar fractional species distribution in the year 2000 as they had in 1982, then the same A matrices that were determined by Gray can be used.

In this study, each scenario uses the same A matrix for determining carbon aerosol concentrations at a specific location and time period. Changes in carbon aerosol concentrations come from changes in the total source emissions levels, which are assumed to be uniformly distributed across all sources within a single source category. However, different source locations and time periods have different A matrices. Therefore, the next step in determining particulate concentration levels is to determine source emissions for the different scenarios considered in this study.

7.2.3 Source Emissions of Fine Carbon

The first step in determining atmospheric fine carbon concentrations as a function of time and location is to determine source emissions into the atmosphere. The CARB particulate emissions inventory (Avlani, 1986) is separated into source types, such as various types of on-road and off-road mobile sources, stationary internal combustion engines, surface coating processes, and so on. This study uses a grouping of 74 source types. Source types within each group share emissions patterns as a function of time, and effective stack height. The CARB inventory gives the locations and emissions of these source types within the basin. By combining the data for all the source types, total emissions by location and time for the entire study area can be obtained. The emissions sources can also be kept separate, to show what percent of total emissions are made up by emissions from a specific source type.

The next step is to update the carbon particulate matter emissions inventory to reflect year 2000 emissions. This is done by using carbon particulate matter emissions information from 1982 and 2000. The year 2000 stationary source carbon aerosol emissions were obtained by scaling the 1982 carbon aerosol emissions by the expected increase (or decrease) in carbon aerosol emissions from 1982 to 2000. This gives the baseline year 2000 emissions. For stationary sources, the scaling data for 1982 to 2000 does not exist for each of the approximately 70 groups but rather for 6 major groups: petroleum processes, solvent processes, internal combustion, waste burning, industrial processes, and miscellaneous processes (which included all processes which did not fit into one of the previous five processes). The off road vehicles, likewise, had one 1982 to 2000 scaling factor. For on road vehicles, scaling was done separately for each of the following groups: Catalyst Light Duty Autos, Non-Catalyst Light Duty Autos, Diesel Light Duty Autos, Catalyst Light Duty Trucks, Non-Catalyst Light Duty Trucks, Diesel Light Duty Trucks, Catalyst Medium Duty Trucks, Non-Catalyst Medium Duty Trucks, Motorcycles, Heavy Duty Gasoline Vehicles and Heavy Duty Diesel Vehicles. This scaling information was determined by calculating the fine particulate emissions for each vehicle type in 1982, as estimated by SCAQMD, with the same emissions forecast for 2000.

The base case inventory, detailed above, is then scaled to determine emissions for the other year 2000 scenarios. There are two methodologies for scaling the emissions, one for the on-road mobile sources, and one for all other sources. The carbonaceous aerosol emissions of each class of on-road CFVs is assumed to scale linearly with the THC emissions. For example, if one scenario considers use of advanced technology CFVs with 30% lower THC emissions, then the resulting fine carbon and elemental carbon emissions will also be 30% lower than in the base case. MFVs are assumed to emit negligible amounts of carbon containing aerosols. For simplicity, this was extended to assume both M100 and M85 fueled MFVs. The total fine carbon and elemental

carbon emissions for on-road mobile sources is the sum of the emissions for all the on-road vehicle groups.

Source types other than on-road mobile sources that are affected by scenarios include regulated off-road mobile sources, utility boilers, power generation equipment, and industrial heaters and boilers. For the cases studied here, these sources either experience total conversion to methanol fuel, or no change at all. Therefore, a source type will either have negligible fine carbon and elemental carbon emissions, or the same emissions as it had in the base case.

Emissions from all source types can be added up to get emissions for the modeling region. Table 7.1 shows the total and elemental carbon emissions for the region in 1982 and for various year 2000 emissions scenarios. These results are repeated graphically in Figures 7.1 and 7.2. In Table 7.1 and Figures 7.1 and 7.2 is the reference to more than one scenario for certain sets of data indicating that similar carbon emissions and concentrations are expected. It is important also to realize that the ratio of fine elemental carbon to fine total carbon is not constant from one source to another. Therefore, a particular set of strategies in one scenario may affect emissions of fine total carbon differently than it affects elemental carbon.

7.2.4 Determining Fine Carbon Concentrations

The matrix equation for determining carbon aerosol concentrations either areawide or at a particular site is given in Equation 7.1. Since only particulate fine and elemental carbon levels are being investigated, the number of species, n , in Equation 7.1 is two. This reduces Equation 7.1 to a set of two algebraic equations

$$c_f = a_{f1}S_1 + a_{f2}S_2 + \dots + a_{fm}S_m \quad (7.3a)$$

$$c_e = a_{e1}S_1 + a_{e2}S_2 + \dots + a_{em}S_m \quad (7.3b)$$

In these equations, c_f is the atmospheric concentration of fine carbon, and c_e is the atmospheric concentration of elemental carbon. a_{f1} is the amount of source 1 emissions that are fine carbon and that are transported to the receptor site. s_1 is the total emissions of source one, and so on. The values of a_{f1} through a_{fm} and a_{e1} through a_{em} are taken from Gray, so atmospheric levels of fine carbon and elemental carbon can be calculated by substituting the appropriate source emissions into Equations 7.3a and 7.3b. The values of a_{f1} through a_{fm} and a_{e1} through a_{em} are different for each location (basinwide and specific site) and for each time period. The results of these calculations are presented in the next section.

7.2.5 Results

7.2.5.1 Areawide Fine Carbon Levels

Areawide levels of fine total carbon and fine elemental carbon refer to the total emissions each day into the 80km x 80km modeling region used by Gray. Table 7.1 and Figures 7.1 and 7.2 show that the sources of the atmospheric fine total carbon are relatively evenly distributed across the major source groups, not all of which are affected by converting to methanol. Converting on-road motor vehicles (except motorcycles), off-road vehicles, and convertible stationary sources to methanol can only reduce fine total carbon by 26% over the baseline year 2000 emissions. This is because the largest contributing groups, fugitive combustion and tire, brake and road dust, are unaffected by the conversions. Also, even though particulate emissions of gasoline vehicles decrease by 93% and diesel vehicles by 48%, the emissions of fine total carbon decrease by only 14%. This is because the improvements in on-road motor vehicle emissions are offset by the

**Table 7.1 Total Emissions of Fine and Elemental Carbon
Within the Modeling Region (kg/day)**

Fine Total Carbon	Gasoline	Diesel	Other	Stationary	Industrial	Tire, Brake	Fugitive	Other	Total	Change
	On-Road	On-Road	Mobile	Combustion	Processes	& Road Dust	Combustion			w.r.t Base 2000
Base 1982	5242	7395	2929	1678	4154	8094	7541	774	37807	1.13
Base 2000, Adv Conv	394	3820	4029	1925	4573	10080	7903	811	33535	1.00
No Mobile, Adv Meth	0	0	855	1625	4264	10080	7903	811	25538	0.76
M100, M85, High Form	11	1607	4029	1925	4573	10080	7903	811	30939	0.92
Full Meth	2	0	855	1040	4264	10080	7903	811	24955	0.74
Meth 50	202	2713	4029	1925	4573	10080	7903	811	32236	0.96

Fine Elemental Carbon	Gasoline	Diesel	Other	Stationary	Industrial	Tire, Brake	Fugitive	Other	Total	w.r.t
	On-Road	On-Road	Mobile	Combustion	Processes	& Road Dust	Combustion			Base 2000
Base 1982	1261	5665	2372	402	438	830	481	1	11450	1.31
Base 2000, Adv Conv	164	2926	2968	461	465	1242	504	1	8731	1.00
No Mobile, Adv Meth	0	0	590	459	457	1242	504	1	3253	0.37
M100, M85, High Form	2	1231	2968	461	465	1242	504	1	6874	0.79
Full Meth	0	0	590	318	457	1242	504	1	3112	0.36
Meth 50	83	2079	2968	461	465	1242	504	1	7803	0.89

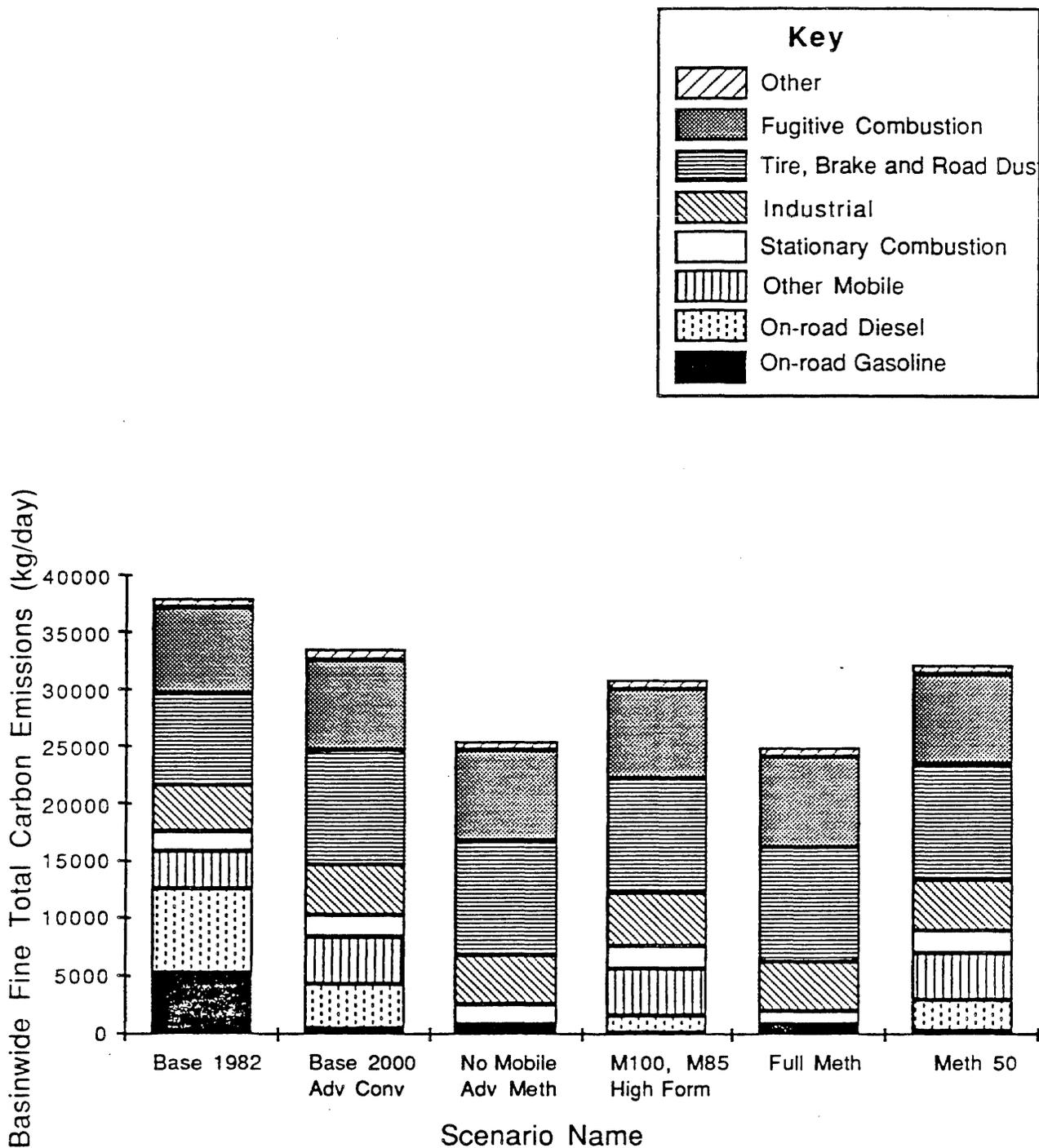


Figure 7.1 Basinwide Fine Total Carbon Emissions as a Function of Scenario

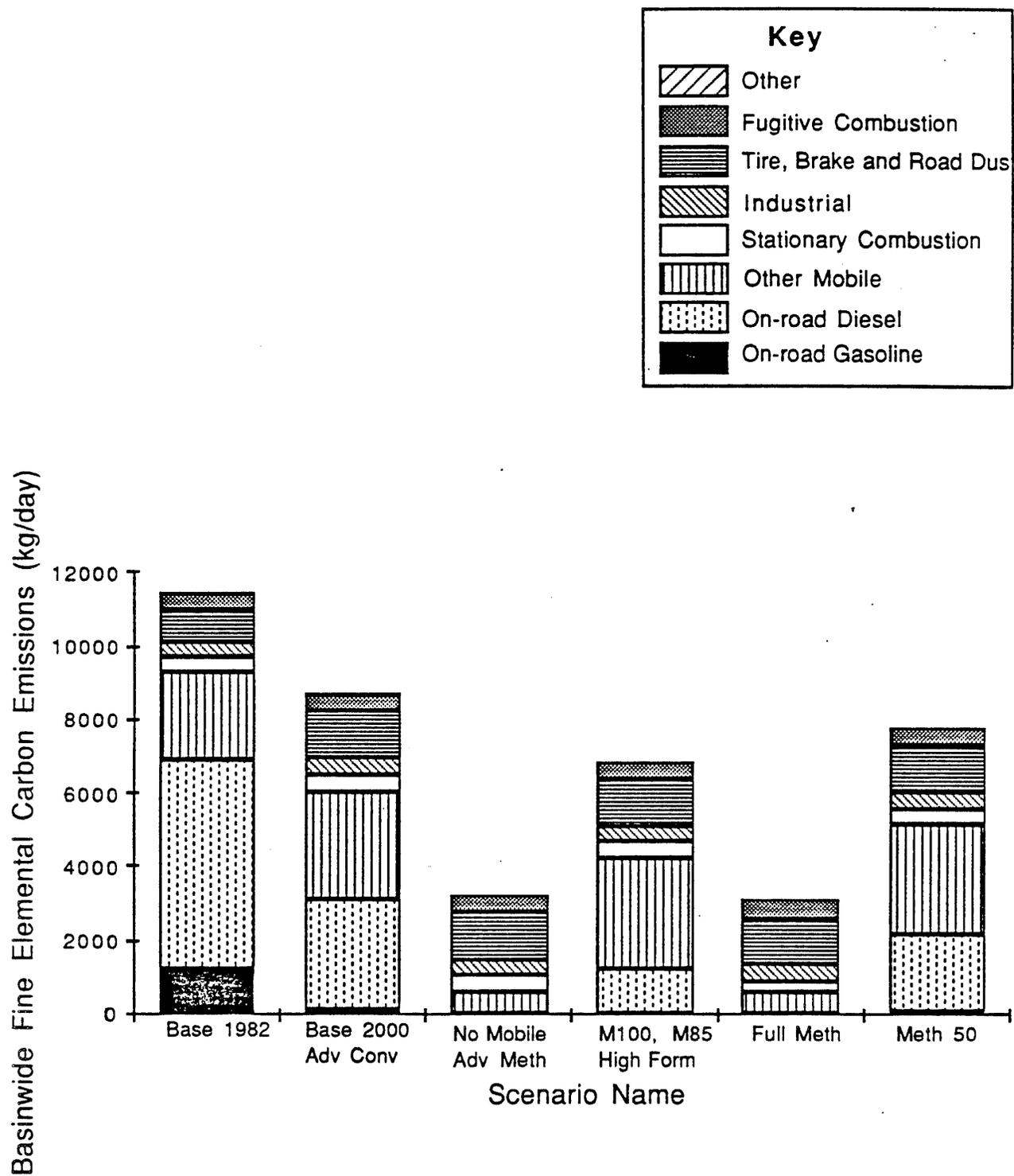


Figure 7.2 Basinwide Fine Elemental Carbon Emissions as a Function of Scenario

increased emissions of industrial sources, tire, brake and road dust, and stationary combustion. These all increase from increased population and commercial activity in the basin between 1982 and 2000.

On the other hand, fine elemental carbon emissions come primarily from diesel engine vehicles and machinery. Therefore, converting diesel cycle on-road, off-road, and stationary sources to methanol fuel can decrease emissions of fine elemental carbon up to 63% below the year 2000 baseline. Additionally, the baseline fine elemental carbon emissions are 31% below the 1982 emissions. This is due to on road diesel emissions comprising 33% of the total emissions, and increased regulations on diesel exhaust will effectively reduce baseline emissions. Diesel sources are also the primary contributors in industrial and other stationary sources and the same benefits would be realized.

7.2.5.2 Fine Carbon Levels at Specific Locations

In addition to reviewing the effects of methanol fuel usage on total basinwide emissions, it is instructive to review the effects at specific locations. This is because specific sites experience different impacts by each source type. For example, the Long Beach area is heavily impacted by refinery emissions, and downtown Los Angeles is impacted by traffic and railway emissions. Reducing the refinery emissions may significantly reduce the particulate emissions near Long Beach but may not help areas such as San Bernardino. However, if particulate levels were excessive at Long Beach, but not at San Bernardino, this might be a more cost effective strategy for reducing particulate matter concentrations than reducing the particulate emissions of other industrial sources which are present at both locations.

The two locations chosen for in-depth review were Los Angeles and Lennox. Los Angeles was selected for several reasons. First, a large amount of the emissions that impact Los Angeles are from on-road mobile sources. Since these are the source types that would primarily be affected by the emissions scenarios studied here, the effects will be more pronounced in this area. Second there is a large population concentration around Los Angeles, so any changes in carbon aerosols will affect a very large number of people. Lennox was chosen because the sources that affect that area have a different distribution than does Los Angeles. Also, the concentrations at two different months at each site were reviewed. September concentrations were reviewed because the photochemical modeling portion of this study looked at emissions during an August 30 to September 1 period. December was also studied because that is when the peak particulate concentrations occurred.

Table 7.2 and Figures 7.3 through 7.10 show the concentrations and sources of fine and elemental carbon at Los Angeles and Lennox. (Again, certain scenarios will share expected concentration results.) Los Angeles generally follows basinwide emission estimates in that total fine carbon concentrations are only decreased a maximum of 38%, while elemental carbon concentrations can be decreased up to 85%. The amount of reduction is less in December than in warmer months. Non-mobile source emissions increase in December, most likely to satisfy seasonal heating requirements. As a result, mobile sources, which are primarily being perturbed, make up less of the total carbon particulate burden.

At the Lennox site, a major source of fine total carbon is aircraft, which are not subject to state emissions regulations, so less improvement is found from converting to MFVs. Total fine carbon is reduced up to 35%, and elemental carbon is reduced up to 62%.

**Table 7.2 Fine and Elemental Carbon Concentrations
at Specific Locations**
Particle Concentrations in $\mu\text{g}/\text{m}^3$

	Los Angeles (Sept) Fine Total Carbon Concentrations					
	Base 1982	Base 2000	No Mobile	M100,M85, Full Meth	Meth 50	
		Adv Conv	Adv Meth	High Form		
gasoline on road	2.8	0.2	0.0	0.0	0.0	0.1
diesel on road	4.1	2.1	0.0	0.9	0.0	1.5
other diesel	2.0	2.8	0.6	2.8	0.6	2.8
aircraft	0.0	0.0	0.0	0.0	0.0	0.0
stationary comb	0.2	0.2	0.2	0.2	0.1	0.2
industrial	1.3	1.4	1.3	1.4	1.3	1.4
tire,brake&road	1.8	2.2	2.2	2.2	2.2	2.2
fugitive comb	2.3	2.4	2.4	2.4	2.4	2.4
background	1.8	1.8	1.8	1.8	1.8	1.8
total	16.3	13.2	8.6	11.8	8.5	12.5
change wrt BASE	1.2	1.0	0.6	0.9	0.6	0.9

	Los Angeles (Sept) Elemental Carbon Concentrations					
	Base 1982	Base 2000	No Mobile	M100,M85, Full Meth	Meth 50	
		Adv Conv	Adv Meth	High Form		
gasoline on road	0.9	0.1	0.0	0.0	0.0	0.1
diesel on road	3.0	1.5	0.0	0.7	0.0	1.1
other diesel	1.5	1.9	0.4	1.9	0.4	1.9
aircraft	0.0	0.0	0.0	0.0	0.0	0.0
stationary comb	0.0	0.0	0.0	0.0	0.0	0.0
industrial	0.0	0.0	0.0	0.0	0.0	0.0
tire,brake&road	0.4	0.6	0.6	0.6	0.6	0.6
fugitive comb	0.0	0.0	0.0	0.0	0.0	0.0
background	0.2	0.2	0.2	0.2	0.2	0.2
total	6.0	4.3	1.2	3.3	1.2	3.8
change wrt BASE	1.4	1.0	0.3	0.8	0.3	0.9

	Los Angeles (Dec) Fine Total Carbon Concentrations					
	Base 1982	Base 2000	No Mobile	M100,M85, Full Meth	Meth 50	
		Adv Conv	Adv Meth	High Form		
gasoline on road	2.5	0.2	0.0	0.0	0.0	0.1
diesel on road	3.8	2.0	0.0	0.8	0.0	1.4
other diesel	2.0	2.8	0.6	2.8	0.6	2.8
aircraft	0.0	0.0	0.0	0.0	0.0	0.0
stationary comb	0.5	0.6	0.5	0.6	0.3	0.6
industrial	0.8	0.9	0.8	0.9	0.8	0.9
tire,brake&road	1.7	2.1	2.1	2.1	2.1	2.1
fugitive comb	3.3	3.5	3.5	3.5	3.5	3.5
background	2.3	2.3	2.3	2.3	2.3	2.3
total	16.9	14.2	9.8	12.9	9.6	13.6
change wrt BASE	1.2	1.0	0.7	0.9	0.7	1.0

Los Angeles (Dec) Elemental Carbon Concentrations

	Base 1982	Base 2000	No Mobile	M100,M85, Full Meth	Meth 50
		Adv Conv	Adv Meth	High Form	
gasoline on road	0.5	0.1	0.0	0.0	0.0
diesel on road	2.9	1.5	0.0	0.6	1.1
other diesel	1.5	1.9	0.4	1.9	1.9
aircraft	0.0	0.0	0.0	0.0	0.0
stationary comb	0.0	0.0	0.0	0.0	0.0
industrial	0.2	0.2	0.2	0.2	0.2
tire,brake&road	0.3	0.4	0.4	0.4	0.4
fugitive comb	0.3	0.3	0.3	0.3	0.3
background	0.4	0.4	0.4	0.4	0.4
total	6.0	4.7	1.6	3.8	4.2
change wrt BASE	1.3	1.0	0.3	0.8	0.9

Lennox (Sept)**Fine Total Carbon**

	Base 1982	Base 2000	No Mobile	M100,M85, Full Meth	Meth 50
		Adv Conv	Adv Meth	High Form	
gasoline on road	2.1	0.2	0.0	0.0	0.1
diesel on road	3.5	1.8	0.0	0.8	1.3
other diesel	0.4	0.6	0.1	0.6	0.6
aircraft	1.6	1.8	1.6	1.8	1.8
stationary comb	0.3	0.3	0.2	0.3	0.3
industrial	1.1	1.2	1.1	1.2	1.2
tire,brake&road	1.3	1.6	1.6	1.6	1.6
fugitive comb	1.3	1.4	1.4	1.4	1.4
background	1.7	1.7	1.7	1.7	1.7
total	13.3	10.5	7.7	9.3	9.9
change wrt BASE	1.3	1.0	0.7	0.9	0.9

Lennox (Sept)**Elemental Carbon Concentrations**

	Base 1982	Base 2000	No Mobile	M100,M85, Full Meth	Meth 50
		Adv Conv	Adv Meth	High Form	
gasoline on road	0.5	0.1	0.0	0.0	0.0
diesel on road	2.6	1.3	0.0	0.6	1.0
other diesel	0.4	0.5	0.1	0.5	0.5
aircraft	1.4	1.6	1.6	1.6	1.6
stationary comb	0.0	0.0	0.0	0.0	0.0
industrial	0.0	0.0	0.0	0.0	0.0
tire,brake&road	0.2	0.3	0.3	0.3	0.3
fugitive comb	0.0	0.0	0.0	0.0	0.0
background	0.0	0.0	0.0	0.0	0.0
total	5.1	3.8	2.0	3.0	3.4
change wrt BASE	1.3	1.0	0.5	0.8	0.9

Lennox (Dec)	Fine Total Carbon Concentrations					
	Base 1982	Base 2000	No Mobile	M100,M85, Full Meth	Meth 50	
		Adv Conv	Adv Meth	High Form		
gasoline on road	4.7	0.4	0.0	0.0	0.0	0.2
diesel on road	6.5	3.4	0.0	1.4	0.0	2.4
other diesel	1.5	2.1	0.4	2.1	0.4	2.1
aircraft	1.5	1.7	1.5	1.7	0.9	1.7
stationary comb	1.3	1.5	1.3	1.5	0.8	1.5
industrial	2.2	2.4	2.3	2.4	2.3	2.4
tire,brake&road	3.0	3.7	3.7	3.7	3.7	3.7
fugitive comb	6.3	6.6	6.6	6.6	6.6	6.6
background	2.3	2.3	2.3	2.3	2.3	2.3
total	29.3	24.1	18.0	21.8	17.1	22.9
change wrt BASE	1.2	1.0	0.8	0.9	0.7	1.0

