Final Report

Proximate Modeling of Weekday/Weekend Ozone Differences for Los Angeles

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TABLE OF CONTENTS

Page

TABLES

FIGURES

GLOSSARY OF ACRONYMS

ARB	(California) Air Resources Board
AQMP	Air Quality Management Plan
CAMx	Comprehensive Air quality Model, with extensions
CARB	California Air Resources Board
CB4	Carbon Bond mechanism, version 4
CRC	Coordinating Research Council
DOE	US Department of Energy
DTIM	Direct Travel Impact Model
EPA	US Environmental Protection Agency
EMFAC	California on-road mobile source emission factor model
HDV	Heavy-duty vehicle
LDV	Light-duty vehicle
MM5	PSU/NCAR Meteorological Model, version 5
MV	On-road motor vehicle
NCAR	National Center for Atmospheric Research
NO	Nitric oxide
NO_2	Nitrogen dioxide
NOx	Nitrogen oxides, nominally the sum of NO and NO_2
NREL	National Renewable Energy Laboratory
O_3	Ozone
ROG	Reactive organic gases
SAPRC99	Statewide Air Pollution Research Center mechanism, 1999 version
SCAQMD	South Coast Air Quality management District
SCAG	Southern California Association of Governments
SCOS97	Southern California Ozone Study in 1997
TOG	Total organic gases
UV	Ultra Violet Radiation
VOC	Volatile Organic Compounds

EXECUTIVE SUMMARY

Emissions of nitrogen oxides (NOx) and volatile organic compounds (VOCs) from both man-made and natural sources react in the presence of sunlight to form ground-level ozone. In the Los Angeles basin (LA basin), ozone levels now tend to reach higher peak levels on weekends than weekdays. This systematic difference between weekend and weekday ozone is referred to as the "weekend effect." Understanding the weekend effect may provide important scientific insight into the ozone formation process in the LA basin including the relationships between ozone and precursor emissions. The weekend effect also has implications for the development of emission reduction strategies to attain ambient ozone standards in the LA basin because high ozone levels now tend to occur on weekends and emission reduction strategies must be effective for both weekday and weekend conditions. Another important reason to study the weekend effect is to test the accuracy of air quality model responses to an observable emissions change. As long as there is relatively little carryover of ozone and emissions from one day to the next, the weekday/weekend effect provides a good test of whether an air quality model can predict the impact of emission changes.

Detailed studies of ambient ozone in the LA basin have found both increases and decreases in elevated ozone levels on weekends depending upon time and location. In the mid 1990s, daily maximum ozone levels were higher on weekends than weekdays throughout the LA basin. In contrast, in the late 1980s ozone concentrations were only slightly higher on weekends in the western LA basin and were slightly lower on weekends in the eastern LA basin. These observations raise questions about why the weekend effect has changed over time, and whether it will change again in the future. The changes in the Los Angeles ozone weekend effect also provide an opportunity to test potential explanations for the weekend effect against a range of atmospheric conditions.

Analyses of ozone precursor data suggest that VOC/NOx ratios have been higher on weekends throughout the 1980s and 1990s. This appears to imply that changes in the weekend ozone effect must be associated with changes in the sensitivity of ozone to precursors (i.e., VOCs and NOx) over this time period. However, a full understanding of the weekend effect is complicated by need to consider a variety of potential emissions changes combined with the relationships between emissions and ozone. Integrating information on emissions changes with atmospheric dispersion and atmospheric chemical relationships requires some form of modeling, either informal "conceptual modeling" or formal "numerical modeling". Conceptual models have advantages of accessibility and flexibility, but suffer disadvantages of being non-quantitative and potentially speculative. Formal numerical modeling, for example photochemical grid modeling, provides an opportunity to test hypotheses quantitatively. This study uses numerical models to investigate the weekend ozone effect for Los Angeles.

OBJECTIVES

The objective of this study is to test weekend effect hypotheses in a photochemical grid model for Los Angeles. In some cases, full descriptions of the emissions changes hypothesized to cause the weekend effect are not yet available, and so the term "proximate modeling" is used to describe experiments that are based on the best available approximation to the emission changes.

The goal to is to rigorously and quantitatively test hypotheses in a full scale 3-D air quality model for Los Angeles of the type that is used to develop ozone attainment strategies.

METHODS

Potential causes of the Los Angeles weekend effect were discussed extensively at Weekend Effects Research Group meetings held at the California Air Resources Board (ARB) and are summarized in presentations available from the Weekend Effects Research Group web page[1]. The ARB subsequently drafted a report[2] that listed six hypotheses:

(1) *NOx-reduction*. Lower NOx emissions on weekends cause the weekend effect. Under this hypothesis, higher weekend ozone results from less NOx titration/inhibition of ozone on weekends. Changes to on-road mobile source emissions are expected to be a major factor in reducing weekend NOx emission, especially reductions in heavy-duty diesel truck traffic.
(2) *NOx-timing*. Changes in driving patterns, e.g., the lack of morning/evening rush-hours on weekends, change the timing of NOx emissions and ozone formation. This hypothesis proposes that the same total amount of NOx emissions can produce different ozone levels if the timing of the emissions is altered.
(3) *Carryover near ground-level*. Accumulation of overnight emissions in the atmosphere near ground level changes the amount of emissions available for ozone formation the next day, and is different between weekdays and weekends.
(4) *Carryover aloft*. Carryover of ozone and/or ozone precursors aloft influences next day ozone, and is different between weekends and weekdays.
(5) *Increased weekend emissions*. Higher weekend ozone results from higher weekend emissions.
(6) *Soot and sunlight*. Lower weekend aerosol levels, especially soot, increase the amount of photolysis caused by solar radiation and increase ozone formation on weekends.

Proximate modeling experiments were designed to investigate five of these six hypotheses. The "increased weekend emissions" hypothesis was not investigated because of uncertainty in what categories of emissions to adjust, and because the ARB draft report considered this hypothesis not credible.

The main series of proximate modeling experiments were performed for an August 3-7, 1997 ozone episode that occurred during the 1997 Southern California Ozone Study (SCOS97). The emission inventories were provided by the ARB and were based on the EMFAC2000 mobile source emission model. The meteorology was modeled using the PSU/NCAR Mesoscale Model, version 5 (MM5) with assimilation of observational data from the SCOS97 study. Ozone modeling was performed using the Comprehensive Air Quality Model with extensions (CAMx). Most of the ozone modeling used the Carbon Bond 4 (CB4) chemical mechanism, but the SAPRC99 mechanism was also used to investigate sensitivity to changes in chemical mechanisms. The MM5/CAMx modeling system with the CB4 chemical mechanism performed very well in simulating the ozone levels observed during the August 3-7, 1997 SCOS episode.

[1] Weekend Effects Research Group web page, http://www.arb.ca.gov/aqd/weekendeffect/weekendeffect.htm.
[2] ARB draft staff report, http://www.arb.ca.gov/aqd/weekendeffect/web_SR.html .

Weekend effect hypotheses were evaluated from the differences between model scenarios where every day was treated as a weekday and scenarios where model inputs were changed according to the weekend hypothesis being tested. Modeled concentration differences were compared to corresponding analyses of ambient data. Specifically, the evaluation considered hourly time-series of ozone and precursors at a fixed location and the spatial distribution of ozone differences across the LA basin. This methodology was successful in clearly distinguishing hypotheses that are consistent or inconsistent with the observed weekend effect.

Weekend effect hypotheses were also evaluated with emission levels adjusted to reflect 1987 and projected 2010 conditions. Emission inventories for 1987 were provided by the ARB and were based on EMFAC2000. The ARB's 2010 emission inventories were not available for this study so an alternative source of data was used. The most recent (1999) Los Angeles Air Quality Management Plan (AQMP) includes emission inventories for 2010 that are the basis of the current State Implementation Plan. The 1999 AQMP emission inventory was based on the EMFAC7G mobile source emissions model, so for this study the mobile source emissions were adjusted by applying ratios of EMFAC2000 to EMFAC7G emission factors. The 2010 emission inventories contain greater uncertainty than the historical (1997 and 1987) emission inventories because they rely upon projections for growth in emissions activity and assumptions for the effectiveness of emission reduction strategies.

CONCLUSIONS

The results of the proximate modeling experiments are consistent with the following major conclusions:

- Changes to the mass of on-road motor vehicle emissions on weekend days (i.e., the NOx-reduction hypothesis) are the main cause of the weekend effect observed in Los Angeles.

- Changes to the spatial distribution of motor vehicle emissions on the weekend could also contribute to the weekend ozone effect. Weekend travel demand models are needed to investigate this further.

- Weekend ozone is relatively insensitive to changes in the timing of motor vehicle emissions (i.e., the NOx-timing hypothesis).

- There is little carryover of effects from one weekend day to the next. The weekend ozone effect is primarily a "same-day" phenomenon for Los Angeles.

- The modeled weekend effects were robust against a large change in the chemical mechanism (from CB4 to SAPRC99) indicating that uncertainties in chemical mechanisms do not compromise the study conclusions about the causes of the weekend effect.

- Changes in photolysis rates due to changes in the amount of aerosol (i.e., the soot and sunlight hypothesis) are not the cause of the Los Angeles weekend effect.

- Modeling the weekend effect for 1987 suggests that the VOC/NOx ratio may be too low in the latest ARB emission inventories for 1987.

- The SCAQMD Air Quality Management Plan 2010 on-road motor vehicle emissions for ROG and NOx are 86% and 69% lower, respectively, than the ARB 1997 emissions. The AQMP 2010 control plan includes advanced technology controls that do not yet exist. If the projected emission reductions are realized, the weekend effect for ozone will decrease in magnitude and extent by 2010.

- Because the projected 2010 emissions are uncertain, the future weekend effect scenarios should be repeated with alternate assumptions.

- Modeled ozone responses to weekend effect scenarios in 2010 showed ozone-precursor relationships that are not explained by changes to the emission inventory alone, which should be investigated further.

- The photochemical modeling system (CAMx with meteorology from MM5 and emission inventories from the ARB based on EMFAC2000) performed very well for the 1997 August 3-7 episode when the Carbon Bond 4 chemistry was used.

- The ozone model response to weekend emission changes in 1997 agreed very well with the observed weekend effects.

- The fact that a photochemical modeling system with good model performance also performs well in describing an observed emissions perturbation (the weekend effect) supports the use of photochemical models for ozone air quality planning.

1. INTRODUCTION

Emissions of nitrogen oxides (NOx) and volatile organic compounds (VOCs) from both man-made and natural sources react in the presence of sunlight to form ground-level ozone. Since human activity patterns vary between weekdays and weekends, NOx and VOC emissions and therefore ozone concentrations may be expected to vary over the course of the week. This provides an opportunity to study the effect of emission changes on ozone levels in the real atmosphere, and an opportunity to evaluate the ability of models to reproduce an observable emissions-ozone relationship. If the weekday/weekend ozone differences are large, they may play a role compliance with ozone air quality standards, in which case they should be considered in the design of ozone control strategies.

Differences in the magnitude and spatial patterns of elevated ozone concentrations in metropolitan areas between weekdays and weekend days have been studied since at least the mid 1970s (Cleveland et. al., 1974; Lebron, 1975; Levitt and Chock, 1976; Elkus and Wilson, 1976; Graedel et al., 1977; Zeldin and Mirabella, 1989). Comparisons of ozone concentrations between weekdays and weekend days described in these studies reveal mixed results depending on location and the particular ozone summary statistic examined. Conclusions regarding the implications of these results on the likely efficacy of future control measures were equally mixed, as well as being hampered by somewhat outdated information on the photochemistry of urban atmospheres in some of the older studies. Interest and research into the Los Angeles weekend effect was renewed in late 1990s with studies such as Blier and Winer (1996) and Stoeckenius et al., (1998). The California Air Resources Board (ARB) and stakeholders, such as DOE and CRC, started a weekend effects research group which has provided new information on weekday/weekend emissions and air quality differences for Los Angeles (Fujita et al., 2002 and Chinkin et al., 2002). The ARB also drafted a report presenting the ARB's interpretation of the Los Angeles weekend effect (ARB, 2001c).

WEEKEND OZONE DIFFERENCES IN LOS ANGELES

Studies of the Los Angeles ambient ozone data have found both increases and decreases in elevated ozone levels on weekends depending upon time and location. Stoeckenius et al. (1998) compared seasonal (May-October) mean daily maximum ozone levels for Wednesday and Sunday. Comparisons are shown here for six monitoring site locations that form a transect across the Los Angeles basin from west to east (Figure 1-1 for the late 1980s (1986-89 average) and the mid 1990s (1994-96 average). In the mid 1990s, daily maximum ozone concentrations on Sundays were higher compared to Wednesdays throughout the basin (Figure 1-2) with statistically significant differences at several locations. In contrast, absolute weekday-weekend differences were generally smaller in the late 1980s with slightly higher weekend values in the coastal, metropolitan, and San Gabriel Valley subregions (West Los Angeles to Azusa) and slightly lower weekend values farther inland (Upland, Riverside and Crestline). Ozone precursor data were also analyzed by Stoeckenius et al., (1998) and the shift in weekend ozone differences between the late 1980s and mid 1990s was attributed to a shift in the chemistry of ozone formation toward a more VOC sensitive condition in the mid 1990s. Other studies have also explained weekend ozone effects in terms of ozone sensitivity to changes in the emissions of ozone precursors, especially NOx.

ROLE OF PRECURSOR EMISSIONS IN OZONE FORMATION

Changing patterns in ozone distributions derived from analyses of ambient data such as those shown in Figures 1-2 and 1-3 can be attributed to changes in the magnitude and spatial distribution of ozone precursor emissions. Central to any emissions-based explanation of the weekend effect is the chemical interaction between VOC and NOx emissions in the meteorological environment(s) of the Los Angeles (LA) basin. Given the complexity of these relationships, one must be cautious of simple chemical explanations for the changing ozone distributions and avoid over-interpretation. However, it is worthwhile to ask whether the observed changes in ozone and precursors make sense within the framework of our current understanding of ozone formation chemistry.

Current understanding of ozone formation is embodied in condensed chemical mechanisms such as CB4 and SAPRC99. While there are uncertainties in quantitative aspects of these relationships (resulting from limitations in knowledge/representations of the chemistry), key qualitative features are clear:

- The existence of VOC and NOx limited regimes
- Titration of ozone by fresh NO emissions
- A NOx inhibition effect in strongly VOC limited regimes
- Changes in the timing of ozone formation resulting from NOx inhibition effects

These key features are captured in the familiar EKMA diagrams calculated using condensed chemical mechanisms.[1] The chemical basis for these features, including the NOx inhibition effect, was described in the 1991 National Research Council report, "Rethinking the Ozone Problem in Urban and Regional Air Pollution." Gunst and Kelly (1993) confirmed that air in the Los Angeles basin shows these same features when the VOC/NOx ratio is perturbed in smog chamber experiments with ambient air samples from the basin. It is important to establish this framework of understanding since the interpretation of the ambient signatures depends upon the presumed chemical relationships.

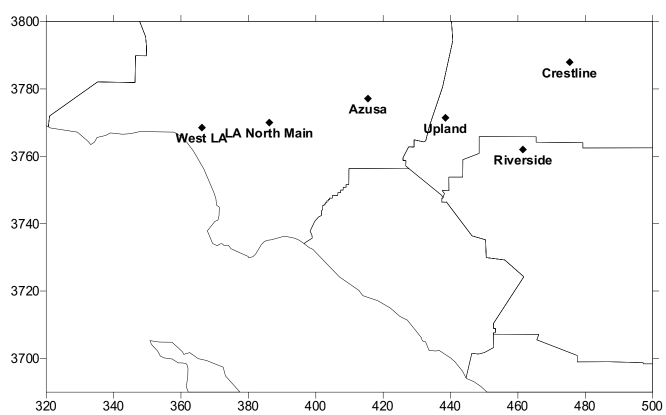


Figure 1-1. Locations of six monitoring sites that form a transect across the Los Angeles basin.

[1] This discussion is not to suggest that an EKMA diagram is adequate to explain ozone formation in the LA basin.

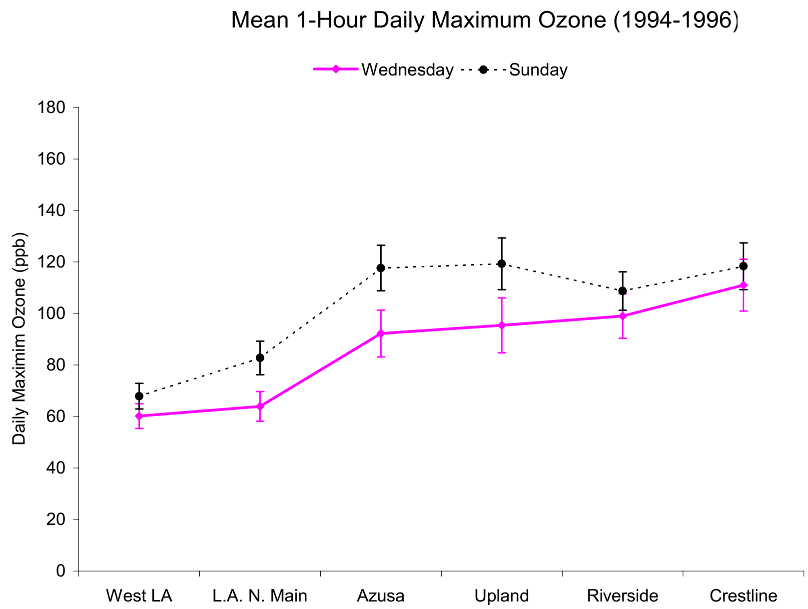


Figure 1-2. Seasonal (May-October) mean daily maximum 1-hour ozone concentrations on Wednesdays and Sundays at monitoring sites in the Los Angeles basin in 1994-1996.

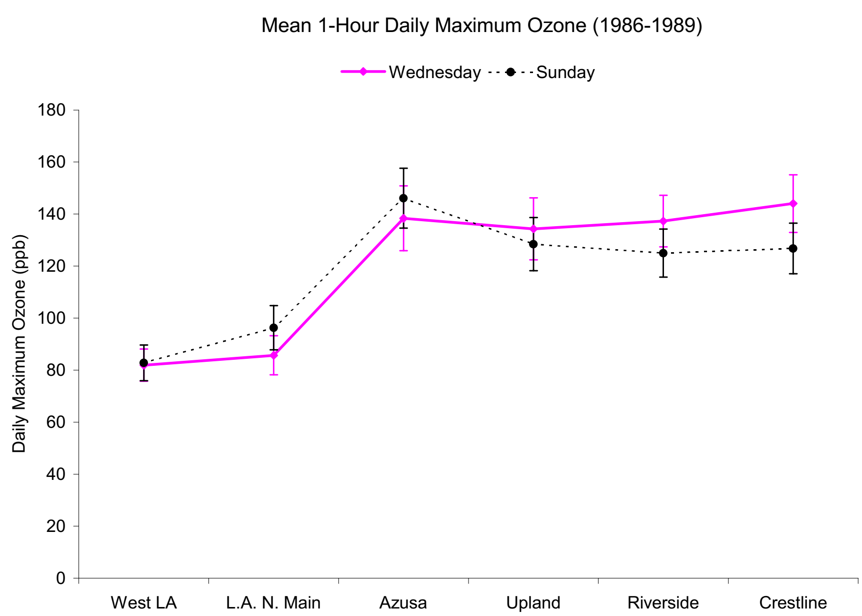


Figure 1-3. Seasonal (May-October) mean daily maximum 1-hour ozone concentrations on Wednesdays and Sundays at monitoring sites in the Los Angeles basin in 1986-1989.

PROXIMATE MODELING

Hypotheses proposed to explain the weekend effect involve relationships between ozone and precursor emissions, which are understood in terms of chemical mechanisms of ozone formation and ozone models. Thus, modeling is involved in virtually all evaluations of weekend effect hypotheses, either explicitly or implicitly. Conceptual modeling approaches that synthesize information from several sources into a qualitative explanation of the weekend effect have advanced our understanding of the weekend effect. Conceptual models have advantages of accessibility and flexibility, but suffer disadvantages of being non-quantitative and potentially speculative. Formal numerical modeling, for example photochemical grid modeling, provides an opportunity to test hypotheses quantitatively.

The objective of this study is to test weekend effect hypotheses in a photochemical grid model for Los Angeles. In some cases, full descriptions of the emissions changes hypothesized to cause the weekend effect are not yet available, and so the term "proximate modeling" is used to describe experiments that are based on the best available approximation to the emission changes. The goal to is to rigorously and quantitatively test hypotheses in a full scale 3-D air quality model for Los Angeles of the type that is used to develop ozone attainment strategies.

THE ARB HYPOTHESES

Potential causes of the Los Angeles weekend effect were discussed extensively at the ARB Weekend Effects Research Group meetings and in presentations available from the Weekend Effects Research Group web page. (http://www.arb.ca.gov/aqd/weekendeffect/weekendeffect .htm). The ARB subsequently drafted a report (ARB, 2001c) that proposed six hypotheses: (1) NOx-reduction; (2) NOx-timing; (3) Carryover near ground-level; (4) Carryover aloft; (5) Increased weekend emissions and (6) Soot and sunlight. Proximate modeling experiments were performed to investigate five of these six hypotheses. The "increased weekend emissions" hypothesis was not investigated because of uncertainty in what categories of emissions to adjust, and because the ARB draft report considered this hypothesis not credible.

2. METHODS

This section of the report describes the methods and modeling databases used to investigate weekend ozone effects in the Los Angeles (LA) basin. This includes discussions of the emission inventories, analyses of weigh-in-motion (WIM) traffic count data to estimate weekday/weekend traffic differences, CAMx photochemical modeling databases and CAMx model performance evaluation.

EMISSION INVENTORIES

Emission inventories were prepared for the August 3-7, 1997 SCOS episode period to reflect 1997, 1987 and 2010 emission levels. The approach was to obtain the latest available emissions information for these years from the California Air Resources Board (ARB) or the South Coast Air Quality Management District (SCAQMD). The ARB provided emission inventories for 1997 and 1987 that will be used in the next Air Quality Management Plan (AQMP) for Los Angeles. The ARB did not provide 2010 emission inventories, so the emissions developed by the SCAQMD for the 1999 AQMP were used to model 2010. For all three years, the emission inventories provided by the regulatory agencies were adapted to a standardized "weekday base case" and then weekend adjustments were made to carry out a series of proximate modeling experiments.

1997 Emissions

The 1997 emission inventory was provided by the ARB in July, 2001. Emissions were in the gridded MEDS format (ARB 2001) and split into separate files for different components of the inventory. The ARB's Gridded Emissions Model (GEM) was used to chemically speciate and temporally allocate emissions. The ARB provided chemical speciation for both the Carbon Bond 4 (Gery et al., 1989) and SAPRC99 "fixed parameter" mechanisms (Carter, 2000). The ARB inventory covered the SCOS modeling domain area (Figure 2-1), but since modeling for this study was performed only for the smaller AQMP domain (Figure 2-1), emissions outside of the AQMP area were discarded in the emissions processing. Emission totals by major category are summarized in Table 2-1 and selected emissions density plots are shown in Figure 2-2.

Table 2-1. ARB model ready emission totals (ton/day) for the AQMP domain area for August 3-7, 1997.

	Sunday 3-Aug	Monday 4-Aug	Tuesday 5-Aug	Wednesday 6-Aug	Thursday 7-Aug
NOx					
MV – SCAG area	742.7	1025.1	1110.6	1070.8	1048.7
MV – non-SCAG	40.8	40.8	41.0	40.5	39.9
Other surface	400.8	470.5	471.1	471.1	455.5
Point source	133.5	133.8	163.7	355.1	235.2
Biogenic	0.0	0.0	0.0	0.0	0.0
Total	**1317.8**	**1670.1**	**1786.4**	**1937.5**	**1779.3**
CB4-ROG					
MV – SCAG area	693.2	765.9	839.9	793.8	743.7
MV – non-SCAG	24.9	24.9	26.1	25.3	25.1
Other surface	894.5	753.4	753.1	753.2	750.0
Point source	72.9	41.2	460.3	2143.7	978.7
Biogenic	361.3	381.8	494.2	419.8	313.7
Total	**2046.8**	**1967.2**	**2573.6**	**4135.6**	**2811.2**
CO					
MV – SCAG area	6493.0	7758.5	8364.7	8185.6	7732.5
MV – non-SCAG	297.2	297.2	308.3	302.2	292.3
Other surface	2598.8	1157.4	1157.4	1157.4	1148.2
Point source	212.0	79.0	1869.1	9062.5	4102.5
Biogenic	0.0	0.0	0.0	0.0	0.0
Total	**9601.0**	**9292.1**	**11699.5**	**18707.7**	**13275.5**

1. MV is on-road mobile.
2. SCAG is the Southern California Association of Governments.
3. By convention, CB4-ROG is the sum of CB4 species assuming molecular weights of 16 per Carbon to account for average carbon/hydrogen/oxygen ratios in ROG.
4. NOx includes HONO emissions.
5. Wildfire emissions are included in the point sources.

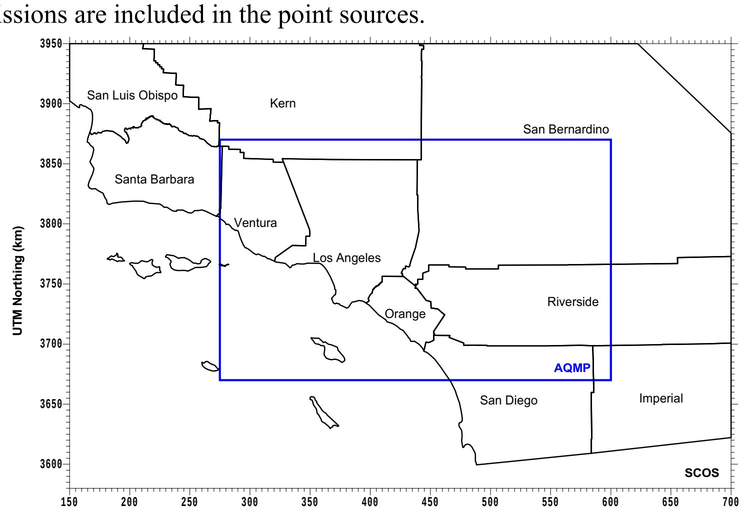


Figure 2-1. Relationship between historical AQMP modeling domain and expanded SCOS modeling domain for Southern California.

The ARB on-road motor vehicle emissions were based on EMFAC2000 and transportation model activity data for a 1997 weekday. The gridded emissions were prepared using version 4 of the DTIM model; however, because of inconsistencies between emission totals from EMFAC2000/DTIM4 and the EMFAC2000 internal activity data (corresponding to the old ARB BURDEN methodology), the ARB developed a methodology where emission totals from the DTIM calculation were re-scaled to match the "BURDEN" methodology. The ARB provided separate emissions files for light-duty and heavy-duty vehicles for each county in the SCAG area (Los Angeles, Orange, Riverside, San Bernardino and Ventura). For counties outside the SCAG area, light-duty and heavy-duty motor vehicle emissions were combined in a single emissions file. Within each motor vehicle emissions file, the emissions were resolved by pollutant type (ROG, NOx, CO) and emissions mode (gasoline exhaust, diesel exhaust, several gasoline evaporative emissions modes). The design of proximate modeling experiments was influenced by the available emissions information. For example, weekday/weekend MV emission adjustments were applied just to the SCAG counties because the split between light-duty and heavy-duty vehicle emissions was available only within this area.

