How New Chemistry Findings Affect Our Understanding of the Weekend Effect — A Modeling Study

FINAL REPORT

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ABSTRACT

High ozone mixing ratios are a serious concern of public health. While ozone concentrations are high on weekdays due to anthropogenic emissions, they are often higher on weekends despite lower emissions. This phenomenon has been named the weekend effect. This study uses the UCI-CIT air quality model to assess the weekend effect in the South Coast Air Basin (SoCAB) of California. The weekend effect is reproduced by the model using an emissions inventory that includes representative weekday and weekend emissions. There are four main objectives in this study. First, to examine the influence of renoxification process on the weekend effect. Second, to quantify the impact of heterogeneous/multiphase chlorine reactions on the weekend effect. Third, to analyze the contribution of distributed generation (DG) to the weekend effect in the year 2010. Finally, to study the consequences of reducing NO_x emissions on ozone concentration aloft and the subsequent impact on the weekend effect. The Caltech Atmospheric Chemistry Mechanism (CACM), used in the UCI-CIT model, is modified to accommodate these scenarios by introducing new heterogeneous reactions involving nitrogen oxides and chlorine. The emissions inventory from the 2003 Air Quality Management Plan is used to simulate a one-week episode in 2010. Results demonstrate that both renoxification and chlorine chemistry lead to a net decrease in the average weekend effect intensity. With the implementation of DG, the weekend effect intensity estimated for 2010 is significantly lower than in 1997, although it is still present even though the emissions for 2010 are significantly lower than in 1997. These results suggest that the SoCAB will still be under a VOC-limited regime in the year 2010. Emissions from DG contribute to a small percentage of the total basin-wide emissions. In the study of the pollutants aloft, the weekend effect is shown to be more prominent at the layer immediately above the ground level. The increasing weekend effect from ground level to altitudes up to 670m is heavily attributed to the decrease in NO_x emissions and the increase in the VOC/NO_x ratios in altitudes between 38 – 154m from weekdays to weekends.

EXECUTIVE SUMMARY

Several studies have reported decreases in concentrations of ozone precursors on weekends with respect to weekdays; observed ozone concentrations, on the other hand, are higher on weekends than on weekdays. This phenomenon has been recognized as the ozone weekend effect. The California Air Resource Board has expressed interest in further exploring the causes for the weekend effect. This modeling study addresses issues relating to the weekend effect by examining four major scenarios. First, the effect of surface-mediated renoxification reactions is studied. Second, the impact of heterogeneous chlorine chemistry is examined. Third, the impacts on ozone formation of the future implementation of distributed generation (DG) in the South Coast Air Basin (SoCAB) of California under NO_x emissions are redistributed is explored. Finally, the carryover aloft hypothesis for the weekend is investigated. In this study, the University of California, Irvine – California Institute of Technology (UCI-CIT) atmospheric chemical transport model is used. The model employs an updated version of the CalTech Atmospheric Chemistry Mechanism (CACM), where the mechanism is intended for use in three-dimensional regional atmospheric models, with ozone formation and secondary organics aerosol production.

Modeling results show that the surface-mediated renoxification reactions are found to increase ozone levels during both weekdays and weekend days. However, increases in weekdays are generally larger than weekend increases. As a result, a net decrease in the average weekend effect intensity is observed with the implementation of renoxification reaction. The influence of renoxification on the weekend effect depends on the reaction probability, *P*, of the reaction

$$NO + HNO_{3,(surface)} \rightarrow NO_2 + HONO,$$

the impact on the weekend effect is significant for *P* larger than 0.1.

Similarly, the introduction of new chlorine chemistry into the model also leads to a net decrease in the average weekend effect intensity, due to the greater increase in ozone level on weekdays compared to weekends. The influence of chlorine chemistry on the weekend effect depends strongly on the sea-salt source function that activates the chlorine chemistry. An amplification factor of 10 for the sea-salt source function produces the best agreement with

observed chlorine levels in the SoCAB. With respect to the base case, the increase in the magnitude of the chlorine source decreases the basin-wide average weekend effect intensity by approximately 30%.