Lennox (Dec)	Elemental Carbon Concentrations					
	Base 1982	Base 2000	No Mobile	M100,M85, Full Meth	Meth 50	
		Adv Conv	Adv Meth	High Form		
gasoline on road	1.1	0.1	0.0	0.0	0.0	0.1
diesel on road	4.9	2.5	0.0	1.1	0.0	1.8
other diesel	1.3	1.6	0.3	1.6	0.3	1.6
aircraft	1.0	1.2	1.2	1.2	0.8	1.2
stationary comb	0.4	0.5	0.5	0.5	0.3	0.5
industrial	0.0	0.0	0.0	0.0	0.0	0.0
tire,brake&road	0.5	0.7	0.7	0.7	0.7	0.7
fugitive comb	0.6	0.6	0.6	0.6	0.6	0.6
background	0.4	0.4	0.4	0.4	0.4	0.4
total	10.2	7.7	3.7	6.1	3.2	6.9
change wrt BASE	1.3	1.0	0.5	0.8	0.4	0.9

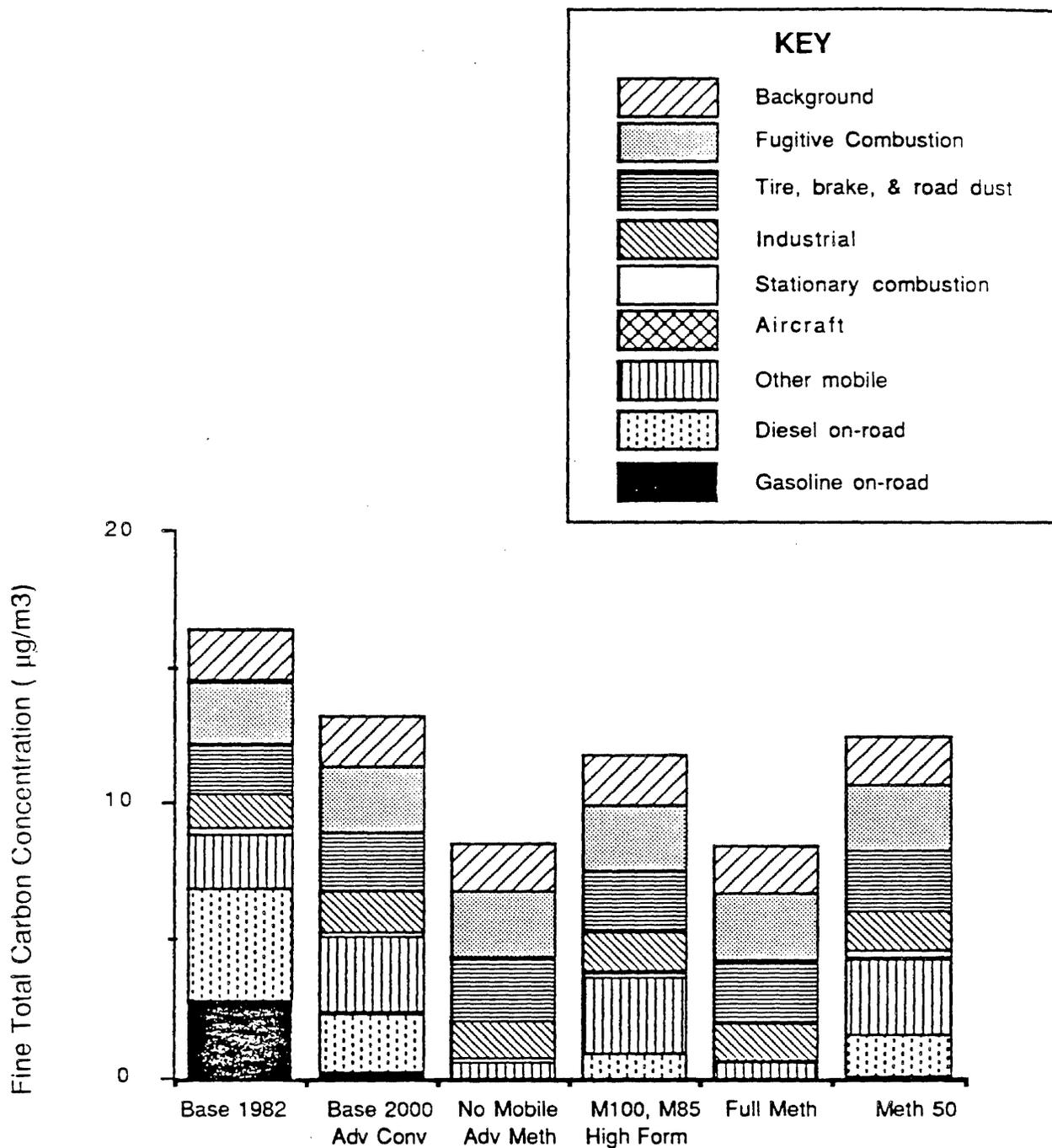


Figure 7.3 Fine total carbon concentrations at Los Angeles in September as a function of scenario and source.

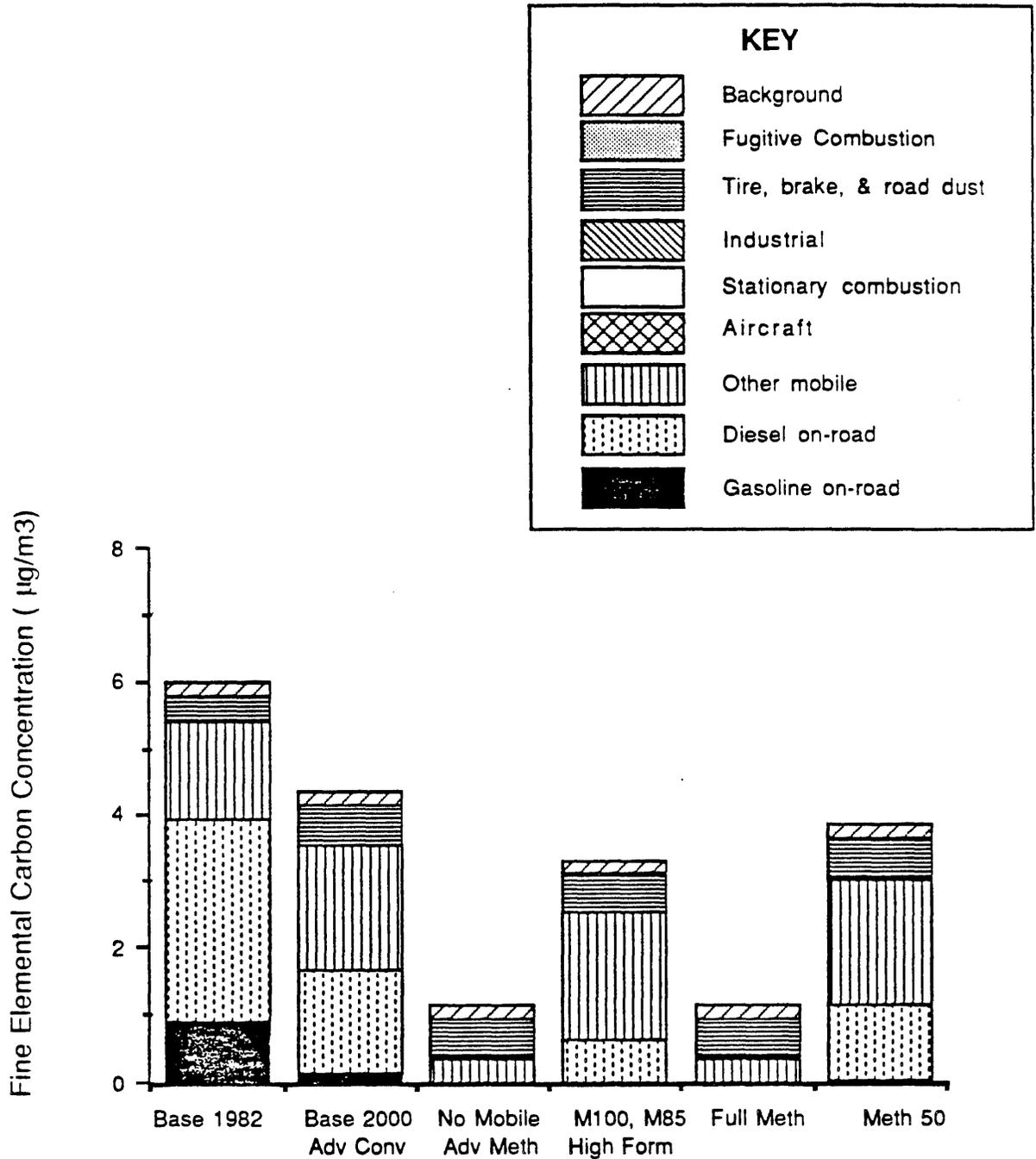


Figure 7.4 Fine elemental carbon concentrations at Los Angeles in September as a function of scenario

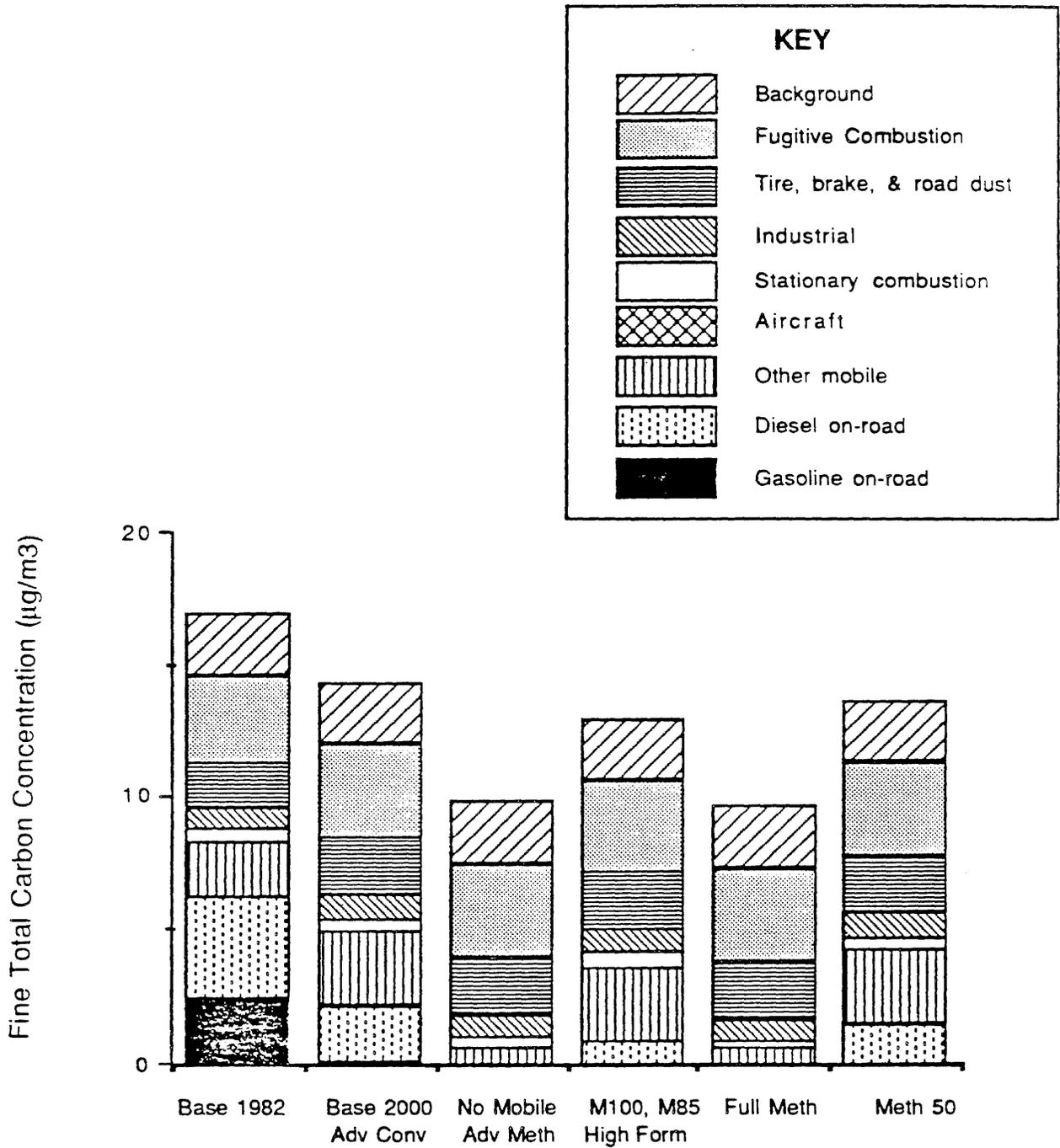


Figure 7.5 Fine total carbon concentrations at Los Angeles in December as a function of scenario and source.

Fine Elemental Carbon Concentration ($\mu\text{g}/\text{m}^3$)

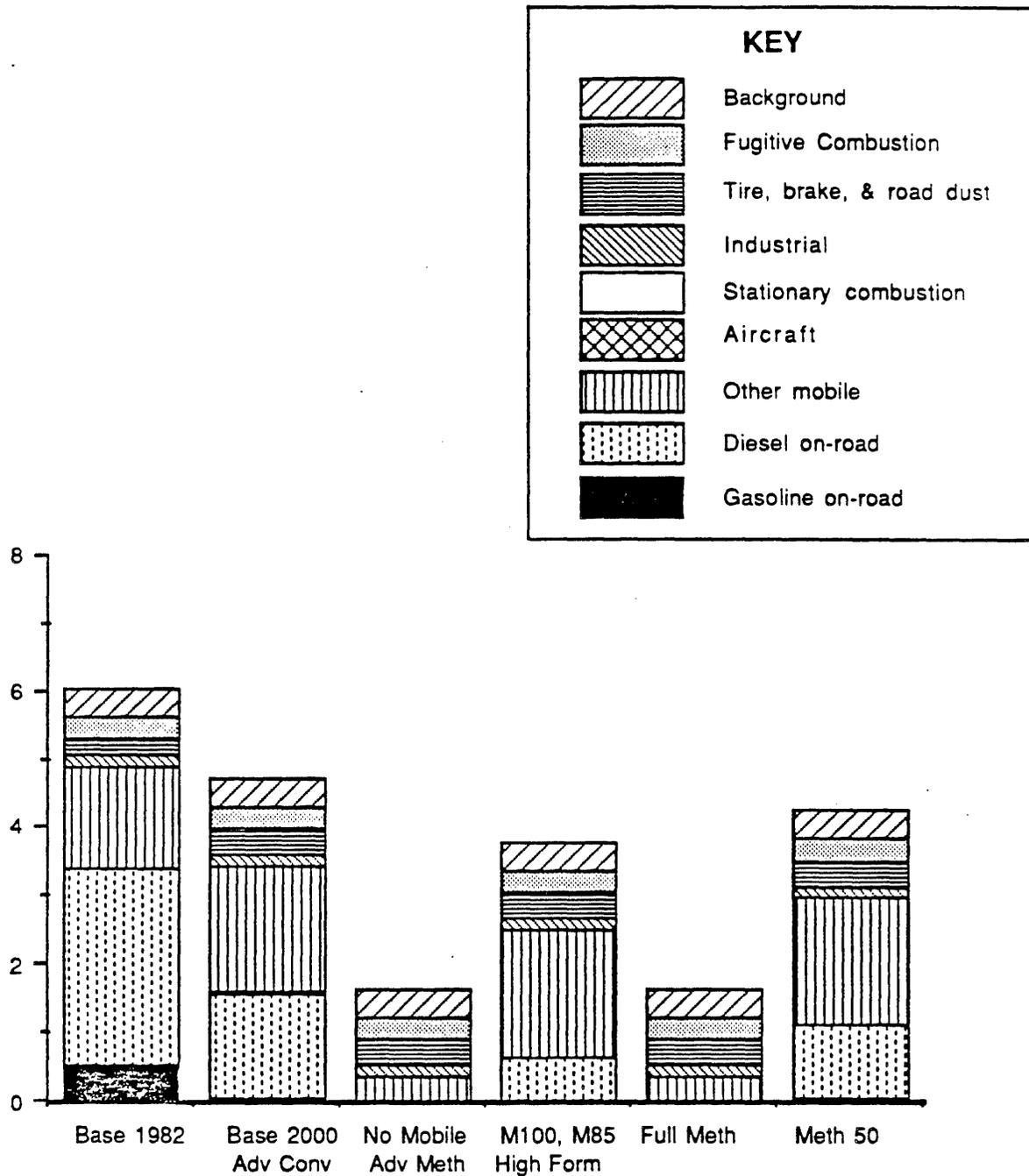


Figure 7.6 Fine elemental carbon concentrations at Los Angeles in December as a function of scenario.

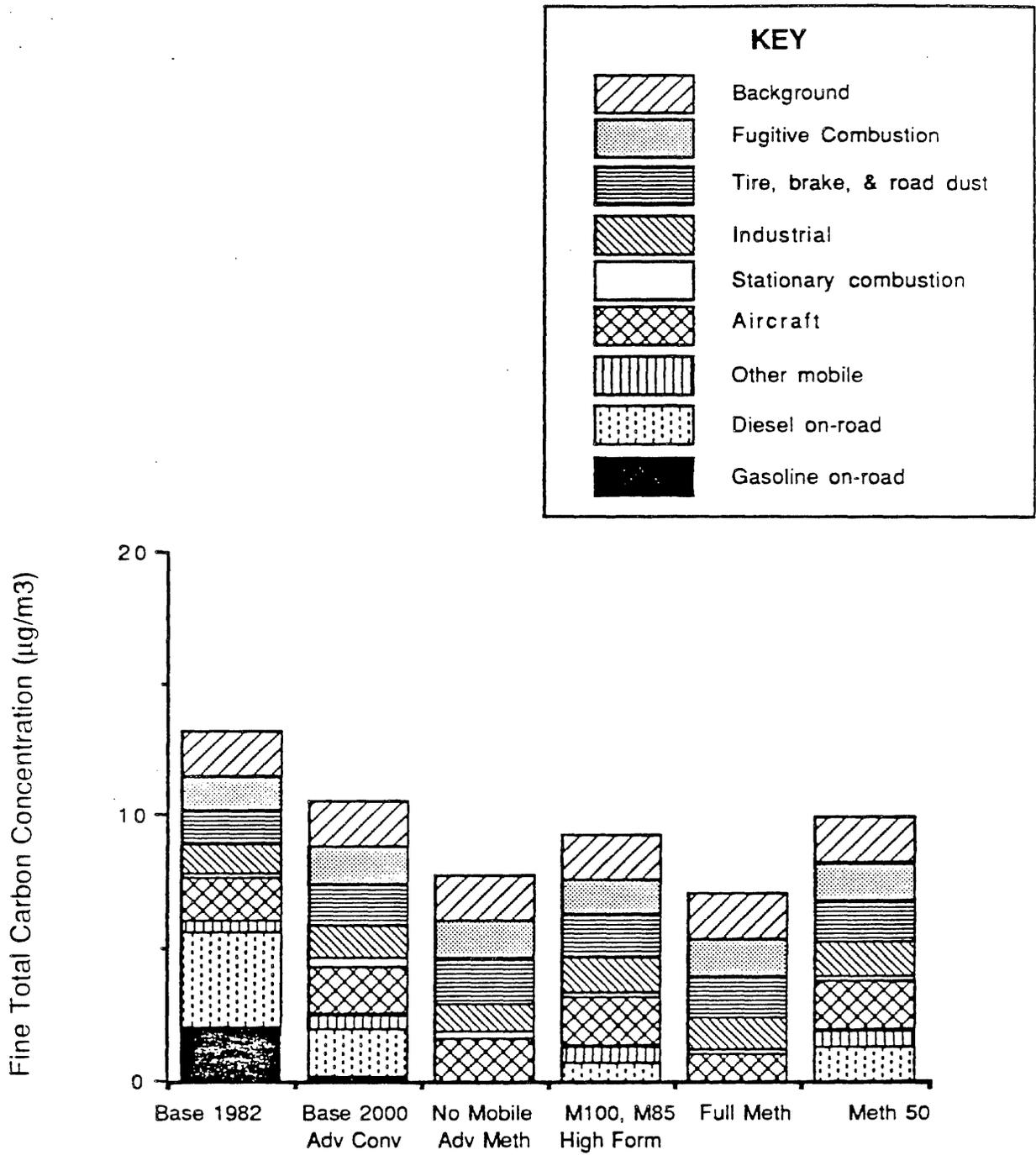


Figure 7.7 Fine total carbon concentrations at Lennox in September as a function of scenario and source.

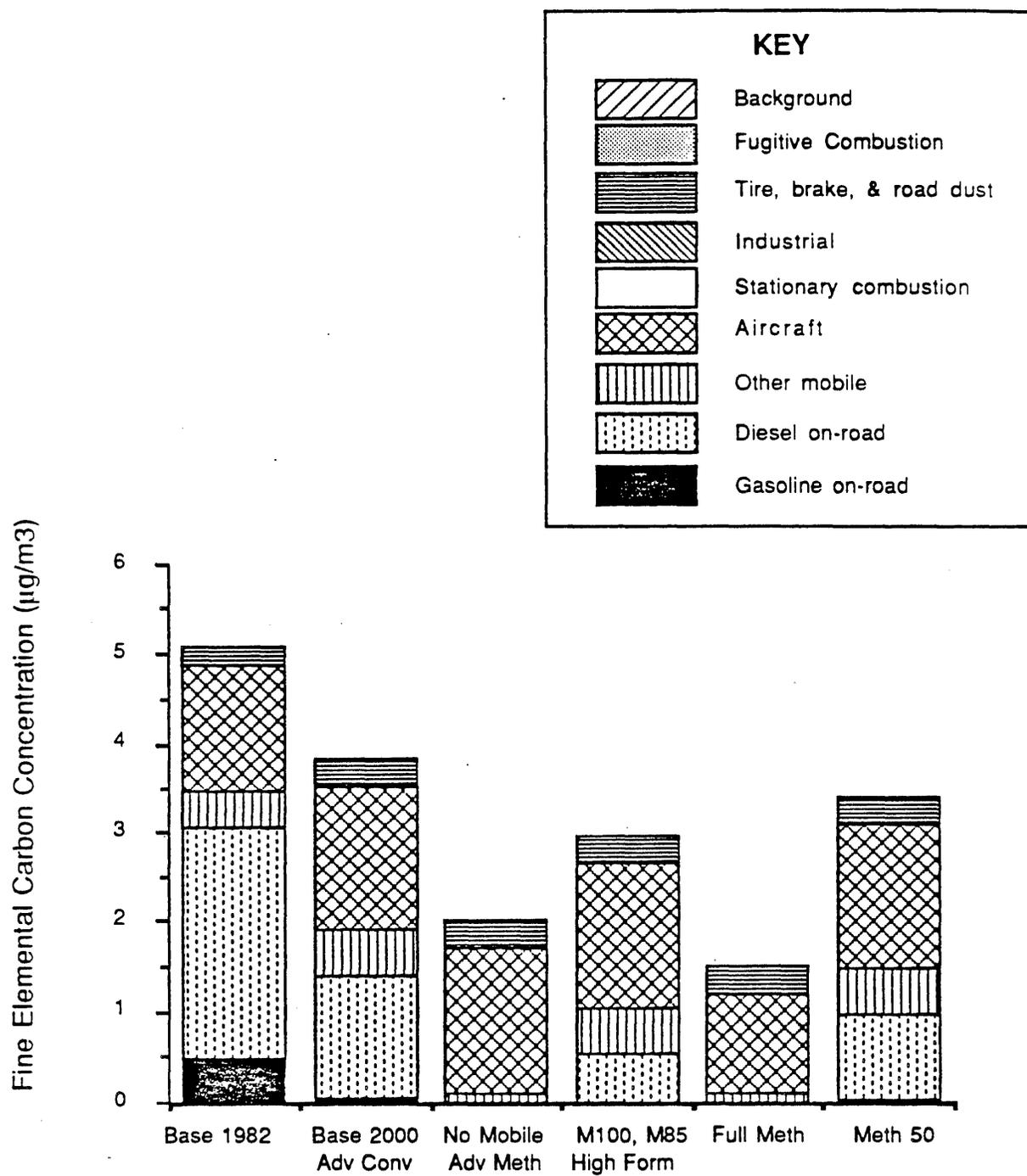


Figure 7.8 Fine total elemental concentrations at Lennox in September as a function of scenario and source.