The other anthropogenic emissions from the ARB's emissions databases included some day-to-day variations. In particular, the shipping and aircraft emissions are day specific. Wildfire emissions are included as point sources and make significant contributions to emission totals on August 5-7, 1997 because of a wildfire in the inland hills of Ventura county. Wildfire emissions were not included when modeling 1987 or 2010.

Biogenic emissions for August 3-7, 1997 were estimated by ARB using the BEIGIS model (ARB, 2001b). The emissions were provided in MEDS format and contained emissions for isoprene only; i.e., there were no VOC's beside isoprene and no NOx emissions. The model ready biogenic emissions totals are shown in Table 2-1. The biogenic emissions are day specific, with higher isoprene emissions on hotter days. The 1997 biogenic emissions were also used in modeling of 1987 and 2010.

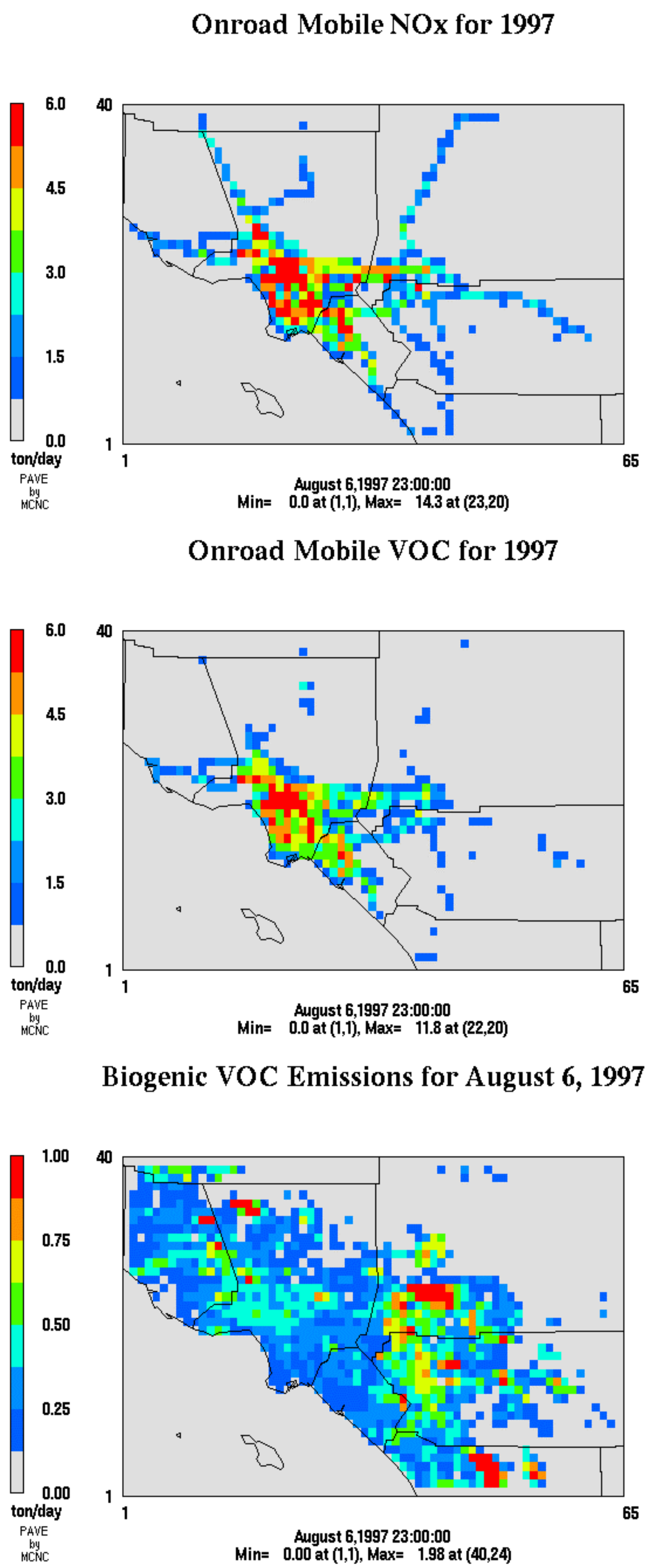


Figure 2-2. Emission density plots for August 6, 1997 showing daily total on-road mobile NOx (top) and ROG (middle) and biogenic ROG emissions (bottom).

1997 Weekday Base Case

The base case emissions provided by the ARB were used for the model performance evaluation because they are the best estimate of the actual emissions for Sunday-Thursday August 3-7, 1997. However, for the proximate modeling experiments, it was more convenient to start from a base case where every day was modeled as a weekday. The changes made to the emission inventory to create a "weekday base case" were as follows:

1. The other anthropogenic emissions for August 3 (which was a Sunday) were replaced by the anthropogenic emissions for August 4.

2. In the SCAG area, on-road mobile emissions for August 6 (which was a Wednesday) were used for every day to eliminate day-to-day emissions differences from the base case.

Otherwise, the original ARB emissions for each day were used. In particular, the day-specific biogenic emissions were used as they depend strongly upon the temperature for each day.

Day of Week Assignment for Proximate Modeling Experiments

The proximate modeling experiments required changes to emission inventories to represent specific days of the week. The August 3-7, 1997 period was actually a Sunday-Thursday, which is not suited to investigating weekend effects; therefore, we assumed that the episode corresponded to a Thursday- Monday period. This assumption is possible because only the emissions depend upon the day of week. In all of the proximate modeling experiments, August 5 was considered a Saturday and August 6 was considered a Sunday. This design aligns the main days of interest (the weekend) with the heart of the modeling period when ozone levels are highest. In addition, the carryover of weekend effects to Monday can be seen on August 7 and the influence of Friday emission changes can be investigated by changing emissions for August 4.

1987 Emissions

The 1987 anthropogenic emissions were based on SCAQS emission inventories for August 28, 1987 developed by the ARB. The emissions were provided by the ARB in MEDS format in December 2001. The on-road mobile emissions were based on the ARB's EMFAC2000/DTIM4 methodology where emission totals from the DTIM calculation were re-scaled to match the "BURDEN" methodology. This is a similar methodology to the 1997 on-road mobile emissions. Unlike the 1997 emissions, there was no separation between light-duty and heavy-duty motor vehicle emissions in the 1987 inventory. Emission totals by major category are shown in Table 2-2 and selected emissions density plots are shown in Figure 2-3.

Table 2-2. ARB model ready emission totals (ton/day) for the AQMP domain area for Friday, August 28, 1987.

	August 28
NOx[1]	
On-road mobile	1250.0
Other surface	558.8
Point source	217.6
CB4-ROG[2]	
O-road mobile	1512.0
Other surface	1661.1
Point source	31.3
CO	
On-road mobile	13518.8
Other surface	1327.2
Point source	54.5

1. NOx includes HONO emissions.
2. CB4-ROG is the sum of CB4 species assuming molecular weights of 16 per Carbon.

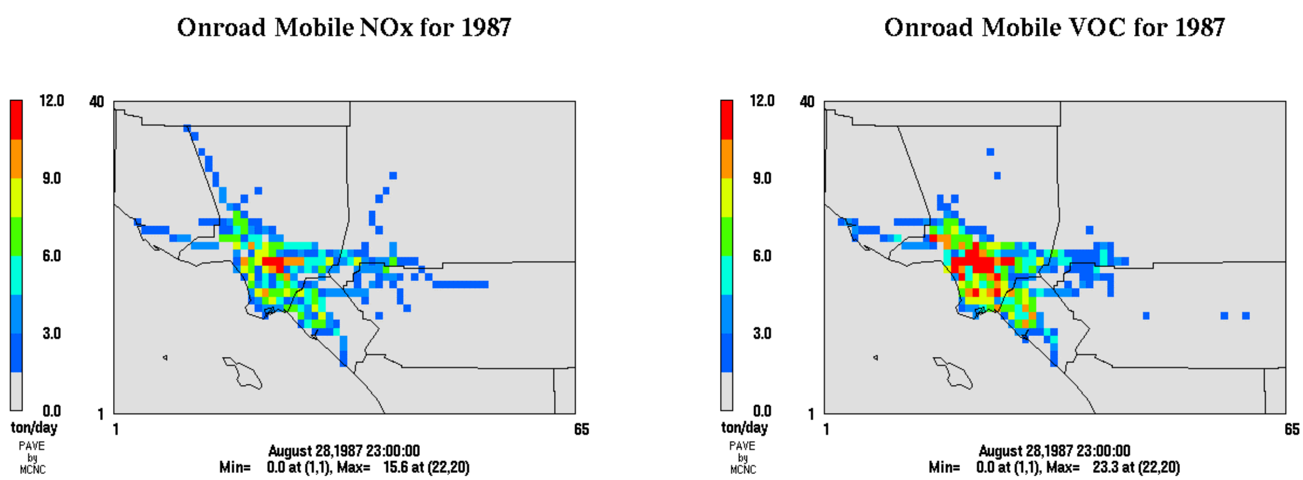


Figure 2-3. Emission density plots for Friday, August 28, 1987 showing daily total on-road mobile NOx (left) and ROG emissions (right).

1987 Weekday Base Case

A 1987 weekday base case inventory for the August 3-7 episode period was prepared by combining the Friday, August 28 anthropogenic emissions shown in Table 2-2 with the day-specific biogenic emissions shown in Table 2-1 for each episode day.

2010 Emissions

The 2010 anthropogenic emissions were based on SCAQS emission inventories for August 28, 1987 adjusted to projected 2010 levels by the SCAQMD for the 1999 AQMP. These emissions include the effects of projected activity growth and emissions control measures. Section 182(e)(5) of the 1990 Clean Air Act amendments (CAAA) allows an extreme ozone nonattainment area (i.e., Los Angeles) to specify emission reductions based on unknown control measures in a SIP control plan. These so-called "advanced technology" control measures were included in the 2010 emission inventories used for this study because they represent the current regulatory plan for Los Angeles in 2010. The 2010 emission inventories from the 1999 AQMP are the same as from the 1997 AQMP. The on-road mobile emissions were based on EMFAC7G. The EMFAC7G emissions were adjusted to reflect EMFAC2000 emission levels by applying ratios of EMFAC2000 to EMFAC7G emission factors. Emission totals by major category are shown in Table 2-3 and selected emission density plots are shown in Figure 2-4.

Table 2-3. SCAQMD model ready emission totals (ton/day) for the AQMP domain area for August 28, 2010.

	August 28
NOx	
On-road mobile	325.8
Other surface	242.3
Point source	72.3
CB4-ROG	
On-road mobile	107.9
Other surface	310.3
Point source	90.5
CO	
On-road mobile	1626.6
Other surface	651.2
Point source	193.8

1. CB4-ROG is the sum of CB4 species assuming molecular weights of 16 per Carbon.

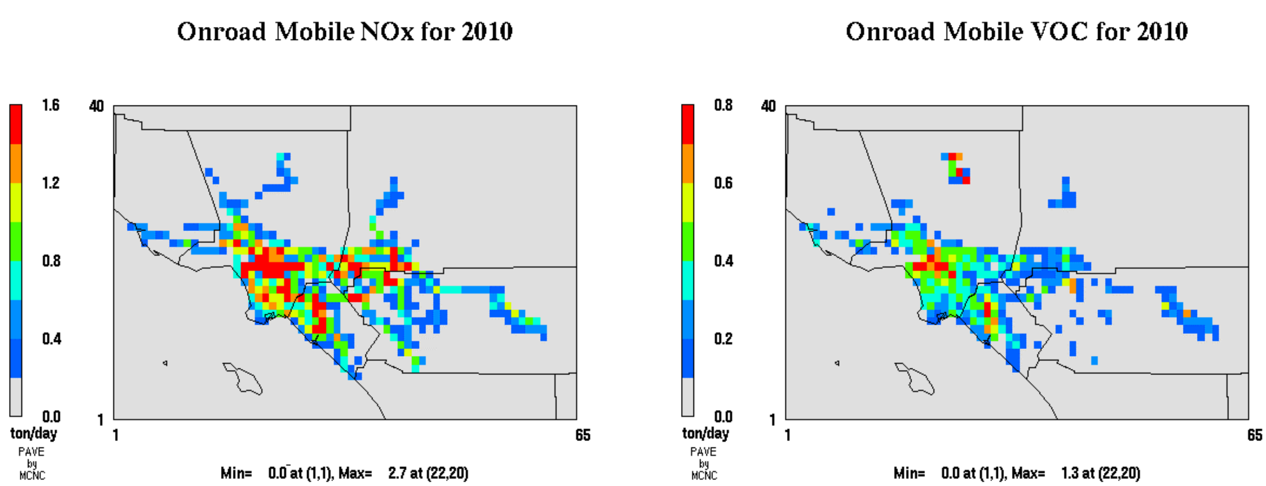


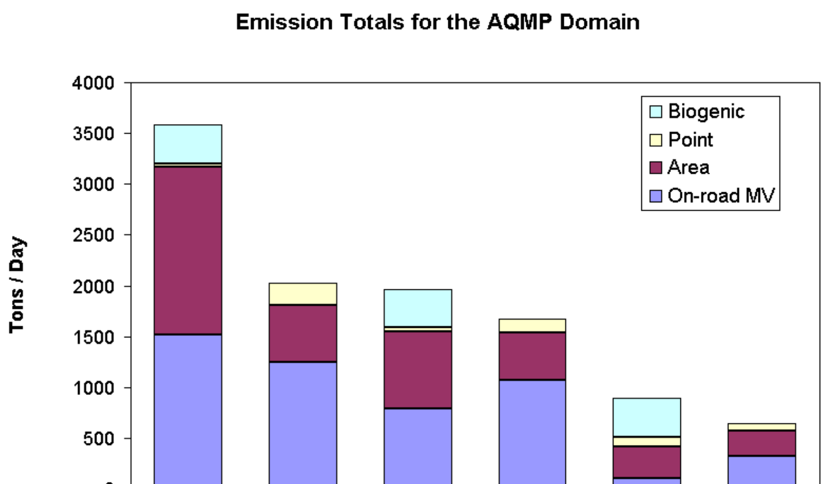
Figure 2-4. Emission density plots for August 28, 2010 showing daily total on-road mobile NOx (left) and ROG emissions (right).

2010 Weekday Base Case

A 2010 weekday base case inventory for the August 3-7 episode period was prepared by combining the August 28 anthropogenic emissions shown in Table 2-3 with the day-specific biogenic emissions shown in Table 2-1.

Comparison of 1997, 1987 and 2010 Emissions

The AQMP domain emission totals for ROG and NOx in 1997, 1987 and projected 2010 are compared in Figure 2-5. This figure is based on the August 4 episode day because this day is treated as a weekday in all years and because there were no wildfire emissions on this day in 1997. This figure is intended to show the trend in emissions across years. Area emissions include all surface anthropogenic emissions except on-road mobile (e.g., off-road mobile, solvents, low-level points). A detailed evaluation of the basis for these three different emission inventories is outside the scope of this study.



	1987 ROG	1987 NOx	1997 ROG	1997 NOx	2010 ROG	2010 NOx
Biogenic	381.8	0.0	381.8	0.0	381.8	0.0
Point	31.3	217.6	41.2	133.8	90.5	72.3
Area	1661.1	558.8	753.4	470.5	310.3	242.3
On-road MV	1512.0	1250.0	790.8	1065.9	107.9	325.8

Figure 2-5. Comparison of weekday emission totals by major source category for the 1987, 1997 and 2010 CAMx-ready emission inventories.

WEEKEND/WEEKDAY DIFFERENCES FOR ON-ROAD MOBILE SOURCES

The ARB SCOS97 August 6 on-road inventory was the foundation for the 1997 on-road MV inventory development for this study. This episodic inventory, which originally occurred on a Wednesday, was used to represent the typical weekday inventory. The typical weekday was assumed to cover Monday through Thursday. Adjustments were then applied to this inventory to represent other days of the week (Friday, Saturday and Sunday). Three types of adjustments were applied to account for changes in (1) daily total emissions, (2) hourly distribution of emissions, and (3) spatial distribution of emissions. Independent adjustments were developed so that effects could be examined separately and together in modeling experiments.

Recently collected, local traffic count data were used as the basis for the day-of-week adjustments. The general, underlying assumption is that vehicle traffic counts are a reasonable surrogate for temporally allocating vehicle emissions.[1] This hypothesis was evaluated by comparing the hourly traffic count profile with the hourly emissions profile in the August 6 inventory, and reasonable agreement was found.

This documentation of the on-road inventory development is broken down into the following topics:

Traffic Count Data
Mass and Temporal Adjustments
Adjustments for 1987 and 2010
Weekend Spatial Shift

Traffic Count Data

The traffic count data used for this study were collected by Sonoma Technology, Inc. (STI) in a project sponsored by NREL and DOE's Office of Heavy Vehicle Technologies. The data contained in the May 21, 2001 presentation, "Weekday versus Weekend Emissions Activity Patterns in the South Coast Air Basin" to the California Air Resources board were obtained from STI. These data consist of traffic counts collected over a two month sampling period (September and October 2000) at various locations in the South Coast Air Basin.

In processing these data, considerations were made in regard to distinguishing vehicle class, day-of-week, location and roadway type. Each of these is discussed below.

For vehicle classes, separate traffic counts for light and heavy-duty vehicles were collected. In processing the traffic count data for this study, these two vehicle classes were evaluated separately in order to identify the unique temporal activity characteristics of light and heavy-duty vehicles.

For day-of-week variation, traffic count data were provided as an average over the sampling period for each day of the week. For light-duty vehicles, the data for Monday through Thursday were indistinguishable and were averaged to represent a typical weekday. For heavy-duty, the data for Monday through Friday were indistinguishable and were averaged to estimate a typical weekday.

In reviewing the roadway types sampled, only a single surface street was included in the data along with several freeway locations. For light-duty vehicles, the temporal profiles for the surface street site were quite similar to those of the freeways. For heavy-duty vehicles, the temporal profiles for the surface street site were quite different than those of the freeways. It was decided to use the freeway count data for this study because of the greater number of sampling

[1] Start, running and soak emissions were assumed to be directly related to vehicle count data. Diurnal and resting loss emissions, whose occurrence is related to vehicle off time, were treated by a separate set of assumptions.

locations and because the freeway-based temporal profiles were considered a better surrogate. For light-duty, more activity occurs on surface streets than on freeways (about 1/3 on freeways, nationally); however, the temporal profiles were similar, so the distinction by roadway type was not considered significant. For heavy-duty, the temporal profiles were quite different, which was expected, however, most of the emissions come from the heaviest vehicles (greater than 33,000 lbs. gross vehicle weight) of which the majority of travel is occurring on the freeways.

In reviewing the sampling locations, the in-basin freeway data were most suitable for quantifying weekday/weekend traffic differences and their impact on ozone precursor emissions in the South Coast Air Basin. Of the seven in-basin freeway sites, the data for the Long Beach site were excluded because they may be overly influenced by a local condition. The Long Beach site was a freeway branch (I-710) that terminated at the Los Angeles and Long Beach port areas and was reflective of those local conditions (and not reflective of the basin as a whole). The vehicles from the Long Beach site likely traveled on the remainder of the in-basin freeway network and were partially counted at other sites, so excluding this site is not considered significant. The remaining six in-basin freeway sites served as the basis for the temporal profiles for this study.

Mass and Temporal Adjustments

Two types of temporal adjustments were applied based on the traffic count data. The first accounted for the change in daily total emissions and the second accounted for the change in hourly distribution of these emissions. All inventories began with the SCOS97 August 6 on-road inventory, which served as the typical weekday inventory. All adjustment factors were developed from the traffic count data and were estimated relative to the typical weekday. As noted above, a typical weekday was assumed to be the average of Monday through Thursday for light-duty vehicles and the average of Monday through Friday for heavy-duty vehicles.

<u>Daily Changes</u>

For total daily emissions, the following were the assumptions and methods used to develop adjustment factors by emissions process.

- For exhaust (running and start-up), hot soak, and running loss emissions, the temporal adjustments were directly related to total vehicle counts. For example, if total daily counts decreased by 10 percent (relative to the typical weekday), then it was assumed that total daily emissions for these processes were those of the typical weekday less 10 percent.

- For resting loss emissions, it was assumed that these would remain constant for all days of the week. Resting losses are related to vehicle off-time, and the amount of vehicle off-time is nearly constant for any day of the week.

- Diurnal emissions occur when a vehicle is not operated and ambient temperatures are rising. The daily temporal adjustments for diurnal emissions were estimated as the inverse proportion to the total activity occurring during the temperature rise period of the day – assumed to between 6am to 2pm. For example, if there were 20% less traffic counts occurring from 6am to 2pm (a multiplicative factor of 0.8), then diurnal emissions would be raised by a multiplicative factor of 1/0.8 or 25%. This accounts for operation during the temperature rise period, which purges the vehicle canister and reduces the amount of diurnal emissions.

Hourly Changes

For hourly temporal profiles, the following were the assumptions and methods used to develop adjustment factors by emissions process.

- For exhaust (running and start-up), hot soak, and running loss emissions, the hourly temporal adjustments were directly related to total vehicle counts. For example, if 5 percent of the counts occurred between 5am and 6am, then 5 percent of the emissions were assumed to occur during that period.

- For resting loss and diurnal emissions, the hourly emissions profile is directly related to hourly temperature characteristics, which is unaffected by vehicle activity. It was assumed that the hourly temporal profile for resting losses and diurnal emissions would not vary by day of week, and the hourly temporal variation for the SCOS97 August 6 episode was used in all cases.

Testing the Use of Vehicle Counts as an Emissions Surrogate

To test the hypothesis that vehicle count data can be used as a surrogate for temporal allocation of emissions, we compared the hourly temporal profiles of the vehicle count data with those of the August 6 SCOS97 on-road inventory. Using the six freeway sites in the manner described above, the hourly temporal profiles for the typical weekday vehicle counts were compared against the temporal profile for the activity-related emissions (exhaust, hot soak and running losses combined). The results are presented in Figure 2-6 with separate plots shown for light-duty and heavy-duty vehicles.

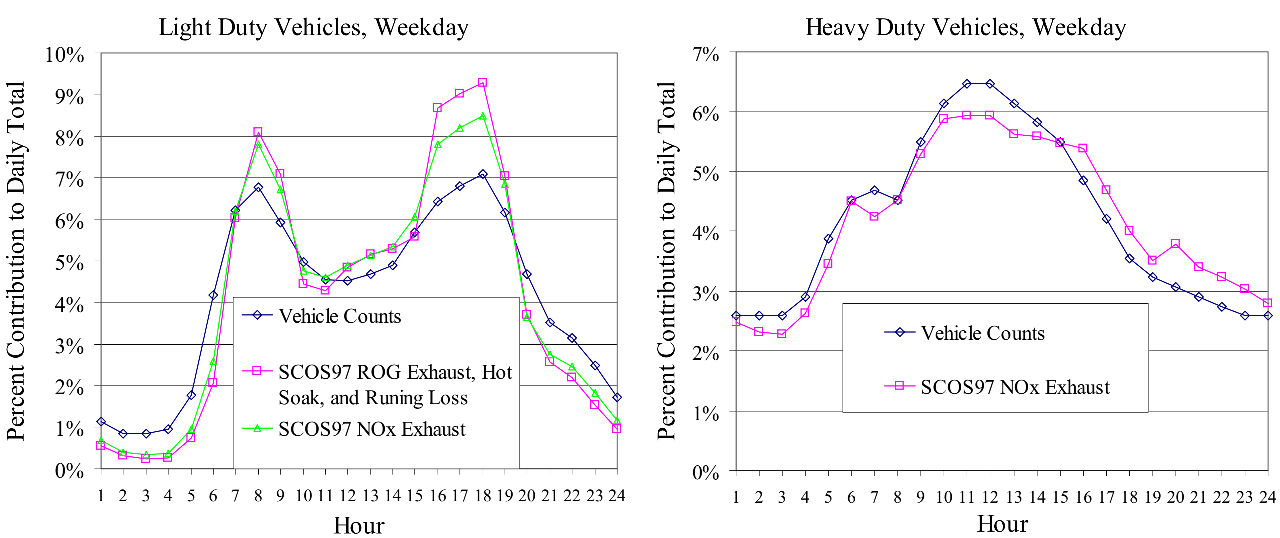


Figure 2-6. Comparison of hourly temporal profiles vehicle count data and SCOS inventory data.

For both vehicle classes, the vehicle count temporal profiles match the emissions profiles reasonably well. The light-duty bimodal and the heavy-duty modal vehicle-count distributions are similar to the emissions distributions. These comparisons confirm the reasonableness of using vehicle count data as a surrogate for temporal allocation of on-road emissions.

Temporal Adjustment Factors and Resulting Inventories

The first set of temporal adjustment factors was used to adjust daily total emissions. The calculated adjustment factors based on the vehicle count data are presented in Table 2-4. Table 2-4 shows the percent change in estimated emissions relative to the typical weekday.

Table 2-4. Daily adjustment factors, percent change relative to typical weekday.

Vehicle Class	Emissions Process	Friday	Saturday	Sunday
Light-Duty	Exhaust, Hot Soak and Running Loss	10%	-7%	-19%
	Diurnal	-3%	23%	59%
Heavy-Duty	Exhaust, Hot Soak and Running Loss	0%	-57%	-66%
	Diurnal	0%	136%	289%

For light-duty vehicles, exhaust, soak and running loss emissions were estimated to increase by 10 percent on Friday and decrease by 7 and 19 percent on Saturday and Sunday, respectively. The change in diurnal emissions was estimated to decrease by 3 percent on Friday and increase by 23 and 59 percent on Saturday and Sunday, respectively.

For heavy-duty vehicles, Friday was included in the typical weekday average, thus there was no change in emissions on Friday by definition. Exhaust, soak and running loss emissions were estimated to decrease by 57 and 66 percent on Saturday and Sunday, respectively. Diurnal emissions were estimated to increase by 136 and 289 percent on Saturday and Sunday, respectively.
Applying these adjustment factors resulted in the on-road inventories shown in Table 2-5. The inventory presented for Monday through Thursday is that of the August 6 SCOS97 episode. The inventories for Friday, Saturday and Sunday were estimated by applying the adjustment factors shown in Table 2-4 to the August 6 inventory.

Table 2-5. 1997 South Coast Air Basin on-road MV inventories (ton/day) by day of week.

	NOx	CB4-ROG	CO
Monday-Thursday	1111.3	819.1	8487.8
Friday	1169.5	881.7	9218.3
Saturday	810.2	755.8	7548.0
Sunday	696.6	692.1	6614.9

1. CB4-ROG is the sum of CB4 species assuming molecular weights of 16 per Carbon.

A second set of adjustment factors was used to translate daily total emissions (Table 2-5) to hourly emissions. As noted in the method discussion above, the hourly temporal profiles for exhaust, soak and running losses were based on vehicle count data. The vehicle count based on hourly temporal profiles are presented in Figure 2-7. These data show the distinct temporal characteristics by day of week. The hourly temporal profiles estimated were applied in a spatially uniform manner throughout the modeling region.