The future scenario of 2010 still exhibits a weekend effect. However, the estimated weekend effect intensity is significantly lower than the observations made in the recent years. If only considering emissions from DG, then SoCAB will still be under a VOC-limited regime in the year 2010 since emissions from DG only contribute a small percentage to the total basin-wide emissions. However, the future most likely indicates that motor vehicle emissions will be a driving factor that could move SoCAB out of the VOC-limited regime. Although weekly ozone concentrations vary within a 3 ppb range, DG emissions do not contribute significantly to the weekend effect.

Results from the ozone aloft study suggest that the weekend effect is more prominent in the layer immediately above the ground level, from 40m to 300m. The increase of ozone concentrations from ground to upper layers coincides with a decrease of NO_x concentrations from ground to upper levels. In areas where the weekend effect is present, the VOC/NO_x ratios during the weekdays are lower than on weekends. As the modeling domain approaches the uppermost layer, no significant weekend effect is observed, which correspond to the insignificant difference in VOC/NO_x between weekdays and weekends.

1 INTRODUCTION

The observation that ozone concentrations are higher on weekends than on weekdays, despite lower atmospheric levels of ozone precursors on weekends, has been long recognized as the ozone weekend effect. Several studies have analyzed the weekly variation in the concentration of ozone and its precursors between the years of 1981 and 2001 (Qin et al., 2004; Blanchard and Tanenbaum, 2003; Chinkin et al., 2003; Fujita et al., 2003). These studies report decreases in concentration of ozone precursors on weekends with respect to weekdays in the order of 25-41% and 12-30% for nitrogen oxides (NO_x) and non-methane hydrocarbons (NMHC), respectively. Data obtained from previous studies suggest that the most plausible cause of the weekend effect is the reduction of NO_x emissions from weekdays to weekends (Yarwood et al. 2003). Weekly differences in the timing of emissions, carry-over of ozone aloft from weekdays to weekends and lower light scattering due to lower aerosol concentrations on the weekends are other causes believed to have a marginal influence on the weekend effect.

Fujita et al. (2003) analyzed trends in volatile organic compounds (VOC) to NO_x ratios from 1981 to 2000, and observed that the reductions in VOC/NO_x ratios were greater in weekdays than on weekends. Trends in the VOC/NO_x ratio variations lead to lower peak ozone levels, a shift of the peak concentration in the domain from central areas of Los Angeles to inland areas towards the eastern portion of the basin, and an increase of the magnitude and spatial extent of the weekend effect. Qin et al. (2004) analyzed the weekday/weekend variation of the concentration of NO_x, NMHC, CO, particulate matter (PM) and ozone in eight monitoring stations in the South Coast Air Basin of California (SoCAB), during the summer months of the years 1995 to 2001. Analyses on the observations showed a prominent weekend effect - more than 15 ppb increase in ozone concentration from weekdays to weekend - in near downwind areas of Los Angeles. On the contrary, far downwind areas and coastal areas showed no weekend effect.

Limitations in data availability require a thorough, holistic analysis only feasible with the help of a state-of-the-science air quality model using a comprehensive treatment of the latest chemistry findings and physical processes. Yarwood et al. (2003) examined the weekend effect in the South Coast of California using the Comprehensive Air Quality Model.

Weekday/weekend differences in emissions were estimated by changing the on-road motor vehicle emissions based upon weekly traffic activity. Yarwood concluded that ozone increases during the weekend are mainly due to changes in NO_x emissions due to VOC-limited regime predominant in the Los Angeles area.

The California Air Resources Board (CARB) has spent a considerable amount of resources on measurements that have characterized this ozone increase. CARB has considered seven hypotheses that potentially could help to explain the nature of this phenomenon, and concluded that five of the seven were plausible contributors to the ozone weekend effects. In the past, photochemical models have been a crucial tool to develop control strategies and also to test hypotheses regarding the formation of pollutants at global, regional, and local scales.

This modeling study addresses several shortcomings of the preceding works by including important processes previously ignored and neglected by other researchers. Namely, this work is the first to include several heterogeneous chemical reactions, and be the first to consider the influence of Distributed Generation (DG) on the dynamics of ozone formation during weekends in the South Coast Air Basin of California (SoCAB). Specifically, the present work focuses around four major objectives. First, it examines the effect of including a series of surface-mediated renoxification reactions, previously neglected, that have the potential to increase the availability of NO_x and hence modify ozone formation. Second, it investigates the impacts on the weekend effect due to ozone increase by heterogeneous chlorine chemistry, particularly in coastal areas. Third, it explores impacts associated with the implementation of DG in the SoCAB, which affects ozone formation on weekends by redistributing NO_x emissions. Finally, it tests the carryover aloft hypothesis proposed to explain the weekend effect under a new framework which includes all the new discoveries described above.