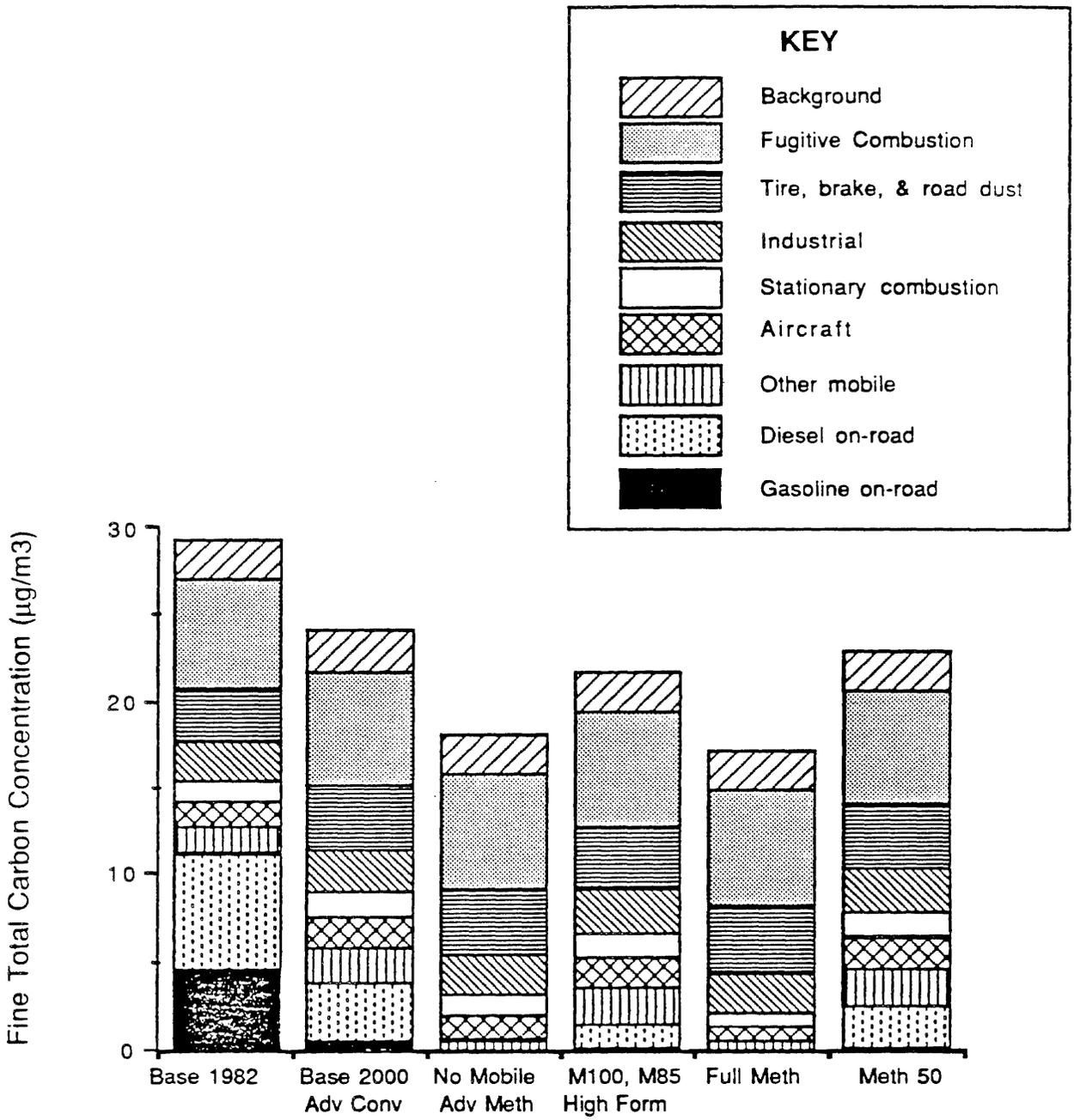


Figure 7.9 Fine total carbon concentrations at Lennox in December as a function of scenario and source.

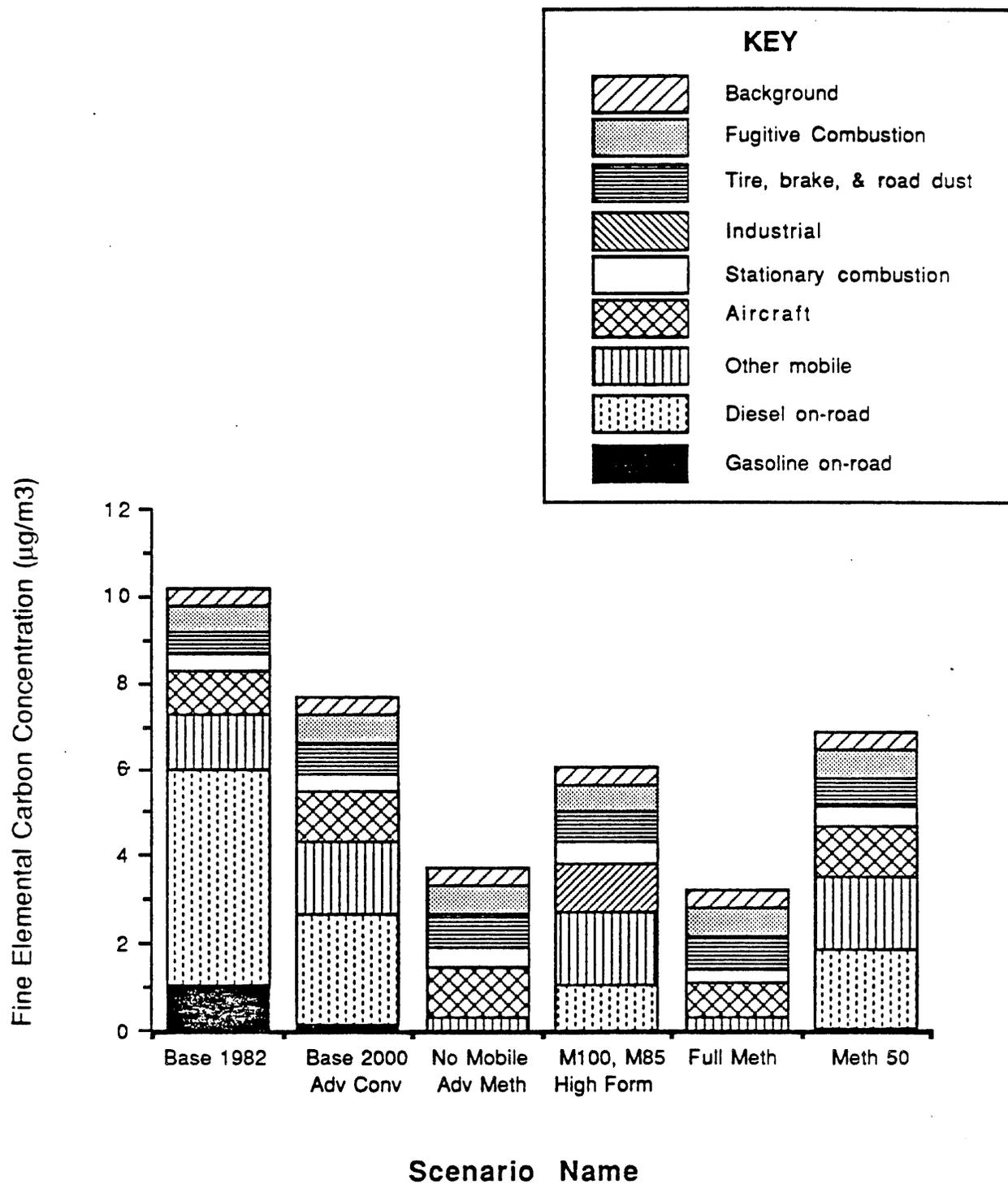


Figure 7.10 Fine elemental carbon concentrations at Lennox as a function of scenario and source type.

7.2.6 Summary of Carbon Particulate Modeling

Converting mobile sources and applicable stationary sources to methanol fuel has a significant effect in reducing concentrations of elemental carbon, but a substantially lesser impact on reducing total carbon. Elemental carbon concentration reductions of up to 85% are predicted if mobile sources completely converted to methanol. Fine total carbon concentrations are reduced a maximum of 38%. Both of these maximum reductions occurred in Los Angeles in September. Since elemental carbon contributes to light extinction, methanol conversion could potentially offer substantial visibility improvements within the basin. Also, many suspected carcinogenic carbon compounds are emitted from diesel cycle engines, so their concentrations would be reduced.

7.3 Aerosol Nitrates

Recent measurements (Solomon, et al., 1988) found that inorganic nitrate, and the associated ammonium, is the major component of PM_{10} on peak days in the SoCAB, and is a large contributor to the annual average. For example, the highest measured concentration (24-hour average) during the 1986 study was $299 \mu\text{g m}^{-3}$ measured at Rubidoux, of which $85.6 \mu\text{g m}^{-3}$ was inorganic nitrate. Further study (Dunwoody, 1986; SCAQMD, Appendix V-F, 1988) has indicated that this value may be low due to nitrate loss during transport and storage. An additional $23 \mu\text{g m}^{-3}$ could be due to associated ammonium. Thus, about 37% would be due to inorganic nitrate formation alone, more than any other component. Virtually all the other measurement stations in the SoCAB also recorded PM_{10} concentrations in excess of the state and federal levels, with nitrate being a major contributor.

7.3.1 Aerosol Nitrate-Emission Relationships

Modeling studies (Russell and Cass, 1986; Russell et al., 1988ab) using the series of photochemical models employed in the present study were able to accurately predict aerosol nitrate levels as a function of emissions. These modeling studies also showed that aerosol nitrate levels would be effectively reduced by controlling NO_x emissions, the precursor of nitrate. Methanol use in diesel engines and stationary sources would reduce NO_x emissions and, thus, could be an effective component in a strategy to reduce nitrate and PM_{10} levels in the SoCAB.

Nitric acid formation is an integral path in the photochemical cycle. The nitric acid formed then can react with ammonia to form aerosol nitrate. These two processes are described in detail by the airshed model used in Chapter 6, and results from those simulations are used here to determine how methanol would affect aerosol nitrate concentrations. An output of the photochemical airshed model discussed in Chapter 6 is predicted aerosol nitrate concentrations across the Basin. The predicted peak nitrate concentration occurs near Chino, upwind of Rubidoux. This agrees with measurements, and can be explained by the emissions of ammonia from confined livestock feeding reacting with nitric acid to form aerosol ammonium nitrate. Accurate calculation of ammonia into the SoCAB is critical to predicting NH_4NO_3 concentrations.

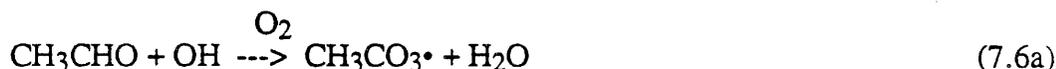
The ammonia inventory used in the previous studies (Cass et al., 1982) was updated to account for increasing numbers of catalyst cars and changes in the distribution of automotive emissions. Catalyst equipped light duty vehicles, methanol and conventional alike, were assumed to emit, nominally, $35 \text{ mg km}^{-1} NH_3$. For larger catalyst equipped vehicles, the NH_3 emissions are scaled to NO_x emissions. NH_3 emissions from non-

catalyst and diesel fueled vehicles follow the recommendations found in the appendix of Russell and Cass (1987). Livestock waste decomposition remains the major source of NH_3 in the SoCAB.

Besides being sensitive to NO_x and NH_3 emissions, aerosol nitrate levels will be affected by the composition of ROG emissions. For example, decreasing the reactivity of the ROG mixture can decrease radical production and the oxidation of NO_x to nitric acid:



Also, certain organics can react to form nitrogen containing compounds, especially PAN, e.g. (Carter, et al., 1986).



This series of reactions inhibits the formation of nitric acid, acting as a reservoir of NO_2 . Methanol is not a precursor to PAN or other heavier organic nitrate compounds, so this will change the apportionment between organic and inorganic nitrate. ROG emissions for each scenario discussed are given in Chapter 6.

7.3.2 Results and Discussion

Airshed modeling results indicate that methanol utilization could lead to lower aerosol nitrate levels across the SoCAB. As shown in Table 7.3, the base case, year 2000, (BASE1) predicted peak nitrate is $93 \mu\text{g m}^{-3}$ NH_4NO_3 , and the basinwide average is $6.8 \mu\text{g m}^{-3}$. The peak 24-hour average was $32 \mu\text{g m}^{-3}$. These values are consistent with the findings of Solomon, et al. (1988), and the findings used in the AQMP, though the observations are not for the same time period. The comparison is mentioned as a basis for interpreting the control scenario predictions below.

Changes in aerosol nitrate levels resulting from methanol utilization and more stringent emission controls on CFVs are shown in Table 7.3. Reducing emissions from CFVs decreased peak 24 hour average nitrate by 22%, about the same as the reduction in NO_x emissions. Basinwide average levels decreased by a similar proportion.

Low emitting MFVs would reduce aerosol nitrate levels further. The 24-hr. peak is reduced 47% from the base, and the basinwide average is reduced 46% to $3.8 \mu\text{g m}^{-3}$. If M100 vehicles start penetrating the vehicle fleet starting in 1990 (i.e. the STD M100 scenario), peak 24-hr. average aerosol nitrate is reduced 46%. Finally, if full use of methanol in stationary and mobile sources is used, peak 24-hr. average aerosol nitrate drops to $16 \mu\text{g m}^{-3}$, a 50% reduction. Population exposure is reduced proportionally to peak 24-hr. average aerosol levels.

An important result of these calculations is that the average aerosol nitrate levels do not scale directly with NO_x emissions. This is because the reactivity of the emissions, and hence oxidation rate of NO_x , is reduced. Also, the formation of NH_4NO_3 from NH_3 and

Table 7.3 Projected Nitrate Emissions, Concentrations and Exposures

	NOx Emissions	1-hr Peak Nitrate	Basinwide Average Nitrate	Peak 24-hr Nitrate	Exposure	Conversion, F_c
SCENARIO	1000 kgs day ⁻¹	($\mu\text{g m}^{-3}$)	($\mu\text{g m}^{-3}$)	($\mu\text{g m}^{-3}$)	($10^6 \mu\text{g m}^{-3}$ -person-hours)	(Compared to Base Case)
Base Case 2000 (BASE1)	700	93	6.8	32	3,170	1.00
Advanced Conventional (ADV CONV)	580	79	5.6	25	2,752	0.94
Advanced Methanol (ADV METH)	500	63	3.8	17	1,669	0.74
Standard M100 (STD M100)	640	64	3.8	18	1,672	0.61
Full Methanol (FULL METH)	460	60	3.6	16	1,577	0.76

HNO₃ is not linear. The right column of Table 7.3 compares the relative formation of aerosol nitrate from the NO_x emissions. The value shown is:

$$F_c = \frac{[\text{Predicted NH}_4\text{NO}_3]_i}{[\text{NO}_x \text{ Emissions}]_i} \times \frac{[\text{NO}_x \text{ Emissions}]_{\text{base}}}{[\text{Predicted NH}_4\text{NO}_3]_{\text{base}}}$$

where the subscript *i* refers to the different scenarios. In essence, this is a measure of the relative fraction, F_c , of the NO_x emissions that form NH₄NO₃, as compared to the base case. These results indicate that converting to methanol reduces the conversion rate of NO_x to NH₄NO₃. The fraction converted is reduced as much as 39% when methanol is used.

7.3.3. Summary of Aerosol Nitrate Results

Aerosol nitrate levels would be expected to decrease if methanol fuel is widely utilized. First, utilizing methanol will reduce NO_x emissions, a precursor to aerosol nitrate, in mobile source diesel engines and stationary source applications. Secondly, the reduction in the reactivity of the ROG emitted reduces the oxidation of NO_x to HNO₃. In the control simulations, peak 24-hr. aerosol nitrate was reduced from 32 μg m⁻³ for the base case to as low as 16 μg m⁻³ for the case with full utilization of methanol. An interesting result is that the use of "standard" methanol fueled vehicles results in less aerosol nitrate than going to stringently controlled CFVs (18 vs. 25 μg m⁻³). This is because of the lower reactivity of the MFV emissions and slightly lower NO_x emissions.

7.4 Particulate Sulfate

Methanol contains no sulfur and its use in the motor vehicle fleet will decrease SO₂ and particulate sulfate concentrations. Particulate sulfate is formed by the oxidation of SO₂ in the gas or liquid phase (e.g., Jacob, et al., 1986), and can be directly emitted. Characteristic of particles formed by gas phase condensation, the resulting particulate matter is found in the fine particle (PM₁₀) fraction of the aerosol. As such, it is an efficient light scatterer, and a major contribution to visibility reduction in the SoCAB (Cass, 1979; Larson, et al., 1988; Hidy, et al., 1974; Groblicki, et al., 1981). Solomon, et al. (1988), found that about 10% of the PM₁₀ aerosol was sulfate. This section describes how an estimate of the potential decrease in sulfate was derived from the change in emissions resulting from methanol use.

7.4.1 Sources of Sulfur in the SoCAB

Major sources of sulfur in the SoCAB are (percentage contribution in the year 2000 shown in parentheses): electricity generation (6%), petroleum refining (16%), ships (20%), diesels (8.6%), automobiles (6.9%), other on-road vehicles (4.7%), and smaller miscellaneous sources (19%) (SCAQMD and SCAG, 1982). Of these, heavy duty diesel vehicles, automobiles, and a fraction of the stationary sources (e.g., stationary I.C. engines) can be converted to methanol. Methanol overfiring of utility boilers would not be expected to decrease sulfur emissions significantly. A more detailed inventory of SO_x emissions for the year 2000 is given in Table 7.4. About a third of the SO_x is from sources convertible to methanol under a clean-fuels plan.

Table 7.4

**SO_x Emission Sources, and their Contribution
to Particulate Sulfate in the Year 2000
at Los Angeles and Rubidoux**

Source	Emissions in Year 2000 (1000 kgs day ⁻¹)	Contribution to Sulfate($\mu\text{g m}^{-3}$)			
		Base Case		Full Methanol	
		Los Angeles	Rubidoux	Los Angeles	Rubidoux
On-Road Mobile	28.16	3.14	2.07	1.72	1.13
Residential Space Heating	0.13	0.02	0.01	0.02	0.01
Residential Water Heating	0.08	0.01	0.01	0.01	0.01
Refinery Boilers & Heaters	3.24	0.28	0.15	0.28	0.15
Utility IC Engines	0.17	0.01	0.00	0.00	0.00
Non-Utility IC Engines	2.23	0.09	0.33	0.04	0.13
Refinery FCCU	17.50	0.58	0.56	0.58	0.56
Cement Kilns	0.10	0.00	0.02	0.00	0.02
Glass Melting	2.09	0.28	0.10	0.28	0.10
Non-Farm Equip.	0.22	0.19	0.13	0.19	0.13
Railroads	3.74	0.14	1.85	0.14	1.85
Commercial Jet & Aircraft	1.25	0.15	0.10	0.15	0.10
Shipping	26.96	1.18	1.17	1.17	1.17
Utility Boilers	8.14	0.09	0.13	0.09	0.13
Industrial Boilers	13.74	0.27	0.30	0.27	0.30
Miscellaneous	25.17	1.79	1.46	1.78	1.46
TOTAL	132.92	8.23	8.41	6.72	7.27

7.4.2 Aerosol Sulfate Concentrations

Annual average sulfate concentrations within the SoCAB were consistently about 5 to 7 $\mu\text{g m}^{-3}$ during the study of Solomon, et al. (1988). This agrees with Gray (1986), and is significantly less than historical levels (Cass, 1979; SCAQMD, 1978). The oxidation product of sulfur dioxide is sulfuric acid, a strong acid, which readily bonds with ammonia. Associated ammonia, assuming sulfate is found as $(\text{NH}_4)_2\text{SO}_4$, would be about 3 $\mu\text{g m}^{-3}$ on an annual average basis. During peak particulate events in the SoCAB, sulfate concentrations ranged from 3.9 to 21.7 $\mu\text{g m}^{-3}$. Peak 24-hr sulfate levels from routine measurement stations within the SoCAB ranged up to 20.6 $\mu\text{g m}^{-3}$ in 1987 (SCAQMD, 1988).

7.4.3 Calculation Methodology

As part of the 1988 AQMP (see appendix V-O), the source contributors to sulfate aerosol are detailed for a number of receptor sites in the SoCAB. Table 7.4 lists the forecast year 2000 source contributions of SO_x and the predicted sulfate levels at Los Angeles and Rubidoux given no new controls. Of those sources listed, on-road mobile sources and utility and non-utility i. c. engines show the greatest promise for conversion to methanol. The impact of methanol can be calculated by changing the individual source emission rates to reflect extensive methanol utilization. Individual source contributions at the two receptor sites can then be scaled proportional to the emission changes to calculate the revised source contribution. Next, contributions can be summed to find the predicted sulfate levels in the year 2000 under a full methanol utilization scenario.

In Chapter 6, it was assumed that only the vehicles registered in California would be converted to methanol, including about 40% of the on-road heavy-duty diesel trucks. Likewise, 50% of the stationary i. c. engines might effectively be converted under the full methanol utilization scenario. Using these conversion levels, individual contributions to annual average sulfate was recomputed to reflect how extensive methanol utilization would impact sulfate levels in the year 2000, as shown in Table 7.4. Annual average sulfate at Los Angeles would decrease from 8.23 $\mu\text{g m}^{-3}$ to 6.72 $\mu\text{g m}^{-3}$. Predicted sulfate at Rubidoux would be reduced 14% from 8.41 $\mu\text{g m}^{-3}$ to 7.27 $\mu\text{g m}^{-3}$.

7.4.4 Summary of Impact on Sulfate

Methanol can be used to reduce sulfate aerosol concentrations in the SoCAB. Calculations at two receptor locations show that sulfate could be reduced up to 14% as a result of extensive conversion to methanol. In the year 2000, the predicted annual average sulfate concentration at downtown Los Angeles could be reduced from 8.82 $\mu\text{g m}^{-3}$ to 6.72 $\mu\text{g m}^{-3}$. At Rubidoux, the maximum reduction would be from 8.41 to 7.27 $\mu\text{g m}^{-3}$.

7.5 Organic Aerosols

Organic particulate matter can be either primary or secondary in nature. In the first section of this chapter, the impact methanol utilization would have on primary organic material was calculated. In this section, the photochemical trajectory model is used to calculate the reduction in secondary organic aerosol that could be realized by converting to methanol.

Secondary organic aerosol is produced by the photooxidation of organic gases, especially aromatics, cycloalkenes, and diolefins. Hydroxyl radical attack on these three classes of compounds and ozone reaction with the alkenes can lead to the formation of low vapor pressure compounds such as dicarboxylic acids and dinitrocresol (referred to as DI-ACID and DNC). These compounds then condense out of the gas phase, forming small particles in the PM₁₀ size range. Because of their size, the aerosol formed is effective at scattering light and is also easily respired. The chemistry of secondary organics is highly non-linear, involving ozone, radical production, and NO_x, as well as the precursor organics. For this reason, secondary organic aerosol formation is treated separately from primary aerosols. The photochemical trajectory model described previously is used. Processes particular to organic aerosol formation are reviewed below, along with the implementation of these steps within the trajectory model. Results from the calculations are discussed for ten of the scenarios described in Chapter 5, emphasizing the impact on PM₁₀.

7.5.1 Formation of Organic Aerosols

7.5.1.1. Cyclic Olefins and Diolefins

It has long been recognized that cycloalkenes form light scattering aerosols at ppm concentrations when irradiated with NO_x in air. The atmospheric oxidation of cycloalkenes has been studied recently to discover more about the reactions and mechanisms that form the majority of organic aerosols in photochemical smog.

As discussed previously, the property of low vapor pressure is important in the formation of aerosols. In order for a particle to exist stably, the partial pressure of that compound must be greater than or equal to its saturation vapor pressure. Organic aerosol formation requires accumulation of condensable species in excess of their gas phase saturation concentrations. Therefore, the lower the vapor pressure of a species, the more likely it will be to form atmospheric aerosols. As shown in Table 7.5, the vapor pressures of the reaction products of cycloalkenes and diolefins are much lower than that of other common alkenes, due to the formation of dicarboxylic acids (organics with two acid groups per molecule). Also shown in this table is the minimum concentration of the precursor species required to form aerosols. Cycloalkenes and diolefins have minimal concentration requirements in order to form particulate matter. The chemical reactions of cyclopentene and cyclohexene in particular have been studied recently to discover more about the products and reactions of cycloalkene with ozone and/or the hydroxyl radical. The steps leading to the formation of aerosols from cycloalkene and ozone reactions have been extensively reported elsewhere (Hatakeyama et al., 1985, 1987; Finlayson-Pitts and Pitts, 1986) and will not be discussed in detail here. The recent findings of the products of these reactions are of interest to this study and will be discussed.