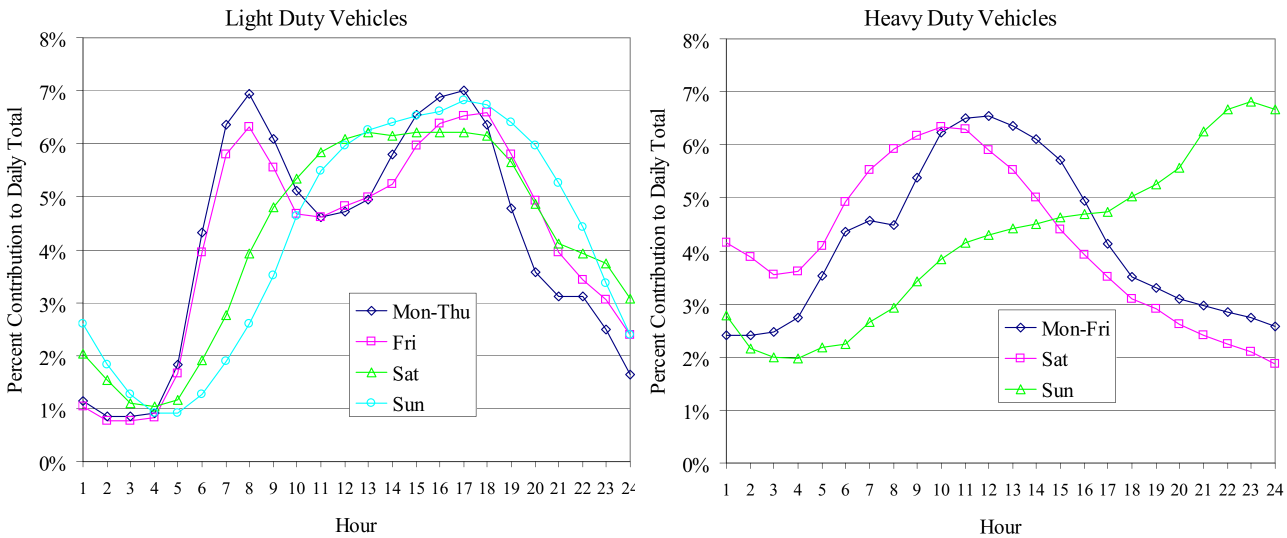


Figure 2-7. Hourly temporal profiles based on vehicle counts used for exhaust, soak and running loss emissions.

Adjustments for 1987 and 2010

The 1987 and 2010 on-road vehicle emission inventories did not separate emissions from light- and heavy-duty vehicles. For these years, mass and temporal adjustments for light- and heavy-duty vehicles were combined to weighted average adjustments for the entire on-road fleet. The weighting factors were determined from the EMFAC 2000 emissions for the South Coast Air Basin.

Weekend Spatial Shift

Adjustments were also developed to represent changes in the spatial distribution of on-road MV emissions on weekends. The major expected difference is less commute driving on weekends, which should place a greater percentage of the total emissions in the residential areas where people live. STI suggested analyzing the freeway traffic count data to see whether they show this effect. STI provided ratios of traffic counts to weekday (Monday-Thursday) values for Friday, Saturday and Sunday for light and heavy-duty vehicles (Table 2-6). These adjustment factors for specific locations were turned into gridded adjustment factors by spatial interpolation using the Kriging algorithm.

The spatially interpolated adjustment factors for light and heavy-duty vehicles on Saturday are shown in Figure 2-8. These figures show some spatial coherency in the changes in freeway driving observed between Saturday and Weekdays. For light-duty vehicles, less weekend driving was observed at the sites near downtown Los Angeles and Irvine, about the same amount of driving was observed at inland suburban locations (Van Nuys, Glendora, Fontana) and more driving was observed at sites further inland at points of exit/entry to the LA basin. For heavy-duty vehicles, less driving was observed everywhere on the weekend, especially near the port at

Long Beach. The changes to the MV NOx emissions for Friday, Saturday and Sunday are shown in Figure 2-9. The NOx emissions change is the net effect of the separate light and heavy-duty effects, and some freeways are apparent in Figure 2-9 because the freeways have different light to heavy-duty emissions ratios than surrounding areas. The emissions re-distribution was applied only for roads within the Southern California Association of Government's region because separate light and heavy-duty emissions were available only within this area. The emission changes shown in Figure 2-9 are roughly consistent with the expected weekend differences in driving and were considered useful for a proximate modeling sensitivity test. These changes are not be intended to represent all the differences in the spatial distribution of emissions on weekends which are likely much more complex. Since there is no information on the change in spatial distribution of surface sheet activity on weekends, the freeway adjustment factors were applied to both surface streets and freeways.

Table 2-6. Ratios of freeway vehicle counts to Monday-Thursday values by vehicle class.

WIM Station	UTM East	UTM North	Fri LDV	Fri HDV	Sat LDV	Sat HDV	Sun LDV	Sun HDV
VanNuys	364.6	3786.2	1.071	0.974	0.981	0.563	0.797	0.340
Castaic	352.1	3813.0	1.361	0.950	1.278	0.474	1.360	0.380
Long Beach	389.0	3747.1	1.058	0.979	0.866	0.262	0.673	0.170
Artesia	383.5	3748.3	1.028	0.883	0.769	0.215	0.673	0.294
Glendora	420.7	3775.6	1.089	0.962	0.941	0.427	0.809	0.281
Irvine	427.7	3729.0	1.052	0.989	0.847	0.409	0.703	0.242
Indio	576.9	3730.1	1.671	0.950	1.255	0.584	1.668	0.592
Fontana	452.0	3774.3	1.186	1.037	1.053	0.490	1.082	0.403

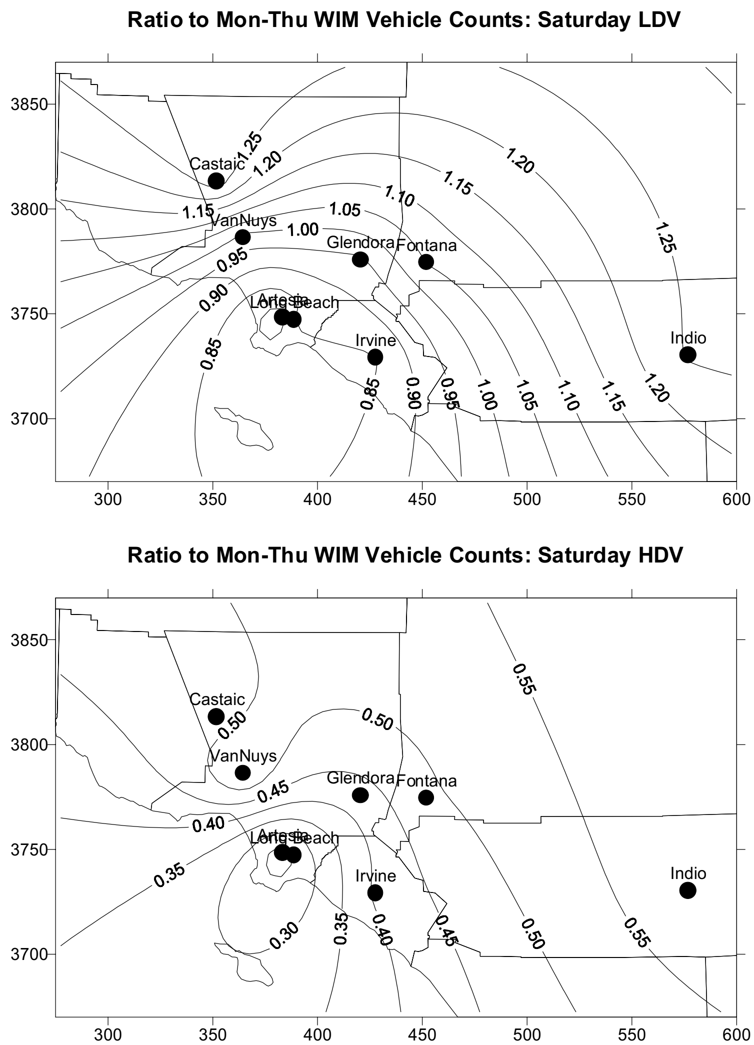


Figure 2-8. Spatially interpolated change in vehicle counts for Saturday light-duty vehicles (top) and heavy-duty vehicles (bottom).

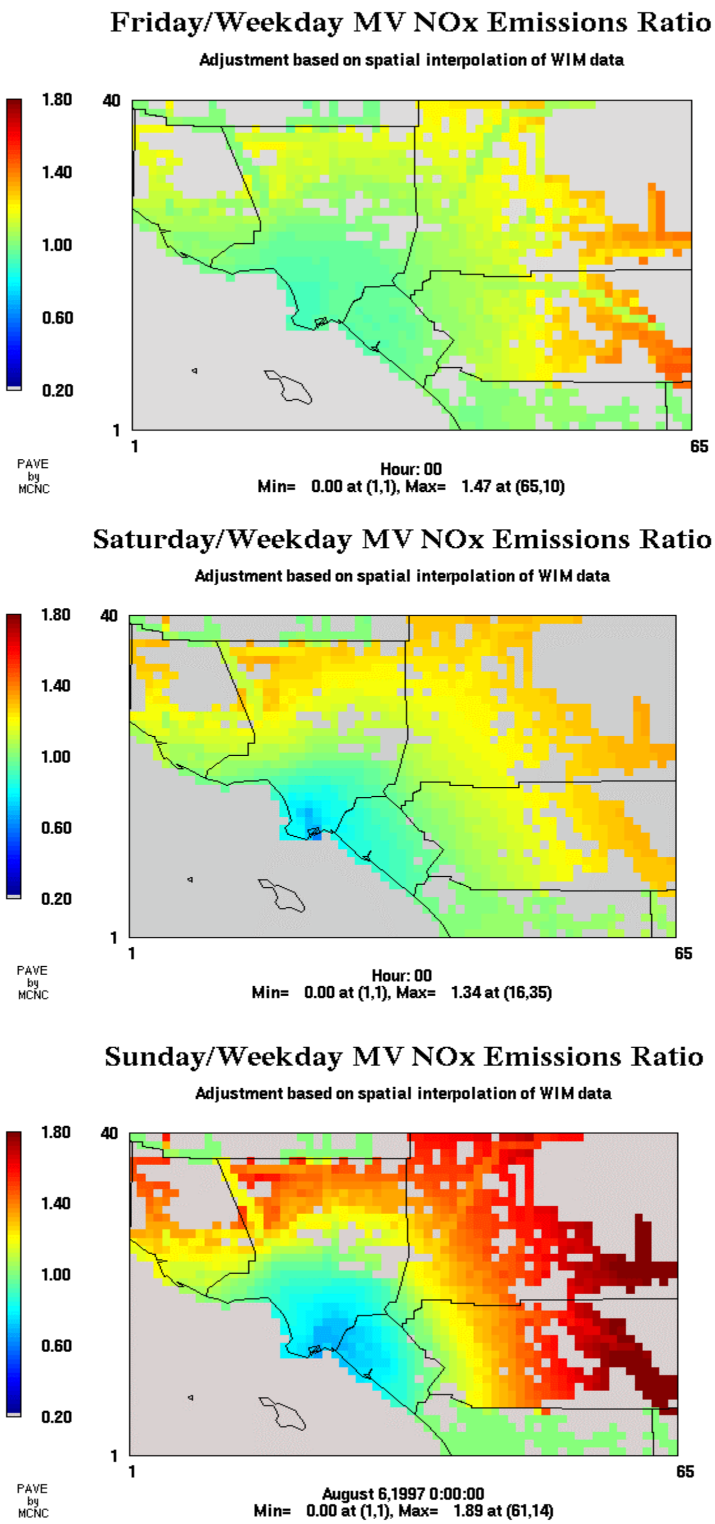


Figure 2-9. Ratio of MV NOx emissions on weekend days to weekdays. Gray areas have zero MV NOx emissions.

CAMx DATABASE

Photochemical grid modeling was performed for August 3-7, 1997 SCOS episode using version 3.01 of the Comprehensive Air-quality Model with extensions (CAMx). The CAMx model is publicly available from www.camx.com. In the past, photochemical grid modeling of the SoCAB has been performed on the "AQMP" or "SCAQS" modeling domain that is the smaller domain depicted in Figure 2-1. For the emerging 1997 SCOS episode modeling, models are being applied to the larger "SCOS" modeling domain (Figure 2-1). Some of the emissions information needed for this study was available only for the AQMP domain and so models were set up on the AQMP domain of 65 by 40, 5-km grid cells.

Meteorological data were developed using the MM5 model. MM5 uses a Lambert Conformal Projection (LCP) coordinate system, whereas the AQMP domain is in a UTM coordinate system. MM5 was configured on an LCP domain that closely matched the AQMP domain so that no horizontal interpolation was necessary to transfer meteorological data from MM5 to CAMx. MM5 was run with data assimilation of both the SCOS measurement database assembled by ARB (e.g., radar wind profiler upper-air data and surface sites) and the Eta Data Analysis System (EDAS) analysis fields data available from the National Center for Atmospheric Research (NCAR).

CAMx was run with 10 layers, a surface layer of 60 meters and a model top at about 4-km. The CAMx layer interfaces were defined to exactly match the MM5 layer interfaces to facilitate the mapping of meteorological parameters from MM5 to CAMx with the MM5CAMx program. Initial and boundary conditions for the CAMx AQMP grid were set to relatively clean values: 40 ppb ozone, 3 ppb NOx, 103 ppbC VOC, and 200 ppb CO.

CAMx PERFORMANCE EVALUATION

Most of the modeling for this study used the Carbon Bond 4 (CB4) condensed chemical mechanism, but sensitivity tests were also performed using the SAPRC99 mechanism. Model performance is discussed first for the CB4 mechanism and then differences for SAPRC99 are discussed. The simulations discussed in the model performance evaluation use the original emissions provided by the ARB and do not include any weekend adjustments developed here. Model performance for ozone was evaluated based on 1-hour ozone data for 48 sites in the modeling domain that were compiled by the ARB. Performance was evaluated using:

- Tables of EPA statistical measures in Table 2-7.
- Daily maximum 1-hour ozone isopleth plots in Figure 2-10.
- Time series plots for 1-hour ozone in Figure 2-11 for several representative sites.

August 3-4, 1997 are considered "spin-up" days and are not included in the performance statistics in Table 2-7. The model performance statistics in Table 2-7 show that good model performance is obtained with the CAMx/MM5 modeling system when the CB4 mechanism is used. The statistical measures meet EPA goals on all episode days. The ozone bias is positive on each day (+5 to +7 percent), which suggests a slight tendency toward over-prediction but is well within EPA's ±15 percent performance goal. However, the modeled episode peak (176 ppb) is still 6 percent lower than the observed episode peak (187 ppb). Overall, model performance is far superior to the performance obtained in the past with UAM-IV as used in the 1997 AQMP for

Los Angeles (i.e., an under-prediction bias of approximately -30%, which is outside the EPA performance goal of within 15%).

Table 2-7. CAMx/MM5 1-hour ozone model performance statistics for CB4.

	EPA Goal	5-Aug	6-Aug	7-Aug
Observed Peak (ppb)		187	154	150
Modeled Peak (ppb)		167	176	159
Unpaired Peak (%)	<±20	-11	15	6
Normalized Bias (%)	<±15	5	7	7
Normalized Error (%)	<35	22	24	28

Statistical measures were calculated for valid data pairs with observed values > 60 ppb at 48 stations.

The ozone isopleth plots for August 6-7 (Figure 2-10) and time-series plots for August 4-7 (Figure 2-11) show why the model performance statistics are good. The model generally does well in predicting high ozone near the observed high ozone on each day, and conversely predicting low ozone where observed levels were low.

August 6, 1997: The observed ozone peak on August 6 was 154 ppb at Crestline (Lake Gregory). CAMx/MM5 predicted a maximum of 152 ppb at this location. The predicted peak was 176 ppb (15 percent higher than the unpaired peak) just to the north of Redlands approximately 25-km to the southeast of Crestline. High ozone levels were also observed in the San Fernando Valley on this day, 134 ppb at Simi Valley and 132 ppb at Santa Clara, where CAMx predicted 145 ppb and 146 ppb, respectively. Model performance is particularly good on this day.

August 7, 1997: The observed ozone peak on August 7th was 150 ppb at Lake Elsinore. CAMx predicted a maximum of 97 ppb at this location. The predicted peak was 159 ppb (6 percent higher than the unpaired peak) near Redlands/San Bernardino and approximately 60-km to the northeast of Lake Elsinore. The highest observed ozone levels were in the San Gabriel Valley whereas the highest predicted ozone was further east around San Bernardino/Redlands. High ozone levels are predicted in the eastern basin and through the passes (near Banning, Crestline and Santa Clara) which is a pattern consistent with the observations on this day.

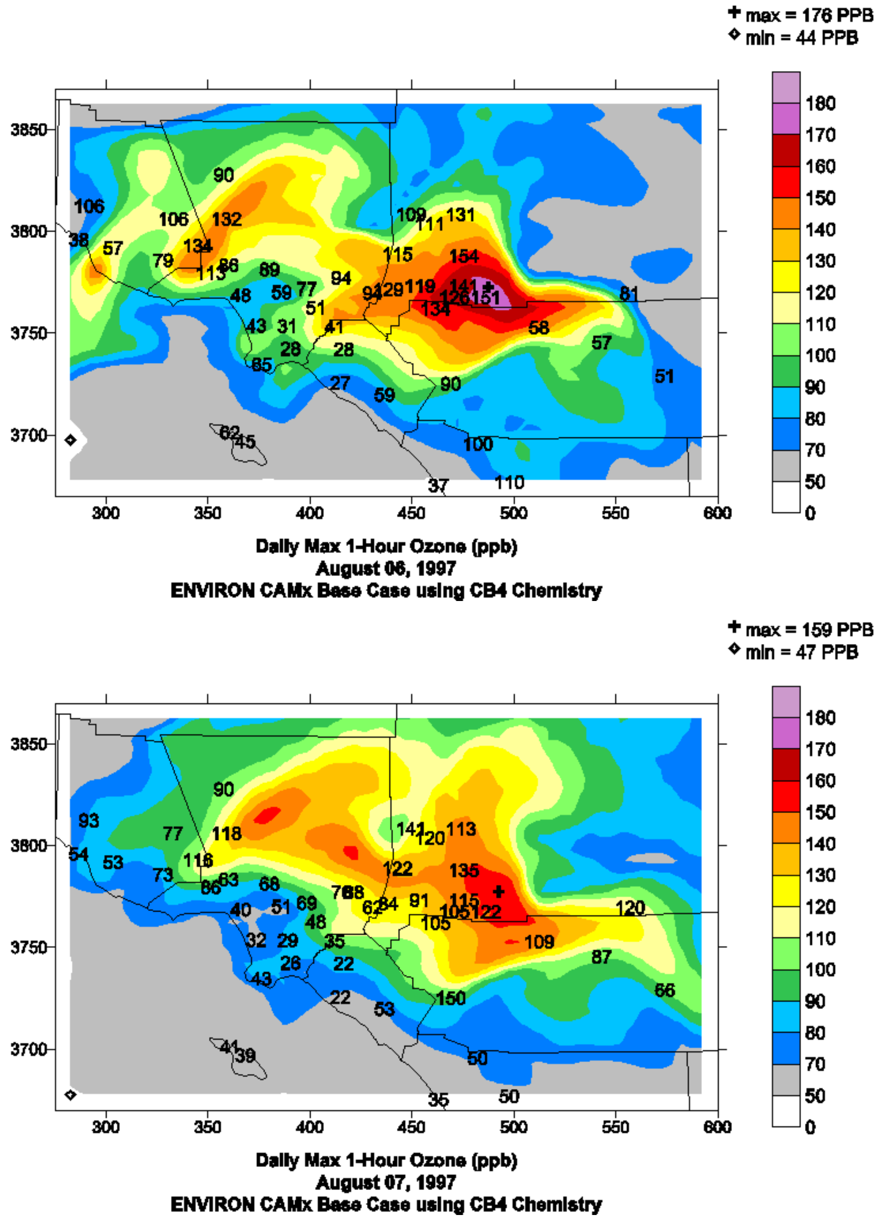


Figure 2-10. Daily maximum 1-hour ozone plots on August 6-7, 1997 showing the CAMx/MM5 estimates with CB4 chemistry with superimposed observations.

The time series plots (Figure 2-11) show that CAMx with CB4 does well in replicating many features of the diurnal variations in the hourly-observed ozone at different sites. The diurnal profiles have different characteristic shapes at upwind sites such as Los Angeles North Main and Burbank versus mid-basin sites like Azusa and Fontana versus downwind sites like Crestline-Lake Gregory and Hesperia.

Excellent performance was obtained for ozone using the CAMx and MM5 models with the ARB emission inventories and the Carbon Bond 4 mechanism. The good performance suggests that all major aspects of the modeling system are being well represented. It is possible for good model performance to mask underlying problems, and it has been hypothesized that good model performance can be obtained even when models and/or model inputs contain errors if these errors compensate. There was little opportunity for inadvertent model tuning in the development of this application because key inputs were developed independently. The MM5 simulations were performed at ENVIRON without access to the ARB emission inventories. The ARB emissions were developed and tested with different photochemical modeling databases.

The MM5 meteorological fields show desirable characteristics in addition to providing good statistical model performance for ozone. For example, the high ozone levels in the inland valleys clearly reflect the influence of terrain (e.g., the San Gabriel mountains and mountain passes) much more realistically than in past diagnostic wind modeling studies. Another advantage of prognostic model fields over diagnostic model fields is that the meteorological parameters are inherently consistent and balanced by the prognostic model physics.

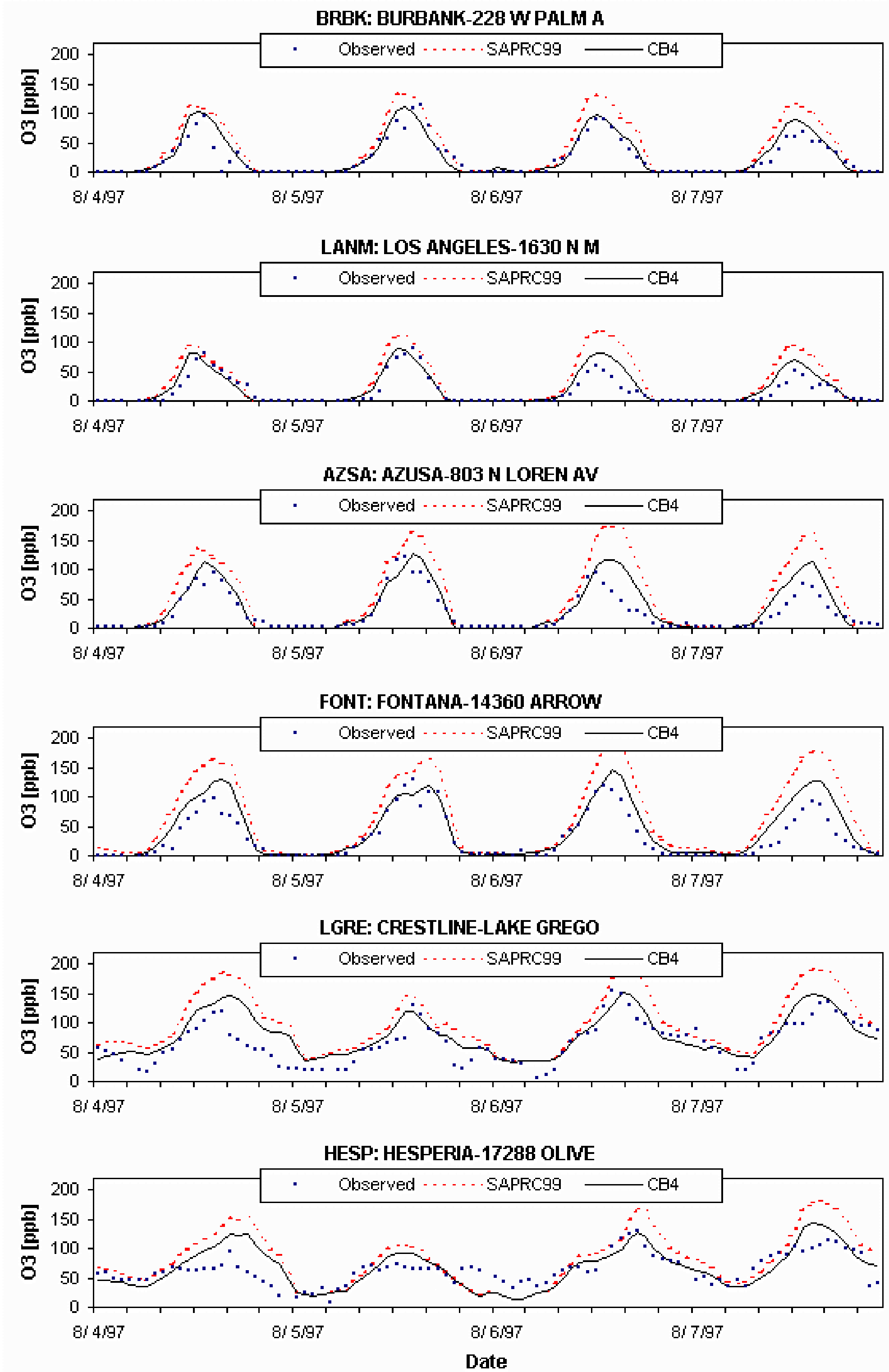


Figure 2-11. Time series of predicted and observed hourly ozone concentrations at representative sites for the CAMx/MM5 modeling system and the August 4-7, 1997 SCOS episode.

Model Performance with SAPRC99

The ARB provided emission inventories for the SAPRC99 mechanism as well as for CB4. Unlike CB4, the SAPRC99 mechanism can have many different configurations depending upon the scheme selected for VOC lumping. In this study, SAPRC99 refers to the "fixed parameter" version of the mechanism (Carter, 2000) developed for use in EPA's MODELS-3 system. ENVIRON implemented the fixed parameter SAPRC99 mechanism in CAMx version 3.01 while this project was being performed, and has since released the SAPRC99 mechanism for general use in CAMx version 3.1. The mechanism implementation was reviewed by the ARB modeling staff.

Model performance with SAPRC99 was evaluated in the same way as for CB4, and the following results are presented:

- Tables of EPA statistical measures in Table 2-8.
- Daily maximum 1-hour ozone isopleth plots in Figure 2-12.
- Time series plots for 1-hour ozone in Figure 2-11 for several representative sites.

The EPA statistical performance measures were poor with SAPRC99 (Table 2-8) in contrast to the good performance with CB4 (Table 2-7). Measures falling outside the performance goal are shaded gray in these tables showing that and eight of nine measures failed the performance goal using SAPRC99 compared to none for CB4. The daily maximum ozone plots (Figure 2-12) show why model performance was poor with SAPRC99. Ozone levels were much higher throughout the basin than with CB4 and over-predicted observed levels at upwind, mid-basin and downwind sites. This resulted in a large positive bias of 30% to 36% which exceeded the performance goal of ±15%. The large bias also produced large normalized errors of 39% to 44%, which exceeded the performance goal of 35%.