Results from this study will improve the scientific foundation upon which regulators will base their decisions on emissions controls for reducing peak ambient ozone concentrations. For instance, the required updates to the State Implementation Plan, the Low-Emission Vehicle light-duty vehicle rules, the federal Tier 2 light- and medium-duty vehicle regulations, the heavy-duty vehicle rules, and the NO_x SIP must include modeling studies of weekend episodes. Thus, the results of this study will be of direct benefit to CARB.

2 PREVIOUS WORK ON WEEKEND EFFECT

The observation that ozone concentrations are higher on weekends than on weekdays despite the lower atmospheric levels of ozone precursors on weekends has been long recognized as the ozone weekend effect. Local air quality districts and CARB have spent a considerable amount of resources on measurements that have characterized this ozone increase. CARB has identified seven hypotheses that may explain the nature of this phenomenon:

1. *NO_x reduction*. Based on well-established O_3 formation chemistry, NO_x reductions in areas that are VOC-limited increase O_3 formation. On the other hand, NO_x reductions in areas that are NO_x limited decrease O_3 formation. In the transition region between these two limiting cases, either VOC or NO_x reductions will reduce O_3. The transition region, however, tends to be a region of maximum O_3 formation.
2. *NO_x timing*. The timing of NO_x emissions on weekends is very different from weekdays. Traffic studies indicate that NO_x emissions on weekends are substantially lower than on weekdays for several hours following sunrise. However, midday vehicle counts are similar on weekdays and weekends. The NO_x timing hypothesis states that later timing of NO_x emission on weekends causes the midday emissions to produce O_3 more efficiently compared with NO_x emitted on weekdays.
3. *Carryover near the ground.* Increased VOC and NO_x emissions from traffic on Friday and Saturday nights may carry over near ground level and lead to greater O_3 formation after sunrise on the following day.
4. *Carryover aloft*. The reservoir of pollutants that is carried over above the nocturnal boundary layer may exert a greater influence on weekends than on weekdays for O_3 surface concentrations.
5. *Increased weekend emissions*. Higher weekend O_3 levels may be caused by increased emissions from activities that occur more often on weekends than on weekdays.
6. *Increased sunlight* caused by decreased soot emissions. Since soot absorbs UV sunlight, it reduces the incoming solar radiation needed to initiate the O_3 formation cycle. The lower levels of soot from heavy-duty trucks on weekends may result in increased UV sunlight near ground level and hence greater O_3 formation.

7. *Ozone quenching*: This assumes that NO emissions during the morning are greater on weekdays than on weekends and that they destroy more of the available ozone in the layer of air near the ground where air monitoring instruments are located. Thus, ozone is suppressed more and ozone formation is retarded more on weekdays compared to weekends, leading to the weekend effect.

Among the seven hypotheses, many studies based on historical measurements and modeling studies suggest that the factor stated in the first hypothesis – reduction of NO_x emissions from weekdays to weekends – is the main cause of the weekend effect. The factors considered in the other hypotheses have a limited influence on weekday-weekend variations in ozone concentration.

2.1 Historical data

Several studies have analyzed the weekly variation in the concentration of ozone and its precursors between the years of 1981 and 2001 (Qin et al., 2004; Blanchard and Tanenbaum, 2003; Chinkin et al., 2003; Fujita et al., 2003). These previous studies report decreases in concentration of ozone precursors on weekends with respect to weekdays on the order of 25-40% and 10-30% for NO_x and NMHC, respectively.

Fujita et al. analyzed trends in VOC/NO_x ratios from 1981 to 2000, and observed that reductions in VOC/NO_x ratios were greater on weekdays than on weekends (Fujita et al., 2003). These reductions resulted in higher VOC/NO_x ratios on weekends with respect to weekdays. These trends in VOC/NO_x ratios have led to lower peak O_3 levels, a shift of the peak from central areas of Los Angeles to inland areas towards the eastern portion of the basin, and an increase of the magnitude and spatial extent of the weekend effect.