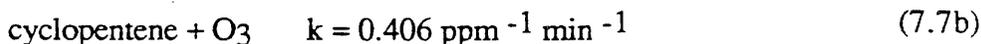
The reaction of cyclohexene with O₃ leads to a series of reactions in which aldehydes and five carbon and six carbon aerosols have been discovered to form (Finlayson-Pitts and Pitts, 1986). Hatakeyama et al. (1985) have done extensive studies on the reactions and formation of products. In this report, the estimated yield of aerosols as a result of ozone-cyclohexene reactions was estimated to be 13 ± 3 %. Further studies by Hatakeyama et al. (1987) on cyclopentene and cycloheptene reactions with ozone confirmed previous findings on cycloalkene reactions. Aerosol yields for cycloalkenes were reported according to carbon number. The following yields for C₅, C₆, and C₇ cycloalkenes were found to occur:

**Table 7.5 Olefinic Precursors and Condensing Species
leading to Organic Aerosol Formation
(from Finlayson-Pitts and Pitts, 1986)**

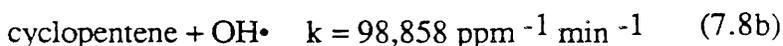
Olefinic Precursor	Least Volatile Photooxidation Product	Product Vapor Pressure (Torr)	Minimum Precursor Concentration
Propylene	Acetic acid	16	21,000 ppm
1-Butene	Propionic acid	4	5,200 ppm
1-Hexene	Pentanoic acid	0.25	327 ppm
1-Heptene	Hexanoic acid	0.02	26 ppm
1-Octene	Heptanoic acid	9.0E-03	12 ppm
1-Decene	Nonanoic acid	6.0E-04	0.8 ppm
1-Tridecene	Dodecanoic acid	1.0E-05	13 ppb
Cyclopentene	Glutaric acid	2.0E-07	0.3 ppb
Cyclohexene	Adipic acid	6.0E-08	0.08 ppb
1,7-Octadiene	Adipic acid	6.0E-08	0.08 ppb
3-Methylcyclohexene	Methyladipic acid	2.0E-08	0.03 ppb

<u>Cycloalkenes</u>	<u>C5</u>	<u>C6</u>	<u>C7</u>
lower limit	1±1%	3±1%	4±1%
upper limit	5%	13±3%	10%

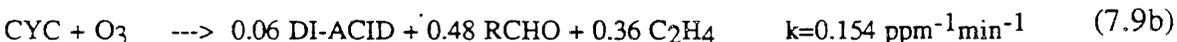
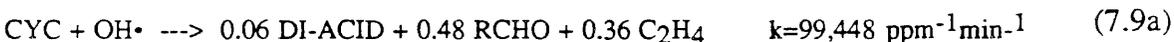
Reaction rates for cycloalkene-ozone reactions are (Atkinson et al., 1983) :



Atkinson et al. also reports on the rate constants for cycloalkene reactions with the hydroxyl radical (1985) :



Using the data from these studies on the formation of aerosols from cycloalkenes, an estimate was derived for the amount of aerosol expected to form as a result of the oxidation of atmospheric cycloalkenes. These updates are made in addition to the results derived by Bouvier (1986). A 6% conversion of cycloalkenes to aerosol organic carbons is estimated from the average of the ranges provided above for aerosol yields. The following condensed reaction is used for cycloalkene and diolefin reactions in the trajectory model:



where CYC is the lumped cycloalkene and diolefin, DI-ACID is the dicarboxylic acid aerosol product, RCHO is the aldehyde, and C₂H₄ is the ethene resulting. The rate constants for cyclohexene have been adopted for the lumped reaction.

The emissions estimates of cycloalkenes for the year 2000 are utilized in this report (Avlani, 1986). Previously, data from the Grosjean and Fung (1984) provided an estimate of the composition of organics in the Los Angeles atmosphere in 1974. At that time, cycloalkenes comprised of approximately 5% of the alkenes present in the atmosphere. According to emissions estimates for the year 2000 provided by the California Air Resources Board (Allen, 1986; Avlani, 1986), only 0.27% of the alkenes present in emissions (on a molar basis) are cycloalkenes and diolefins.

7.5.1.2 Aromatic Hydrocarbons

Photooxidation of aromatics in the air is prompted by the hydroxyl radical reaction with aromatic compounds. Aromatic hydrocarbons are precursors for what constitutes a large portion of secondary particulate organic carbons in urban air, some of which are known to be mutagenic. Toluene is the most prevalent of these aromatics since it is a part of automobile exhaust and is used as an industrial solvent (Bouvier, 1986). Due to its fraction of aromatic hydrocarbons in the atmosphere, approximately 55% (Grosjean and Fung, 1984), toluene has been the most studied of these compounds. Studies of o-cresol,

a compound formed from toluene-OH• reactions prior to aerosol formation, have also been studied to get a clearer understanding of aerosol formation.

Stern et al. (1987) have conducted a study on aerosol formation and growth of aromatic hydrocarbon/NO_x systems. In an outdoor smog chamber the quantity of initial hydrocarbon converted to aerosols was measured on a mass basis. The average yields by mass were found to be:

toluene	4.8%
m-xylene	3.5%
ethylbenzene	1.9%
1,3,5-trimethylbenzene	2.4%

The study of reactions of o-cresol and dinitrocresol (Grosjean, 1984) provides further information concerning the conversion of aromatics to aerosols. O-cresol is a key product of the toluene-OH• reaction, and acts as a precursor for aerosol formation. Aerosol yields of 5 - 19% on a carbon basis are reported for these reactions.

A following study by Grosjean (1985) of o-cresol and nitrocresol reactions in sunlight and in the dark provides further analysis into the reactions and aerosol yield. For our purposes we will use data collected for the reactions in sunlight. With this study, experimental effects such as wall losses and aerosol size distribution measurements were taken into consideration. The amount of particulate formed from o-cresol was found to be significantly higher. Aerosol yields ranged from 5.1% - 44.5% on a carbon basis.

The estimate used for the aerosol yield of aromatic hydrocarbons is based on the above findings. A predicted 17% conversion of toluene to o-cresol is reported by Leone and Seinfeld (1984). This provides an estimate of 1 - 8% conversion of toluene to aerosol, in agreement with Stern et al. (1987). To account for the contributions of all aromatics to total aerosol yield, the results of Stern et al. (1987) are weighted by the fraction of aromatic emitted. From Stern et al.'s results, a 4.6% conversion of aromatics to aerosols is used in the trajectory model. This is in accordance with the range cited from other recent studies (Grosjean, 1984, 1985). For the purpose of this study, the aerosol formed from oxidation of toluene is classified as dinitrocresol (DNC).

7.5.2 Results and Discussion

Analysis using the trajectory model described in Chapter 5 is used to determine concentration changes of three additional lumped species: dicarboxylic acids, cyclic olefins, and dinitrocresols (DI-ACIDS, CYC, and DNC). The trajectory model of Bouvier is used and has been updated to include recent findings in atmospheric chemistry (Stern et al., 1987; Grosjean, 1984, 1985). Ten scenarios were chosen to test how the DI-ACID, CYC, and DNC concentrations respond to methanol utilization. These scenarios include scenarios for the year 2000, including the base case, mobile sources removed, conversion to advanced methanol vehicles, and selected conventional and methanol fuel scenarios. The ten scenarios are as follows: BASE, AR (mobile sources and refinery emissions removed), SC01, SC02, SC03, SC04, SC11, SC14, SC20, and SC21. Scenario descriptions are listed in Table 5.1.

Results of the trajectory runs are discussed as a relative percent of reduction as discussed in Chapter 5:

$$R_i^A = \frac{[AER]_{\text{base}} - [AER]_i}{[AER]_{\text{base}} - [AER]_{\text{source-removed}}} \quad (7.10)$$

where R_i^A is the effective reduction obtained with the scenario being analyzed, $[AER]_i$ is the aerosol concentration of the scenario being analyzed, $[AER]_{\text{source-removed}}$ is the aerosol concentration level when the mobile and petroleum sources are removed (scenario AR), and $[AER]_{\text{base}}$ is the aerosol level in the base 2000 year estimates.

Selected results for DI-ACID and DNC concentrations are shown in Table 7.6. Averages of the reduction sensitivities for advanced MFVs, advanced CFVs, current MFVs, and M85 fuel on six carbon aerosols and dinitrocresol are shown in Figure 7.11. The sensitivity reduction, or $1-R_i$, is shown. Therefore, the smaller the bar, the lower the aerosol concentrations. Important to note in the table and the figures, is that while the effective reductions at the Pasadena and San Bernardino trajectories agreed to within approximately 10%, improvements in Norco were often twice as great. This could be accounted for by the reduction in refinery emissions.

Base case (BASE) predictions of the levels of dinitrocresol type aerosols ranged from $7.22 \mu\text{g m}^{-3}$ in Norco to $8.8 \mu\text{g m}^{-3}$ in San Bernardino. Dicarboxylic acid aerosol concentrations ranged from $5.33 \times 10^{-3} \mu\text{g m}^{-3}$ in Norco to $9.51 \times 10^{-3} \mu\text{g m}^{-3}$ in Pasadena. From these calculations, aromatic derived aerosols are significantly more prevalent than those derived from olefins. This is a result of much lower precursor olefin emissions, as reflected in the emissions inventory. If mobile sources and petroleum refineries are removed (case AREA), predicted dinitrocresol and dicarboxylic acid aerosols decrease by 15% and 62%, respectively, averaged across the three trajectories. The AREA calculation shows that about 15% of the DNC aerosol is, in some sense, due to mobile sources and refinery emissions. Likewise, a much larger fraction, 62%, of the DI-ACID is attributable to the same sources, though this amounts to a small amount of aerosol mass.

Full penetration of advanced methanol fueled vehicles provided the greatest improvements for both secondary organic aerosol species. Advanced MFVs offered an average of 96% effective reduction in the formation of the dicarboxylic acid from olefin reactions relative to no mobile source emissions. In concentration levels, this is equivalent to a reduction of 7.42×10^{-3} to $3.03 \times 10^{-3} \mu\text{g m}^{-3}$. The formation of dinitrocresols was reduced more than removing the mobile and petroleum sources altogether when simulating full use of advanced MFVs. This is a result of the reduction of NO_x emissions from mobile sources. With a certain amount of NO_x still present, as in the advanced methanol fuel scenario, scavenging of the radical species will occur, thus reducing the total concentration of aerosol species. The concentrations of DNC were reduced by an average of $1.58 \mu\text{g m}^{-3}$, from 8.09 to $6.51 \mu\text{g m}^{-3}$.

Advanced CFVs do not offer as great an improvement compared to advanced MFVs, in most cases only half as good. For the dicarboxylic acid species, the decrease was approximately 50% of the advanced MFV case, or a concentration reduction from 7.42×10^{-3} to $5.11 \times 10^{-3} \mu\text{g m}^{-3}$. The effective reduction was a little higher, approximately 60%, for dinitrocresol. In this case, concentrations were reduced $0.73 \mu\text{g m}^{-3}$, from $7.93 \mu\text{g m}^{-3}$ to $7.19 \mu\text{g m}^{-3}$.

Table 7.6 Secondary Organic Aerosol Concentrations

DI-ACID DATA	Scenario	TRAJECTORY		
		San Bernardino ($\mu\text{g}/\text{m}^3$)	Pasadena ($\mu\text{g}/\text{m}^3$)	Norco ($\mu\text{g}/\text{m}^3$)
	BASE	7.42 E-03	9.51 E-03	5.33 E-03
	AREA	3.28 E-03	3.69 E-03	1.63 E-03
	SC01 (ADV METH)	3.69 E-03	3.73 E-03	1.68 E-03
	SC04 (ADV CFV)	5.38 E-03	6.50 E-03	3.44 E-03
	SC11 (STD M100)	4.80 E-03	5.42 E-03	2.60 E-03
	SC14 (STD M85)	5.87 E-03	6.87 E-03	3.82 E-03
DNC DATA				
	BASE	8.80	7.76	7.22
	AREA	7.63	6.37	6.25
	SC01 (ADV METH)	7.54	5.90	6.08
	SC04 (ADV CFV)	8.14	6.80	6.63
	SC11(STD M100)	7.88	6.39	6.39
	SC14 (STD M85)	8.27	6.99	6.76

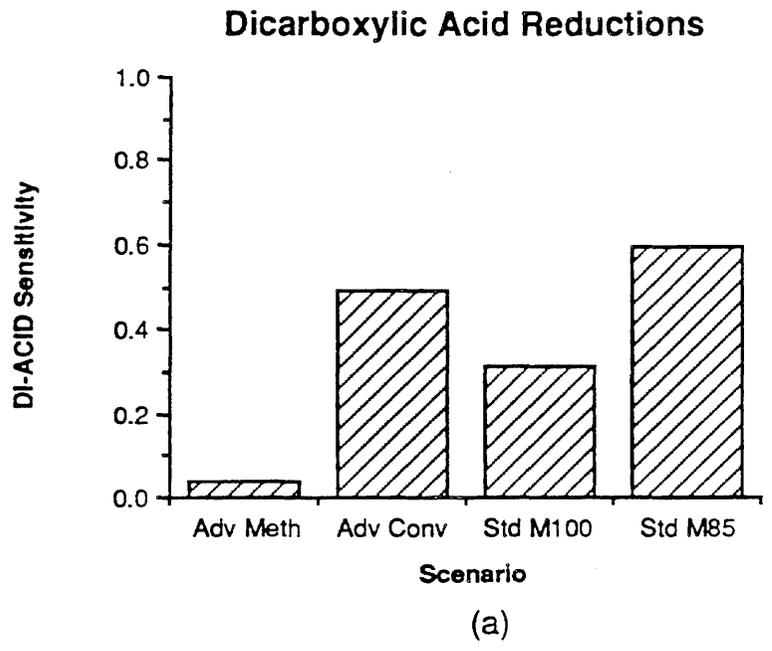


Figure 7.11 Effective Reductions of Secondary Organic Aerosols a) Dicarboxylic acid b) Dinitrocresol

The improvements resulting from CFV implementation are comparable to that of using either M85 methanol fuel or implementing MFV in only 50% of the LDA and LDT fleet. M85 fuel offers only 40-50% improvements in the formation of secondary organic aerosols as compared to M100. Fifty percent implementation of LDA and LDT (SC21) offers approximately 40% reduction in dicarboxylic acids and 45% improvements in dinitrocresol with approximately 15% reductions in cyclic olefins.

7.5.3 Summary of Secondary Organic Aerosol Modeling

Trajectory modeling of the SoCAB indicates that use of methanol fuel, particularly in mobile sources, would effectively reduce the formation of secondary organic aerosol. The amount of improvement has been found to be nearly proportional to its use. Advanced CFVs, M85 methanol fueled vehicles, or only 50% implementation of methanol in LDA and LDT (with 100% implementation in MDT and HDT) offer only half the benefit received from standard or advanced technology M100 MFVs. Maximum use of M100 vehicles lowered the predicted organic aerosol concentration (DI-ACID + DNC) at Pasadena from a base case level of 7.76 to 5.90 μgm^{-3} . The effective at Norco was from 7.22 to 6.06 $\mu\text{g m}^{-3}$. Reductions in the San Bernardino trajectory ranged up to 14%.

Effective reductions in DNC averaged greater than 100% with the use of Advanced MFVs for the three trajectories. Use of Standard M100 Vehicles resulted in substantial improvements, as well, with effective relative reductions averaging over 80% compared to removing mobile sources. Advanced CFVs and 50% utilization of MFVs offered substantially less improvement.

7.6 Future PM₁₀ Levels

The role that methanol fuel utilization could assume in reducing PM₁₀ concentrations in the SoCAB was found by summing up the results for the individual species. From the results above, it was seen that methanol would reduce primary carbon aerosol emissions, as well as the secondary formation of nitrate, sulfate, and organic aerosol. These are 4 of the 5 main source categories contributing to PM₁₀, as listed in Table 7.7. Thus, methanol utilization would be expected to be effective at reducing total PM₁₀ concentrations.

Methanol's impact on total fine particulate matter (PM₁₀) will vary throughout the SoCAB, just as the impact on specific components differs between receptor sites. Given the spatial inhomogeneity in particulate matter levels and that a very large fraction of the PM₁₀ is secondary in nature, it is difficult to describe a simple measure of the basinwide response to methanol use. Instead, the approach taken is to use the information developed above for carbon, sulfate, nitrate, and particulate, with the combined dispersion and receptor modeling structure used in the AQMP (SCAQMD, 1988, Appendix V-O), to predict the effect on annual average levels. The analysis here concentrates on the impact at Rubidoux because this site is the most heavily impacted by high particulate matter loadings.

7.6.1 Description of AQMP PM₁₀ Modeling Methodology

Dispersion and receptor modeling techniques were combined in the 1988 AQMP to estimate the current contributors to PM₁₀ levels, and to determine future PM₁₀ concentrations and the impact of controls. The receptor model employed was the Chemical Mass Balance (Version 6.0, Axtell and Watson, 1987), and was used for source apportionment of primary particulate matter. The dispersion model used was an enhanced

Table 7.7

Source Contributions to PM₁₀ at Rubidoux in 1986¹

	Contribution to PM ₁₀ ($\mu\text{g m}^{-3}$)	
	Annual Average	Peak 24-hr Average
Nitrates	25.7	166.5 ²
Sulfates	7.5	30.6
Diesel Exhaust	4.8	9.8
Paved Road Dust	39.2	57.7
Secondary Carbon	5.6	18.6
Other	7.4	6.5
Unexplained	<u>0.0</u>	<u>32.2</u>
TOTAL	90.3	321.7

¹ From Table VI of Appendix V-O of the 1988 Draft AQMP.

² Corrected for nitrate loss during measurement and storage.

version of the model described in the primary carbon aerosol modeling section (7.2) above. These models are detailed elsewhere, and readers are referred to Appendix V of the AQMP for information (SCAQMD, 1988). Specific aspects pertinent to this project are discussed below.

In the 1988 AQMP, the enhanced EQL dispersion model was used to predict PM₁₀ levels in 2000 and 2010. For the non-secondary components, such as road dust and diesel exhaust, as well as secondary organics, this was accomplished by scaling the historic concentrations by the ratio of the future emissions divided by historic levels. This is similar to the roll back procedure, applied to individual components. An assumption made in rolling back emissions is that the spatial and temporal distribution of emissions does not change significantly.

A significant enhancement was made to predict future secondary nitrate and sulfate levels that will be affected by changing precursor emissions, and changes in ROG emissions. In this case, the chemical transformation rate is determined by a parameterized chemistry submodule. The parameterized oxidation rates were determined by a series of chemical kinetic simulations. These simulations did not include replacing a large portion of the CFV with MFV type emissions, concentrating on bulk changes in emissions levels.

The Eastern SoCAB, especially around the Rubidoux-Riverside area, experiences some of the highest PM₁₀ levels in California. As part of the AQMP, the PM₁₀ contributors at Rubidoux were quantified using the dispersion model described above. This was broken down into primary sources, and secondary nitrate, sulfate, and carbon, with corresponding fractional source contributions. For 1985, the annual average PM₁₀ level at Rubidoux was measured to be 86.0 $\mu\text{g m}^{-3}$. Source contributions to the aerosol loading, as found by receptor modeling, are given in Table 7.7 (Table VI of App. V-O). Contributors to the secondary nitrate and sulfate were further delineated as shown in Table 7.8, (Table 1X of App. V-O), along with the precursor emissions.

7.6.2 Integration of PM₁₀ Modeling of Methanol Utilization

Results of the photochemical airshed and trajectory models were used in conjunction with the results of the AQMP model to look specifically at how the use of methanol will impact PM₁₀ levels in the Year 2000. Predictions of how methanol will affect aerosol sulfate and primary carbon levels is done analogously to the procedure used in the AQMP. Aerosol nitrate, and secondary organic aerosol changes, are calculated by supplementing the AQMP methodology with results of the photochemical airshed and trajectory modeling described above. This is warranted because of the non-linear dependence of secondary aerosol formation. Here, the analysis concentrates on annual average and peak PM₁₀ levels at Rubidoux.

Aerosol nitrate contributions to PM₁₀ at Rubidoux were found on a source-by-source basis, as shown in Tables 7.8 and 7.9 for 1985 and as predicted for the year 2000. Future predicted levels are shown for a base level of emissions, a standard methanol case, and a case depicting the use of advanced MFVs. (The four future predictions correspond to **BASE1**, **ADV CONV**, **STD M100**, and **FULL METH**, respectively.) Predicted nitrate loadings include the effect of changing NO_x emissions and, when appropriate, the lower oxidation rate found when methanol is utilized.

Table 7.8

**Source Contributions to Annual Average,
Secondary Sulfate and Nitrate PM₁₀ Formation
at Rubidoux in 1985**

Source	Source Contribution ($\mu\text{g m}^{-3}$)	
	Nitrate	Sulfate
On-Road Mobile Sources	15.274	2.553
Residential Space Heating	0.320	0.010
Residential Water Heaters	0.283	0.005
Refinery Boilers & Heaters	0.767	0.214
Utility IC Engines	0.069	0.001
Non-Utility IC Engines	1.681	0.141
Refinery FCCU	0.132	0.593
Cement Kilns	1.281	0.017
Glass Melting Furnaces	0.100	0.096
Non-Farm Equipment	0.660	0.107
Railroads	2.235	1.180
Commercial Jet & Aircraft	0.153	0.073
Shipping	0.775	1.024
Utility Boilers	0.589	0.072
Industrial Boilers	0.218	0.135
Miscellaneous	<u>1.153</u>	<u>1.307</u>
ALL SOURCES	25.69	7.53

Table 7.9

**Projected, Year 2000 Source Contributions to
Annual Average Aerosol Nitrate (PM₁₀) Levels
at Rubidoux**

	Contribution ($\mu\text{g m}^{-3}$)			
	Base 1985	Base 2000	Roll-in	Full-Methanol
On-Road	15.274	8.853 ¹	4.804	2.390
Residential Space	0.320	0.324	0.197	0.239
Residential Water	0.283	0.208	0.127	0.154
Refinery Heaters & Boilers	0.767	0.490	0.166	0.181
Utility IC Engines	0.069	0.078	0.026	0.029
Non-Utility Engines	1.681	0.778	0.264	0.288
Refinery FCCU	0.132	0.088	0.054	0.065
Cement Kilns	1.281	1.081	0.659	0.799
Glass Melting	0.100	0.054	0.032	0.040
Non-Farm Equip.	0.600	0.722	0.441	0.534
Railroads	2.235	3.520	2.147	1.301
Aircraft	0.153	0.199	0.121	0.147
Shipping	0.775	0.898	0.558	0.664
Utility Boilers	0.589	0.552	0.336	0.204
Industrial Boilers	0.218	0.529	0.327	0.313
Miscellaneous	<u>1.153</u>	<u>1.463</u>	<u>0.892</u>	<u>1.081</u>
	25.69	19.83	10.34	8.43

¹ Does not agree with AQMP because a different base level of NO_x is used. Compare emissions inventory in Ch. 4 with Table VII of AQMP appendix V-O.

As an example, in the year 2000, base case (**BASE1**) NO_x emissions from on-road motor vehicles are forecast to be $310 \text{ tons day}^{-1}$, compared to $620 \text{ tons day}^{-1}$ in 1985. Thus, aerosol nitrate contributed by on-road mobile sources in 2000 is:

$$15.274 \mu\text{g m}^{-3} \times \frac{310 \text{ tons day}^{-1}}{620 \text{ tons day}^{-1}} = 7.64 \mu\text{g m}^{-3} \quad (7.11)$$

where $15.274 \mu\text{g m}^{-3}$ is the 1985 annual average small particle nitrate at Rubidoux due to on-road mobile sources.