The time series plots (Figure 2-11) compare hourly ozone levels with SAPRC99 and CB4 to observed values for several sites. Peak ozone levels were higher with SAPRC99 than CB4 at all sites on all days with the largest differences at the mid-basin sites Azusa and Fontana. It is evident that the SAPRC99 mechanism is much more reactive than CB4, resulting in faster rise in ozone and higher peak ozone levels. The time of the peak ozone levels does not differ substantially between SAPRC99 and CB4, which may be because the timing of the peak is strongly influenced by meteorological factors. A more detailed evaluation of the differences between the SAPRC99 and CB4 simulations could be performed using the process analysis tools in CAMx version 3.1.

Table 2-8.CAMx/MM5 1-hour ozone model performance statistics for the August 5-7, 1997 SCOS episode with SAPRC99 chemistry. Gray shaded cells fail the performance goal.

	EPA Goal	5-Aug	6-Aug	7-Aug
Observed Peak (ppb)		187	154	150
Modeled Peak (ppb)		204	223	200
Unpaired Peak (%)	<±20	9	45	34
Normalized Bias (%)	<±15	30	35	36
Normalized Error (%)	<35	39	44	44

Statistical measures were calculated for valid data pairs with observed values > 60 ppb at 48 stations.

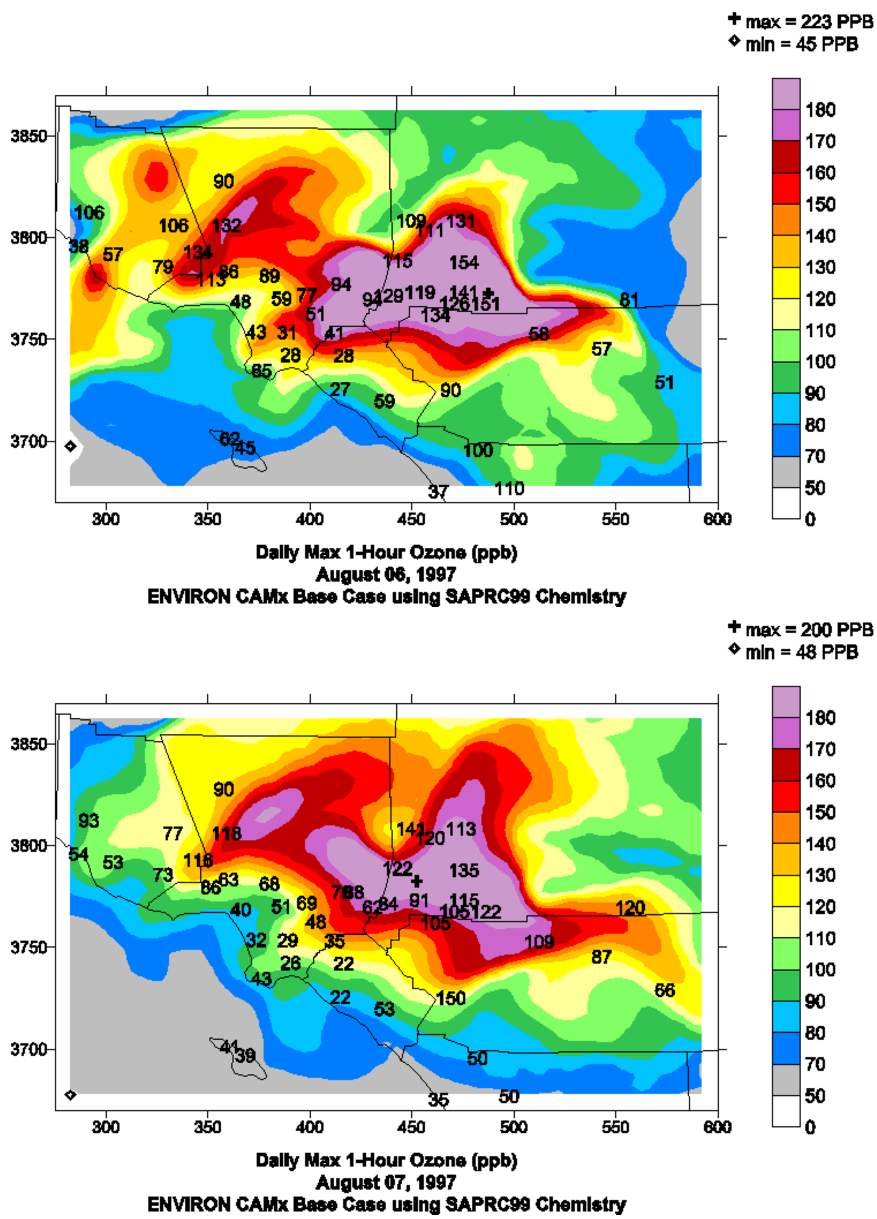


Figure 2-12. Daily maximum 1-hour ozone plots on August 6-7, 1997 showing the CAMx/MM5 estimates with SAPRC99 chemistry and superimposed observations.

3. RESULTS

A series of experiments were performed to investigate potential causes of the weekend ozone effect in the Los Angeles basin. This report section describes the experiments, the results and their interpretation. Experiments were designed to address the following questions, as summarized below and in Table 3-1:

- What are the impacts of changes to the mass and timing on-road motor vehicle (MV) emissions on weekends? Model runs wd_base, h1a, h2a, h2c and h3a.
- What is the impact of Friday MV emission changes? Model runs h3a and h2c.
- What is the role of carryover in the MV emission change scenarios (h3b, h3a and h4a)?
- Could changes to the spatial distribution of MV emissions on weekends cause the weekend effect? Model runs h2e and h2f.
- Could changes in aerosol loading produce the weekend effect via impacts on the rates photolytic reactions? Model run h5a.
- Does uncertainty in the chemical mechanism alter the impact of MV emission changes on weekends? Model runs wd_base_s99, h1b and h2d.
- What are the impacts of MV emissions changes with 1987 emission levels? Model runs 87_wd_base and 87_h3a.
- What are the impacts of MV emissions changes with 2010 emission levels? Model runs 10_wd_base and 10_h3a.

Table 3-1. Summary of modeling experiments by run numbers.

Run Number	Description
wd_base	Weekday base case with every day modeled as a weekday
wd_base_s99	Weekday base case with SAPRC99
h1a	Change MV emissions mass for Sat/Sun based on activity data
h1b	Repeat run h1a using SAPRC99
h2a	Change MV emissions temporal profile on Sat/Sun based on activity data
h2c	Change MV emissions mass and temporal profile on Sat/Sun
h2d	Repeat run h2c using SAPRC99
h2e	Combine h3a and h2f – change Fri/Sat/Sun MV mass/temporal/spatial
h2f	Change MV emissions spatial distribution on Fri/Sat/Sun
h3a	Combine h2c and h3b – change Fri/Sat/Sun MV mass/temporal
h3b	Change MV emissions mass and temporal profile on Friday
h4a	Repeat run h2c for Sunday only – change Sunday MV mass/temporal
h5a	Change photolysis rates on Sat/Sun to reflect lower aerosol load
87_wd_base	Weekday base case for 1987 emission levels
87_h3a	Change Fri/Sat/Sun MV mass/temporal for 1987 emission levels
10_wd_base	Weekday base case for 2010 emission levels
10_h3a	Change Fri/Sat/Sun MV mass/temporal for 2010 emission levels

1. Run h2b was dropped from the workplan.

EMISSIONS MASS AND TIMING EFFECTS

The first series of experiments investigated the effects of weekend changes to the mass and timing of on-road motor vehicle (MV) emissions. These experiments changed emissions of VOC, NOx and CO, but according to the ARB's NOx reduction and timing hypotheses (ARB, 2001c), the changes to the MV NOx emissions are expected to be the main factor in determining ozone response. The starting point for the experiments was the 1997 weekday base case (described in section 2) where every day is modeled as a weekday. The MV emissions for counties in the SCAG (Southern California Association of Governments) were then changed to represent weekend activity patterns based on traffic count data, as described in Section 2. Separate adjustments were developed for the total mass of emissions and the timing of emissions throughout the day. The Saturday and Sunday mass and timing adjustments were applied separately and in combination to investigate their relative importance in experiments h1a, h2a and h2c.

Spatial Patterns of Ozone Differences

The ozone changes for the MV emissions mass and timing experiments are shown in a series of tile plots displaying the spatial distribution of ozone at 9am, noon and 4pm on Saturday, at 9am, noon and 4pm on Sunday and noon on Monday (Figures 3-1 to 3-7). Times for model experiments are always in Pacific Standard Time. There are four panels in each figure:

- Top left shows the weekday base case ozone;
- Top right shows the difference in ozone due to changing the temporal profile of MV emissions (h2a minus wd_base);
- Bottom left shows the difference in ozone due to changing the mass of MV emissions (h1a minus wd_base), and;
- Bottom right shows the difference in ozone due to changing the mass and temporal profile of MV emissions (h2c minus wd_base).

The main features of the mass change, timing change and mass/timing change in each figure are summarized below:

Saturday 9am: In the base case, ozone levels are depressed by NOx scavenging in the high emission areas, the central and western LA basin. Changing the temporal profile of MV emissions has very little impact on ozone. Changing the mass of MV emissions increases ozone across most of the LA basin and along the Ventura coast by up to 13 ppb. The combined effect of the mass and timing change is very similar to the mass change alone, with ozone increases of up to 14 ppb.

Saturday noon: The base case has elevated ozone (90 to 130 ppb) over most of the LA basin and surrounding areas, except for some areas near downtown LA. Changing the temporal profile of MV emissions has very little impact on ozone. Changing the mass of MV emissions increases ozone across most of the central and eastern portions of the LA basin by up to 20 ppb. The largest increases occur in the central basin, from northern Orange County to the San Fernando Valley. The combined effect of the mass and timing change is very similar to the mass change alone, with ozone increases of up to 19 ppb. There are some areas of ozone decreases, but they are smaller in magnitude (up to 8 ppb) and extent than ozone increases.

Saturday 4pm: The base case has elevated ozone (100 to 160 ppb) over widespread areas. The highest ozone levels are inland along the foothills of the San Gabriel Mountains, through San Bernardino/Riverside and into the desert. Ozone levels in the western LA basin are lower due to the influence of the sea breeze and ozone scavenging by NOx emissions. Changing the temporal profile of MV emissions produces small (up to 5 ppb) increases in ozone in the central LA basin due to reduced NOx scavenging. Changing the mass of MV emissions increases ozone by up to 17 ppb, with the largest increases in the inland areas around San Bernardino/Riverside and also northern Orange County. The combined effect of the mass and timing change is very similar to the mass change alone, with ozone increases of up to 18 ppb. Ozone decreases are smaller in magnitude (up to 10 ppb) and extent than ozone increases.

Sunday 9am: The base case results show ozone levels depressed in central and western LA basin due to NOx scavenging, similar to 9am on Saturday. Changing the temporal profile of MV emissions increases ozone by up to 15 ppb across most of the LA basin and the Ventura coast. This is a larger effect than for Saturday 9am because the change in the temporal profile of HDV emissions is larger for Sunday than Saturday (Figure 2-7) relative to weekdays. Changing the mass of MV emissions increases ozone by up to 22 ppb across most of the LA basin and the Ventura coast. The combined effect of the mass and timing change is similar to the sum of the separate effects, leading to ozone increases of up to 30 ppb.

Sunday noon: The base case has elevated ozone (90 to 150 ppb) over most of the LA basin and Ventura County, except for an area near downtown LA. Changing the temporal profile of MV emissions increases ozone in the central and eastern LA basin by up to 15 ppb. Changing the mass of MV emissions increases ozone across most of the LA basin, with the largest increases in the western basin of up to 38 ppb. The combined effect of the mass and timing change is similar to the sum of the separate effects, leading to ozone increases of up to 45 ppb. Ozone decreases are smaller in magnitude (up to 21 ppb) and extent than ozone increases.

Sunday 4pm: The base case has elevated ozone (100 to 170 ppb) in many inland areas. The highest ozone levels occur to the east of San Bernardino. Ozone levels in the western and central LA basin are lower due to the influx of marine air and ozone scavenging by NOx emissions. Changing the temporal profile of MV emissions produces small (up to 7 ppb) increases in ozone in the eastern LA basin. Changing the mass of MV emissions increases ozone in the central and eastern LA basin by up to 26 ppb, with the largest increases in the San Gabriel Valley/San Bernardino area. The combined effect of the mass and timing change is very similar to the mass change alone, with ozone increases of up to 27 ppb. Ozone decreases are smaller in magnitude (up to 21 ppb) and extent than ozone increases.

Monday noon: The base case has elevated ozone (90 to 150 ppb) over the inland parts of the LA basin. Any ozone differences for noon on Monday in these experiments are due to carryover of the Saturday/Sunday emission changes. Changing the temporal profile of MV emissions increases ozone by up to 7 ppb in some inland areas such as northern LA County near interstate highway 5. Changing the mass of MV emissions decreases ozone by up to 5 ppb across some inland areas. The combined effect of the mass and timing change is very small.

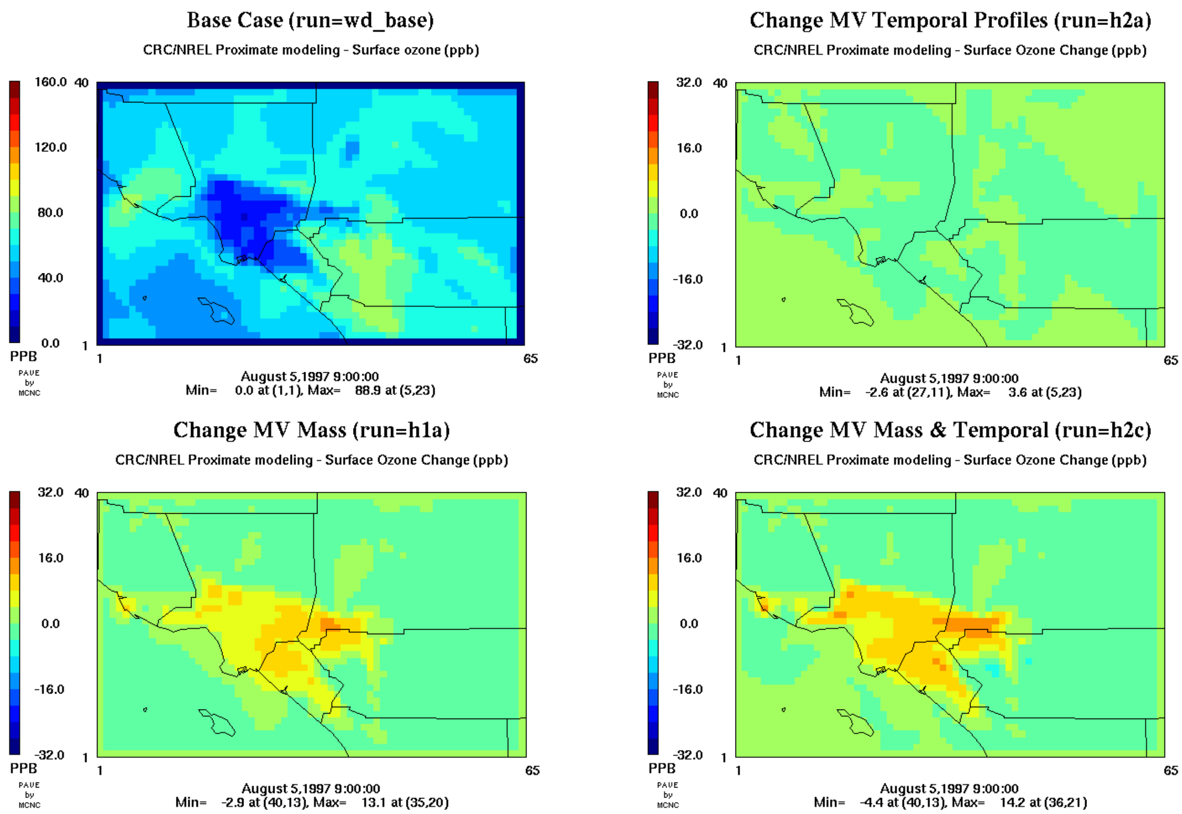


Figure 3-1. 1997 weekday base case ozone (top left) and ozone differences due to changing the mass and/or timing of MV emissions. Saturday, 9am.

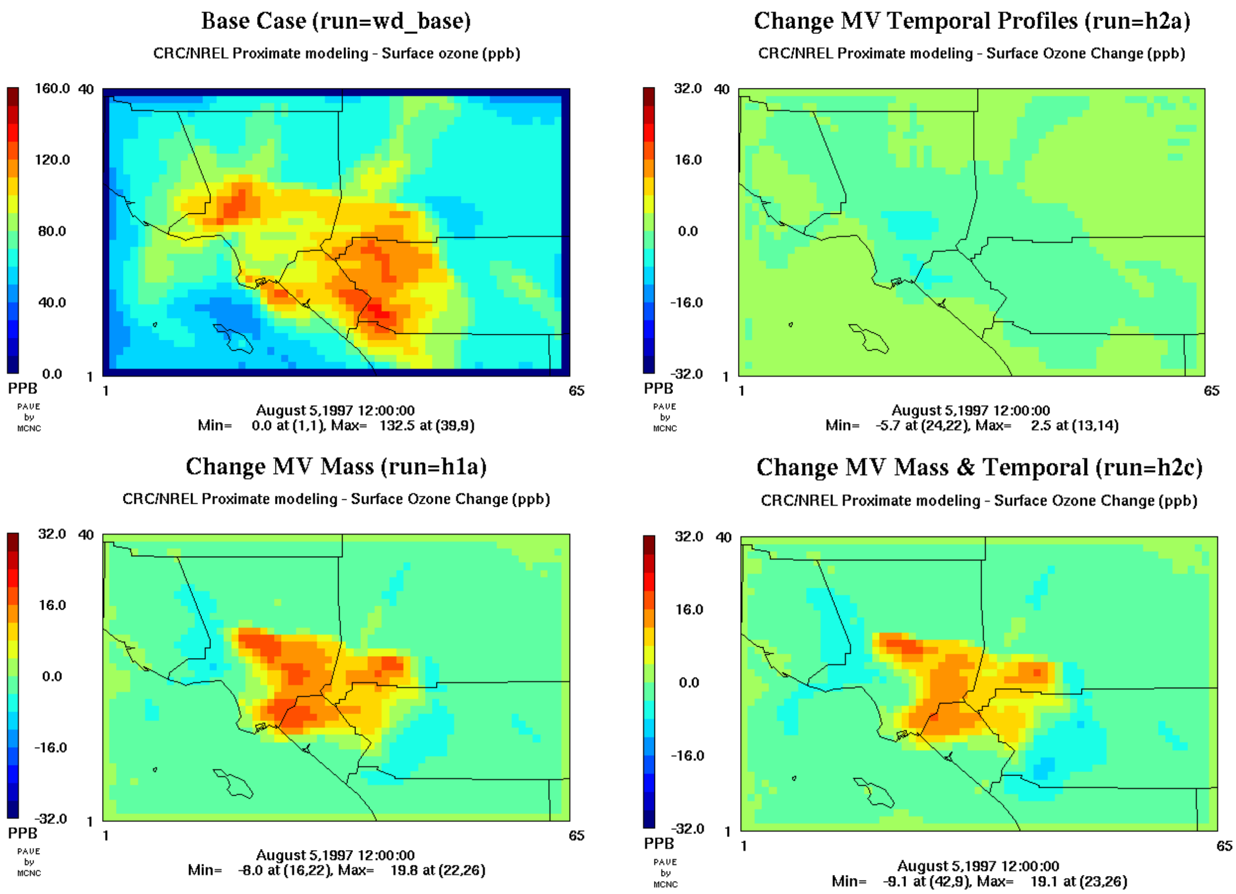


Figure 3-2. 1997 weekday base case ozone (top left) and ozone differences due to changing the mass and/or timing of MV emissions. Saturday, noon.

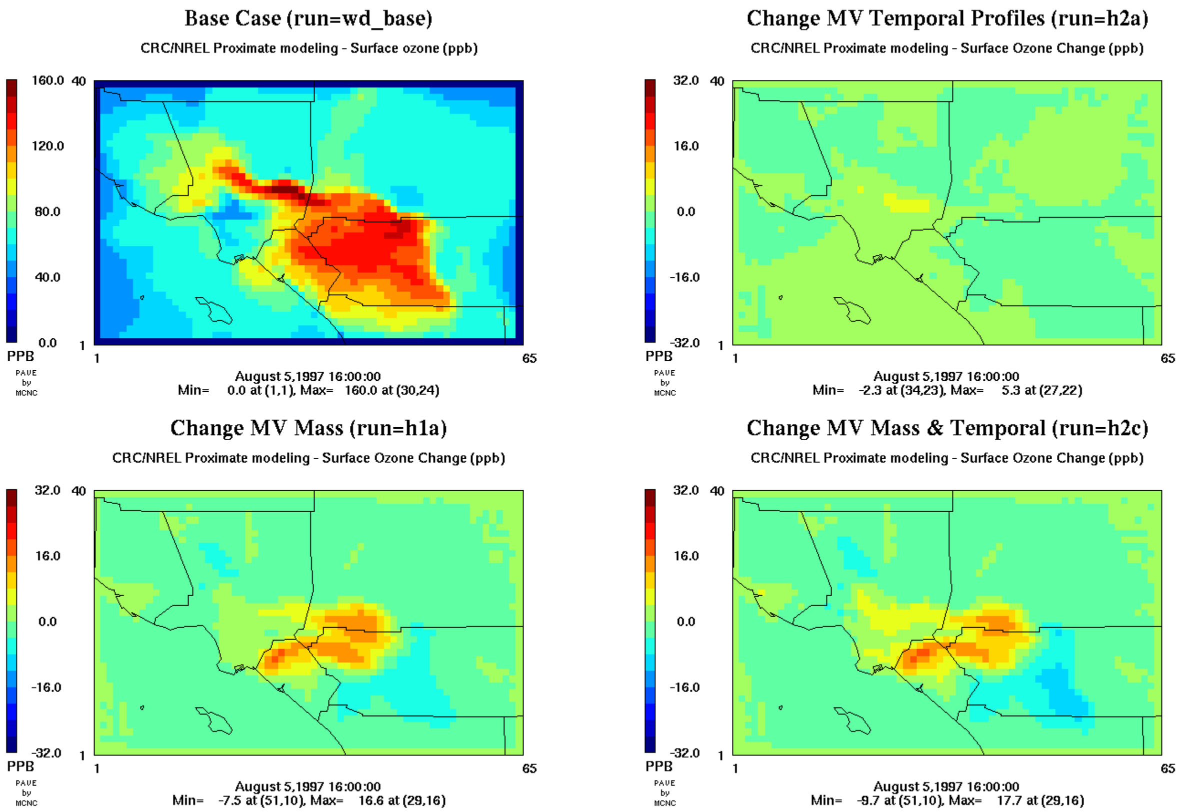


Figure 3-3. 1997 weekday base case ozone (top left) and ozone differences due to changing the mass and/or timing of MV emissions. Saturday, 4 pm.

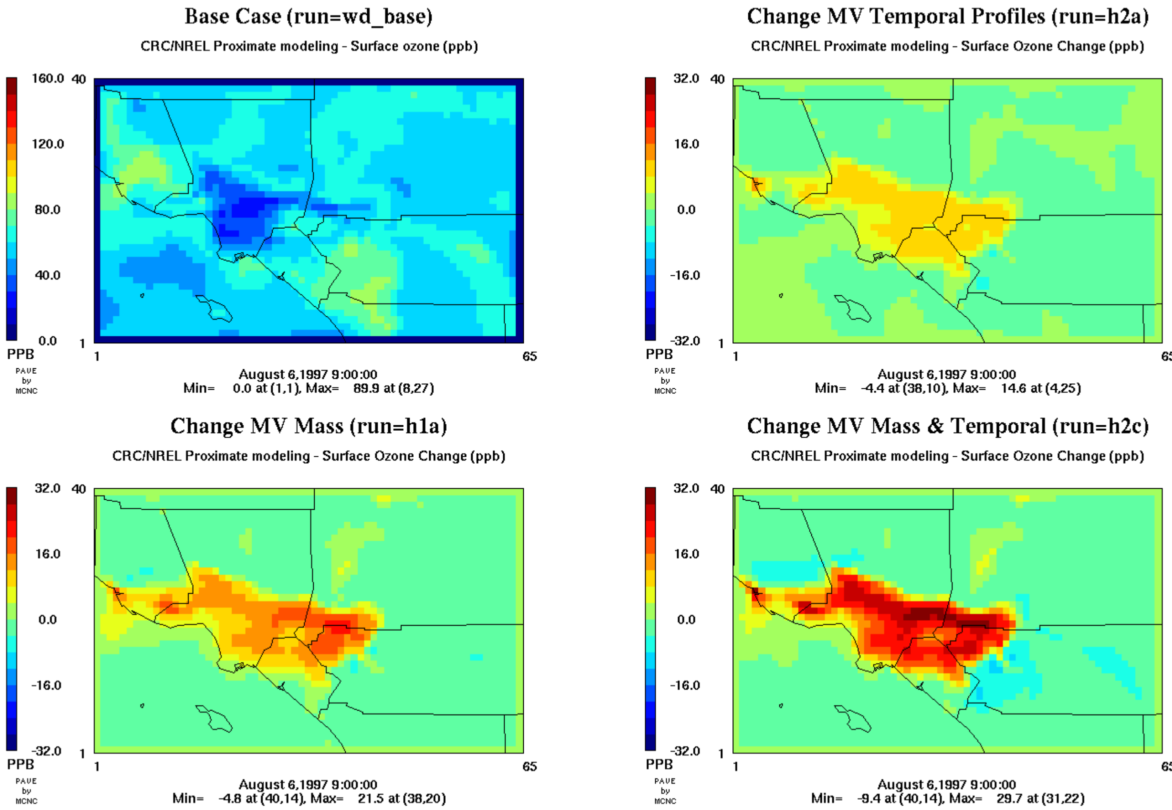


Figure 3-4. 1997 weekday base case ozone (top left) and ozone differences due to changing the mass and/or timing of MV emissions. Sunday, 9am.