Qin et al. analyzed the weekday/weekend variation of the concentration of NO_x, NMHC, CO, PM and ozone in eight monitoring stations in the South Coast Air Basin of California, during the summer months of the years 1995 to 2001 (Qin et al., 2004). This variation was examined at the early morning rush hour (5:00 – 6:00 a.m.) and in the afternoon peak ozone hour. Analyses on the observations showed no weekend effect (less than 5 ppb difference) in two monitoring stations: Hawthorne, upwind from central Los Angeles near the coast, and Palm Springs, far downwind from Los Angeles. Moderate weekend effect (less than 15 ppb

difference) was observed at three stations: Downtown Los Angeles, Santa Clarita and Burbank, which are all in the western half of the basin. Finally, three stations showed an intensive weekend effect (more than 15 ppb difference): Pico Rivera, Azusa and Fontana, which all are downwind stations with respect to downtown Los Angeles.

The current study investigates the concentrations of criteria pollutants at the same monitoring stations considered by Qin et al. (2004). Additionally, this study extends the analysis to the entire modeling domain.

2.2 Previous work on modeling the weekend effect

A previous study was conducted to analyze the weekend effect in the South Coast of California using a modeling approach. Yarwood et al. (2003) used the Comprehensive Air Quality Model with extensions and the meteorological episode of August 3-7, 1997 (Sunday to Thursday) (Yarwood et al., 2003). Emissions estimates elaborated by the CARB for Wednesday, August 6, were used as baseline emissions for weekdays. Weekday/weekend differences in emissions were estimated by changing the on-road motor vehicle emissions based upon weekly traffic activity. The estimated changes in NO_x emissions with respect to weekday emissions were 5% increase on Friday, 27% decrease on Saturday and 37% decrease on Sunday. For VOC, the estimated changes with respect to Monday-Thursday emissions were 8% increase on Friday, 8% decrease on Saturday and 15% decrease on Sunday. This study used the original 5-day, Sunday through Thursday meteorology for a hypothetical Thursday through Monday episode. Then, the simulation results of this hypothetical episode were compared with the original one to determine weekday/weekend differences. Results showed that the mass differences in pollutant emissions explained well the weekend effect. Timing in motor vehicle emissions was also analyzed, but it was found to have a minor influence on the weekend effect compared to the change in mass. Likewise, results showed that the lower light scattering on weekends due to lower PM concentrations had limited influence on ozone concentrations. Therefore, ozone increases during the weekend are mainly due to reductions in NO_x emissions in a predominantly VOC-limited ozone formation regime in the Los Angeles area.

3 APPROACH TO SIMULATE THE WEEKEND EFFECT

Based on results from previous studies, the most important factor that produces the weekend effect is the difference in total emissions between weekdays and weekends. The approach in this study is to use one-day meteorology as the baseline meteorology for a period of two weeks. In this way, simulation results are isolated from the effect of meteorology. This hypothetic meteorological episode is used in conjunction with a set of emissions that reflects the variation between weekdays and weekends.

3.1 Model Formulation

The California Institute of Technology (CIT) atmospheric chemical transport model is used to analyze the air quality in the South Coast Air Basin of California (SoCAB). The three-dimensional CIT model simulates the conditions present during the South Coast Air Quality Study (SCAQS) on August 27-28, 1987 (Meng et al., 1998). The model solves numerically the transport diffusion equation for gas and aerosol-phase species, predicting the temporal and spatial evolution of concentrations in atmosphere,

$$\frac{\partial C_i^m}{\partial t} + u\nabla C_i^m = \nabla(K\nabla C_i^m) + R_i^m(C,t,T) + E_i^m(x,t) - S_i^m(x,t) \qquad \text{(Eq. 1)}$$

where C is concentration, i is an index for chemical species and m is the aerosol size. Time and spatial coordinates are represented by t and x respectively. u is the wind field components, K is the eddy diffusivity tensor, R is the net chemical production or loss of species, and T is the temperature. E and S represent the emission and removal fluxes of species respectively.