If methanol is utilized, (**STD M100** or **FULL METH**), on-road nitrate levels are decreased due to lower NO_x emissions and the lower reactivity of the ROG. As shown in Table 7.3, when comparing the relative fraction, F_c , to the base case, between 24% (**FULL METH**) and 39% (**STD M100**) less nitrate is formed from the NO_x emissions due to the lower reactivity. For the standard M100 case, the on-road mobile source contribution to PM_{10} -sized nitrate is:

$$15.294 \mu\text{g m}^{-3} \times \frac{248 \text{ tons day}^{-1}}{620 \text{ tons day}^{-1}} \times 0.61 = 3.72 \mu\text{g m}^{-3} \quad (7.12)$$

where $248 \text{ tons day}^{-1}$ is the on-road mobile source NO_x emissions, and 0.61 is the relative fraction of nitrate formed when methanol is used (see Table 7.3). This methodology is used to quantify the other source contributions to aerosol nitrate at Rubidoux, shown in Table 7.9. Total aerosol nitrate is predicted to drop from $19.83 \mu\text{g m}^{-3}$ in the base case, year 2000, to $8.43 \mu\text{g m}^{-3}$ in the full methanol utilization case. A similar scaling is used to find source contributions to aerosol nitrate during the meteorology leading to the peak, 24-hr PM_{10} measurement.

Sulfate levels would be reduced by using methanol in internal combustion engines, especially diesels. This affects mobile and stationary I.C. engines. Use in external combustion boilers, such as utility boilers, for NO_x reduction would slightly lower sulfur oxide emissions. This minor effect was not included. Base Case Year 2000 source contributions to sulfate at Rubidoux are detailed in Table 7.10. Sulfate levels assuming 100% penetration of MFVs into the light and medium duty on-road vehicle fleet, and 40% into the heavy duty diesel fleet is also shown. Included in the latter calculation is 40% methanol use in stationary i. c. engines. Sulfate at Rubidoux would be reduced from $8.41 \mu\text{g m}^{-3}$ to $7.27 \mu\text{g m}^{-3}$ on an annual average. The sulfate at the time of the 24-hr peak is reduced the same percentage.

Secondary carbon reductions, as described previously, would result from methanol use in mobile sources. For the case of 100% penetration of MFVs into the fleet from 1990 on, trajectory modeling predicted a 17% reduction in secondary organic. When a fleet of Advanced Technology MFVs is used, the secondary organic was reduced 16% relative to the Base Case. This leads to a reduction of secondary organic from $4.6 \mu\text{g m}^{-3}$ as used in the AQMP, to $4.07 \mu\text{g m}^{-3}$ in the Standard MFV Case, to $3.87 \mu\text{g m}^{-3}$ in the Advanced MFV Case.

Table 7.10

**Projected Source Contribution to
Annual Average Sulfate (PM₁₀) Levels
at Rubidoux
($\mu\text{g m}^{-3}$)**

	Base 1985	Base 2000	Methanol Utilization (40% Diesel Truck, 50% IC Engines)
On-Road	2.553	2.070	1.138
Residential Space	0.01	0.013	0.013
Residential Water	0.005	0.007	0.007
Refinery Boilers	0.214	0.152	0.152
Utility IC	0.001	0.002	0.001
Non-Utility IC	0.141	0.328	0.131
Refinery FCCV	0.593	0.563	0.563
Cement Kilns	0.017	0.018	0.018
Glass Melting	0.096	0.103	0.103
Non-Farm Equip.	0.107	0.131	0.131
Railroads	1.180	1.854	1.854
Aircraft	0.073	0.098	0.098
Shipping	1.024	1.173	1.173
Utility Boilers	0.072	0.131	0.131
Indust. Boilers	0.135	0.300	0.300
Miscellaneous	<u>1.307</u>	<u>1.459</u>	<u>1.459</u>
TOTAL	7.53	8.41	7.27

Diesel exhaust particulate is virtually eliminated by utilizing methanol. Section 7.2 described the impact at two western basin sites. Rubidoux is less impacted by diesel exhaust (SCAQMD, 1988). In 2000, diesel exhaust is expected to contribute $3.87 \mu\text{g m}^{-3}$ to the PM_{10} levels. If methanol is utilized in applicable sources (40% of on-road diesels, 50% of stationary sources), the levels are predicted to drop to $2.13 \mu\text{g m}^{-3}$. If methanol is used in all diesel engines, the diesel exhaust particulate would go to zero.

7.6.3 Discussion of PM_{10} Effects

Predicted annual average PM_{10} levels at Rubidoux could potentially be reduced from $98 \mu\text{g m}^{-3}$ to $79 \mu\text{g m}^{-3}$, as shown in Table 7.11, if methanol is fully utilized. Most of the remaining PM_{10} , 69%, is from road dust. Total concentrations and contributions are portrayed in Figure 7.12. Except for road dust, methanol utilization would reduce particulate matter contributions from the major sources.

Methanol utilization would also greatly reduce peak 24-hr PM_{10} levels, as seen in Table 7.12 and Figure 7.13. The peak measured in the Basin, $321.7 \mu\text{g m}^{-3}$ (corrected for measurement artifacts), included $166.5 \mu\text{g m}^{-3}$ nitrate, $30.6 \mu\text{g m}^{-3}$ sulfate, $9.8 \mu\text{g m}^{-3}$ diesel exhaust, and $18.6 \mu\text{g m}^{-3}$ secondary organic. In 2000, the forecast peak increases slightly to $324 \mu\text{g m}^{-3}$. Using the results from above, extensive methanol utilization potentially could reduce the future peak to $210.4 \mu\text{g m}^{-3}$, of which 38% is road dust,

The AQMP (Appendix V-O) calculated source contributions at Long Beach, Los Angeles, Burbank, and Ontario, as well as at Rubidoux. In each case, sources that are potentially converted to using methanol comprise about half of the total PM_{10} . Thus, similar improvement would be expected at these sites, and throughout the basin.

7.6.4 Summary of PM_{10} Effects

Methanol fuel use has the potential to substantially lower the PM_{10} concentrations in the SoCAB. At Rubidoux, the most heavily impacted site, the annual average concentration in the year 2000 is calculated to drop from a base case of $98 \mu\text{g m}^{-3}$ to $79 \mu\text{g m}^{-3}$. Peak 24-hr. average levels would be reduced more because a larger portion is due to the secondary formation of nitrate aerosol, which can be significantly reduced by converting to methanol. Other sites in the basin would find similar improvements.

7.7 Visibility

Fine particulate matter, especially in the near-micron size range, leads to significant visibility degradation in the SoCAB. In 1979, sections of the basin experienced over 75 days with low visibility (visibility < 3 miles, with relative humidity < 70%) (SCAQMD and SCAG, 1982). The area most frequently experiencing low visibility is, not surprisingly, near Riverside-Rubidoux, where the highest fine particle aerosol levels are found. The potential reduction in PM_{10} levels resulting from extensive use of methanol would also lead to an improvement in visibility.

The relationship between visibility and air quality is complex. Light scattering and absorption is a function of particle loading, aerosol composition, and the size distribution of the aerosol (Friedlander, 1977). Absorption and scattering by gases add to visibility reduction, but to a lesser extent. Except during intensive measurement programs (e.g.,

Table 7.11

Predicted Year 2000 Annual Average PM₁₀ Levels at Rubidoux
($\mu\text{g m}^{-3}$)

	<u>Base 2000</u>	<u>Roll-In From 1990</u>	<u>Full Methanol Use</u>
Nitrates	19.83	10.34	8.43
Sulfates	8.41	7.27	6.04
Elemental	3.87	2.32	0.00
Paved Road	54.25	54.25	54.25
Secondary Carbon	4.60	4.07	3.87
Other	7.39	7.39	7.39
Unexplained	<u>0.00</u>	<u>0.00</u>	<u>0.00</u>
TOTAL	98.35	85.64	79.98

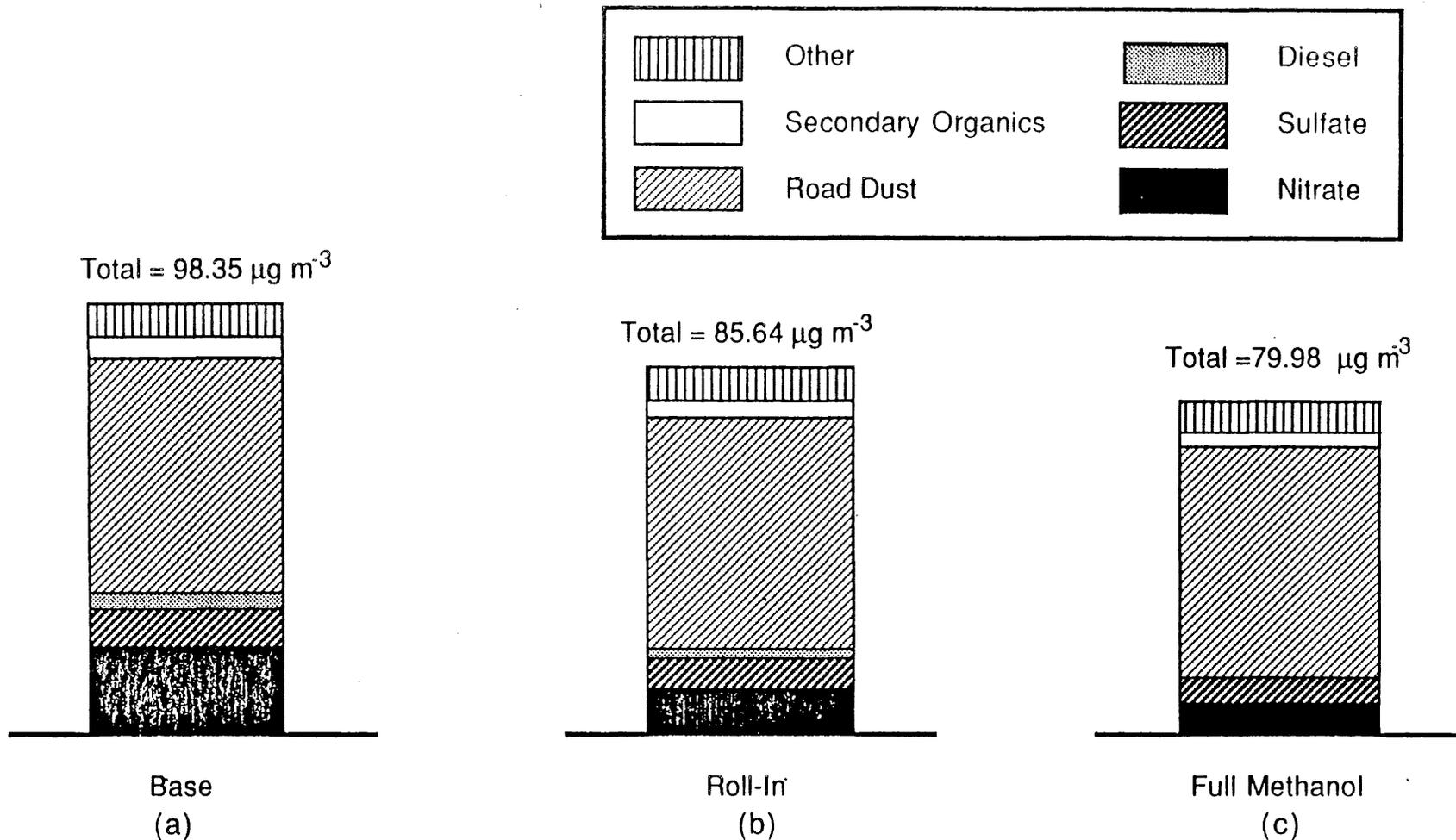


Figure 7.12 Source contributions to annual average PM10 levels at Rubidoux for the year 2000 for a) Conventional (BASE case) fuel use, b) Roll in from 1990 on of M100 MFVs, and c) Full use of methanol fuels in applicable sources.

Table 7.12
Year 2000 Peak 24-hr Average PM₁₀ at Rubidoux
($\mu\text{g m}^{-3}$)

	Base Case ¹	Full Utilization of Methanol
Nitrate	148.01	54.26
Sulfate	34.11	24.50
Diesel Exhaust	7.79	0.00
Paved Road Dust	79.95	79.95
Secondary Carbon	15.23	12.81
Other	6.46	6.46
Unexplained	<u>32.41</u>	<u>32.41</u>
TOTAL	323.97	210.39

¹ Source: Table XIV, Appendix V-O, SCAQMD (1988).

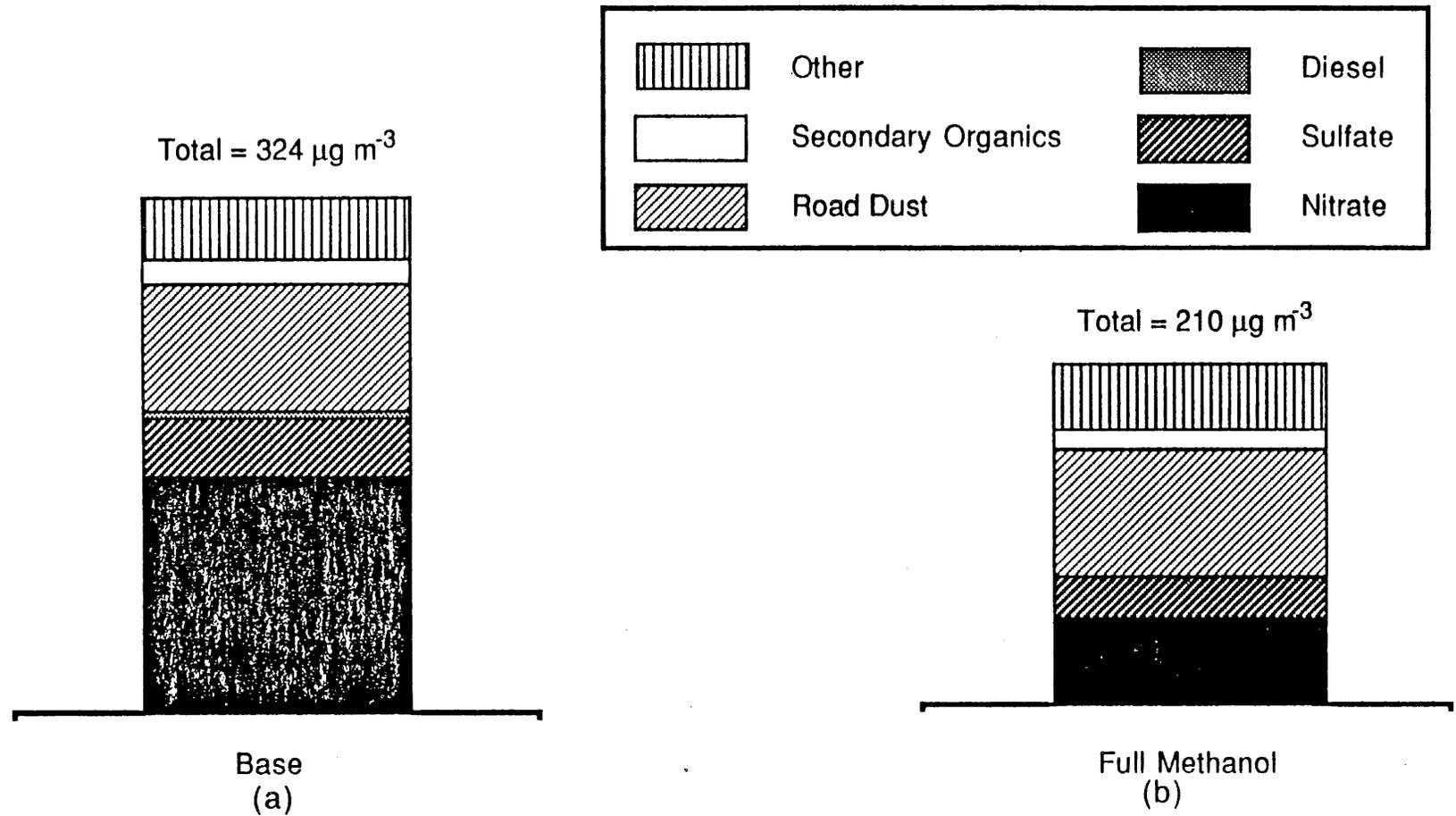


Figure 7.13 Source contributions to peak, 24-hr average PM10 at Rubidoux for a) BASE, year 2000, and b) Full methanol utilization case

Larson and Cass, 1988), there is insufficient data to determine visibility from first principles, and investigators have developed empirical relationships between visibility and more easily collected quantities, such as relative humidity and sulfate, nitrate, and carbonaceous aerosol concentrations (Cass, 1979; Groblicki, et al., 1981; Trijonis, 1979; White and Roberts, 1979).

In general, the underlying premise of the correlations is to find an extinction coefficient, b_{ext} , which relates visibility degradation to molecular and aerosol light scattering and absorption. Then, visibility, s , is found as (Friedlander, 1977):

$$s = \frac{3.912}{b_{\text{ext}}}$$

Groblicki, et al. (1981) found that for the Denver aerosol:

$$b_{\text{ext}} = \left(0.066 + \frac{0.0147}{1 - \mu}\right) S + \left(0.028 + \frac{0.0147}{1 - \mu}\right) N + 0.053 \text{ ORG} + 0.16 \text{ ELEM} + 0.017 R - 0.17 \quad (7.13)$$

where b_{ext} is in 10^{-4} km^{-1} , correlated visibility to measured pollutant concentrations. Here, S , N , ORG , and ELEM are the sulfate, nitrate, organic and elemental carbon aerosol concentrations (in $\mu\text{g m}^{-3}$). R is the remainder of the small particle aerosol matter, and μ is the relative humidity divided by 100 ($\%RH/100$, assumed to be 0.50). A limitation with using this correlation is that it was developed for the Denver aerosol, not Los Angeles. However, other correlations did not include an explicit dependence on the five visibility reducing compounds considered here. The sensitivities to aerosol loadings were similar to the Los Angeles based correlations. This equation will be used, along with the PM_{10} calculations above, to estimate the visibility improvement that can be realized from employing methanol.

As seen in Table 7.13 and Figure 7.14, the aerosol nitrate, sulfate, secondary carbon, and elemental carbon contributions to the extinction coefficient, b_{ext} , are decreased when extensive use of methanol is employed. The most significant decreases in light extinction are noted for nitrate and elemental carbon. If full use of methanol is employed, the predicted visibility is increased from 6 to 11 miles. Road dust, instead of nitrate, would become the major contributor to visibility impairment.

7.8 Summary of Aerosol and Visibility Modeling

Four different approaches were used to predict how methanol fuel use would change SoCAB aerosol levels in the year 2000. Airshed model results were used to develop emissions-to-air quality relationships for aerosol nitrate. The photochemical trajectory model was updated to include recent findings on secondary organic aerosol yields, and was used for establishing how methanol utilization would impact concentrations when methanol was used. Future primary particulate carbon concentrations were calculated using the particle-in-cell model results of Gray (1985). Sulfate concentrations, and how methanol use would affect them, were predicted using a roll-back approach and the results of the AQMP PM_{10} modeling. The results of the individual approaches for each species were integrated to show how methanol use would result in decreased PM_{10} levels and hence, improved visibility.

Table 7.13
Visibility Extinction at Rubidoux
Using Predicted Annual Average PM₁₀
Concentrations¹

Particulate Component	Extinction (b_{ext} , 10^{-4} km ⁻¹)		
	Base Case	Std. M100	Full Methanol
Sulfate	0.84	0.72	0.60
Nitrate	1.13	0.59	0.44
Elemental ²	0.62	0.37	0.00
Secondary Organic	0.24	0.21	0.20
Road Dust	0.92	0.92	0.92
Other	<u>0.12</u>	<u>0.12</u>	<u>0.12</u>
Intercept	<u>-0.17</u>	<u>-0.17</u>	<u>-0.17</u>
TOTAL	3.70	2.70	2.11
Visibility (km)	10.4	14.2	18.5

$$(s = \frac{3.912}{b_{ext}})$$

- 1) PM₁₀ levels taken from Table 7.11 and the correlation shown in Eq. 7.8 is used to calculate the extinction coefficient.
- 2) Most of the elemental carbon at Rubidoux is assumed to be diesel exhaust, and the value from Table 7.11 is used.

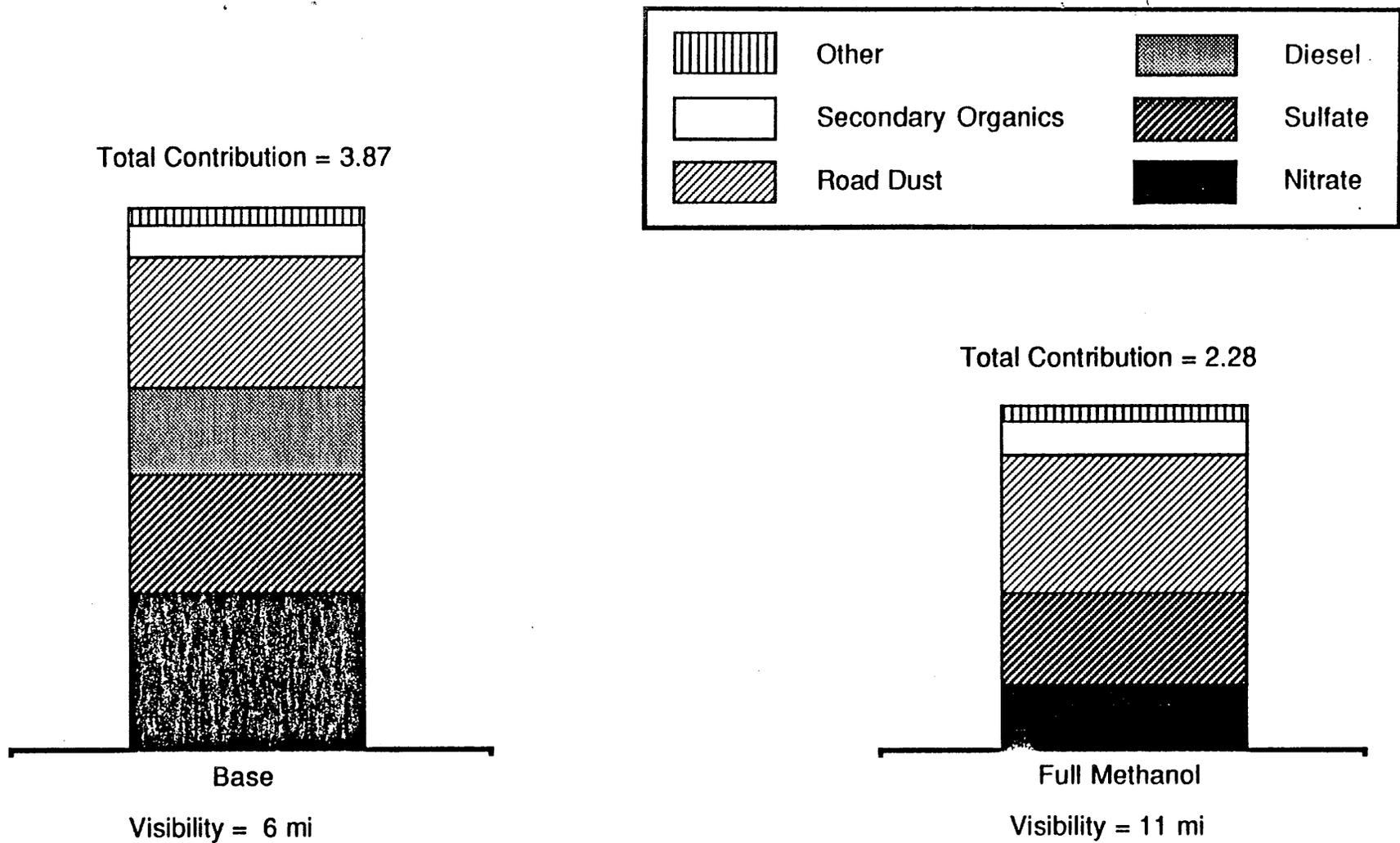


Figure 7.14 Source contributions to visibility extinction at Rubidoux (b extinction in 1/10000 km, annual average)

Diesel vehicles are a major contributor to primary organic and elemental carbon aerosol concentrations within the basin. If on-road and off-road diesel engines are converted to methanol, those emissions would be reduced because methanol fueled diesel cycle engines emit little particulate. In downtown Los Angeles, predicted total fine carbon concentrations were reduced 38%, and elemental carbon was reduced 85%, when full use of methanol was employed.

Reduced NO_x emissions, and the lower reactivity of the exhaust ROG, lead to decreased aerosol nitrate concentrations when methanol fuel is employed. Methanol application in stationary sources leads to further reductions in NO_x emissions, and still lower nitrate concentrations. Peak 24-hr. nitrate concentrations, as predicted by the airshed model, were lowered from a base level of $32 \mu\text{g m}^{-3}$ to as low as $16 \mu\text{g m}^{-3}$ in the methanol utilization scenarios. On an annual basis at Rubidoux, this corresponds to a reduction from 19.83 to $8.42 \mu\text{g m}^{-3}$.

Sulfate levels would be lowered slightly by methanol penetrating into the vehicle fleet. Again, the primary benefit is from use in diesel cycle engines. Annual average sulfate levels at Rubidoux would decrease 14%, from 8.41 to $7.27 \mu\text{g m}^{-3}$. A similar decrease was noted at Los Angeles.