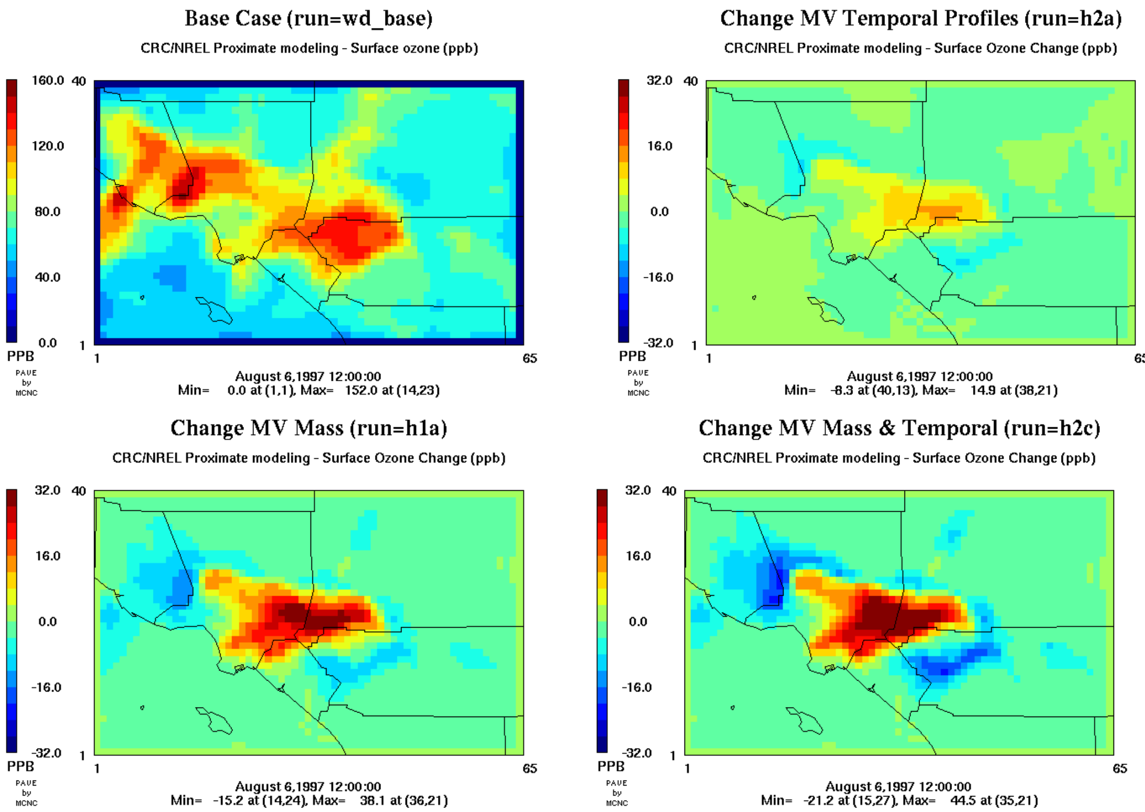


Figure 3-5. 1997 weekday base case ozone (top left) and ozone differences due to changing the mass and/or timing of MV emissions. Sunday, noon.

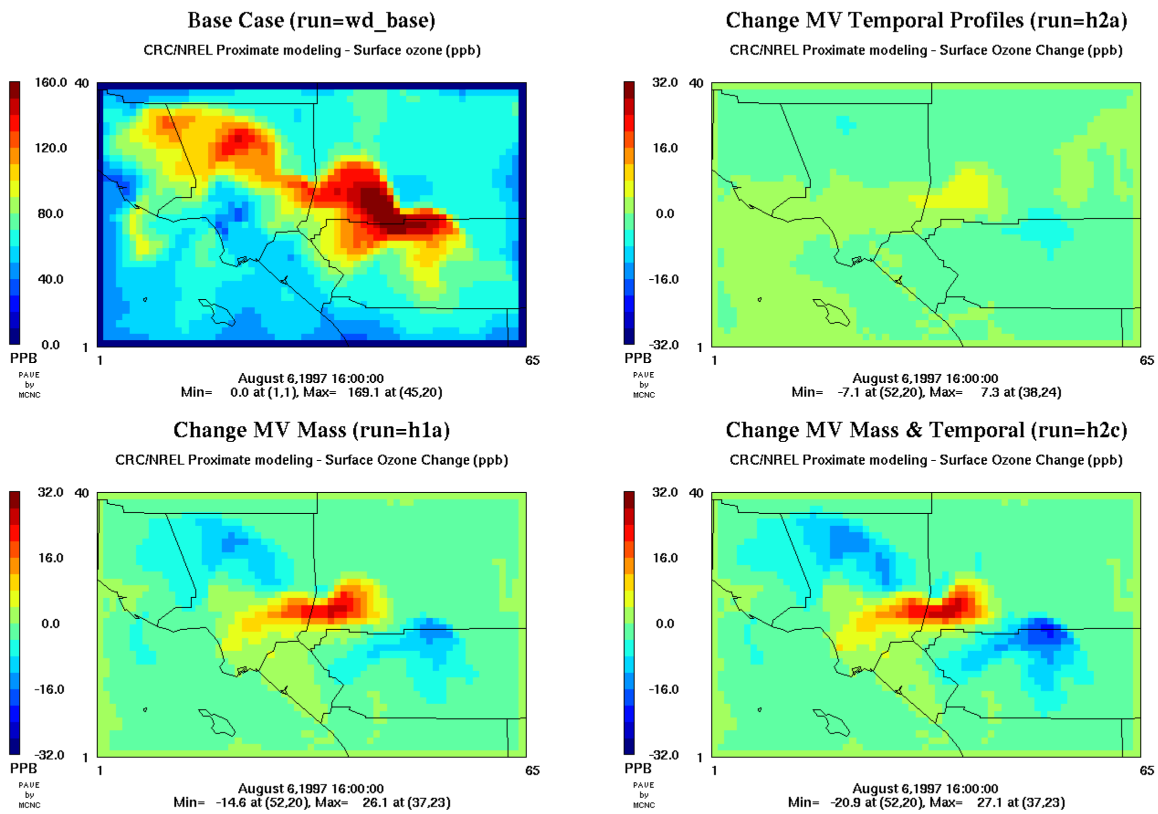


Figure 3-6. 1997 weekday base case ozone (top left) and ozone differences due to changing the mass and/or timing of MV emissions. Sunday, 4pm.

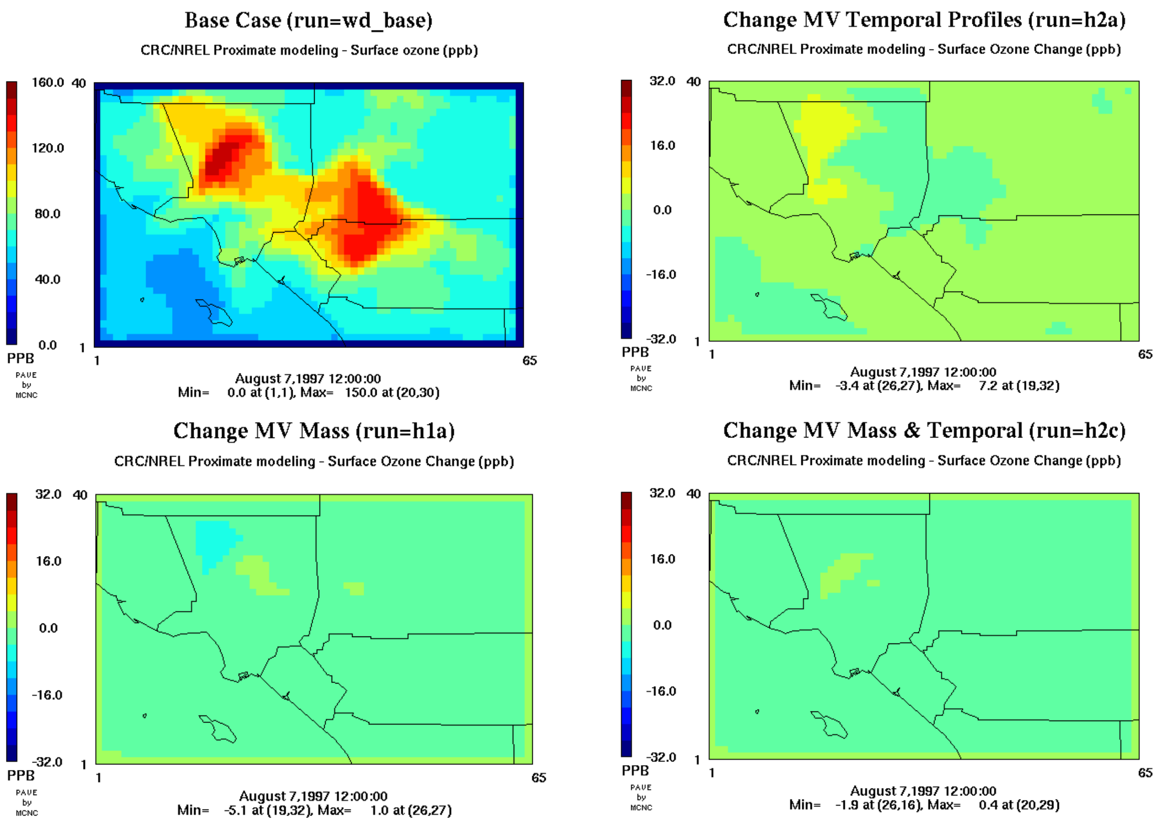


Figure 3-7. 1997 weekday base case ozone (top left) and ozone differences due to changing the mass and/or timing of MV emissions. Monday, noon.

Figures 3-1 through 3-7 show the spatial and temporal distributions of the ozone response changes in the mass and/or timing of MV emissions changes. From these figures it is clear that the mass effect is larger than the timing effect on both Saturday and Sunday, though there are differences between the days. It is also helpful to see the impact of the emissions changes on daily maximum ozone levels. Figure 3-8 shows the daily maximum ozone for the weekday basecase alongside the difference in daily maximum ozone due to the MV emissions mass/timing change (h2c minus wd_base) for Saturday and Sunday. There are increases in maximum ozone across much of LA basin, and decreases in maximum ozone in surrounding areas. The largest ozone increases are in the mid-basin close to areas of high base case ozone, with the increases tending to be on the upwind (coastal) side of the highest base case ozone levels. Decreases in maximum ozone tend to be toward the downwind (inland) side of highest ozone areas. This pattern is consistent on Saturday and Sunday, although larger ozone differences occur on Sunday, and there are changes in the locations of high ozone and ozone changes due to differences in meteorology. The response of ozone to the MV emissions mass/timing change is consistent with lower mass of MV NOx emissions on the weekend reducing the NOx inhibition of ozone formation in the upwind (coastal) and central basin areas. This results in higher ozone in the mid basin areas. Several factors likely contribute to the lower weekend ozone in downwind (inland) areas, including the upwind shift in ozone peaks due to reduced NOx inhibition, and reduced ozone production in the downwind areas in response to lower MV emissions. These effects could also be described in terms of the upwind areas being VOC sensitive (and therefore showing ozone increases due to NOx reduction) and the downwind areas being NOx sensitive (and therefore showing ozone decreases due to NOx reduction).

The spatial variations in modeled and observed weekend effects in 1997 are compared in Figure 3-9. This figure compares modeled and observed weekday/weekend ozone differences at six sites across the Los Angeles basin from West (upwind) to East (downwind). The observed weekend effect is characterized by the Sunday and Wednesday maximum ozone levels for the summers of 1994 to 1996, whereas the modeled effect is characterized by the wd_base and h3a maximum ozone levels for August 6th (Sunday). The observed weekend (Sunday) effect in 1994-1996 was an increase in ozone at all sites from West LA to Crestline. This is consistent with most of the Los Angeles basin being VOC sensitive, such that weekend decreases in MV NOx emissions produce ozone increases. The modeled weekend (Sunday) effect shown in Figure 3-9 is very similar to the observed effect, suggesting that the MV emissions mass and timing change provides a good description of the observed weekend effect in the mid-1990s.

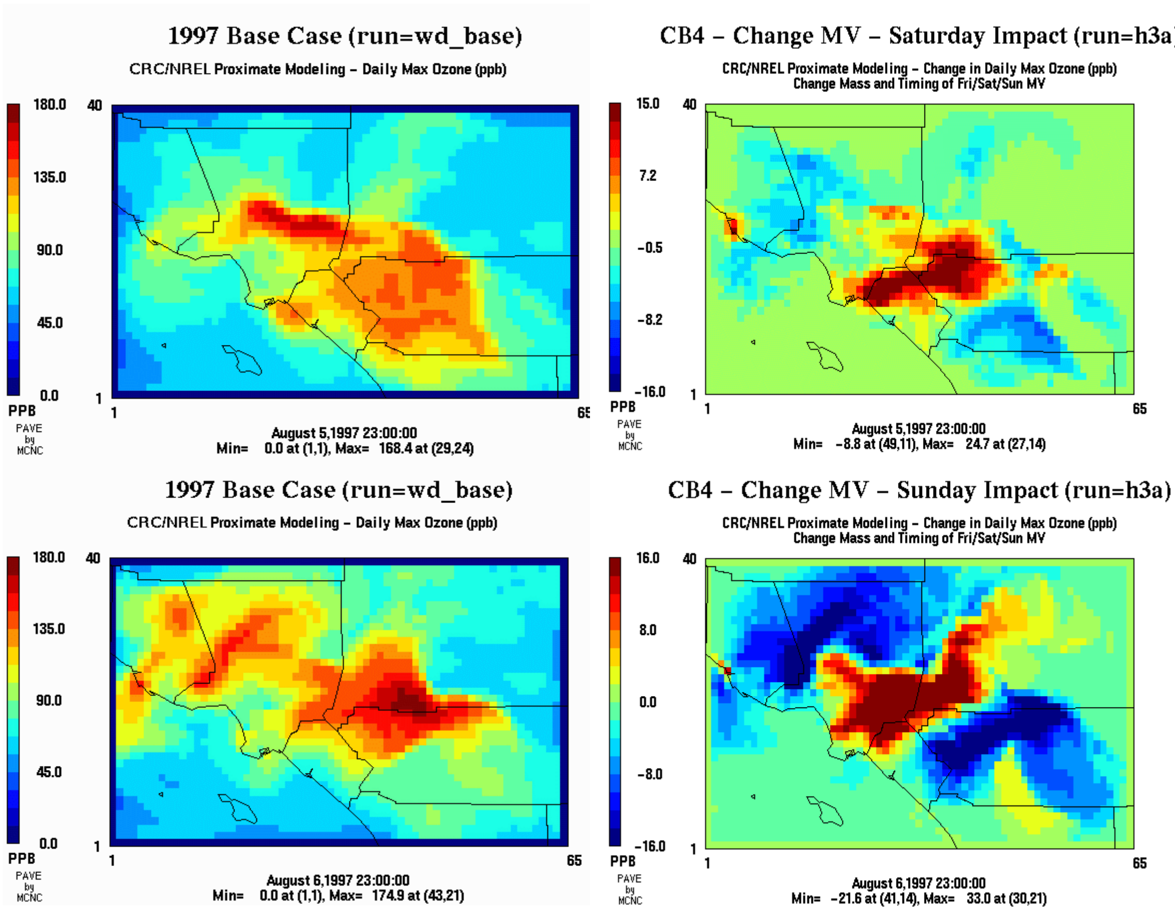
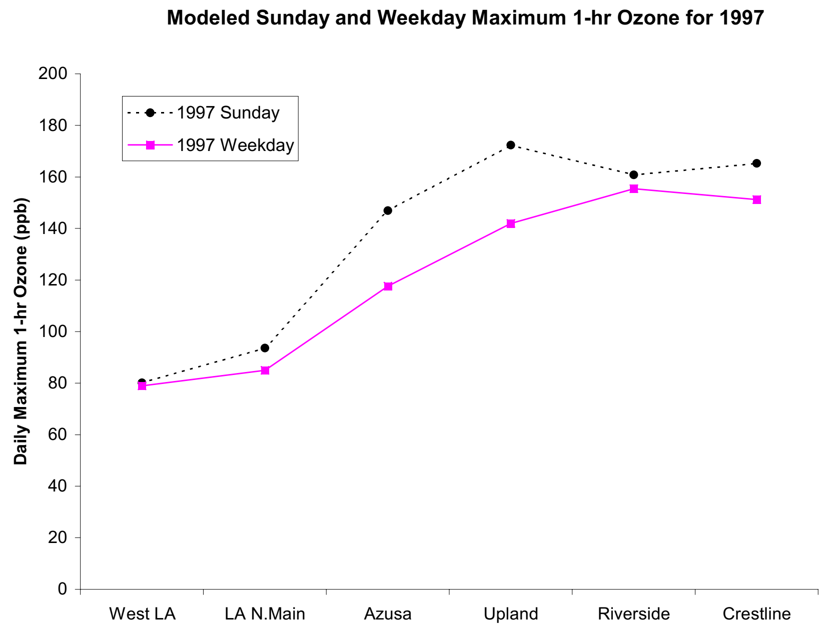


Figure 3-8. 1997 daily maximum ozone (left) and ozone difference due to changing the mass and timing of MV emissions (right) for Saturday (top) and Sunday (bottom).



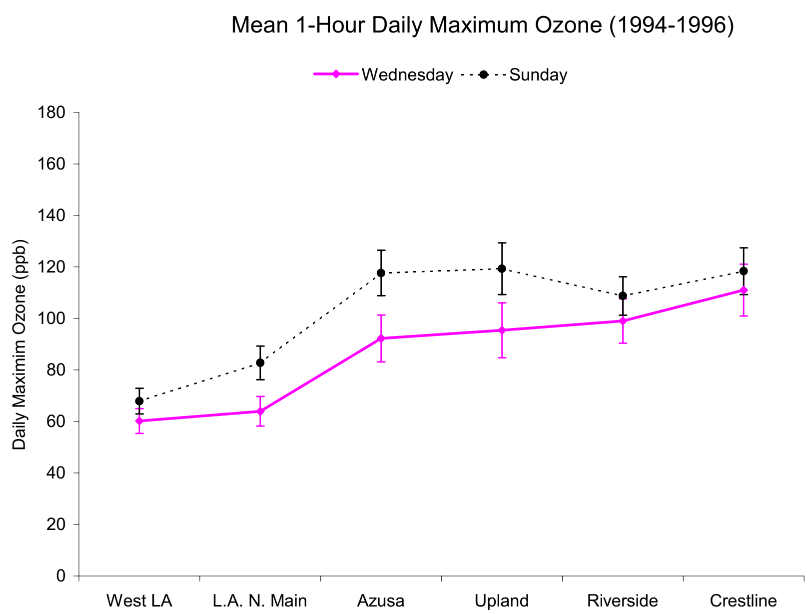


Figure 3-9. Comparison of the modeled Sunday ozone effect of changing the mass and timing of MV emissions in 1997 (top) to seasonally averaged Sunday effect for 1994-1996 (bottom) for monitoring sites across the LA basin.

ENVIRON

Ozone and Precursors at Azusa

The effects of the MV emissions mass and timing changes were investigated in detail for the location of the Azusa monitoring site. The location of the Azusa monitor is shown in Figure 1-1. Several studies have analyzed the weekend effect at Azusa, for example (Stoeckenius et al. (1998) and Fujita et al. (2002), and concluded that in the mid-1990s Azusa showed a large weekend effect typical of mid-basin sites. Therefore, Azusa was selected as a representative location for detailed comparisons of the modeled and observed weekend effects for ozone and precursors.

Modeled concentrations for the Azusa monitoring site location were determined by extracting the model results for the single 5-km grid cell that contains the monitor location. A time series of ozone at Azusa is shown in Figure 3-10 for the base case (wd_base) and mass/timing experiments (runs h1a, h2a and h2c). Changing the MV emissions timing has little impact on ozone levels on Saturday and produces a small increase in Sunday ozone. Changing the mass of MV emissions produces a small increase in ozone on Saturday and a large increase in Sunday ozone. The combined effect of changing the MV emissions mass and timing is approximately the same as the sum of the separate mass and timing changes, which overall makes the mass/timing impact similar to the mass impact alone. There is almost no difference on Monday ozone at Azusa due to the Saturday/Sunday emissions and ozone changes. These results are consistent with Figures 3-1 through 3-7 (which show the same experiments). Figures 3-1 through 3-7 show the spatial distribution of impacts whereas Figure 3-10 provides a more detailed look at the timing of impacts for one representative location.

Fujita et al. (2002) developed a combined analysis of the weekday/weekend differences in ozone and precursors at Azusa (Figure 3-11) by averaging data from the summer of 1995 for weekdays and weekends. Figure 3-11 shows the weekend effects for ozone, NO, NO_2 and CO. CO was used as a surrogate for VOC because VOC data were unavailable. Fujita et al, analyzed 1995 data whereas the modeling performed here is for 1997; but this is not expected to introduce a large bias, because there were no large changes in emissions between 1995 and 1997. For example, Los Angeles had Federal reformulated gasoline (RFG) in 1995 and California RFG in 1997 and these fuels are expected to generally have similar impacts on the ozone forming potential of vehicle emissions.

The analysis by Fujita et al. in Figure 3-11 shows that ozone “accumulation” starts earlier, proceeds faster, and reaches a higher midday peak on weekends at Azusa. Ozone accumulation starts after a morning period (about 6-9am) of high NOx levels that inhibit ozone. Both NO and NO_2 are lower on the weekend in this morning period, and the earlier/faster accumulation of weekend ozone is consistent with less “NOx inhibition” of ozone on the weekend. The morning NO/NO_2 ratio is lower on weekends because lower NOx emissions mean that a larger proportion of the NOx is converted to NO_2 by NO-O_3 titration. The lower weekend NO/NO_2 ratio accelerates weekend ozone accumulation because having more of the NOx in the form of NO_2 gives a “head start” to the ozone formation process on weekend mornings. Morning CO levels are lower on the weekend and so, assuming CO is a good surrogate for VOC, the faster weekend ozone formation is not due to higher weekend morning VOC levels. This pattern of relationships between ozone and precursors has been observed and described in previous analyses of the weekend effect for Los Angeles (e.g., Stoeckenius et. al., 1998, and led to the hypothesis that lower weekend NOx levels are the cause of the Los Angeles weekend effect (Stoeckenius et. al, 1998). The ARB later split this hypothesis into separate NOx reduction and timing hypotheses (ARB, 2001c).

The modeled weekend effects of changing the MV emissions were analyzed using an approach designed to be comparable to the ambient data analysis shown in Figure 3-11. The modeled weekend effect was taken as the difference between the weekday base case and run “h3a” where the mass and timing of on-road MV emissions were changed for Friday, Saturday and Sunday. Figure 3-12 shows the modeled ozone, NO, NO_2 and VOC at Azusa for these weekday and weekend emission scenarios. The modeled VOC concentrations should be compared qualitatively to the observed CO concentrations in Figure 3-11. Fujita et al. combined ambient data for Saturdays and Sundays to a single weekend day, and so the model results for weekend days (August 5 and 6) were similarly combined by averaging the concentrations at each hour on August 5 and 6.

The modeled weekend effect due to the MV emissions change (Figure 3-12) is strikingly similar to the observed weekend effect (Figure 3-11). Specific points of similarity are: (1) Ozone “accumulation” starts earlier, proceeds faster, and reaches a higher midday peak on weekends than weekdays. The modeled ozone peak is about 20 ppb higher on weekends which agrees well with the observed magnitude of the weekend effect at Azusa. (2) Morning (6 to 9 am) NO and NO_2 are lower on weekends than weekdays. (3) The morning (6 to 9am) NO/NO_2 ratio is lower on weekends than weekdays. (4) The modeled VOC concentrations are lower in the morning and throughout the day on weekends than weekdays, consistent with the observed CO as a surrogate for VOC.

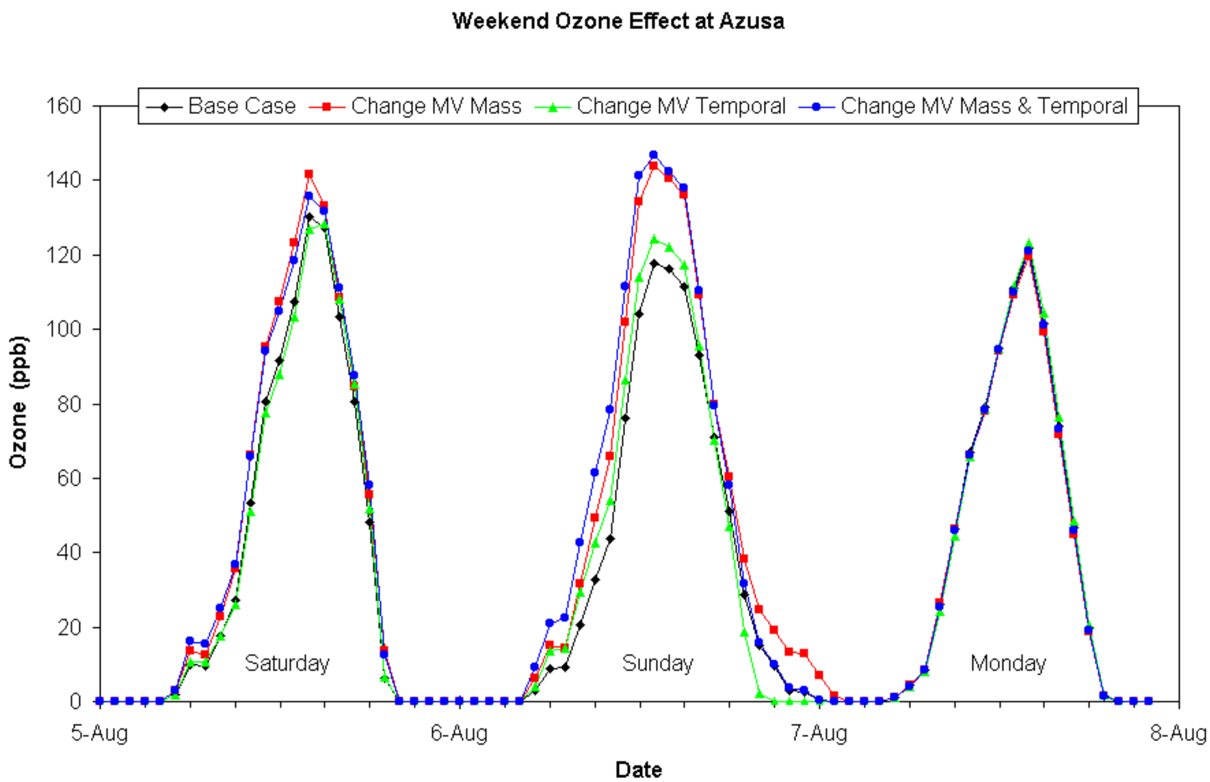
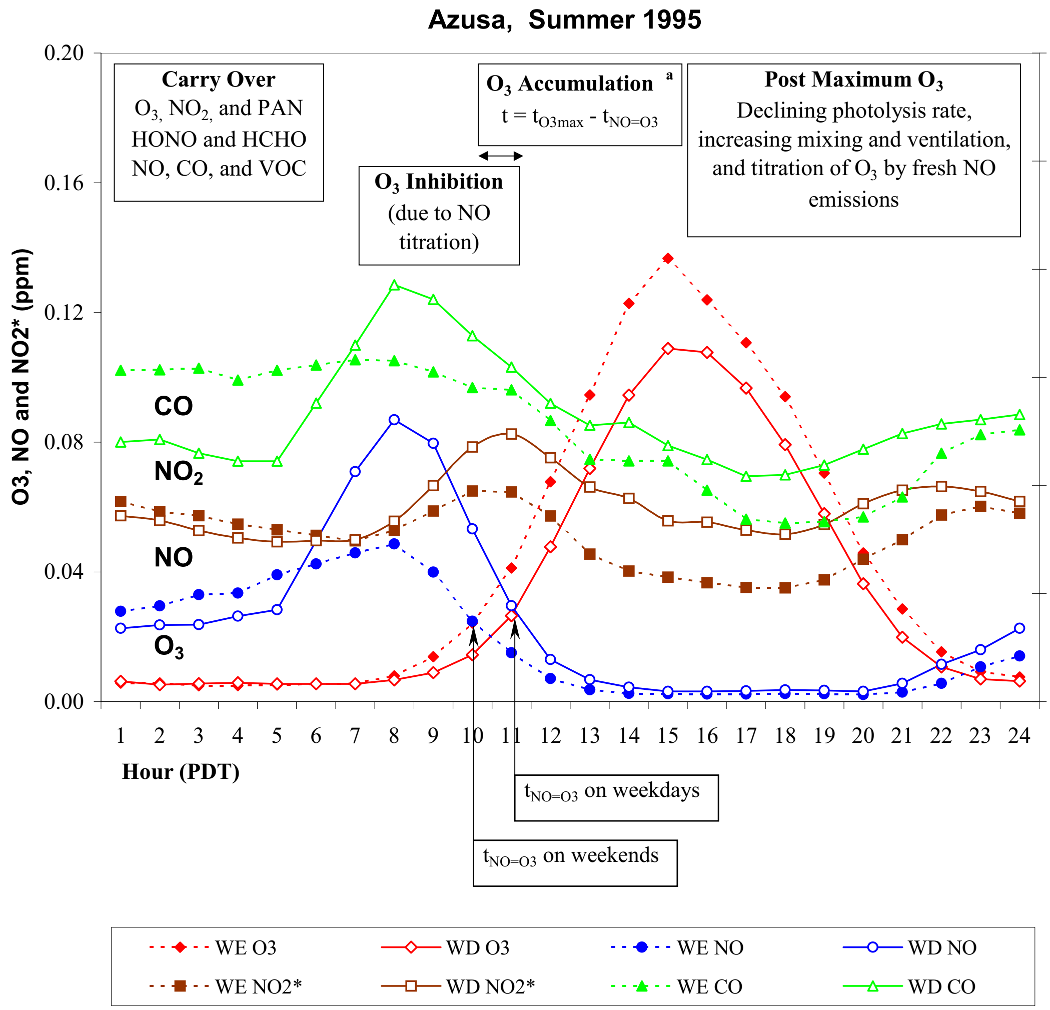


Figure 3-10. Times series of ozone at Azusa in 1997 for experiments changing the mass and/or timing of MV emissions on Saturday and Sunday.



a. O3 accumulation rate = [O3(max) - O3 ($t_{NO=O3}$)]/(t_{O3max} - $t_{NO=O3}$)

Figure 3-11. Observed weekday/weekend differences in ozone and precursors at Azusa for summer 1995 (from Fujita et al., 2002 with permission).