The computational domain, shown in Figure 1, corresponds to an irregular region composed of 994 columns of cells. Each column corresponds to a 5 km by 5 km region in the x, y plane and extends 1100m in height. The columns are partitioned into 5 cells in the vertical direction.

The CIT model includes the CalTech Atmospheric Chemistry Mechanism (CACM) (Griffin et al., 2002a; Pun et al., 2002; Griffin et al., 2002b). This chemical mechanism is intended for use in three-dimensional urban/regional atmospheric models, with O_3 formation and secondary organics aerosol (SOA) production. CACM includes 191 species and 361 reactions

attaining an accurate description of the chemical processes. The model also includes some new refinements to minimize influence of initial conditions in the results. Table 1 summarizes the boundary conditions used in this study. The values of the boundary concentrations tend to affect only the computational cells near the boundary of the domain. Carreras-Sospedra et al. (2006) showed that boundary conditions do not impact the basin-wide peak ozone concentration significantly.

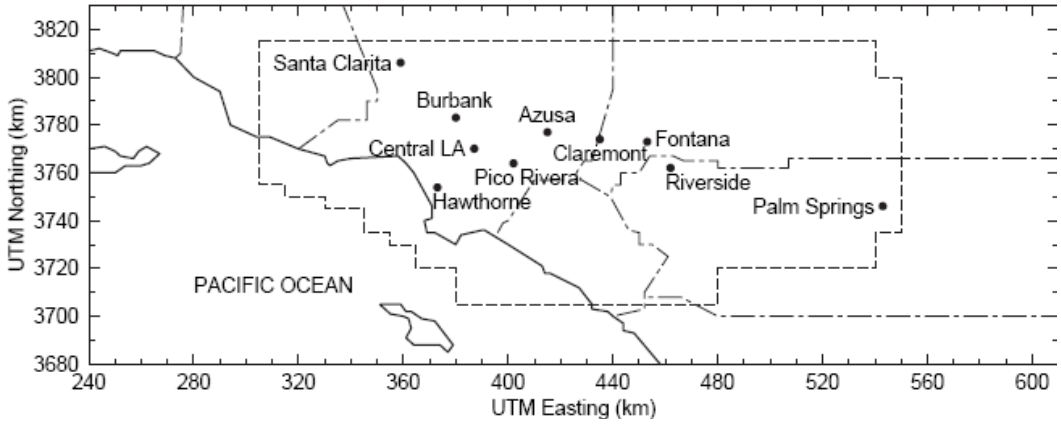


Figure 1. Computational domain of the CIT Airshed Model that represents the South Coast Air Basin of California.

Table 1. Boundary conditions used for the simulations of this study (in ppb).

		Vertical layer in model				
		Surface	**Level 2**	**Level 3**	**Level 4**	**Level 5**
Species	**Boundary**[e]	(0-38m)	(38-154m)	(154-308m)	(308-671m)	(671-1100m)
NO_2	N, S, W	1	1	1	1	1
NO_2	E	aq[a]	aq	1	1	1
NO	N, S, W	1	1	1	1	1
NO	E	aq	aq	1	1	1
O_3	N	aq	70	70	70	60
O_3	E	aq	aq	60	70	70
O_3	S, W	40	40	40	40	40
RHC[b]	N	aq	100	100	100	100
RHC	E	aq	aq	100	100	100
RHC	S, W	100	100	100	100	100
HCHO	N, E	aq	aq	3	3	3
HCHO	S, W	3	3	3	3	3
ALD2[c]	N, E	aq	aq	5	5	5
ALD2	S, W	5	5	5	5	5
MEK[d]	N, E	aq	aq	4	4	4
MEK	S, W	4	4	4	4	4
CO	N, E	aq	200	200	200	200
CO	S, W	200	200	200	200	200

[a]aq refers to values based upon measurements obtained during Aug 27-29th 1987 SCAQS episode. These values are scaled down so that the maximum boundary value is 120 ppb of ozone.
[b]RHC = Reactive Hydrocarbons
[c]ALD2 = Aldehydes with two or more carbons
[d]MEK = Methyl ethyl ketone and other ketones with higher number of carbons
[e]N = north, S = south, E = east, W = west