Secondary organic concentrations would be decreased due to the displacement of CFV emissions by methanol. CFV emissions are rich in aromatics, which can form particulate matter upon photooxidation. MFV emissions would be expected to have little particulate formation potential. Photochemical trajectory modeling predicted a 24% decrease in secondary organic aerosol formation when methanol was used.

The results from the four approaches were integrated to show how PM_{10} concentrations and visibility would change at Rubidoux. Rubidoux is one of the most heavily impacted sites in the SoCAB. Using methanol could reduce PM_{10} by 19% from $98 \mu\text{g m}^{-3}$ to $80 \mu\text{g m}^{-3}$. Peak 24-hr. concentrations could be reduced more: 35% from $324 \mu\text{g m}^{-3}$ to $210 \mu\text{g m}^{-3}$. The reduction in PM_{10} would lead to increasing visibility. Without further control, annual average visibility at Rubidoux would be about 6 miles. Switching to methanol would almost double the visible range to 11 miles.

This analysis indicates that extensive use of methanol would be effective in reducing particulate matter levels and improving visibility. Methanol use would result in decreases in sulfate, nitrate, primary carbon, and secondary carbon particulate matter. Decreases are most dramatic in nitrate and primary aerosol carbon.

8.0 Wintertime Formaldehyde and Methanol Levels Under Low Ventilation, and the Impact on Benzene

8.1 INTRODUCTION

One area of concern not addressed in the photochemical modeling studies described previously is the buildup of formaldehyde and methanol during periods of low ventilation and pollutant dispersion. During these periods, primary pollutants, such as carbon monoxide and NO_x ($\text{NO} + \text{NO}_2$) reach high levels -- particularly in areas of high traffic density. Lynnwood, Lennox and Downtown Los Angeles typically experience high CO and NO_x levels, and would be most susceptible to buildup of HCHO and CH_3O from the primary emissions of methanol fueled vehicles.

Related to the possible buildup of primary emittants from methanol fueled vehicles is the simultaneous reduction in compounds directly emitted by conventionally fueled vehicles. Benzene, a carcinogen, is emitted from CFVs, and on-road motor vehicles are the largest contributor within the SoCAB. Recent measurements by the South Coast Air Quality Management District (1988) have found high levels of exposure to benzene by commuters.

Methanol's impact on concentrations of formaldehyde, methanol, and benzene emitted directly from on-road motor vehicles during periods of low ventilation are calculated using an empirical model relating future concentrations to historical CO levels. The calculated future levels of HCHO and methanol are then compared to suggested ambient standards and levels of concern. Benzene at any level is of concern since it is a carcinogen.

8.2 Formaldehyde

Recent measurements (Lawson, et al., 1988) and the photochemical modeling conducted as part of this study found two diurnal HCHO peaks of comparable magnitude. The first occurred around the time of the morning rush hour, and the second occurred in the afternoon. The morning peak can be ascribed to direct emissions of HCHO and rapidly reacting olefins. The morning peak drops quickly, due to HCHO oxidation, photolysis, and vertical ventilation. The afternoon peak can be explained by photochemical production. If primary emissions, as opposed to photochemical production, are going to lead to HCHO concentrations of concern, the most likely time would be in the morning on days of low photochemistry and minimal ventilation. Similar conditions lead to high CO concentrations and are experienced during the late fall and winter months. Emissions of HCHO would build up during the evening, night and morning rush-hour traffic. Oxidation and ventilation are minimal during this time. NO_x and CO levels reach their maximums in the morning.

If methanol does penetrate significantly into the vehicle fleet, motor vehicles would be the dominant source of direct emissions of HCHO in the SoCAB. Currently on-road vehicles are the major source of CO, elemental carbon and NO_x (Gray, 1985; SCAQMD and SCAG, 1982). (Though CO is formed as a reaction product of organic compounds, in Los Angeles the photochemical production of CO is negligible compared to direct emissions.) A conservative method to calculate future peak HCHO concentrations is to use the historical peak CO concentration data, the corresponding CO emission inventories, and the forecast emissions of HCHO in future years, then use the ratio of relative emission levels to get expected peak HCHO levels. This section describes the procedure, limitations and results of those calculations for the SoCAB.

8.2.1 Calculation Methodology

The method chosen to calculate peak atmospheric HCHO concentrations during periods of low photochemistry and ventilation is to scale forecast HCHO emissions by the ratio of the measured CO concentration to the corresponding emissions. This is, in essence, an application of the linear roll-back procedure (see, for example, Seinfeld, 1988). An example of the procedure is given in Appendix 8.A.

A slight modification of the standard rollback calculation procedure is used to predict future HCHO concentrations resulting from direct emissions. The method requires historical CO concentration data, the corresponding emissions, and the future HCHO emissions estimate. Yearly, peak 1-hr average CO concentrations measured in the SoCAB are given in Table 8.1. The peak values range from 26 to 33 ppm, and are usually measured at Lynnwood. (In the photochemical modeling section, the peak morning HCHO at Lynnwood was one of the highest in the modeling region. This, along with the measured CO concentrations show its susceptibility to direct emissions from automobiles.) In 1979 the peak was 30 ppm, about the mid range of the observed peaks. A detailed emissions inventory is also available for 1979 as part of the 1982 AQMP (SCAQMD and SCAG), so this year was chosen as the base for predicting future concentrations. Approximately 6100 metric tons of CO were emitted daily in the SoCAB in 1979.

The forecast HCHO emissions for 100% penetration from 1990 on of standard technology MFVs, with high HCHO emissions (55 mg mi^{-1}), is 19 metric tons per day, of which 84% is from mobile sources. The background HCHO level is taken to be 2.5 ppb, representing the lower levels measured at Long Beach by Mackay, et al. (1988) during the SCAQS study. The predicted future, 1 hr. peak HCHO concentration during a meteorological period similar to the 1979 day corresponding to the CO peak is found as:

$$\left[\begin{array}{l} \text{Historical Peak} \\ \text{CO Concentration} \end{array} \right] \times \frac{(\text{Future Emissions of HCHO, in Moles})}{\left(\begin{array}{l} \text{Mole Emission Rate of CO} \\ \text{at Time of 1979 Peak} \end{array} \right)} + (\text{background HCHO})$$

$$= 30 \text{ ppm} \times \frac{\left(\begin{array}{l} 19 \times 10^6 \text{ grams/day} \\ 30 \text{ grams/mole} \end{array} \right)}{\left(\begin{array}{l} 6100 \times 10^6 \text{ grams/day} \\ 28 \text{ grams/mole} \end{array} \right)} + 2.5 \text{ ppb} = 89 \text{ ppb} \quad (8.1)$$

where emissions have been converted to moles because the concentration measurements are on a mole basis. (89 ppb is equivalent to 0.118 mg m^{-3} .) The 24 hr. average would be considerably lower due to dilution. The calculated concentration is close to the maximum value of 86 ppb measured by Grosjean and Fung (1984) in Los Angeles during a limited measurement program. Historical HCHO measurements have ranged still higher.

A similar calculation for the case when the MFVs are not high HCHO emitters (e.g. the STD M100 scenario) gives a peak HCHO concentration of 40 ppb. This is similar in magnitude to the predicted summertime peaks. If MFVs were to emit only 3 mg mi^{-1} (i.e. the ADV METH case), on-road sources no longer dominate HCHO emissions, and the above calculation procedure is no longer valid, though one would expect significantly lower HCHO levels than for the other two cases.

**Table 8.1 Annual Maximum CO Concentrations in the South Coast Air Basin
1979 - 1987¹**

Year	Maximum Concentrations in ppm. 1-hr Average	Location of Peak
1979	30	Lynnwood
1980	31	Lynnwood
1981	31	Lynnwood
1982	27	Lynnwood
1983	31	Lennox
1984	29	Lynnwood
1985	33	Lynnwood
1986	27	Lynnwood
1987	26	Lynnwood

¹ South Coast Air Quality Management District, 1988b.

A number of limitations are inherent in the above, empirical calculation. First, to scale the HCHO concentrations to CO, the source distribution must be similar. In this case, mobile sources accounted for 85% of the CO in 1979, and would account for 84%, or essentially the same fraction, of the HCHO in the Year 2000 scenario used. Stationary sources, distributed across the basin, account for the rest. Thus, the source distribution is very nearly the same. Secondly, the atmospheric processes affecting the dynamics of CO in the 1979 case should be similar to those that would affect the HCHO in the future years. The peak CO concentration from 1979 was chosen to represent particularly severe events. The 1979 peak can be compared to maximum measurements over the last ten years, ranging from 26 ppm to 33 ppm. The 1979 value is near the middle. HCHO is photochemically active, and is reduced by photolysis and radical attack. Formaldehyde is believed to deposit out at the earth's surface faster than CO (Walcek, et al., 1988). Both the photochemical destruction and ground level deposition would tend to reduce HCHO concentrations from that predicted, and would indicate that the calculation is even more conservative.

The empirical nature of the calculation also assumes that the general spatial and temporal patterns of the emissions are similar. While the temporal pattern of the year 2000 HCHO emissions are dominated by morning and evening rush-hour traffic, as are the 1979 CO emissions, the spatial pattern is expected to change. Growth in the Basin is expected to spread the emissions out, especially eastward. The historical CO peak, used above, was observed at a midbasin (Lynnwood) monitoring station. If the same level of emissions are spread out over a larger area, the spatial peaks would tend to be more uniform and reduced. Again, this would indicate that the 89 ppb is a conservative estimate.

Correct emission estimates are integral to the accuracy of the calculation. The predicted peak scales linearly with HCHO emissions and inversely with CO emissions. If the future HCHO emissions were under predicted, the predicted peak is, too, by a similar percentage. Conversely, if historical CO emissions were underestimated, the predicted peak HCHO is overestimated. If less than 100% penetration is realized, the estimated HCHO would be proportionally less.

Methanol fueled vehicles emit significantly more HCHO when cold-starting than when running hot, similar to CO emissions from a CFV. The above calculation accounts for significant differences in the relative amounts of the two compounds being emitted during cold-start vs. running emissions, though it assumes

$$\frac{\{\text{HCHO}\}_{\text{Cold Start MFV}}}{\{\text{CO}\}_{\text{Cold Start CVF}}} \sim \frac{\{\text{HCHO}\}_{\text{Running MFV}}}{\{\text{CO}\}_{\text{Running}}} \quad (8.2)$$

where {HCHO} and {CO} are the emission rates of formaldehyde and carbon monoxide respectively. The two ratios will depend on future catalyst and engine technology. Sufficient data is not available to determine the validity of this assumption, nor the direction of the bias. In the airshed modeling, cold-start emissions of HCHO are explicitly treated spatially and temporally, though not here. The predicted peak at Lynnwood was related to morning commuter traffic, and was on the same order as the predicted levels at Downtown Los Angeles (e.g., 15.6 ppb vs. 15.3 ppb for the advanced methanol case). It would appear that using the peak at Lynnwood is a good surrogate for the future HCHO peak under high methanol utilization scenarios.

A final limitation to the calculation is that the historic data base has CO measurements only at discrete monitoring locations within the basin. Other "hot spots" could exist, in particular street canyons, parking garages, and near freeways in the SoCAB. HCHO and methanol buildup in street canyons and garages has been studied by Harvey, et al. (198), Gold and Moulis (1988) and HEI (1987). Freeway concentrations can be estimated by using data from the Lennox monitoring station, which is very near Interstate 405 and Imperial Highway, on La Cienega Boulevard. It is a good example of a location heavily impacted by freeway traffic as is evidenced by some of the highest CO levels in the basin. The one year that the peak CO was not measured at Lynnwood, it was found at Lennox, again around 30 ppm. Thus, the 30 ppm value used in the previous calculations would be representative of a site near a freeway.

8.2.2 Discussion of Formaldehyde Buildup

Under the most severe conditions considered, high primary emissions of HCHO and very limited mixing, the peak 1-hr formaldehyde is predicted to be 89 ppb, corresponding to emissions of 19 metric tons day⁻¹. The calculated maximum is less than or comparable to concentrations previously measured in the Los Angeles area during special programs. The limited nature of the measurement programs would indicate that actual peak HCHO levels are higher. It is estimated that direct emissions of HCHO from mobile and stationary sources will continue to decrease. Thus, even under extreme circumstances, ambient HCHO should decline from historic levels. For example, the 1974 inventory for the SoCAB estimated HCHO emissions of 27 metric tons day⁻¹. This is 42% more than in the high HCHO case, and more than double the standard case.

One measure of the severity of the possible buildup is how the predicted maximum compares to standards suggested for HCHO in various environments and known health problems. The calculated maximum, 89 ppb, can be compared to the OSHA standard of 1 ppm (8 hour weighted average). NIOSH recommends a ceiling of 2 ppm, which is also the California OSHA ceiling. 89 ppb is below the odor threshold in most people, and near the lower end of where eye irritation has been found in sensitive individuals (Consensus Workshop on Formaldehyde, 1984). Respiratory difficulties are evident at concentrations significantly higher: 10 - 20 ppm.

A second perspective is gained by looking at the likely exposure to HCHO from different environments. Indoor concentrations of HCHO usually exceed outdoor levels because of the use of the formaldehyde based compounds used in building materials (National Research Council, 1981) Indoor concentrations are frequently above the maximum 1 hr peak of 89 ppb calculated here, and significantly higher than the expected average concentrations. Using typical daily activities for different people in different occupations, Gold and Moulis (1988) concluded that the exposure to direct HCHO emissions from methanol fueled vehicles would be a small fraction of the total. Midwest Research (1984), in a separate study, concluded that even in street canyons and parking garages HCHO from mobile sources would be less than the EPA level of concern. A final note is that the 89 ppb value was derived using the worst case HCHO emissions. If the standard MFV emissions are used, the predicted 1 hr peak would be about 40 ppb, less than encountered in many, if not most, indoor environments.

8.2.3 Summary of Peak, Wintertime Formaldehyde Levels

In this section, an empirical set of calculations were conducted to predict maximum HCHO concentrations under conditions of minimal photochemical activity and low ventilation. The procedure was to use historical CO concentration and emissions data, and future HCHO

emissions rates. The peak historical CO concentrations were then scaled by the ratio of the forecast, HCHO emissions and historical CO emissions.

Using 1979 CO data, a maximum HCHO concentration of 89 ppb is calculated for the scenario where high HCHO emitting MFVs replace CFVs from 1990 to the Year 2000. The 89 ppb is conservative because the calculation did not include deposition or photochemical destruction of HCHO, nor the spreading of emissions within the basin. The calculation, however, does not account for the possibility of very local high concentrations, such as in parking garages. If the standard, expected technology, MFV scenario is used, the predicted peak HCHO is 40 ppb.

These levels can be compared to previously observed HCHO concentrations and to levels of concern due to health effects. Grosjean and Fung (1984) measured HCHO concentrations of up to 86 ppb in Downtown Los Angeles in 1982. Irritation occurs between 100 and 3000 ppb, and respiratory difficulties are experienced between 10,000 to 20,000 ppb. Thus, if HCHO levels were to reach the predicted peak under the most conservative assumptions, eye irritation may be noticed by the most sensitive individuals. A more likely scenario would lead to levels about one third of the level where irritation usually is noticed. When the standard MFV scenario is considered, the predicted 1 hr peak HCHO is on the order of measured, summertime, formaldehyde levels (Lawson et al., 1988; Grosjean and Fung, 1984).

8.3 Peak Methanol Concentrations

Atmospheric methanol would be expected to reach maximum concentrations under the same conditions leading to the high CO and HCHO concentrations just discussed. A similar calculation can be conducted to estimate the peak methanol concentration that would be expected under worst case scenarios. This value can then be used to determine if unhealthy concentrations of methanol are likely to occur in the Los Angeles atmosphere.

The major difference between calculating peak methanol and peak HCHO concentrations is the difference in the forecast emission estimates for the two compounds. Methanol emission estimates are reviewed below, and the calculation of expected peak concentrations is given. These results are discussed with reference to the expected levels of concern and other studies, estimating peak levels.

8.3.1 Expected Ambient Methanol Concentrations

As part of the photochemical modeling section of this study, Year 2000 inventories of methanol emissions were constructed for various penetration scenarios. The maximum emission rate of 190 metric tons/day is forecast for 100% penetration of standard MFVs on a summer day. MFVs, including refueling, would be contributing 91% of the CH₄O in this case. Using this value, in the calculation procedure used above for formaldehyde, provides a worst case concentration estimate:

$$30 \text{ ppm} \frac{\left[\frac{190 \times 10^6 \text{ g CH}_4\text{O}}{32 \text{ g/mole}} \right]}{\left[\frac{6,154 \times 10^6 \text{ g CO}}{28 \text{ g/mole}} \right]} = 0.93 \text{ ppm} = 1.2 \text{ mg m}^{-3} \quad (8.3)$$

This is consistent with the range of values predicted by Harvey, et al. (1984) for street canyons and expressways under severe conditions.

In calculating the 0.93 ppm value, a number of assumptions similar to those previously stated for the formaldehyde concentrations were made. First, this value assumes complete conversion to methanol fueled vehicles emitting between 0.25 and 0.4 g C mi⁻¹ (0.58 - 0.92 g CH₄O mi⁻¹). If a smaller percentage of the conventional vehicle fleet is replaced, the resulting CH₄O level will be correspondingly less. If the vehicles emit more methanol, the calculated value would be low. MFVs in the above scenario, would be responsible for a slightly higher percentage of the methanol than CFVs were responsible for the CO (91 vs. 85%). However, the difference is small, and inclusion of this in a more detailed calculation would not be expected to alter the results significantly. Other limitations are as described, above, for formaldehyde.

8.3.2 Discussion

It is of interest to compare the calculated peak concentration to levels considered to be of concern for health related reasons. Severe intoxication requires a dose of approximately 900 ppm (Roe, 1982). The threshold limit value set by the American Conference of Governmental Industrial Hygienists is 200 ppm (ACGIH, 1980). Each of these values is well above the predicted maximum atmospheric methanol concentration. For these reasons, "It is unlikely that a normal human being could ever be exposed to enough of it (methanol) by inhalation to experience acute toxicity" (Marnett, 1988). The Health Effects Institute (HEI, 1987) concluded that exposures in worst-case ambient exposures, and in traffic situations, would produce a negligible effect. Further discussion relevant to the health effects of extreme MFV related exposure to methanol can be found in Harvey, et al. (1984) and HEI (1987). Those reports discuss exposure in personal and public parking garages, and refueling stations.

8.4 Ambient Benzene Concentrations

Benzene, a carcinogen, would be reduced if methanol fueled vehicles replaced conventionally fueled vehicles. This is because conventionally fueled, on-road motor vehicles are the largest source of benzene in the SoCAB. Grosjean and Fung (1984) measured benzene levels of up to 29 ppb in Downtown Los Angeles, during the morning rush hour peak in 1982. Methanol fueled vehicles emit virtually no benzene, and their use would lead to a reduction in ambient benzene levels.

A similar calculation to those conducted for HCHO and CH₄O can be used to estimate the maximum traffic related benzene concentrations. Benzene emissions in 1982 were approximately 13,000 Kgs/day⁻¹. Using rollback modeling, this would lead to a peak of

$$30 \text{ ppm} \times \frac{\left[\frac{13 \times 10^6 \text{ g/day}^{-1}}{78 \text{ g/mole}^{-1}} \right]}{\left[\frac{6,100 \times 10^6 \text{ g/day}^{-1}}{28 \text{ g/mole}^{-1}} \right]} = 28.6 \text{ ppb} \quad (8.4)$$

The 28.6 ppb calculated compares well to the 29 ppb measured. The predicted value does not account for any background benzene due to non-mobile, distributed sources.

In the Year 2000, mobile source benzene emissions are forecast to drop to 4496 Kgs/day⁻¹, corresponding to a traffic related benzene peak of up to 10 ppb of benzene. Use of methanol will reduce the traffic related benzene proportionally to the penetration of MFVs into the fleet. Full use of methanol would lead to reducing benzene to the much lower levels arising

from distributed benzene emissions from sources besides on-road motor vehicles. In particular, this would lower exposure to benzene while commuting.

8.5 Summary of Methanol, Formaldehyde and Benzene Concentrations Resulting from MFV Use

Use of methanol as a motor vehicle fuel would result in raising peak, winter morning methanol levels and would lower benzene concentrations from a similar case involving conventionally fueled vehicles in the Year 2000. Formaldehyde levels would be reduced from 1982 levels whether MFVs are used or not, even if the MFVs emit HCHO at 55 mg mi^{-1} .

Using a rollback methodology, the peak predicted HCHO level was 89 ppb under low-mixing, stagnation conditions in the morning. In this calculation, MFVs with high HCHO emission rates were used. 89 ppb is well below the 2 ppm CAL/OSHA standard. Average levels would be significantly less than 89 ppb. If MFVs emitting at the proposed CARB regulated rate of $15\text{-}18 \text{ mg mi}^{-1}$ are considered, or if there is less than 100% penetration of MFVs into the fleet, the predicted peak will be proportionally less. This would lead to levels well below historical peak levels. The peak ambient concentration predicted is below levels commonly found indoors. Using similar values, Gold and Moulis (1988) showed that exposure to MFV-related HCHO would be small compared to other sources, especially in houses and offices due to building materials.

Methanol levels would increase substantially. The predicted peak under full penetration of MFVs into the vehicle fleet is 0.93 ppm. This is a factor of 200 times less than the threshold limit value, and has led to the conclusion that worst case exposure to ambient methanol would have a negligible effect. Benzene levels would drop proportionally to MFV use. Exposure to benzene while commuting would, in particular, be reduced.

These results indicate that methanol fueled vehicle use should not lead to ambient HCHO and methanol concentrations above levels of concern set by health agencies. Formaldehyde levels should decrease from historical levels resulting from less effective controls of CFVs. Benzene would be reduced substantially.

APPENDIX 8.A

As an example of the linear rollback procedure, the predicted future peak CO concentration can be calculated from historical measurements. In Table 8.1 the peak CO in the SoCAB in 1979 was 30 ppm, corresponding to a daily emission rate of 6770 tons of CO per day. In the Year 2000, CO emissions are expected to be reduced to 3885 tons/day-1. Scaling the forecast, Year 2000 emissions by the historical, 1979, emissions, times the historical peak ambient CO in the Basin gives

$$\begin{aligned}
 \text{[Historical Peak CO]} * \frac{\text{[Future CO Emissions]}}{\text{[CO Emissions at Time of Historical Peak CO]}} &= 30 \text{ ppm} \times \frac{3885 \text{ tons/day}^{-1}}{6700 \text{ tons/day}^{-1}} \\
 &= 17 \text{ ppm} \quad (8.A.1)
 \end{aligned}$$

In essence, an emissions reduction of 42% should lead to a similar decrease in ambient concentrations. If there were a significant background CO level, this must be accounted for using the general form of linear rollback

$$\text{[Historical Peak]} = \alpha \text{ [Historical Emissions]} + \text{[Background]}$$

so

$$\alpha = \frac{\text{[Historical Peak]} - \text{[Background]}}{\text{[Historical Emissions]}}$$

Then,

$$\text{[Future Peak]} = \alpha \text{ [Future Emissions]} + \text{[Background]}$$

The background level of CO, however, is small compared to 17 ppm, so it has been neglected.

The above calculation has inherent limitations. First, the CO must be either emitted directly, or its formation must be linear in precursor emissions. While CO is formed by photochemical oxidation, in Los Angeles this contribution is small compared to direct emissions. A second limitation is that the spatial and temporal pattern of emissions should not change appreciably. In Los Angeles, mobile source emissions will continue to be concentrated in the urban and suburban areas, though a slight shift eastward is expected. A third limitation is that the calculation relies on the accuracy of the input emission estimates. Finally, any loss process, such as deposition, should be linear in the species concentration. If each of these limitations holds, rollback models can be used effectively.

9.0 Recommendations For Future Work

The three-tiered design of this project was developed, specifically, to identify areas of uncertainty, and to quantify how those uncertainties may affect conclusions of this report. By identifying important uncertainties it is possible to suggest further studies to improve our capability to predict how utilizing methanol will impact future air quality. Each tier identified specific concerns. In this section reasons for the major uncertainties, and projects to alleviate their impacts, are described. It is worth noting that the openness of this project, both through the in-progress meetings and other forums, has helped identify areas of concern as the project progressed. Those concerns, when possible, were then addressed within the project.