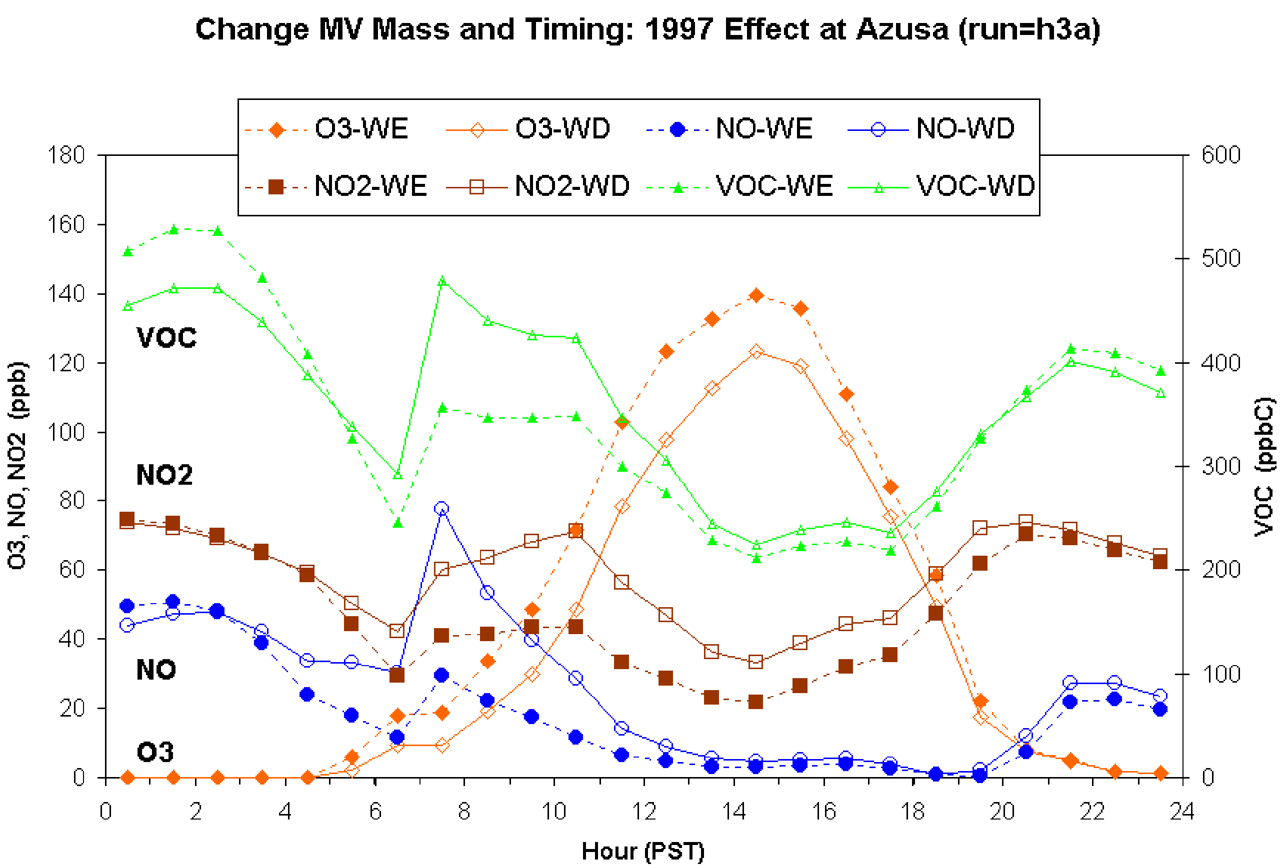


Figure 3-12. Modeled weekday/weekend differences in ozone and precursors at Azusa for 1997 (experiments h3a and wd_base).

Conclusions about Emissions Mass and Timing Effects

- The good agreement between the modeled and observed weekend effects for both ozone and precursors at Azusa demonstrate that weekend changes to the MV emission inventory provide a good explanation for the observed weekend effect.

- The good agreement for the spatial variation in modeled and observed weekend ozone effect further demonstrate that changes to the MV emission inventory provide a good explanation for the observed weekend effect.

- The modeled ozone-precursor relationships for this weekend effect show that the higher weekend ozone results from lower weekend NOx emissions. This is the same mechanism that several studies (Stoeckenius et. al., 1998, Fujita et. al., 2002) have concluded causes the observed weekend effect in Los Angeles.

- Modeling permits quantitative investigation of the relative importance of mass and timing changes and shows that the mass effect explains almost all of the Saturday ozone change and dominates the Sunday ozone change.

- The modeled impact of changing the timing of MV emissions is greater on Sunday than Saturday because the change in the timing of heavy-duty (NOx) emissions is much greater for Sunday than Saturday, relative to weekdays.

- The modeled impact of changing the mass of MV emissions is greater on Sunday than Saturday because the change in the mass of heavy-duty (NOx) emissions is much greater for Sunday than Saturday relative to weekdays.

- The weekend effect is consistent with the ARB NOx reduction hypothesis, but is not consistent with the ARB NOx timing hypothesis alone.

CARRYOVER

Several hypotheses have been developed that attribute the weekend effect to carryover of ozone and/or precursors from one day to the next. This includes carryover of ozone and precursors at the surface and aloft. For example, surface carryover could be the overnight accumulation of emissions in model layers close to the ground adding to the precursors available for ozone formation on the next morning. This might result from slow movement of air within a high emissions area or from surface wind re-circulation patterns. One type of re-circulation that may operate in the Los Angeles basin is the nocturnal land breeze carrying emissions out over the Pacific Ocean followed by a daytime sea breeze bringing the pollutants back over land. Carryover aloft is the storage or re-circulation of ozone or precursors aloft followed by mixing down the next day to influence surface ozone levels. Rather than trying to design experiments to focus on specific carryover mechanisms and hypotheses, experiments were designed to investigate the importance of carryover from any mechanism that is operative within the CAMx/MM5 models.

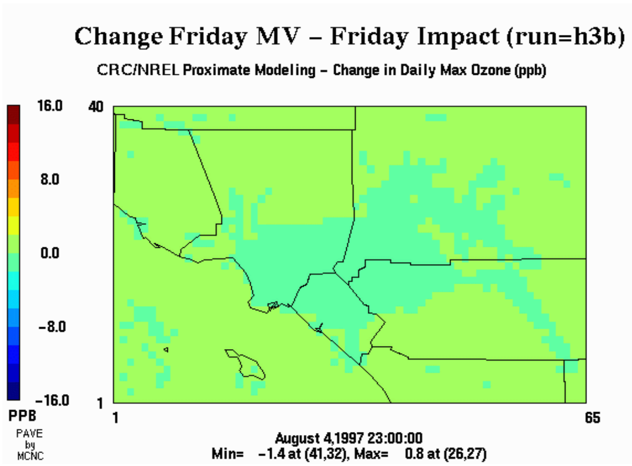
Answers from model experiments to investigate carryover are limited by the extent to which the model replicates actual carryover mechanisms that may operate in the Los Angeles basin. Since carryover results from the movement of pollutants in air, the amount of carryover in the CAMx model is primarily dependent upon the meteorological fields developed using the MM5. There are several reasons to expect that the CAMx/MM5 models can realistically represent carryover effects for Los Angeles. Carryover implies some concerted air movement pattern lasting several hours. A prognostic meteorological model, such as the MM5, inherently has the potential to capture this type of phenomenon because air motions are governed by "physical constraints" imposed by the prognostic equations. In contrast, the diagnostic meteorological models used in many other Los Angeles modeling studies are unlikely to capture any but the simplest of carryover mechanisms. This is because in diagnostic models the air motions are not fully constrained by physical equations, because the wind fields at each hour are independent of the wind fields at the preceding hour, and because there are always gaps in data used to diagnose the wind fields (e.g., aloft, over the ocean). The CAMx meteorological inputs for this study are from the MM5, and the quality of model performance strongly suggests that the meteorological inputs are describing many aspects of the meteorological simulations correctly. The CAMx results shown in Figures 3-1 through 3-7 and below show that land/sea breeze re-circulations are represented in the MM5 simulations because ozone and precursors move off shore with the land breeze then move back over land with the sea breeze. These factors suggest that the CAMx/MM5 models are a good tool to investigate the role of carryover in the LA weekend effect.

The role of carryover was investigated using the MV emission change scenarios, discussed above, because these simulations had proved to be capable of explaining the observed weekend effect and because the experiments provide opportunities to look at carryover from Friday to Saturday to Sunday. Several experiments were conducted to look at carryover between different days, which is important because both the emissions and meteorology differ by day.

Friday Impacts

Experiment h3b changed the mass and timing MV emissions on Friday alone and Figure 3-13 shows the Friday impact on daily maximum ozone, i.e, the difference between run h3b and the weekday base case on Friday. The same day impacts of the Friday MV emissions change are small decreases (up to 1.4 ppb) in ozone levels throughout the Los Angeles basin. In experiment h3b the Friday MV NOx emissions were increased relative to weekdays, so the decrease in ozone is explained by greater NOx inhibition/titration of ozone by Friday MV emissions than weekday emissions. This response is consistent with the ozone increases in response to Saturday and Sunday MV NOx emissions decreases that were discussed above.

Figure 3-14 shows the change in daily maximum ozone on Saturday due to the Friday MV emissions change, i.e., the impact of carryover from Friday to Saturday. The next day impact of the Friday emissions change is small. In most areas there is no change in ozone but there are some ozone increases (up to 2.4 ppb) near the coast in Orange County and some very small ozone decreases (up to 0.4 ppb).



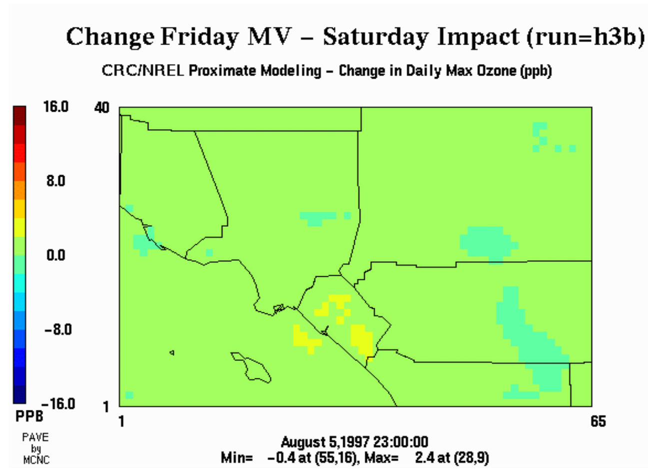


Figure 3-13. Change in Friday daily maximum ozone due to changing the mass and timing of Friday MV emissions (i.e., the same day impact).

Figure 3-14. Change in Saturday daily maximum ozone due to changing the mass and timing of Friday MV emissions (i.e., the next day impact).

The results of experiment h3b show very little impact from carryover of Friday MV emission changes on Saturday ozone levels. However, experiment h3b also shows that land/sea-breeze re-circulation patterns do exist within the CAMx/MM5 simulations. The Friday ozone decreases over the Pacific Ocean shown in Figure 3-13 are due to increased Friday MV NOx emissions being carried offshore by the nocturnal land breeze. The higher ozone levels near the Orange County coast on the next day shown in Figure 3-14 result from Friday MV emissions impacts being carried back over the land by the daytime sea breeze. This confirms the presence of a land/sea breeze re-circulation over the Pacific Ocean in the MM5/CAMx models; however, the ozone impact of this re-circulation is small relative to the ozone formation from same-day (Saturday) emissions.

Experiment h3b shows that changing the mass and timing of Friday MV emissions has little impact on ozone levels on Friday or Saturday. Therefore, neither the Friday MV emissions change, nor carryover of the Friday MV emissions change, are an important component of the weekend effect.

Carryover Between Days

Three experiments were performed to investigate ozone impacts due to carryover of MV emissions changes from Friday to Saturday to Sunday:

h3a – change Friday/Saturday/Sunday MV emissions
h2c – change Saturday/Sunday MV emissions
h4a – change Sunday MV emissions

In each experiment, the mass and timing of MV emissions were changed as described in section 2. The ozone impacts were evaluated at Azusa because this location shows a large weekend ozone effect. Figure 3-15 shows changes in ozone levels at Azusa relative to the weekday basecase. On Friday, changing Friday emissions leads to small decreases in ozone, which is consistent with Figure 3-13. On Saturday, the MV emissions changes increase ozone, and the effect is very similar regardless of whether just Saturday emissions are changed, or Friday/Saturday emissions are changed. This shows that the Saturday ozone effect at Azusa is dominated by the same day emissions change and that there is little carryover of the Friday change, which is consistent with Figure 3-14. On Sunday, the MV emissions change increases ozone even more than for Saturday, and the effect is very similar regardless of whether just Sunday emissions were changed, or emissions were also changed on the preceding days. This shows that the Sunday ozone effect at Azusa is dominated by the same day emissions change, that there is little carryover of the Saturday change to Sunday, and negligible carryover of the Friday change to Sunday. Figure 3-15 also shows that there is little carryover of effects from Sunday to Monday, as shown previously in Figures 3-7 and 3-10. To generalize from Figure 3-15, these experiments show that ozone impacts due to carryover from the previous day are small relative to same day impacts, and that carryover from 2 days previously is negligible.

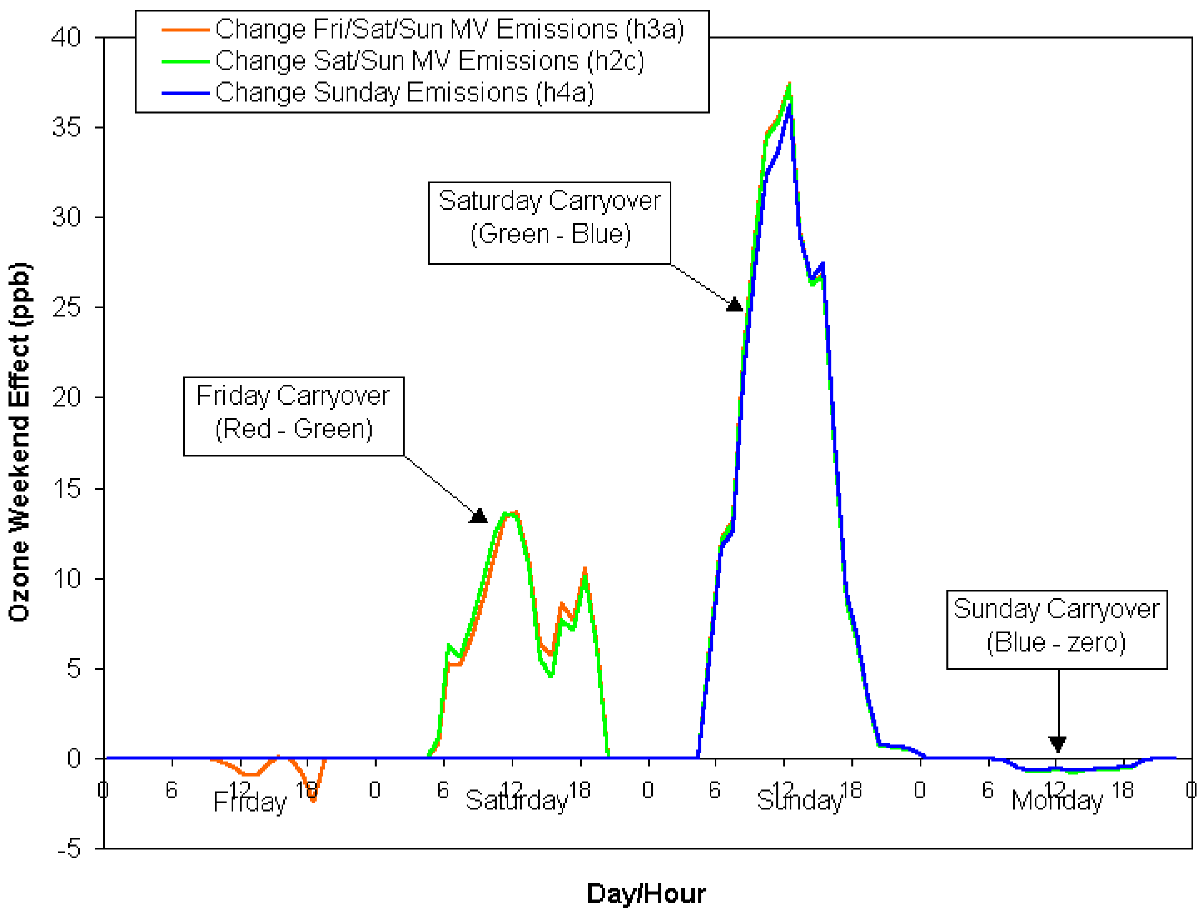


Figure 3-15. Carryover of ozone differences at Azusa due to changing the mass and timing of MV emissions in 1997.

Conclusions on Carryover

The main conclusion from the carryover experiments is that ozone impacts are primarily a "same day" effect for MV emissions changes. This suggests strongly that carryover is not an important factor in the Los Angeles weekend effect. This finding encompasses all potential mechanisms for carryover of MV emissions changes, surface and aloft, ozone and precursors, because the experiment design includes all potential mechanisms. This result for MV emissions changes is likely to be a good indicator that carryover is generally less important than same day effects, because the MV emissions changes impacted a large emissions category with a widespread distribution of emissions.

SPATIAL SHIFT IN VEHICLE EMISSIONS

The experiments described above investigated the impacts of weekend changes to the mass and timing of MV emissions. It is likely that the spatial distribution of MV emissions also differs on weekdays and weekends. For example, there is less commute driving on the weekend, but more household related (e.g., shopping) and recreational driving. The freeway weigh-in-motion vehicle count data were analyzed, as described in Section 2, to investigate whether they could provide a weekend difference in the spatial distribution of emissions that was suitable for a sensitivity test. Modified spatial distributions of MV emissions were developed for Friday, Saturday and Sunday and modeled in runs h2e and h2f. It is not suggested that these spatially redistributed emissions are a complete or accurate representation of the changes that actually occur in Los Angeles on weekends, but rather they provide a simple modeling test to investigate whether this effect is potentially important.

Experiment h2e looked at the effect of just the spatial shift in MV emissions, and Figure 3-16 (left) shows the change in daily maximum ozone on Saturday due to the spatial shift in MV emissions relative to the weekday base case. There are increases in maximum ozone throughout the Los Angeles basin, and the pattern of increases is similar to impact of the MV emissions mass and timing change shown in Figure 3-8. This is because both the spatial and mass/timing changes lower the NOx emissions in the high MV emission density areas of the western and central LA-basin. Consequently, the assumed spatial redistribution of emissions on the weekend increases ozone in the Los Angeles basin by the same mechanism as the MV emissions mass/timing change, i.e., less NOx inhibition of ozone on the weekend. Experiment h2f looked at the impact of the weekend spatial shift in combination with the mass/timing change and, not surprisingly, this leads to larger weekend ozone increases than either the spatial shift or the mass/timing change alone.

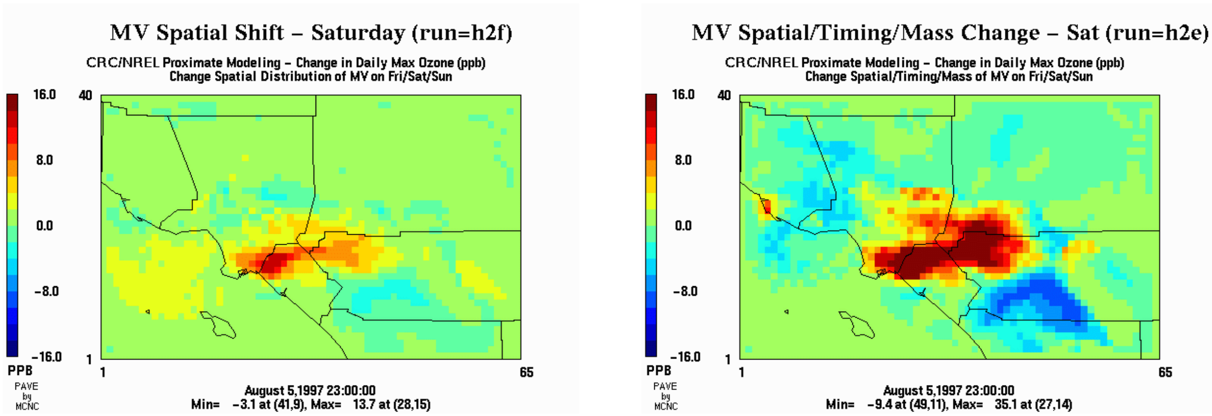


Figure 3-16. Impact of changes in the spatial distribution of MV emissions on Saturday maximum ozone. Spatial shift alone (left) and spatial shift combined with mass and timing change (right).

Conclusions on the Spatial Shift in Vehicle Emissions

The results of the simple experiments performed here show that spatial redistribution of the MV emissions could be an important contributor to the weekend effect in Los Angeles. However, the actual redistribution of emissions modeled here should be considered a sensitivity test rather than an accurate representation of the actual weekend differences in the spatial distribution of MV emissions. A more refined analysis might produce different emissions changes and ozone impacts. An improved modeling approach would be to develop a weekend travel demand model for Los Angeles and use this to develop weekend MV emission inventories for photochemical modeling.

IMPACT OF AEROSOLS

Changes to the atmospheric aerosol burden between weekdays and weekends have been proposed as a potential cause of the weekend effect. The proposed mechanism is that decreases in amount of aerosols on weekends increase the rates of photolytic reactions and thereby increase ozone. Consideration of this hypothesis is complicated by the complexity of the relationships between aerosols and photolysis rates, and between photolysis rates and ozone concentrations, making modeling an ideal tool to investigate this hypothesis. The relationship between aerosols and photolysis rates is complex because aerosols can absorb radiation and thereby attenuate photolysis rates (particularly black carbon particles), but aerosols also scatter radiation which can increase or decrease photolysis rates depending upon solar zenith angle, height above ground and other factors. The ARB has developed a hypothesis called “soot and sunlight” which focuses on one part of the aerosol effect, namely the absorption of solar radiation by black carbon (soot) particles.

Data on aerosol loading were collected during the summer of 1997 as part of the SCOS field study and the ARB sponsored analysis and modeling of these data (Vuilleumier et al., 2000). The optical depth (OD) due to aerosols at 340 nm at Riverside in the summer of 1997 was in the range 0.2 to 1.0, but there is no information on weekday/weekend differences in OD in the report by Vuilleumier et al. (2000). A sensitivity experiment was designed to evaluate whether aerosol effects could explain the observed weekend effect. The experiment assumed that the aerosol OD changed from 1.0 on weekdays to 0.2 on weekends. No changes were made to the spatial distribution or composition of aerosols between the weekday and weekend. This experiment almost certainly overestimates the change in aerosol loading between weekdays and weekends.

CAMx treats photolysis rates as an input parameter that depends upon photolysis reaction, solar zenith angle, height above ground, surface UV albedo, stratospheric ozone column and aerosol OD. This detailed information is input to CAMx via a multi-dimensional lookup table of photolysis rate data that is prepared for the specific conditions of the modeling episode. This approach is designed to allow a detailed treatment of photolysis rate effects while moving the photolysis rate calculation to a pre-processing step where the level of calculation detail is not restricted by computational limitations. The amount of CPU time devoted to the photolysis rate calculation for this episode is comparable to CAMx model run time. Photolysis rates were calculated using the Tropospheric visible Ultra-Violet (TUV) model developed by the National Center for Atmospheric Research (Madronich, 1993 and 2002). TUV is a state-of-the-science radiation scattering model that is designed to be used for photolysis rate calculations and includes the capability to model the effects of aerosols.

Figure 3-17 shows the sensitivity of the NO_2 photolysis rate, J(NO_2), to changing the aerosol OD from 0.2 to 1.0 as a function of zenith angle and height above ground level. The figure shows the ratio of J(NO_2) for an OD of 1.0 relative to 0.2, so values less than one indicate that increased aerosol loading attenuates J(NO_2). At ground level, increased aerosol loading attenuates J(NO_2) at all zenith angles, although the effect is small when the sun is near overhead (midday) and larger when the sun is near the horizon (morning and evening). However, above the surface at 640m or 1.84 km, increased aerosol increases J(NO_2) in the middle of the day but decreases J(NO_2) near sunrise and sunset. A simple explanation for these results is that less absorption by aerosols tends to increase J(NO_2) whereas less scattering by aerosols tends to decrease J(NO_2), and the overall change in J(NO_2) is the net effect of these processes. Figure 3-17 illustrates the complexity of the relationships between aerosols and photolysis rates and cautions against over-simplification in considering the effect of aerosols on ozone formation.