3.2 Meteorological Episodes

The Southern California Air Quality Study (SCAQS) was a comprehensive campaign of atmospheric measurements that took place in the California South Coast Air Basin (SoCAB), during August 27-29, 1987. The study collected an extensive set of meteorological and air quality data that has been used widely to validate air quality models (Meng et al., 1998; Griffin et al., 2002a; Pun et al., 2002; Griffin et al., 2002b, Moya et al., 2002; Knipping and Dabdub, 2002). Temporal and spatial distribution of temperature, humidity and vertical wind profiles were

obtained during SCAQS. These measurements are the basis for a complete set of gridded meteorological data used in air quality simulations. Zeldin et al. (1990) conducted an assessment of the representativeness of meteorological and air quality data for the 1987 SCAQS episode. Zeldin et al. (1990) found that August 28, 1987 represents a 'reasonable central met-class tendency', which makes it suitable for modeling. In addition, the August 27-28, 1987 episode is statistically within the top 10% of severe ozone-forming meteorological conditions. Furthermore, this episode was also used by the South Coast Air Quality Management District of California (SCAQMD). Hence, meteorological conditions for August 28 are appropriate to use as a basis for evaluating the weekend effect.

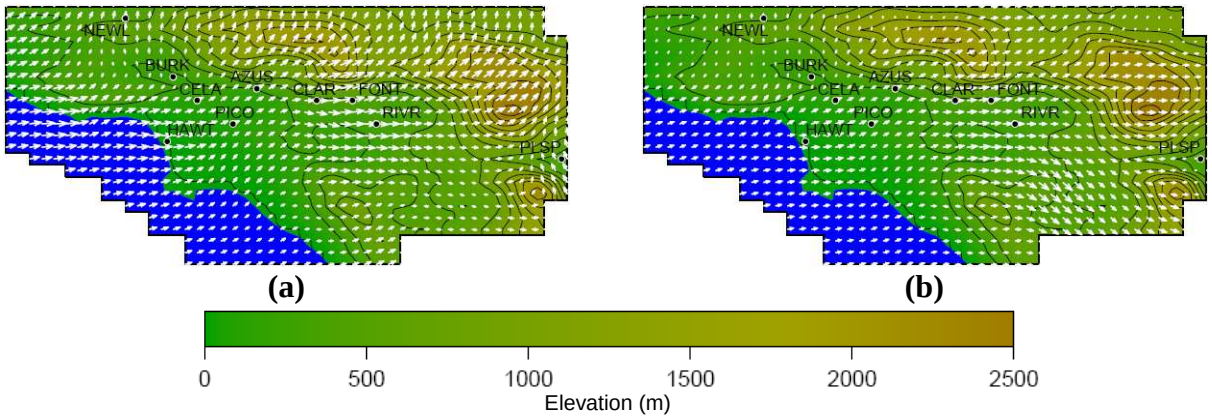


Figure 2. An overlay of the terrain elevation data and wind profiles at 2 p.m. for (a) August 28, 1987 and (b) September 9, 1993 in the South Coast Air Basin of California. Wind speed decreases near the base of the mountain ranges.

The typical dominant direction of winds in the SoCAB is from west to east during the day. The San Gabriel and San Bernardino Mountains form a natural barrier that enhances accumulation of air pollutants in downwind locations like Riverside and San Bernardino. Figure 2 shows increases in wind velocity from Los Angeles County toward Inland Empire locations, such as Riverside, leading to decreases in wind velocity at the base of the mountain ranges, confirming the blocking effects of natural barriers. In addition, the typically warm and sunny conditions in the interior of the basin favor the formation of photochemical smog and ozone.

The SCAQS episode of August 27-29, 1987 was characterized by a weak onshore pressure gradient and warming temperatures aloft. The wind flow was characterized by a sea breeze during the day and a weak land-mountain breeze at night, as shown in Figure 2a. The presence of a well-defined diurnal inversion layer at the top of neutral and unstable layers near the surface, along with a slightly stable nocturnal boundary layer, facilitated the accumulation of pollutants over the SoCAB, and the occurrence of high ozone concentration.