9.1 Exhaust Composition of M85 and M100 Fuel

Chemical sensitivity, trajectory, and airshed modeling all showed that the assumptions concerning the exhaust composition of methanol fuels can dramatically affect the results. In the calculations, this uncertainty was treated by conducting bounding calculations. Key issues in this category are:

- 1) The composition of the reactive organic gases, excluding methanol and formaldehyde, of the exhaust.
- 2) Formaldehyde exhaust fraction. Formaldehyde is very reactive, and if HCHO emissions are not well controlled the environmental benefits of MFVs are decreased. As an example, one of the calculations in Chapter 6 showed that increasing the HCHO emissions from 15 mg mi^{-1} to 55 mg mi^{-1} reduced the ozone reduction by 50%.
- 3) ROG emission rate from M100 and M85 vehicles. Simulations of M85 vehicles showed approximately half the benefits of M100 vehicles because of the ROG fraction of the emissions.

An integral issue here is that the fuel composition is still unknown, and this will affect exhaust and evaporative emissions. What is required to alleviate this problem is to speciate and quantify the organic exhaust components, including the heavy organics. Of interest here is what fraction of the organics are derived from the fuel, what fraction from the oil, and the reactivity of the species emitted. In this study, M100 exhaust was assumed to be purely methanol and HCHO. Data of CARB suggests that the other organics from M100 fueled MFVs account for about 4% of the reactivity. Emissions from M85 fueled vehicles were treated more conservatively. Non-methanol, non-formaldehyde components of M85 vehicles were assumed to have a similar distribution to catalyst light duty vehicles. If a significant fraction of the measured ROG is from lubricating oil, the reactivity, as used in this project, could be overestimated. Thus, the two assumptions bound the likely reactivity of MFV exhaust.

Programs are currently underway to refine the estimates of exhaust composition, both at CARB and in industry. These studies should provide the required data, though continuing evolution in methanol fueled vehicle technology will continue to change the composition and rate of emissions.

One interpretation of the sensitivity to exhaust composition would be to suggest that the reactivity of the methanol exhaust and fuel components be minimized. For example, a

mixed methanol fuel low in olefins and aromatics might be preferred, if engine performance, cold starting, emissions and safety standards can be maintained.

9.2 Modeling of Other Episodes

Ozone formation is a complex system of events and the relative role of different sources in forming ozone can depend on meteorology. The period chosen for modeling in this study was conducive to smog formation, though other periods with different meteorology, also have led to high ozone levels. Calculations could be extended to other events. One such period is June 5-7, 1985, which was used in the AQMP, and as the basis for similar efforts by industrial concerns. This period does not, however, have as detailed evaluation data. A third period could be chosen from the Southern California Air Quality Study (SCAQS) program period.

After proper model evaluation for each of these periods, an airshed model should be used to test the effectiveness of methanol in each period. About six different scenarios corresponding to the use of CFVs and MFVs in the Year 2010 should be tested, including:

- 1) Base 2010, with expected controls
- 2) 100% penetration of M85 vehicles from 1990 (or 1995) to 2010
- 3) 100% penetration of M100 vehicles from 1990 (or 1995) to 2010
- 4) Low-emitting MFVs throughout the fleet
- 5) Low-emitting CFVs throughout the fleet
- 6) No on-road mobile source emissions.

These six should give a very good view of how methanol use would perform under a variety of meteorological periods, and alleviate concerns over designing ozone control strategies based on modeling of a limited time period.

The cost of this project should be limited because two of the periods, August 30 - September 1, 1982 and June 5-7, 1985, have already been used for airshed modeling, and the SCAQS days are expected to be used for model intercomparison. Also, the inventories have been developed and used, and can be readily adapted for the proposed study.

Estimated Cost: \$75,000 (if SCAQS model evaluation has been accomplished)

9.3 Use of a Different Chemical Mechanism

Midway through this study, two new chemical mechanisms appropriate for use in airshed type models were introduced. These two mechanisms are larger (and hence slower) than the Extended Caltech Mechanism, and include recent findings on the atmospheric reactions of pollutants. The Caltech Mechanism has constantly been updated to include what is believed to be the current understanding of atmospheric chemistry; however, the new mechanisms, including the ERT/SAPRC (Lurmann, et al., 1987) mechanism used for parts of this study, have been extensively tested and are shown to perform very well. Very recently, Carter (1988) under contract to CARB has designed a methodology to optimize mechanism performance, and to minimize computational requirements, based on emission inventory composition, and shows very good

performance. Mechanism intercomparison indicates that these mechanisms are more complete descriptions of the atmospheric chemistry than the extended Caltech Mechanism. It is recommended that future studies use one of these mechanisms.

In the study here, the results obtained using the Caltech Mechanism were compared against those obtained using the SAPRC/ERT Mechanism, using both the trajectory and chemical kinetics models. The sensitivities to methanol and HCHO were shown to be very similar. In trajectory modeling, the results were comparable, though the SAPRC/ERT Mechanism showed slightly more sensitivity to ROG reductions than did the Caltech Mechanism.

In recent studies (unpublished) airshed modeling of the June 5-7, 1985 period, using both the CIT Model (conducted by A. Russell and G. McRae) and the SAI Model (conducted by SAI), showed similar response to ROG and NO_x controls. The comparison of the two models was informal, but relied on essentially the same meteorological data sets. Given the testing of the models using the Caltech Mechanism against models using the other mechanisms, and the similarity in the response, a separate study testing the effectiveness of methanol using a model based on a different mechanism is not warranted, but one of the recent mechanisms should be used in future studies of other periods. No separate cost is given as this is integral to modeling of other episodes.

9.4 Other Alternative Fuels

Methanol is one of the proposed clean, alternative fuels. Other candidates include liquified propane gas, compressed natural gas, ethanol, hydrogen, butane and ethane. Each fuel has its benefits, and will impact the formation of photochemical smog and other pollutants. A recommended follow-on topic would be to test competing alternatives in a similar fashion to the methanol tests, though not as exhaustive list of calculations is necessary. Four scenarios for each fuel would give a foundation for good intercomparison of the air quality benefits of each.

Estimated cost: \$65,000 - \$85,000. (dependent upon number of fuels tested)

9.5 Impact of Methanol Downwind of Los Angeles

The atmospheric lifetime of methanol is about 20 days. This has led to the concern that the methanol emitted in the SoCAB could be transported, and become a problem in downwind regions. Model predictions of methanol concentrations during the afternoon in the Eastern Basin are about 0.1 ppm. Further dilution and reaction would decrease those levels further as the air parcels are advected downwind. Using the results of previous tracer experiments, calculations could be conducted to indicate the downwind concentrations of methanol outside of the SoCAB, and be used to indicate if the methanol would have a significant impact. In interpreting the results of such a study, it should be noted that ozone formation in rural areas without NO_x emissions is NO_x limited, minimizing the impact of slightly higher ROG levels.

9.6 Incorporating the Results of the Adoption of the Air Quality Management Plan

Ozone formation is highly nonlinear, and the effect that utilizing methanol will have depends on the emissions from unaffected sources, such as solvents. Controls proposed in the AQMP, the adoption of which is being discussed, will change the relative benefits of switching to methanol. Depending on the controls adopted, the role of methanol in improving air quality could be more, or less, dramatic. It is recommended that future

calculations be conducted that incorporate the controls on sources that are projected to be in place by 2010.

Estimated Cost: \$10,000 (if conducted as part of the study on other alternative fuels, or modeling of other episodes).

9.7 Impacts on Aqueous Phase Chemistry

During the course of this study, it has been hypothesized that the increased levels of methanol might lead to the formation of potentially harmful, trace compounds in fogs and clouds. One such possibility is the formation of dimethyl sulfate (DMS). While the thermodynamics are unfavorable to the formation of DMS, it has been suggested that under extreme circumstances, it could be important. It is recommended that a set of equilibrium calculations be conducted to indicate the likely level of DMS in a fog exposed to a polluted atmosphere containing methanol, NO, NO₂, ammonia, SO₂ and other organics. A similar set of calculations for rain droplets should also be conducted. If these calculations indicate that potentially significant levels of DMS or other aqueous compounds are formed, further laboratory study is required to determine rate constants for methylation of sulfuric acid. Insufficient kinetic data is available for doing a kinetic study of DMS formation.

Estimated cost for equilibrium calculations: \$7,000.

9.8 Summary of Recommendations

This project used a three-tiered methodology, with extensive modeling at each level, to determine the air quality benefits of methanol and reduce uncertainties in the interpretation of those results. However, uncertainties still exist, primarily in input data. The most crucial is the composition of MFV exhaust and fuel. Because of the increasing interest in methanol as an automotive fuel, projects are currently underway to determine the levels of emissions, by component, for MFVs. The results of this study can be interpolated to find the likely benefits of different mixtures of emissions (e.g., combining sensitivity analysis of the ozone formation sensitivities of individual species with the results of trajectory and airshed modeling). Future modeling studies will benefit greatly from the data taken from emission measurements.

The second most productive area of future study is to show how methanol will affect air quality during other periods. Two other meteorological periods could be used to show if methanol use is a robust strategy.

Final areas of concern are potential problems of methanol use on the small scale (confined spaces), large scale (downwind transport), and during foggy periods. These studies would concentrate on identifying if a problem may arise and, if so, more study would be required, because the underlying science and health information is inadequate.

Minimizing the uncertainties and concerns has been accomplished by extensive modeling, sensitivity analysis and open discussion of the results of the project. Many of the perceived uncertainties, e.g., dependence on boundary and initial conditions, mechanism employed, emission composition, etc., were dealt with during the project. The large number of calculations allow for interpolating between specific scenarios tested. The major uncertainty is the future composition of MFV emissions, which will unfold MFV technology advances.

10.0 Summary of the Air Quality Effects of Methanol Utilization

Methanol fuel use in mobile and stationary sources has the potential to improve many facets of air quality in the Southern California Air Basin. Extensive photochemical modeling, using a three-tiered methodology employing chemical kinetics, sensitivity analysis, trajectory and airshed models, shows that ozone and other photochemical oxidants could be reduced effectively by methanol use, primarily in motor vehicles. Separate models were used to show that particulate matter (PM₁₀) would also be decreased.

A number of issues were outstanding when this project begun, and it has been the goal to address each one as conclusively as possible, and to do so in a manner to minimize uncertainty. A summary of each issue, and conclusion derived from results of this study follows. Next, quantitative estimates of air quality improvements derived from methanol use are summarized.

10.1 Summary of Issues and Related Conclusions

10.1.1 Multiday Build-Up of Methanol Decreasing Effectiveness

An overriding issue was that methanol could build up over an extended period until it dominated the reactivity of the ROG in the atmosphere, leading to a decrease in the effectiveness of methanol use during multiday ozone episodes. This hypothesis was supported by results of smog chamber experiments that showed, on the third day of the experiment, little or no benefit of replacing one third of the ROG with methanol. This was in contrast to modeling studies, and single day smog chamber experiments, that showed significant benefits. This issue was addressed from two directions. First, the results of the experiments were explained and, secondly, multiday trajectory and airshed modeling were used to show longer period impacts.

Smog chamber modeling, with sensitivity analysis, showed that the reason the experiments showed little benefit from methanol substitution after the first day was that the mixture became severely NO_x-limited and that the bag walls were responsible for driving the photochemistry. The experimental conditions were not representative of those in the atmosphere of the SoCAB. It could be concluded that the actual atmosphere would show trends much more like the results of single day experiments where methanol substitution was found to be beneficial to reducing ozone. (See sections 1.6.2, 2.4 and 3.4)

The second part of this issue, concerning if the multiday buildup of methanol to concentrations so great that even with a significantly lower reactivity, benefits would not be realized, was accomplished by multiday modeling and sensitivity analysis. Each of these tests concluded that the benefits would continue throughout a smog episode. The degree of ozone reduction that can be expected is detailed in the later sections on impacts from particular strategies. (See section 3.4 and Chapters 5 and 6.)

10.1.2 Will Ambient Formaldehyde Levels Increase?

Though much less abundant than methanol, HCHO emissions from MFVs may be significant. It was of concern that extensive penetration of MFVs into the motor vehicle fleet would lead to excessive increases in HCHO levels. This study showed that ambient, summertime HCHO levels will not increase significantly, and may decrease, if MFVs are used. While MFVs have higher direct emissions of HCHO than CFVs, the methanol emitted reacts very slowly to produce secondary HCHO. On the other hand, CFV exhaust reacts relatively rapidly to form HCHO. About 80% of the atmospheric HCHO in the

SoCAB is secondary (Rogozen and Siskind, 1984), so decreasing the reactivity of the exhaust ROG and, hence, secondary HCHO production, offsets direct emissions. Thus, HCHO concentrations are relatively unchanged by switching to MFVs. (See section 5.5.6 and 6.5.4.)

Wintertime levels of HCHO were calculated to reach levels of up to 86 ppb under extreme conditions if HCHO emissions are 55 mg mi⁻¹. This is less than the suggested ambient standard. If vehicles met the proposed level of 15 to 18 mg mi⁻¹, or if there was less than 100% penetration of MFVs into the vehicle fleet, the ambient levels would be lower. (See section 8.2)

10.1.3 Will Methanol Levels Build Up to Unhealthy Levels?

Linear calculations were used to show that the expected methanol levels under severe stagnation conditions should not exceed about 1 ppm, on a one-hour average. Daily and yearly averages would be significantly less. The 1 ppm value can be compared to the ACGIH threshold limit value of 200 ppm (8-hr average) indicating that exposure to ambient, atmospheric methanol should not portend a problem. (See section 8.3.)

10.1.4 How Will Methanol Use Affect Concentrations of Pollutants Other Than Ozone, HCHO and Methanol?

Previous studies concentrated on determining if methanol use would decrease ozone. Little, if any, attention was paid to how other photochemical oxidants, primary pollutants and particulates would be impacted. These other pollutants are known or suspected of materials damage and health concerns. Methanol use will, in general, decrease levels of NO₂ (criteria pollutant), peroxyacetyl nitrate (an eye irritant and phytotoxin), nitric acid (leads to acid deposition, irritant), aerosol nitrate (contributor to PM₁₀, a criteria pollutant, visibility degrader), sulfate (acidic, PM₁₀), particulate carbon (PM₁₀, carries possible carcinogens), and benzene (a carcinogen).

Predicted NO₂ levels decreased up to 28%, as did HNO₃, in the simulations involving 100% penetration of MFVs into the vehicle fleet. PAN exposure decreased up to 23%. Particulate matter could be decreased up to 19% on an annual average basis, and 35% for the peak 24-hr level. Thus, the use of methanol to reduce ozone will be accompanied by beneficial reductions in other pollutants. (See Chapters 5,6 and 7.)

10.2 Summary of Expected Improvement in Air Quality From Utilizing Methanol

Over 150 trajectory calculations and thirty-six airshed model runs were conducted to develop methanol use-air quality relationships and for sensitivity analysis. The trajectory model was used extensively for sensitivity testing because of its computational speed, and because there are limitations in its formulations. The airshed model, though computationally intensive, gives a much more global and concrete view of the air quality impacts throughout the SoCAB. Twenty-five of the airshed simulations were used to determine the impact of various levels of use of methanol in mobile and stationary source applications, as compared to the continued use of conventionally fueled vehicles. Issues were addressed to delineate the relative advantages of various strategies for use in determining public policy. Specific issues investigated include role of exhaust formaldehyde content, fuel composition effects, comparison to conventionally fueled vehicle fleets, the role of developing advanced, low emitting, MFVs and CFVs, and how stationary source use of methanol fuel would impact air quality.

10.2.1 Potential Benefits of Methanol Fueled Vehicle Fleets Compared to Conventionally Fueled Vehicles¹

A first comparison was between predicted air quality resulting from a conventionally fueled vehicle fleet versus the potential benefits of methanol use. The use of two different methanol fuels were tested. There are greater benefits if a nearly neat (M100) fuel, as compared to M85, is used if, as assumed here, the HCHO levels are the same between the two methanol fuels. This section summarizes the benefits of converting to M100 fueled vehicles.

Predicted peak ozone in the Year 2000 using the forecast emissions, assuming a conventionally fueled vehicle fleet was 0.27 ppm, over twice the NAAQS and state standards. Population exposure to Stage 1 ozone levels (0.20 ppm and above) was 2,171,000 person-ppm-hours. If a standard M100 fueled vehicles started displacing conventional vehicles starting in the Year 1990, the predicted peak ozone decreased to 0.22 ppm, and the exposure above 0.20 ppm decreased 83% to 364,000 person-ppm-hours. In the Year 2010, which has generally higher ozone levels, the exposure above 0.2 decreased 26%, and the exposure above 0.30 decreased 92%.

As an example of the effectiveness of methanol, removing mobile sources completely reduced peak ozone in the Year 2000 to 0.21 ppm, and exposure to 58,000 person-ppm-hours. Comparing the results between converting to M100 versus having no vehicles at all shows that the peak ozone reduction with M100 fuel use is 68% of that of having no vehicles. Exposure reduction is 85% of the no-vehicle case. Similarly, comparing M100 use to having no ROG emissions from motor vehicles shows that the peak ozone reduction is almost the same in both cases (0.223 for M100 vs. 0.227 for no mobile source ROG). This indicates that the organic exhaust and evaporative emissions from an M100 vehicle, which are primarily unburned methanol, contribute little to ozone formation.

Switching to methanol reduced both peak HCHO (from 29.7 to 28.9 ppb) and exposure (16%), alleviating concern that formaldehyde levels could be exacerbated by MFV use. Peroxyacetyl nitrate (PAN) exposure was reduced 22%, and the peak dropped from 15.2 to 11.1 ppb. NO₂ and HNO₃ exposure both were predicted to be reduced about 28% if MFVs started penetrating into the vehicle fleet. In summary, M100 use has the potential to reduce levels of the photochemical oxidants, including ozone, HNO₃, PAN, NO₂, and HCHO levels, to nearly the same degree as removing the ROG from vehicle exhaust. (See section 6.5.4.)

10.2.2 Effectiveness of Fuel Types

Technologically M85 fueled MFVs are more viable in the near term, though there are air quality benefits to reducing the emissions of non-methanol organics that are associated with a fuel blend. Comparing air quality benefits from converting to M85 as opposed to M100 shows that the 0.02 ppm reduction in peak ozone (0.26 to 0.24 ppm)

¹ After completion of the modeling portion of this project, CARB revised the mobile source inventories to reflect a more accurate temperature dependency. The revised inventory has significantly greater NO_x emissions (K. Wagner, personal communication, 1989). If NO_x emissions in the future years were to be greater than used in this study, the benefits of switching to methanol would be greater. Higher ambient NO_x concentrations lead to a greater sensitivity to ROG controls and the reactivity of the ROG. In a significant fraction of the modeling region, especially the eastern SoCAB, ozone formation was NO_x-limited, minimizing the impact of switching to methanol. Both peak concentrations and exposures would become more sensitive to substitution. See chapters 2, 5 and 6 for more discussion on this issue.

achieved by M85 fuel is half that of going to M100. The improvement in ozone exposure is also about half of that realized from using M100. This shows the advantage of using a fuel with minimal amounts of organic gas emissions that are more reactive than methanol, and M85 is about half as effective as M100.

The assumed composition of M85 exhaust was 10-15% higher in non-methanol ROG than seen in recent CARB tests. If future vehicles follow this trend, or achieve lower non-methanol emission rates, the benefits from conversion would be greater. Also, if a large portion of the ROG measures in M85 exhaust is less reactive heavy hydrocarbon, such as from fuel oil, the benefit of M85 fuel use would be greater than shown here. The composition of the fuel and exhaust used for the M85 and M100 vehicle simulations brackets the likely reactivity range. When future data becomes available, the results here can be used to interpolate to more accurately estimate the impact. (See section 5.5 and 6.5.4.)

10.2.3 Exhaust Formaldehyde Content

Formaldehyde emissions, which come from the incomplete combustion of methanol, are the largest contributor to the organic reactivity of the exhaust from an MFV. About half the ozone reduction was lost if M100 vehicles emitted 55 mg mi^{-1} , as compared to the similar calculation using an in-use emission rate of 15 to 18 mg mi^{-1} . HCHO exposure would also increase. In the Year 2000, if light-duty MFVs emitted 55 mg mi^{-1} the predicted peak ozone is 0.24 ppm, compared to 0.26 for the base and 0.22 ppm for the standard M100 case.

Ambient HCHO levels would also increase. The peak concentration increased 17% to 35 ppb. This is less than current HCHO levels. The impact on NO_2 and HNO_3 is also marked, increasing peak levels by 36% and 20%, respectively, over the M100 case. This calculation evidences the need to control formaldehyde emissions from MFVs. (See section 5.5 and 6.5.4.)

10.2.4 Low Emitting Methanol and Conventionally Fueled Vehicle Fleets

Advances in technology or increased regulatory stringency could lead to substantial reductions in automotive ROG and NO_x emissions. At issue here is the relative benefits of methanol compared to conventional vehicles if both are stringently controlled to 0.25 g mi^{-1} ROG and $0.20 \text{ g mi}^{-1} \text{ NO}_x$. Three cases bear information in this area. If the entire fleet were advanced, low emitting, conventionally fueled vehicles, the predicted peak ozone in the Year 2000 is 0.245 ppm. If it were an advanced methanol fleet, the predicted peak is 0.223 ppm. If no organics were emitted by either advanced fleet, the peak ozone is 0.215 ppm. That would indicate that at this level of emissions from other sources, the organics from the MFVs produce about one-fourth the peak ozone. Relative ozone exposure to levels above the 0.12 standard is reduced by about the same fraction. Exposure and peak levels to the other pollutants is also significantly less in the advanced methanol case. (See section 5.5 and 6.5.4.)

10.2.5 Stationary Use of Methanol Fuel

Methanol can be used in stationary sources to reduce NO_x emissions which, in turn, can reduce ozone concentrations. Calculations simulating the use of methanol in utility boilers, refinery heaters and stationary internal combustion engines showed that the peak ozone would be reduced slightly, about 2%, corresponding to a 7% decrease in NO_x emissions. Reductions in exposure to other pollutants were between 2% (for HCHO) and

5% (HNO_3 and NO_2), except there was a slight (1%) increase in PAN exposure. The small reduction in NO_x emissions led to a less than proportional (2% to 7%), though beneficial, reduction in ozone, HCHO, NO_2 and HNO_3 . (See section 6.5.4.6.)

10.2.6 Example of Use of Results for 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 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 NMOG and 3 mg mi^{-1} HCHO. The default MFV had HCHO emissions of $15 - 27 \text{ mg mi}^{-1}$ (LDV). These calculations can be used as bounds for interpolating to intermediate cases.

As an example, tests 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 between the M100 and M85 calculation. (The HCHO emission rate is $20 - 30 \text{ mg mi}^{-1}$, 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 as follows:

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. The exposure 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.

10.3 Impact on Particulate Matter and Visibility

Methanol fueled vehicles emit virtually no particulate and the methanol and formaldehyde emitted are not precursors to secondary particulate formation. Also, use of methanol in diesel engines would reduce NO_x and SO_x emissions, and result in reduced formation of nitrate and sulfate particulate. The ability of utilizing methanol to reduce particulate matter is important because of the very high loadings of small particulate throughout the Basin. At some locations, PM_{10} levels are about six times the state standard and double the national standard.

Calculations involving the photochemical airshed and trajectory models, and results of linear dispersion modeling, indicate that converting to methanol has the potential to reduce annual average PM_{10} by 19%. The major reductions are from reduced levels of elemental carbon and nitrate.

Visibility would improve due to the decreased PM₁₀ levels. Maximum use of methanol in the Year 2000 would lead to the predicted average visibility nearly doubling from 6 to 11 miles for the Base Case and Methanol Case, respectively. (See Chapter 7.)

10.4 Benzene Reductions

Benzene, a carcinogen, is emitted by conventionally fueled vehicles. Motor vehicles contribute about 73% of the benzene emissions in the SoCAB, and switching to methanol fuel would help eliminate the major source. A linear calculation showed that maximum levels of mobile source related benzene could be reduced from 29 ppb towards zero. The extent of reduction depends on the fuel type, M85 vs. M100, and the organics in the fuel. (See section 8.4.)

10.5 Future Studies

The three-tiered structure of this study was used to identify, minimize and quantify uncertainties in the calculation. Identifying causes of uncertainties also allows for specifying areas requiring further study.

Benefits of methanol fuel use are very sensitive to the exhaust and fuel composition, including exhaust formaldehyde and other organic emittants. Programs are currently underway to better characterize the emissions of MFVs, and the results here can be used to estimate future air quality corresponding to those emission characteristics.

One question that can be asked in terms of this project, and other photochemical modeling studies, is whether results from one episode are characteristic of others. It is suggested that a future study look at the impact of using methanol during two other smog episodes. Potential periods are the three-day episode used in the 1988 AQMP process and a period during the SCAQS experiment. This will help develop a more robust foundation for interpreting modeling results. This work should incorporate a newer mechanism, such as the SAPRC/ERT mechanism.