Figure 3-18 shows the Saturday and Sunday impacts on maximum ozone of changing the weekend aerosol loading from an OD of 1.0 to 0.2 (less aerosol on the weekend). There are increases in maximum ozone of up to about 5 ppb in parts of the LA basin and larger increases in Ventura County. The distribution of ozone increases is not consistent with expectations that the largest weekend effect should be associated with high ozone levels in the mid LA basin. The magnitude of ozone increases within the LA basin is much smaller than the observed weekend effect.

Figure 3-19 shows the photolysis rate impact on ozone and precursors at Azusa averaged over Saturday and Sunday. Figure 3-19 can be compared to the observed weekend effect for Azusa shown in Figure 3-11 and discussed above. Comparing Figures 3-19 and 3-11 shows that the aerosol impact produces the wrong diurnal pattern of ozone changes (no change at midday, small weekend increases in the morning and afternoon) and the wrong changes in precursor concentrations (almost no changes).

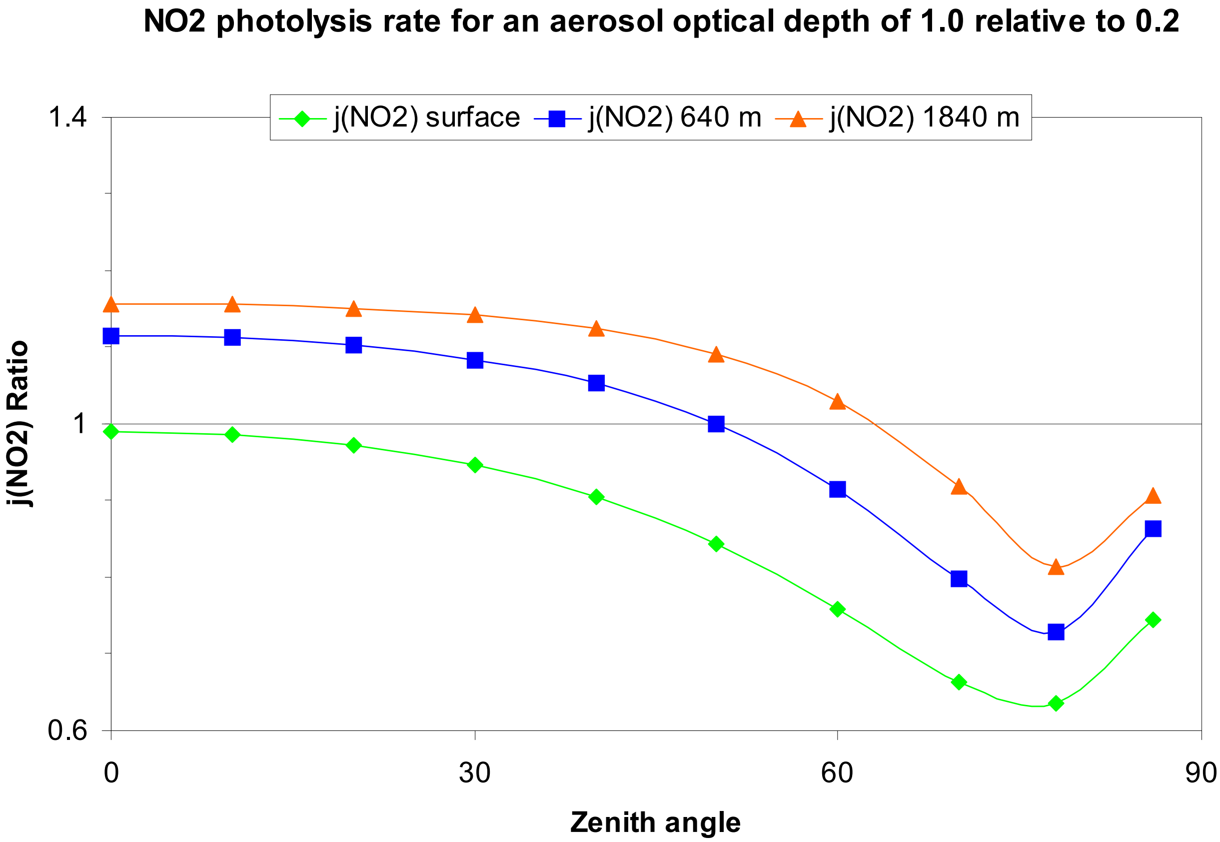


Figure 3-17. Sensitivity of the NO_2 photolysis rate to aerosol optical depth as a function of solar zenith angle and height above ground level.

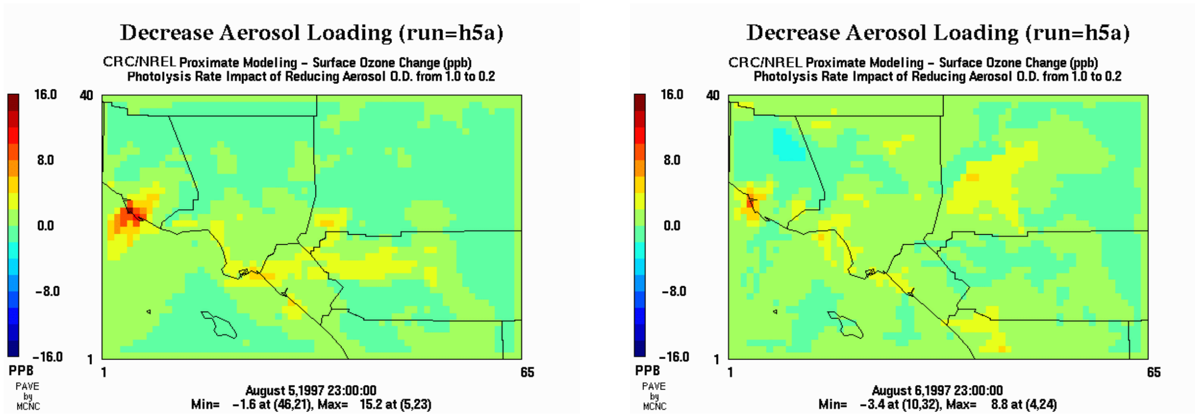


Figure 3-18. Difference in 1997 daily maximum ozone on Saturday (left) and Sunday (right) due to decreasing the aerosol loading from an optical depth of 1.0 to 0.2.

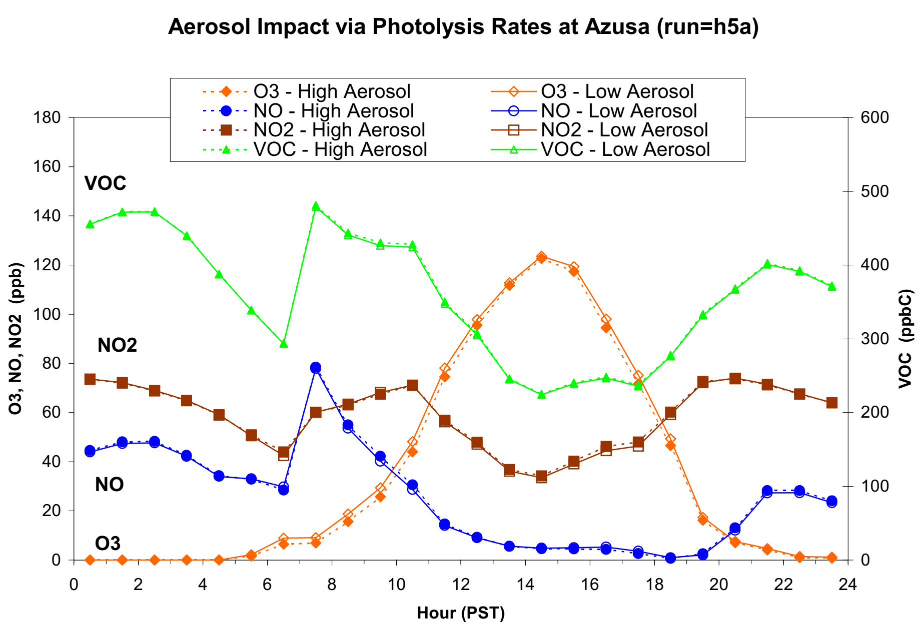


Figure 3-19. Modeled weekday/weekend differences in ozone and precursors at Azusa in 1997 due to decreasing the aerosol optical depth from 1.0 to 0.2.

Conclusions on the Impacts of Aerosols

Available data were insufficient to estimate the weekday/weekend differences in the amount and/or composition of atmospheric aerosol in Los Angeles, so a sensitivity test was conducted changing the aerosol loading from near maximum to near minimum summer levels observed at Riverside in 1997. This sensitivity test should be an upper limit to the magnitude of weekday weekend differences in aerosol loading, but does not account for effects due to weekday/weekend differences in aerosol composition or distribution. The effect on the photolysis rates was modeled using a state-of-the-science radiative transfer model of the atmosphere (the TUV model), which demonstrated that decreasing the aerosol loading can decrease or increase photolysis rates depending upon the solar zenith angle and height above the ground. This complex response is a result of the competing effects of absorption and scattering of radiation by aerosols. This finding cautions against over-simplification in considering the effect of aerosols on ozone formation.

The results of the aerosol impact experiment are inconsistent with changes to the total amount of aerosols being the main cause of the weekend effect. The aerosol impact was directionally correct for ozone, but too small in magnitude for the ozone change, and had the wrong temporal profile of ozone changes. The aerosol impact produced little change in precursor concentrations, which is inconsistent with the observed weekend effect.

CHEMICAL MECHANISM UNCERTAINTY

The modeling experiments that changed the mass and timing of MV emissions, described above, show that observed weekend effect for the mid-1990s is well-explained by lower weekend MV NOx emissions. The response of the modeling system to NOx reduction is closely related to the properties of the chemical mechanism and might be influenced by uncertainties in the chemical mechanism. Certain basic attributes of ozone-NOx-VOC chemistry are well established (NRC, 1991), such as:

- The existence of VOC and NOx limited regimes.
- Titration of ozone by fresh NO emissions.
- A NOx inhibition effect in strongly VOC limited regimes.

Current understanding of ozone formation is embodied in condensed chemical mechanisms such as CB4 and SAPRC99 that are used to develop ozone control plans using photochemical models such as CAMx. Both the CB4 and SAPRC99 mechanisms exhibit all of the attributes listed above; however, there are differences in the formulations of these mechanisms. Experiments were performed to determine whether the modeled effects of changing weekend MV emissions are different using the SAPRC99 mechanism rather than CB4.

The CB4 mechanism was developed in late-1980s (Gery et al., 1989) and has a long history of successful application in ozone modeling studies. There have been updates to the mechanism, specifically for PAN chemistry, radical termination reactions and isoprene chemistry, as described in the CAMx User's Guide (ENVIRON, 2000). Some parts of the mechanism are out-dated in light of more recent data for specific reaction rates and reaction mechanisms. It is difficult to assess how these uncertainties impact the overall performance of the mechanism without updating the mechanism and repeating the evaluation against smog chamber data. A reevaluation of CB4 was undertaken at the University of North Carolina, and a preliminary version of the work was completed and called CB-IV_99 (see http://airsite.unc.edu/soft/cb4/CB4docs.html). However, this work is being re-considered, due to changes to an important rate constant update, and does not yet provide a useable update for CB4.

Dr. Bill Carter developed the SAPRC chemical mechanisms at the University of California at Riverside. The 1999 version of this mechanism (Carter, 2000) was released in CAMx version 3.1 (ENVIRON, 2002). The SAPRC99 mechanism provides an alternative to CB4 that is based on more recent experimental data, includes more species and a larger number of reactions, uses a different approach for lumping VOCs, and has been evaluated against smog chamber data like CB4. SAPRC99 has been used much less extensively than CB4 for ozone modeling studies to date.

The SAPRC99 emission inventories for this study were provided by the ARB and the only difference from the CB4 emission inventories is in the VOC chemical speciation step. Model performance was evaluated using SAPRC99 as described in section 2. Briefly, SAPRC99 produced much higher ozone levels than CB4 for the August 3-7, 1997 episode; consequently, SAPRC99 model performance is poor and falls well short of the accepted goals. This should not be interpreted to mean that “CB4 is right and SAPRC99 is wrong,” since this study provides only one comparison. SAPRC99 may perform as well or better than CB4 with alternate model inputs for this episode or for different episodes. However, the poor model performance with SAPRC99 must be considered in evaluating the results of the SAPRC99 weekend effects experiments.

The impact of changing the chemical mechanism was evaluated using experiments that changed the mass and timing of MV emissions on Saturday and Sunday. With the CB4 mechanism, the mass and timing change (experiment h2c) provide a good description of the observed weekend effect. Experiment h2c was repeated using SAPRC99 as experiment h2d. The 1997 weekday base case was also re-run with SAPRC99 and the daily maximum ozone levels with the CB4 and SAPRC mechanisms for the 1997 weekday base case scenarios are compared in Table 3-2. This table shows the much higher ozone levels generated by SAPRC99 than CB4.

Table 3-2. Daily maximum ozone levels (ppb) with the CB4 and SAPRC mechanisms for the 1997 weekday base case scenarios.

	CB4	**SAPRC99**
4-Aug	148.2	199.4
5-Aug	168.4	206.3
6-Aug	174.9	223.5
7-Aug	163.0	203.5

The changes in daily maximum ozone in the MV emissions mass and timing change experiments are compared in Figure 3-20. The Saturday changes are shown at the top and Sunday changes are shown on the bottom, while CB4 results are shown on the left and SAPRC99 results are shown on the right. The CB4 and SAPRC99 results for each day are similar in the locations and magnitudes of ozone increases and decreases on both Saturday and Sunday. Ozone increases occur in the upwind areas of the Los Angeles basin (coastal and mid-basin), whereas decreases occur in downwind areas (inland). As discussed above, this pattern is explained by the upwind areas being more VOC sensitive and the downwind areas more NOx sensitive. Some difference between the CB4 and SAPRC99 results is apparent on both days in that the transition from areas of ozone increases to decreases occurs closer to the coast with SAPRC99 than CB4. This difference is explained by the SAPRC99 mechanism being "more reactive" than CB4, meaning that ozone formation is more rapid and reaches higher levels further upwind with SAPRC99 than CB4. The more rapid ozone formation is accompanied by faster oxidation of NOx to NOz and therefore the transition from VOC sensitive to NOx sensitive ozone formation also occurs further upwind with SAPRC99 than CB4. Analysis of observed weekend ozone differences in the mid-1990s, shown in Figure 3-9, shows that weekend ozone increases extended all across the Los Angeles basin from upwind West LA to downwind Riverside and Crestline, and the CB4 model results shown in Figure 3-9 are in good agreement with this pattern. The corresponding SAPRC99 experiment results (Figure 3-21) show poorer agreement with observations than CB4 because weekend ozone decreases are predicted for the downwind sites at Riverside and Crestline, contrary to the observations.

The SAPRC99 weekend effect on ozone and precursors for the Azusa monitor location is shown in Figure 3-22. This figure may be compared to the observed effects in Figure 3-11 and the CB4 results in Figure 3-12. (Figure 3-12 shows a slightly different scenario for CB4, run h3a, in which Friday emissions were changed as well as Saturday/Sunday emissions, but this is not a major difference because carryover from Friday is a small effect, as discussed above). The ozone levels are much higher at Azusa with SAPRC99 than CB4, as shown previously in Table 3-2. In spite of the large differences in total ozone levels, the weekend ozone differences are very similar for the SAPRC99 and CB4 experiments. The precursor concentrations and weekend precursor differences are also very similar with CB4 and SAPRC99. Thus, although the SAPRC99 and CB4 mechanisms show substantial differences in the amount of ozone formation, and some differences in the distribution of VOC and NOx sensitive areas within the Los Angeles basin, both mechanisms provide the same chemical explanation for weekend ozone increases at Azusa. The SAPRC99 mechanism shows the same ozone titration and inhibition effects by NOx as the CB4 mechanism. Both SAPRC99 and CB4 show that reduced weekend NOx emissions lead to less NOx inhibition of ozone and higher weekend ozone for most of the Los Angeles basin in 1997.

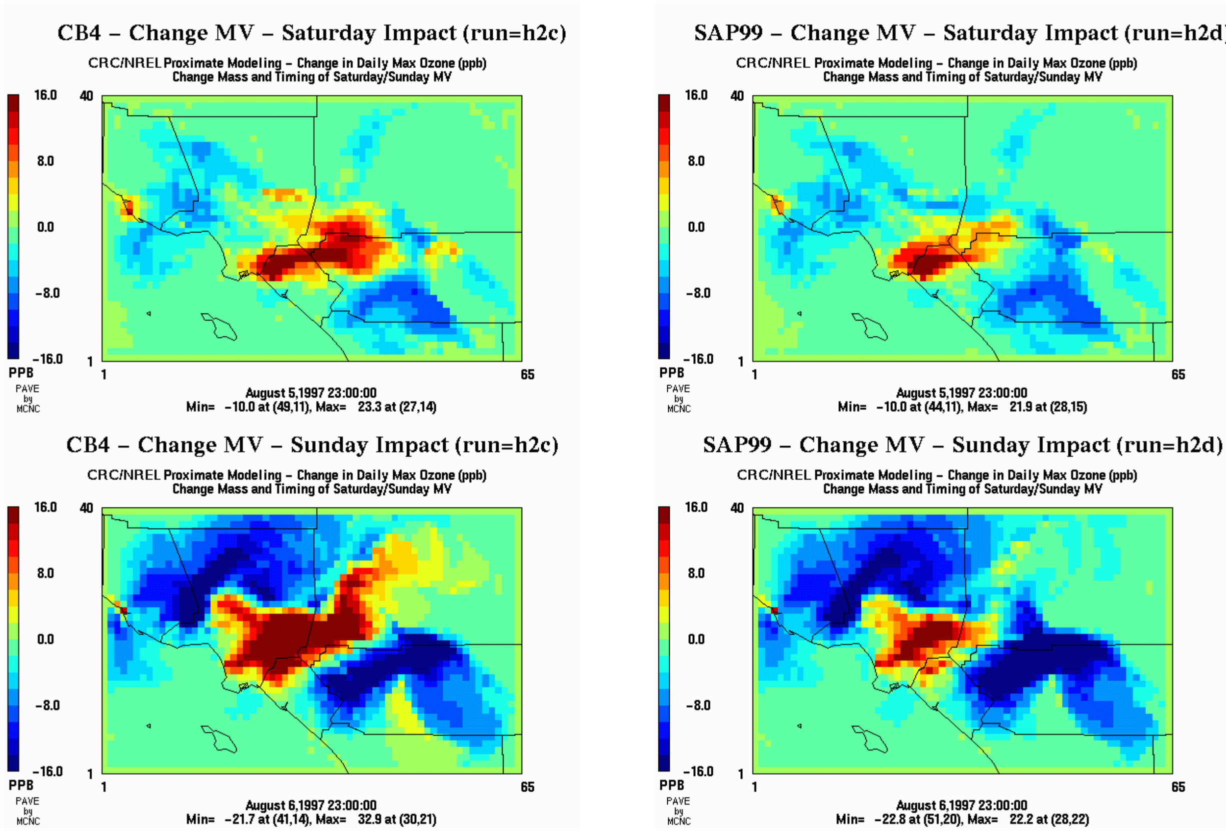


Figure 3-20. Difference in 1997 daily maximum ozone on Saturday (top) and Sunday (bottom) due to changing the mass and timing of MV emissions modeled with the CB4 mechanism (left) and the SAPRC99 mechanism (right).

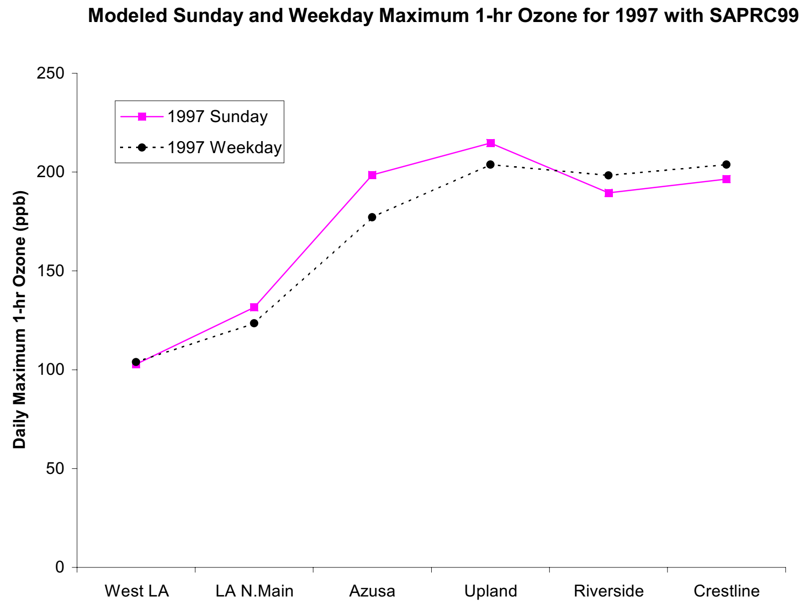


Figure 3-21. SAPRC99 modeled Sunday ozone effect of changing the mass and timing of MV emissions in 1997 for monitoring sites across the LA basin.

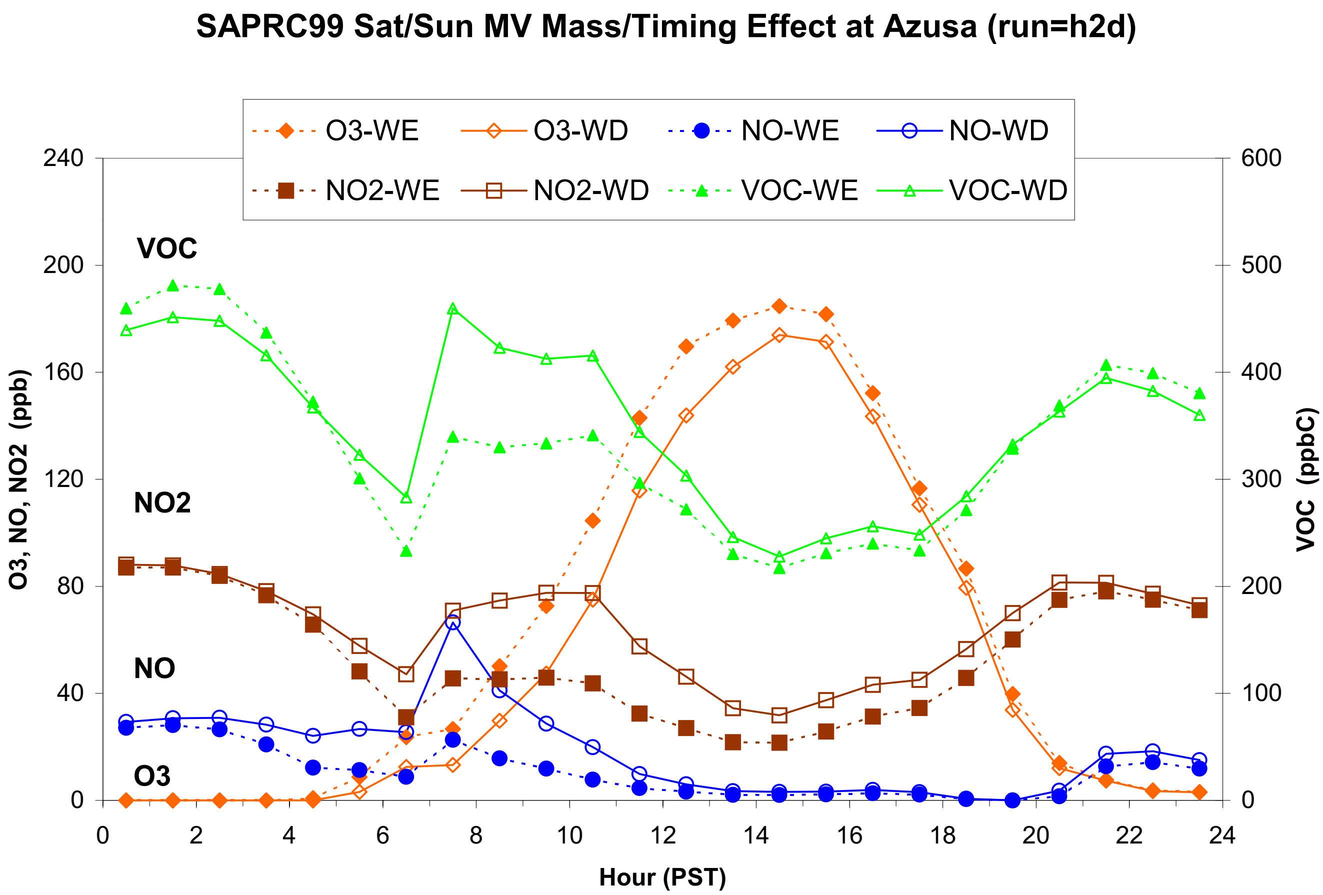


Figure 3-22. SAPRC99 modeled weekday/weekend differences in ozone and precursors at Azusa for 1997 (experiments h2d and wd_base_S99).

Conclusions on Uncertainties in Chemical Mechanisms

The SAPRC99 mechanism produced much higher ozone levels than the CB4 mechanism. The SAPRC99 base case model performance was poor and failed the expected performance goals, in contrast to the good model performance obtained using CB4 (see Section 2). These results show that SAPRC99 has substantial differences from the CB4 mechanism, but model performance results for a single episode should not be used to determine whether one mechanism is more "correct" than another.

The main features of the Saturday and Sunday ozone responses to changing the mass and timing of MV emissions in 1997 are the same with CB4 and SAPRC99: ozone increases occur across most of the Los Angeles basin and ozone decreases occur in some inland (downwind) areas. There are differences in the spatial extent of VOC and NOx sensitive areas between CB4 and SAPRC99, and the CB4 results are more consistent with the observed weekday/weekend ozone differences.

For the large areas of the Los Angeles basin that showed ozone increases, the CB4 and SAPRC99 mechanisms are consistent in showing that the ozone increases resulted from reduced weekend NOx emissions leading to less NOx inhibition of ozone and therefore higher weekend ozone.

The main features of the ozone response to MV emissions changes in 1997 are robust against a large change in the chemical mechanism; i.e., from CB4 to SAPRC99. These features persisted in the SAPRC99 model results even though the underlying model performance was substantially degraded with SAPRC99. This is because the ozone response to weekend NOx emission changes is based on very fundamental attributes of the ozone-NOx-VOC chemical mechanisms (namely, ozone titration by NO, NOx inhibition of ozone formation, and VOC versus NOx sensitivity in ozone formation) that are central to both the CB4 and SAPRC99 mechanisms.

CHANGES IN WEEKEND EFFECTS ACROSS YEARS

Analyses of ambient data for Los Angeles have shown that the weekend effect has changed over time, as discussed in Chapter 1. Therefore, modeling experiments were performed for 1987 and 2010 emission levels for comparison with the 1997 experiments already discussed. Investigating the ability of the modeling system to reproduce historical changes in the weekend effect probes the base case emission inventories and the weekend emission changes. Success in describing weekend effects for several different years would build confidence in the model explanations of the weekend effect.

There is also interest in looking at how the weekend effect changes for estimated future emission levels. One important aspect is to evaluate how important the weekend effect will be as ozone levels in Los Angeles approach the level of the 1-hr ozone standard (124 ppb) and attainment/nonattainment status becomes more sensitive to ozone changes of the magnitude of the weekend effect. There also is interest in the control strategy implications of present and future weekend effects as real-world indicators of the VOC/NOx sensitivity of ozone.

The usefulness of modeling results depends upon uncertainties in the emission inventories. This is especially true for future year results because there are greater uncertainties in future year emission inventories:

- Future year inventories inherit uncertainties from base year inventories.
- Future year emissions projections contain additional uncertainties from assumed activity growth and control strategy effectiveness.

Changes in modeled weekend effects from 1987 to 2010 were investigated for the scenario that changed the mass and timing of onroad mobile (MV) emissions on Friday-Sunday, namely experiment h3a. This scenario was selected because experiment h3a was very successful in describing the observed weekend effect in the mid-1990s, as described above. The 1987 and 2010 emission inventories were developed from the most recent emissions data available for Los Angeles from the ARB (for 1987) and SCAQMD (for 2010), as described in Section 2.

Changes in Emissions and Ozone Levels

The maximum Saturday ozone levels and Saturday weekend effects for 1987, 1997 and 2010 are compared in Figure 3-23. The peak ozone levels for August 5-7th in the 1987, 1997 and 2010 weekday base case simulations are summarized in Table 3-3. The base case ozone levels decrease from 1987 to 1997 to 2010 in response to decreasing anthropogenic emission levels. The trends in total anthropogenic emissions of VOC and NOx over these years are shown in Table 3-4. The biogenic emissions were held constant across all years. From 1987 to 1997 there were large decreases in the VOC emissions and much smaller decreases in NOx emissions, strongly suggesting that the ozone decreases from 1987 to 1997 are primarily attributable to reductions in VOC emissions.

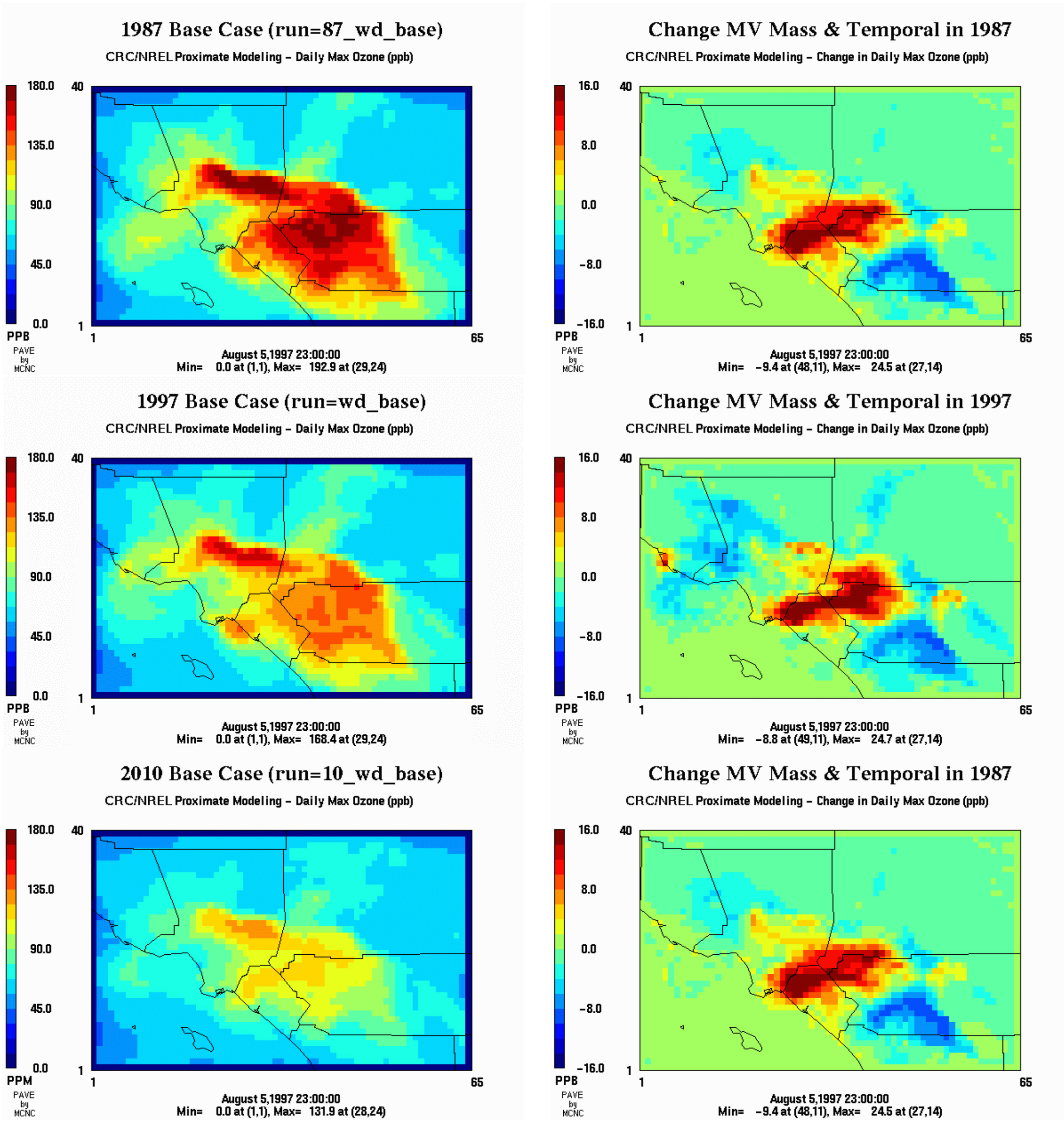


Figure 3-23. Saturday effect on daily maximum ozone due to changing the mass and timing of MV emissions in 1987 (top), 1997 (middle), and 2010 (bottom).

Table 3-3. Peak ozone (ppb) for the weekday base case in 1987, 1997 and 2010.

	1987	1997	2010
5-Aug	192.9	168.4	131.9
6-Aug	228.0	174.9	137.2
7-Aug	191.0	163.0	127.7

Table 3-4. Trends in total weekday anthropogenic ROG and NOx emissions between 1987 and 2010 expressed as ratios to the 1997 emission levels[1,2].

Year	ROG	NOx
1987	2.02	1.21
1997	1.0	1.0
2010	0.32	0.38

1. The actual emission totals are shown in Figure 2-5.
2. Wildfire emissions are not included.

The relative decreases in anthropogenic NOx and VOC emissions from 1997 to 2010 were similar. Therefore, additional analyses would be required to determine the relative contributions of VOC and NOx emission reductions to the modeled reductions in ozone between 1997 and 2010. The modeled peak ozone levels in 2010 are still above the level of the 1-hr ozone standard. The 2010 base case for this study is not expected to show attainment of the 1-hr ozone standard even though the anthropogenic emissions were based on the most recent AQMP for Los Angeles. This is because the episode and meteorology are different from the AQMP modeling, the biogenic VOC emissions are different (higher) than in 1999 AQMP modeling, and the MV emissions were adjusted higher from EMFAC7G to EMFAC2000.

There are differences in the modeled Saturday effect of changing the mass and timing of MV emissions between 1987, 1997 and 2010, as shown in Figure 3-23. Similar differences across years also occurred for Sunday. The results of experiment h3a for 1997 have already been discussed above, and they suggest that the weekend ozone response should be related to the VOC/NOx ratio. This is because the weekend ozone increases result from lower weekend NOx emissions causing less ozone inhibition. The weekday total anthropogenic emission VOC/NOx ratios are shown in Table 3-5 for 1987, 1997 and 2010. Biogenic emissions were excluded from these ratios because a large fraction of the biogenic emissions occur outside the LA basin in forested areas of high terrain. There was a large decrease in VOC/NOx ratio (4.55 to 2.71) between 1987 and 1997 and a small decrease in VOC/NOx ratio (2.71 to 2.28) between 1997 and 2010. The modeled 6-9am VOC/NOx ratios at Azusa are shown in Table 3-6. The modeled weekday inventory (Table 3-5) and atmospheric (Table 3-6) VOC/NOx ratios are very similar for 1987, but differ somewhat for 1997 and substantially for 2010. This reflects increasing influence of biogenic emissions, boundary conditions and chemical reactions in 2010 and 1997 relative to 1987.

Table 3-5. VOC to NOx ratios for weekday anthropogenic emissions in 1987, 1997 and 2010.

Year	VOC/NOx MoleC/Mole
1987	4.55
1997[1]	2.71
2010	2.28

1 Excluding wildfire emissions in 1997.

Table 3-6. Modeled morning (6-9am) VOC to NOx ratios[1] at Azusa for 1987, 1997 and 2010 on weekdays and weekends[2].

Year	Weekday VOC/NOx (ppbC/ppb)	Weekend VOC/NOx (ppbC/ppb)
1987	4.55	5.93
1997	3.71	5.41
2010	6.11	9.20

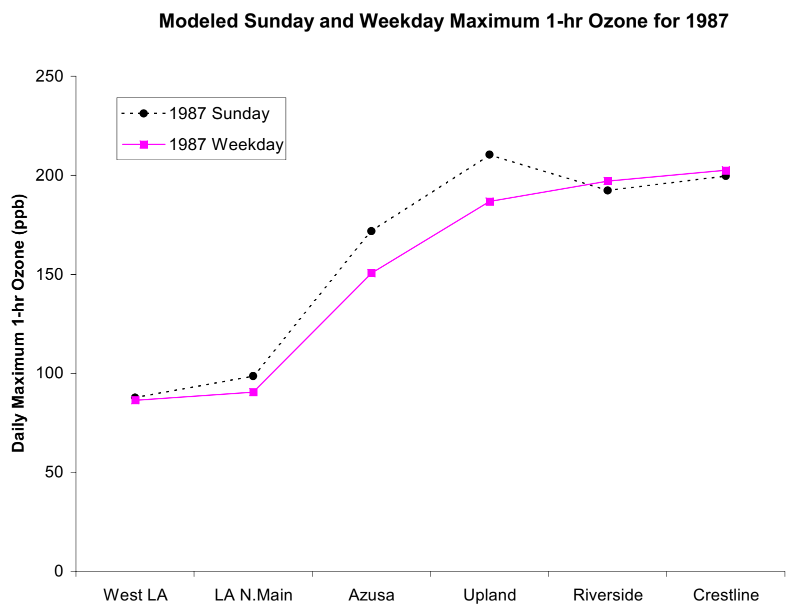
1. Ratios are calculated as the average VOC for August 5th and 6th divided by the average NOx for August 5th and 6th.
2. Weekday values are for the weekday base case and weekend values are for the "h3a" scenarios changing the mass and timing of MV emissions.

1987 Weekend Effect

The spatial variations in modeled and observed weekend effects in 1987 are compared in Figure 3-24. This figure compares modeled and observed weekday/weekend ozone differences at six sites across the Los Angeles basin from West (upwind) to East (downwind). The observed weekend effect is characterized by the Sunday and Wednesday maximum ozone levels for the summers of 1986 to 1989, whereas the modeled effect is characterized by the 87_wd_base and 87_h3a maximum ozone levels for August 6th (Sunday). In 1987, the observed weekend effect was an increase in ozone at the upwind sites (West LA to Azusa) and a decrease in ozone at the downwind sites (Upland to Crestline). This is consistent with the upwind areas being VOC sensitive and the downwind areas NOx sensitive, such that weekend decreases in MV NOx emissions produce ozone increases at the upwind sites and ozone decreases at the downwind sites.

The modeled weekend effect for 1987 shows some similarities to the observed effect just described. Weekend ozone decreases are modeled at the far downwind sites, Riverside and Crestline, but they are relatively small compared to the observed decreases at these sites. Conversely, the modeled weekend ozone increases at upwind sites are relatively large compared to the observed effects and they extend too far East, from West LA to Upland rather than West LA to Azusa. This pattern of differences suggests that the 1987 model has too large an area of VOC sensitivity and too small an area of NOx sensitivity. This is consistent with the VOC/NOx ratio in the 1987 emission inventory being too low. It would be interesting to conduct additional experiments for 1987 with a higher VOC/NOx ratio (higher VOC emissions, lower NOx emissions, or a combination) to see if this resulted in better agreement in Figure 3-24.

The observed weekend effect for 1986-1989 shown in Figure 3-24 is different from the weekend effect observed for 1994-1996 shown in Figure 3-9. By the mid-1990s, weekend ozone increases were observed all across the Los Angeles basin from West LA to Crestline, suggesting that the most of the Los Angeles basin had become VOC sensitive by the mid-1990s. The model results for 1997 shown in Figure 3-9 are very similar to the observations for the mid-1990s confirming that experiment h3a describes the observed weekend effect very well for 1997. The change in modeled weekend effect between 1997 and 1987 is directionally correct in showing a change to ozone decreases at downwind receptors. These results suggest that the model has the right balance between VOC and NOx sensitivity in 1997, but is biased toward VOC sensitivity in 1987.



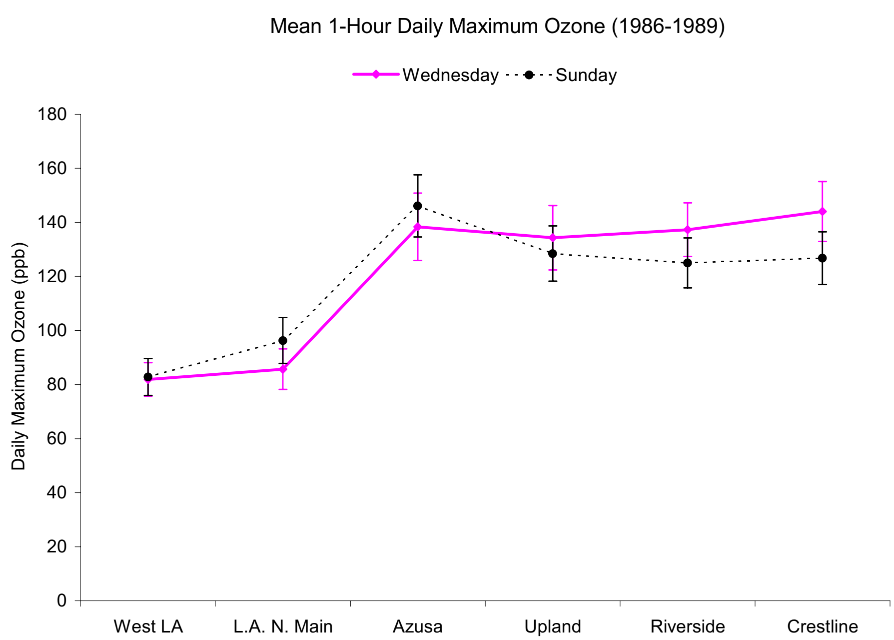


Figure 3-24. Comparison of the modeled Sunday ozone effect of changing the mass and timing of MV emissions in 1987 (top) to the seasonally averaged Sunday effect for 1986-1989 for monitoring sites across the LA basin.

The weekend differences in ozone and precursors at Azusa due to changing the mass and timing of MV emissions in 1987 are shown in Figure 3-25. This figure may be compared to the corresponding1997 modeling results in Figure 3-12. The same features are present in the precursor-ozone relationships at Azusa in 1987 as 1997, showing that the ozone increases in 1987 are due to the mechanism already discussed for 1997; that is, weekend ozone increases are due to reduced weekend NOx emissions and less NOx inhibition of ozone.

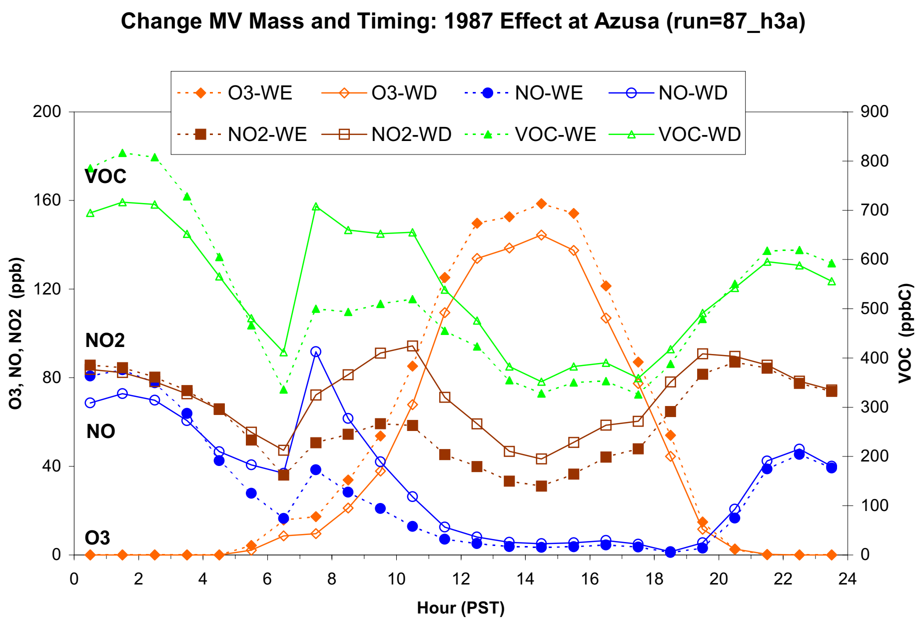


Figure 3-25. Modeled weekday/weekend differences in ozone and precursors at Azusa for 1987 (experiments 87_h3a and 87_wd_base).

2010 Weekend Effect

The modeled weekend effect in 2010 is shown in the tile plot for Saturday (Figure 3-23), the transect of ozone changes at six sites across the LA basin (Figure 3-26) and the detailed comparison for ozone and precursors at Azusa (Figure 3-27). All of these figures may be compared to their counterparts for 1997 and 1987, described above. Figure 3-23 shows that weekend ozone increases were smaller in magnitude and extent in 2010 than for either 1997 or 1987. Weekend ozone increases were confined to high emission areas of the western LA basin. Weekend ozone decreases in downwind areas also were smaller in magnitude in 2010 than either 1997 or 1987. In part, the smaller weekend ozone differences are because ozone levels throughout the basin are lower in 2010 than the earlier years.

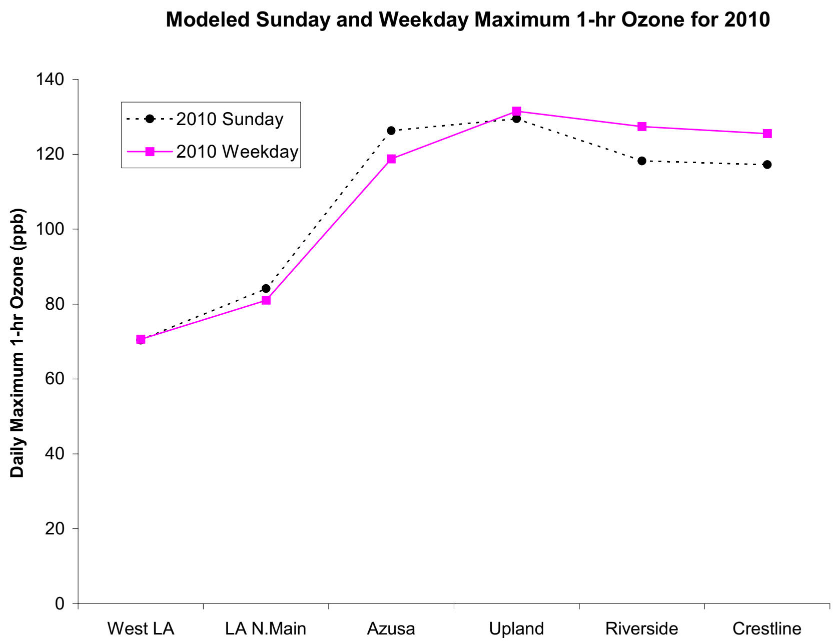


Figure 3-26. Modeled Sunday ozone effect of changing the mass and timing of MV emissions in 2010 for monitoring sites across the LA basin.

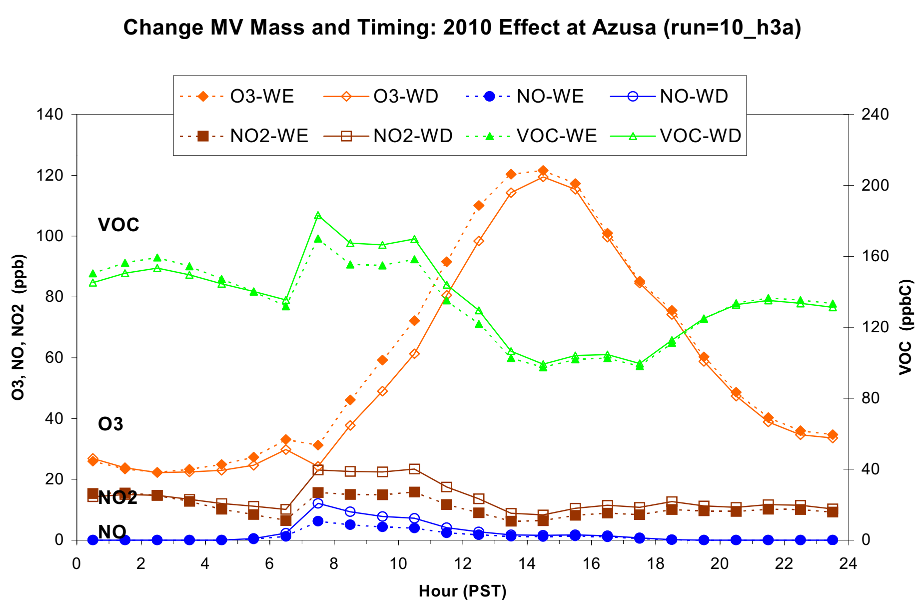


Figure 3-27. Modeled weekday/weekend differences in ozone and precursors at Azusa for 2010 (experiments 10_h3a and 10_wd_base).

The smaller spatial extent of weekend ozone increases in 2010 suggests that less of the Los Angeles basin is VOC sensitive, and more of the basin is NOx sensitive in 2010 compared to 1997. This is also shown in the basin transect in Figure 3-26, which shows weekend ozone increases at upwind locations from West LA to Azusa, and weekend ozone decreases at downwind locations from Upland to Crestline. This pattern of differences is similar to that observed in the late-1980s (Figure 3-24) which was interpreted as indicating more areas of NOx sensitivity in the late-1980s than the mid-1990s (discussed above).

The weekend differences in ozone and precursors at Azusa in 2010, shown in Figure 3-27, also support a shift from VOC sensitive toward NOx sensitive conditions in 2010. In the morning, lower weekend NOx levels together with higher weekend ozone levels still point to a mechanism where lower weekend NOx emissions raise ozone levels by reducing the amount of NOx inhibition of ozone. However, the morning ozone increases are weaker in 2010 than 1997, and at about the time of the midday ozone peak the differences between weekday and weekend ozone levels disappear. Weekday and weekend ozone levels are almost the same in the afternoon, evening and night at Azusa in 2010.

As just discussed, the location and magnitude of weekend ozone increases/decreases is related to the NOx/VOC sensitivity of ozone formation. The shift in model response between 1997 and 2010 toward NOx sensitive ozone formation is not expected simply from the changes to the anthropogenic emission inventory. The VOC/NOx ratio of the anthropogenic emissions decreases between 1997 and 2010 suggesting that in 2010 ozone formation should be more strongly VOC sensitive than in 1997. Further study is needed to investigate the causes and mechanisms of this change in model response between 1997 and 2010. Possible contributing factors include the role of biogenic VOC emissions, the role of boundary conditions and changes in the way the photochemical system processes overnight NOx emissions.

Conclusions on Changes in the Weekend Effects Across Years

The modeled response of ozone to changes in the mass and timing of MV emissions for 1997 agrees well with observations, as discussed above. Both the observed and modeled weekend effects are consistent in showing ozone increases in response to NOx reductions across the Los Angeles basin from West LA to Riverside/Crestline.

The changes to the modeled weekend effect between 1997 and 1987 are directionally correct, but too small in magnitude. Observations show that in the mid-1980s upwind areas were VOC sensitive but downwind areas were NOx sensitive. The 1987 model results show downwind areas being more NOx sensitive in 1987 than 1997, but the shift toward NOx sensitivity is too weak and occurs too far downwind. This could be explained by the VOC/NOx ratios in 1987 base case inventory being too low. Modeling experiments should be performed to investigate whether adjusting the 1987 VOC/NOx higher would improve agreement with the observed weekend effect.

The modeled weekend effect is weaker in 2010 than 1997 with both ozone increases and decreases being smaller in magnitude and extent in 2010 than 1997. This is partly because anthropogenic emission levels and total ozone levels are lower in 2010 than 1997 which reduces the magnitude of the weekend ozone differences. The weekend ozone response to reducing MV emissions in 2010 suggests that ozone formation is more NOx sensitive in 2010 than either 1987 or 1997. This is not expected from changes to the VOC/NOx ratio of anthropogenic emissions, which is lower in 2010 than either 1997 or 1997. This finding is consistent with the changes to model-predicted 6-9am VOC/NOx atmospheric ratios which are higher in 2010 than either 1997 or 1987. Further study is needed to explain this effect.

4. CONCLUSIONS

Conclusions were discussed throughout the presentation of results in section 3, and only the major conclusions are re-stated here. This study is the first to comprehensively investigate the causes of the weekend effect using photochemical modeling. The results demonstrate that a well-performing photochemical model is a powerful tool for rigorously and quantitatively investigating weekend effect hypotheses.

The results of the proximate modeling experiments are consistent with the following major conclusions:

- Changes to the mass of on-road motor vehicle emissions on weekend days are the main cause of the weekend effect observed in Los Angeles.
- Changes to the spatial distribution of motor vehicle emissions on the weekend could also contribute to the weekend ozone effect. Weekend travel demand models are needed to investigate this further.
- Weekend ozone is relatively insensitive to changes in the timing of motor vehicle emissions.
- There is little carryover of effects from one weekend day to the next. The weekend ozone effect is primarily a "same-day" phenomenon for Los Angeles.
- The modeled weekend effects were robust against a large change in the chemical mechanism (from CB4 to SAPRC99) indicating that uncertainties in chemical mechanisms do not compromise the study conclusions about the causes of the weekend effect.
- Changes in photolysis rates due to changes in the amount of aerosol are not the cause of the Los Angeles weekend effect.
- Modeling the weekend effect for 1987 suggests that the VOC/NOx ratio may be too low in the latest ARB emission inventories for 1987.
- The SCAQMD Air Quality Management Plan 2010 on-road motor vehicle emissions for ROG and NOx are 86% and 69% lower, respectively, than the ARB 1997 emissions. The AQMP 2010 control plan includes advanced technology controls that do not yet exist. If the projected emission reductions are realized, the weekend effect for ozone will decrease in magnitude and extent by 2010.
- Because the projected 2010 emissions are uncertain, the future weekend effect scenarios should be repeated with alternate assumptions.
- Modeled ozone responses to weekend effect scenarios in 2010 showed ozone-precursor relationships that are not explained by changes to the emission inventory alone, which should be investigated further.

- The photochemical modeling system (CAMx with meteorology from MM5 and emission inventories from the ARB based on EMFAC2000) performed very well for the 1997 August 3-7 episode when the Carbon Bond 4 chemistry was used.

- The ozone model response to weekend emission changes in 1997 agreed very well with the observed weekend effects.

- The fact that a photochemical modeling system with good model performance also performs well in describing an observed emissions perturbation (the weekend effect) supports the use of photochemical models for ozone air quality planning.

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