A final need is to look into the possible aqueous phase formation of harmful pollutants, such as dimethyl sulfate. Insufficient kinetic rate data exist for an in depth calculation, so an equilibrium calculation is warranted. A variety of pollutant conditions pertaining to both fogs and clouds should be used.

Completing these research recommendations should improve the confidence on the results obtained here, and are not expected to drastically change them. The methodology used was generally conservative, and used upper and lower bounds on emission characteristics to enable quick interpolation of results as further data becomes available. The aqueous phase calculations can be used to alleviate concerns, or identify problems in the formation of compounds in fogs and clouds. (See Chapter 9.)

10.6 Conclusion

A three-tiered modeling approach was used to quantify the extent that methanol fuel utilization would impact air quality in the South Coast Air Basin of California. Model results show that methanol use in stationary and mobile sources can be used to effectively reduce ozone and other photochemical oxidants in future years. Reductions were found in the peak ozone concentrations, and spatial extent of high levels if methanol is used. Results here showed that nearly neat (M100) fuel was about twice as effective as M85, and both were more effective at reducing ozone than more stringently controlled CFVs. Recent test results, as shown in the example above, indicate that M85 fueled vehicles emit less

ROG than modeled. This would lead to the formation of less ozone, and the M85 result would approach that found for M100. In the example in 10.2.6, using data for three M85 fueled, FFV Crown Victorias led to an exposure reduction of 72% of that found for removing mobile sources. Thus, both M100 and M85 use could lead to substantial ozone reduction.

Initial concerns that the benefits of methanol utilization would be lost during multiday smog episodes were shown to be an artifact of the experiments on which that hypothesis was based. Similarly, the buildup of methanol and formaldehyde should not be a health problem. In contrast, using methanol will reduce atmospheric benzene levels.

Methanol utilization will reduce other pollutants besides ozone and benzene. Peroxyacetyl nitrate, nitric acid and NO_2 would also be decreased. Small particulate matter (PM_{10}) concentrations could also be decreased markedly by switching to methanol. This would lead to an improvement in visibility, especially in the more heavily impacted region.

None of the emission scenarios studied led to predicted compliance of the Basin with either the ozone or PM_{10} standard. However, these results suggest that use of methanol as a fuel could be an effective technique, combined with other source controls, in a strategy to help approach the applicable national and state standards. Given the broad range of benefits it could be an integral part of a plan to improve air quality in the Los Angeles area.

REFERENCES

- ACGIH (1985) American Conference of Governmental Industrial Hygienists, Inc., Documentation of the Threshold Limit Values and Biological Exposure Indices, Fifth Edition. Cincinnati, OH.
- Allen, P. (1986) Magnetic disk, personal communication to A. G. Russell.
- Alson, J.A. (1988) The emission characteristics of methanol and compressed natural gas in light vehicles, Presented at the 81st annual meeting of the APCA, June 19-24, Dallas, Texas.
- Atkinson R., Lloyd A. C. and Wings L. (1982) An updated chemical mechanism for hydrocarbon/NO_x/SO₂ photo-oxidations suitable for inclusion in atmospheric simulation models. *Atmos. Environ.* **16**, 1341-1355.
- Atkinson R., Aschmann S. M., Carter W. P. L. and Pitts J., Jr. (1983) Effects of ring strain on gas-phase rate constants. I. Ozone reactions with cycloalkenes. *Int J. Chem. Kin.* **15**, 721-731.
- Atkinson R. and Lloyd A. C. (1984), Evaluation of kinetic and mechanistic data for modeling of photochemical smog. *J. Phys. Chem. Ref. Data* **13**, 315-444.
- Atkinson R. and Carter W. P. L. (1984) Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions. *Chem. Rev.* **84**, 437-470.
- Atkinson R., Plum C. N., Carter W. P. L., Winer W. P. and Pitts J., Jr. (1984) Rate constants for the gas phase reactions of NO₃ radicals with a series of organics in air at 298° ± 1° K. *J. Phys. Chem.* **88**, 1210-1215.
- Austin, T. (1988) Potential Emissions and Air Quality Effects of Alternative Fuels, Sierra Research Inc., Sacramento, CA.
- Avlani P. (1987) California Air Resources Board, Reference magnetic tape Nos. ARE029 and AR2085, personal communication to A. G. Russell.
- Axtell K. and Watson J. G. (1987) Receptor model technical series, volume III (revised): CMB user's manual (version 6.0), U. S. Environmental Protection Agency, Research Triangle Park, N. C., EPA-450/4-83-014R.
- Balentine H. C. (1984) Effects of Emissions from Methanol-Fueled Vehicles on Smog. Presented at U. S. Environmental Protection Agency Methanol Workshop, San Francisco, CA.
- Balentine H. C., Beskid C., Edwards L., Klausmeier R. and Langevin S. (1985) An analysis of chemistry mechanisms and photochemical dispersion models for use in simulating methanol photochemistry. U.S. Environmental Protection Agency, Report No. EPA-460/3-85-008.
- Bauges K. (1986) A review of NMOC, NO_x, and NMOC/NO_x ratios measured in 1984 and 1985. U.S. Environmental Protection Agency, Report No. EPA-450/4-86-015, Research Triangle Park, N. C.
- Baulch D. L., Cox R. A., Crutzen P. J., Hampson R. F., Kerr J. A., Troe J. and Watson R. T. (1982) Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement 1. *J. Phys. Chem. Ref. Data* **11**, 327-496.
- Bechtold R. and Pullman J. B. (1980) Driving cycle economy, emissions, and photochemical reactivity using alcohol fuels and gasoline. SAE Paper 800260.
- Blumenthal D. L. (1984) Sonoma Technology, personal communication.

- Bouvier B. (1986) The atmospheric formation of organic aerosols. M. E. Thesis, Carnegie Mellon University, Pittsburgh, PA.
- Bresnitz E. A. and Rest K. M. (1988) Epidemiologic studies of effects of oxidant exposure on human populations. In *Air Pollution, the Automobile, and Public Health*, Health Effects Institute, National Academy Press, Washington, D. C., pp. 389-413.
- California Air Resources Board (1986) Methodology to calculate emissions factors for on-road motor vehicles, Technical Support Division, California Air Resources Board, Sacramento, CA.
- California Air Resources Board (1988) Draft supplement 1 to methodology to calculate emissions factors for on-road motor vehicles, Technical Support Division, California Air Resources Board, Sacramento, CA.
- Carmichael G. R., Kitada T. and Peters L. K. (1986) A second generation model for regional-scale transport/chemistry/deposition. *Atmos. Environ.* 20, 173-188.
- Carter W. P. L. (1988a) Reactivity Issues Related to Methanol Use. From Proceedings of the APRAC Methanol Workshop, Orange, CA., April 19-21, 1988. CRC Report No. 564, Coordinating Research Council, Inc., Atlanta, Georgia.
- Carter W. P. L. (1988b) Development of a Photochemical Mechanism Compiler, Final Report to the California Air Resources Board, Sacramento, CA.
- Carter W. P. L., Atkinson R., Long W. D., Parker L. N. and Dodd M. C. (1986a) Effects of methanol fuel substitution on multi-day air pollution episodes. Final report on Contract No. A3-125-32, California Air Resources Board, Sacramento, CA.
- Carter W. P. L., Lurmann F. W., Atkinson R. and Lloyd A. C. (1986b) Development and testing of a surrogate species chemical reaction mechanism. U. S. Environmental Protection Agency Contract No. 68-02-4104, Statewide Air Pollution Research Center, Riverside, CA.
- Cass G. R. (1977) Methods for sulfate air quality management with application to Los Angeles. PhD Thesis, California Institute of Technology, Pasadena, CA.
- Cass G. R. (1979) On the relationship between sulfate air quality and visibility with examples in Los Angeles. *Atmos. Environ.* 13, 1069-1084.
- Cass G. R. (1981) Sulfate air quality control strategy design. *Atmos. Environ.* 15, 1227-1249.
- Cass G. R., Gharib S., Peterson M. and Tilden J. W. (1982) The origin of ammonia emissions to the atmosphere in an urban area. Open File Report 82-6, Environmental Quality Laboratory, California Institute of Technology, Pasadena, CA.
- Chang J. S., Brost R. A., Isaksen I. S. A., Madronich S., Middleton P., Stockwell W. R. and Walcek C. J. (1987) A three-dimensional Eulerian acid deposition model: physical concepts and formulation. National Center for Atmospheric Research, Boulder, CO. In press, *J. Geophysical Research*.
- Chang T. (1988) Impact of Methanol-Fueled Vehicles on Ozone Air Quality. From Proceedings of the APRAC Methanol Workshop, Orange, CA., April 19-21, 1988. CRC Report No. 564, Coordinating Research Council, Inc., Atlanta, Georgia.
- Consensus Workshop on Formaldehyde (1984) Report on the Consensus Workshop on Formaldehyde. *Environ. Health Perspect.* 58, 323-381.
- Denbigh, K. (1971) *The Principles of Chemical Equilibria*, Cambridge University Press, Cambridge, U.K.
- Drachand, K.D. (1988) Memorandum to John Holmes, California Air Resources Board, February 16, Sacramento CA.

- Dunker A. M. (1984) The decoupled direct method for calculating sensitivity coefficients. *J. Chemical Physics* **81**, 2385-2393.
- Dunwoody C. L. (1986) Rapid nitrate loss from PM₁₀ filters. *J. Air Pollut. Control Assoc.* **33**, 817.
- Falls A. H. and Seinfeld J. H. (1978) Continued development of a kinetic mechanism for photochemical smog. *Envir. Sci. Technol.* **12**, 1398-1406.
- Falls A. H., McRae G. J. and Seinfeld J. H. (1979) Sensitivity and uncertainty analysis of reaction mechanisms for photochemical air pollution. *Int. J. Chemical Kinetics* **11**, 1137-1162.
- Finlayson-Pitts B. J. and Pitts J. N. (1986) *Atmospheric Chemistry*. John Wiley and Sons, New York.
- Friedlander S. K. (1973) Chemical element balances and identification of air pollution sources. *Envir. Sci. Technol.* **7**, 235-240.
- Gery M. R. (1987) Systems Applications Inc., San Rafael, CA, personal communication to Jana Milford.
- Gold M. D. and Moulis C. E. (1988) Effects of Emission Standards on Methanol Vehicle-Related Ozone, Formaldehyde, and Methanol Exposure. For presentation at the 81st annual meeting of APCA, Dallas, TX, June 19-24, 1988.
- Goodin W. R., McRae G. J. and Seinfeld J. H. (1979) A comparison of interpolation methods for sparse data: application to wind and concentration fields *J. Appl. Met.* **18**, 761-771.
- Gray H. A. (1986) Control of atmospheric fine primary carbon particle concentrations. Ph.D. Thesis, California Institute of Technology, Pasadena, CA.
- Gray H. A., Cass G. R., Huntzicker J. J., Heyerdahl E. K. and Rau J. A. (1986) Characteristics of atmospheric organic and elemental carbon particles in Los Angeles. *Envir. Sci. Technol.* **20**, 580-589.
- Gray, D. and Tomlinson, G (1985) A baseline technology assessment of methanol as an automotive fuel, Presented at the NSF workshop on Automotive Use of Methanol Based Fuels, January 10-11, Washington D.C.
- Groblicki P. J., Wolff G. T. and Countess R. J. (1981) Visibility reducing species in the Denver "Brown Cloud", Part I. Relationships between extinction and chemical composition. *Atmos. Environ.* **15**, 2473-2484.
- Grosjean D. (1982) Formaldehyde and other carbonyls in Los Angeles ambient air. *Envir. Sci. Technol.* **16**, 254-262.
- Grosjean D. and Fung K. (1984) Hydrocarbons and carbonyls in Los Angeles air. *J. Air Pollut. Control Assoc.* **34**, 537-543.
- Grosjean D. (1984) Atmospheric reactions of o-cresol: gas and aerosol phase products. *Atmos. Environ.* **18**, 1641-1652.
- Grosjean D. (1985) Reactions of o-Cresol and nitrocresol with NO_x in sunlight and with ozone-nitrogen dioxide mixtures in the dark. *Envir. Sci. Technol.* **19**, 968-974.
- Harvey C. A., Carey P. M., Somers J. H. and Garbe R. J. (1984) Toxicologically acceptable levels of methanol and formaldehyde emissions from methanol-fueled vehicles. SAE Paper 841357.
- Hatakeyama S., Tanonaka T., Weng J., Bandow H., Takagi H. and Akimoto H. (1985) Ozone-cyclohexene reaction in air: quantitative analysis of particulate products and the reaction mechanism. *Envir. Sci. Technol.* **19**, 935-942.

- Hatakeyama S., Ohno M., Weng J., Bandow H., Takagi H. and Akimoto H. (1987) Mechanism for the formation of gaseous and particulate products from ozone-cyclohexene reactions in air. *Envir. Sci. Technol.* **21**, 52-57.
- Health Effects Institute (1987) Automotive methanol vapors and human health: an evaluation of existing scientific information and issues for future research. Report of the Institute's Health Research Committee. Cambridge, MA.
- Hidy G. M. (1975) Summary of the California aerosol characterization experiment. *J. Air Pollut. Control Ass.* **25**, 1106-1114.
- Jacob D. J., Shair F. H., Waldman J. M., Munger J. W. and Hoffman M. R. (1987) Transport and oxidation of SO₂ in a stagnant foggy valley. *Atmos. Environ.* **21**, 1305-1313.
- Jeffries H. E., Sexton K. G. and Salmi C. N. (1981) The effects of chemistry and meteorology on ozone control calculations using simple trajectory models and the EKMA procedure. U. S. Environmental Protection Agency EPA-450/4-81-034, Research Triangle Park, NC.
- Jeffries H. E., Sexton K. G. and Holleman M. S. (1985) Outdoor smog chamber experiments: reactivity of methanol exhaust. U. S. Environmental Protection Agency EPA-68-03-3162 (prepared under subcontract with Southwest Research Institute).
- Katoh, K., Imamura, Y. and Inoue, T. (1986), Development of a methanol lean burn system, SAE paper #860247
- Killus J. P. (1984) Presented at the XVth Informal Conference on Photochemistry, Stanford, CA, June 27-July 1, 1984.
- Larson S. M., Cass G. R., Hussey K. J. and Luce F. (1988) Verification of image processing based visibility models. *Envir. Sci. Technol.* **22**, 629-637.
- Lawson D. R., Winer A. M., Biermann H. W., Tuazon E. C., Mackay G. I., Schiff H. I., Kok G. L., Dasgupta P. K. and Fung K. (1988) Formaldehyde measurement methods evaluation and ambient concentrations during the carbonaceous species methods comparison study. *Aer. Sci. Technol.*, submitted.
- Leone J. A. and Seinfeld J. H. (1984) Analysis of the characteristics of complex chemical reaction mechanisms: application to photochemical smog chemistry. *Envir. Sci. Technol.* **18**, 280-287.
- Leone J. A. and Seinfeld J. H. (1985) Comparative analysis of chemical reaction mechanisms for photochemical smog. *Atmos. Environ.* **19**, 437-464.
- Lioy P. J., Vollmuth T. A. and Lippmann M. (1985) Persistence of peak flow decrement in children following ozone exposures exceeding the national ambient air quality standard. *J. Air Pollut. Control Ass.* **35**, 1068-1071.
- Lippmann M., Lioy P. J., Leikauf G., Green K. B., Baxter D., Morandi M. and Pasternack B. S. (1983) Effects of ozone on the pulmonary function of children. In *International Symposium on the Biomedical Effects of Ozone and Related Photochemical Oxidants* (Lee S. D., Mustafa M. G. and Mehlman M. A., eds.) Princeton Scientific Publishers, Inc., Princeton, N. J., pp. 423-446.
- Lonnemann W. A., Bellar T. A. and Altshuller A. D. (1968) Aromatic hydrocarbons in the atmosphere of the Los Angeles basin. *Envir. Sci. Technol.* **2**, 1017-1026.
- Lurmann F.W., Carter W.P.L. and Coyner L.A. (1987) A surrogate species chemical reaction mechanism for urban-scale air quality simulation models Vol I. U. S. Environmental Protection Agency EPA- 68-02-4104.

- Mackay, G.I., Karecki, D.R. and Schiff, H.I. (1988) The Southern California Air Quality Study tunable diode laser measurements of H₂O₂ and H₂CO at the Claremont and Long Beach "A" sites," Final report to the California Air Resources Board, Sacramento, CA.
- Mahoney L. (1988) Unlabeled magnetic tape containing year 2010 point, area, and mobile source emissions. Personal communication to A. G. Russell.
- Marnett L. J. (1988) Health effects of aldehydes and alcohols in mobile source emissions. In *Air Pollution, the Automobile, and Public Health*. (Watson A., Bates R. and Kennedy D. eds.), National Academy Press, Washington, D. C., pp. 579-603.
- McCroskey P. S. and McRae G. J. (1987) Documentation for the Direct Decoupled Sensitivity Analysis Method - DDM. Report, Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA.
- McRae G. J. (1982) Mathematical modeling of photochemical air pollution. PhD Thesis, California Institute of Technology, Pasadena, CA.
- McRae G. J., Goodin W. R. and Seinfeld J. H. (1982) Development of a second generation mathematical model for urban air pollution II. Evaluation of model performance. *Atmos. Environ.* 16, 679-696.
- McRae G. J. and Seinfeld J. H. (1983) Development of a second generation mathematical model for urban air pollution, II. Performance evaluation. *Atmos. Environ.* 17, 501-523.
- McRae G. J. (1978) A computer program for the numerical solution of chemical kinetics problems. EQL Report No. 206-40, California Institute of Technology, Pasadena, CA.
- Milford J. B. (1988) Photochemical air pollution control strategy development. Ph.D. Thesis, Carnegie Mellon University, Pittsburgh, PA.
- Murrell, J.D. and Piotrowski, G.K. (1987) Fuel economy and emissions of a Toyota T-LCS-M methanol prototype vehicle, SAE paper #871090.
- National Research Council (1981) Formaldehyde and Other Aldehydes. Committee on Aldehydes, Board on Toxicology and Environmental Health Hazards, Assembly of Life Sciences, National Research Council. National Academy Press, Washington, D. C.
- Nichols R. J. and Norbeck J. M. (1985) Assessment of Emissions from Methanol-Fueled Vehicles: Implications for Ozone Air Quality, presented at the 78th Annual Meeting of the Air Pollution Control Association, Paper No. 85-38.3, June 16-21, 1985, Detroit, MI.
- O'Toole R. P., Dutzi E., Gershman R., Heft R., Maynard D. and Kalema W. (1983) California Methanol Assessment, Volume II, Technical Report. Chapter 6: Air Quality Impact of Methanol Use in Vehicles, JPL Publication 83-18. Report for the California Energy Commission, California Institute of Technology, Pasadena, CA.
- Pefley R. K., Pullman B. and Whitten G. (1984) The Impact of Alcohol Fuels on Urban Air Pollution: Methanol Photochemistry Study. Final Report DOE/CE/50036-1, Department of Energy, Washington, D. C.
- Ranzierra A. (1983) Tape AR3288, 1982-SCAB Point and Area Source Emissions. Personal communication to A. G. Russell.
- Ranzierra A. (1984) Tape AR3292, 1982-SCAB Motor Vehicle Traffic Emissions. Personal communication to A. G. Russell.
- Roe O. (1982) Species differences in methanol poisoning. *CRC Crit. Rev. Toxicol.* 10, 275-286.

- Rogozen M.B. and Ziskind R.A. (1984) Formaldehyde: A survey of airborne concentrations and sources. SAI Publication No. 841624.
- Russell A. G., McRae G. J. and Cass G. R. (1983) Mathematical modeling of the formation and transport of ammonium nitrate aerosol. *Atmos. Environ.* **17**, 949-964.
- Russell A. G. and Cass G. R. (1984) Acquisition of regional air quality model validation data for aerosol nitrate, sulfate, ammonium ion and their precursors. *Atmos. Environ.* **18**, 1815-1827.
- Russell A. G., McRae G. J. and Cass G. R. (1984) Acid deposition of photochemical oxidation products - A study using a Lagrangian trajectory model. In *Air Pollution Modeling and Its Application III* (Edited by C. DeWispelaere), Plenum Publishing Corporation, New York, pp. 539-564.
- Russell A. G., McRae G. J. and Cass G. R. (1985) The dynamics of nitric acid production and the fate of nitrogen oxides. *Atmos. Environ.* **19**, 893-903.
- Russell A. G. (1985) Formation and control of atmospheric aerosol nitrate and nitric acid. Ph.D. Thesis, California Institute of Technology, Pasadena, CA. Available from University Microfilms, Ann Arbor, MI.
- Russell A. G. and Cass G. R. (1986) Verification of a mathematical model for aerosol nitrate and nitric acid formation, and its use for control measure evaluation. *Atmos. Environ.* **20**, 2011-2025.
- Russell A. G. and Harris J. N. (1988) A quantitative estimate of the air quality effects of methanol fuel use. SAE Paper 881687.
- Russell A. G., McCue K. F. and Cass G. R. (1988) Mathematical modeling of the formation of nitrogen containing air pollutants. 1. Evaluation of an Eulerian photochemical model. *Envir. Sci. Technol.* **22**, 263-271.
- Russell A. G. (1988) Mathematical modeling of the effect of emission sources on atmospheric pollutant concentrations. In *Air Pollution, the Automobile, and Public Health* (Watson A. Y., Bates R. R. and Kennedy D. eds.) Health Effects Institute, National Academy Press, Washington, D. C., pp. 161-205.
- SCAQMD and SCAG (1982) South Coast Air Quality Management District and Southern California Association of Governments, Final Air Quality Management Plan, 1982 Revision.
- SCAQMD and SCAG (1988) South Coast Air Quality Management District and Southern California Association of Governments, Draft 1988 Air Quality Management Plan, September, 1988.
- Schiller J. W. (1987) 20-City Study, Ford Motor Company, personal communication to A.G. Russell.
- Scheiler, L., Fischer, M., Dennler, D. and Nettell, R. (1985) Bank of America's methanol fuel program, "An insurance policy that is now a viable fuel, Presented at the NSF workshop on Automotive use of methanol fuel, January 10-11, Washington D.C.
- Seigneur C., Tesche T. W., Roth P. M. and Liu M-K. (1983) On the treatment of point source emissions in urban air quality modeling. *Atmos. Environ.* **17**, 1655-1676.
- Seinfeld J. H. (1975) *Air Pollution: Physical and Chemical Fundamentals*, McGraw Hill Book Co., New York.
- Seinfeld J. H. (1986) *Atmospheric Chemistry and Physics of Air Pollution*. John Wiley and Sons, New York.
- Snow, R. et al. (1989) Characterization of emissions from a methanol fueled motor vehicle, *J. of the Air and Waste management Assoc.*, **39**, 48-54.

- Solomon P. A., Fall T., Salmon L. and Cass G. R. (1988) Chemical characteristics of PM₁₀ aerosols collected in the Los Angeles area. *Envir. Sci. Technol.*, submitted.
- Stern J. E., Flagan R. C., Grosjean D. and Seinfeld J. H. (1987) Aerosol formation and growth in atmospheric aromatic hydrocarbon photo-oxidation. *Envir. Sci. Technol.* 21, 1224-1231.
- Tesche T. W., Seigneur C., Oliver W. R. and Haney J. L. (1984) Modeling ozone control strategies in Los Angeles. *J. Environ. Eng.* 110, 208-225.
- Tilden J. W., Costanza V., McRae G. J. and Seinfeld J. H. (1981) Modelling of chemical reaction systems. *Springer-Verlag Series in Chemical Physics* Vol.18, Springer-Verlag, New York.
- Trijonis J. (1979) Visibility in the Southwest - An exploration of the historical data base. *Atmos. Environ.* 13, 833-843.
- U. S. Congress Office of Technology Assessments (1988) Urban Ozone and The Clean Air Act: Problems and Proposals for Change. Staff Paper (personal communication J. B. Milford to A. G. Russell).
- Wagner K. K. and Ranzierrri A. J. (1984) Model performance evaluations for regional photochemical models in California. Paper No. 84-47.3, presented at the 77th Annual Meeting of the Air Pollution Control Association, San Francisco, CA, June 1984.
- White W. H. and Roberts P. T. (1977) On the nature and origins of visibility reducing species in the Los Angeles basin. *Atmos. Environ.* 11, 803-812.
- Whitten G. Z. and Hogo H. (1983) Impact of methanol on smog: a preliminary estimate. SAI Publication No. 83044.
- Whitten G. Z., Yonkow N. and Myers T.C. (1986) Photochemical modeling of methanol-use scenarios in Philadelphia. U. S. Environmental Protection Agency EPA-406/3-86-001.