An alternative meteorological episode – September 9, 1993 – is used only in two scenarios to determine the influence of meteorology on the prediction of the weekend effect: one is the base case scenario, and the other is the renoxification scenario. The meteorology used in each scenario is indicated along with the graphical representation of modeling results. The September 9, 1993 episode was used previously by Griffin et al. (2002b) to validate the CACM mechanism. The features of this episode are characterized by slow winds and slightly higher temperatures than in the August 27-29, 1987 episode. In addition, the direction of the wind is predominantly towards the eastern desert, as shown in Figure 2b. These conditions lead to some of the highest ozone concentrations in 1993.

3.3 Emission Inventory

The emission inventory used in this study is the August 3-7, 1997 episode used in the 2003 Air Quality Management Plan designed by the South Coast Air Quality Management District of California (SCAQMD). These emissions were used to validate the performance of the model used in the AQMP, and include emissions from Sunday through Thursday (August 3 through 7). The approach in the current study is to run the model using emissions from a representative weekday for five days (Monday through Friday), then use emissions from a representative weekend day for two more days (Saturday and Sunday). More specifically, this study uses Wednesday, August 6 as baseline emissions for weekdays, and Sunday, August 3 as baseline emissions for weekend days. Table 2 shows the characteristic reduction of both NO_x and VOC emissions from the chosen weekday episode to the chosen weekend episode.

Table 2. Weekday-weekend basin-wide emissions of ozone precursors in the South Coast Air Basin of California in 1997 (tons/day).

	Wednesday (August 6)	**Sunday (August 3)**	**Reduction (%)**
NO_x	862	636	26
VOC	1557	1472	5

Emissions of NO_x and VOC during weekdays follow a different temporal profile compared to weekend emissions. As shown in Figure 3, during morning and afternoon rush hours on weekdays (6:00 – 8:00 a.m. and 3:00 – 5:00 p.m.) emissions are significantly higher than on weekends. This indicates that the main factor that contributes to the difference in emissions between weekdays and weekends is traffic activity, which agrees with previous findings (Yarwood et al., 2003). Despite the significant differences in temporal profiles, Yarwood et al. (2003) showed that the main factor that contributes to the weekend effect is the difference in total mass of emissions.

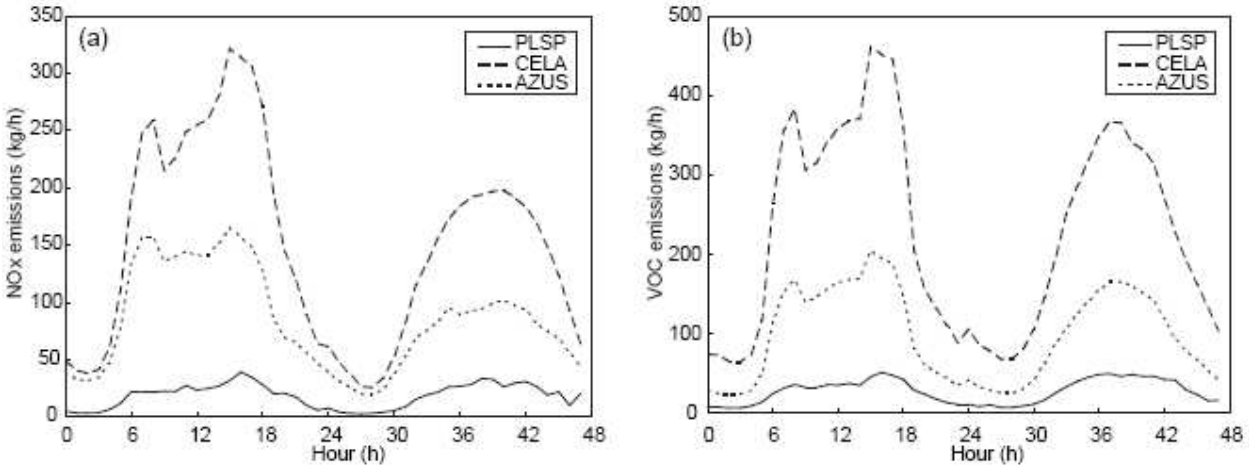


Figure 3. (a) Baseline NO_x and (b) VOC emissions in selected grid cells. Solid line: Palm Springs (PLSP); dotted line: Azusa (AZUS); dashed line: Central Los Angeles (CELA). First 24 hours correspond to emissions estimates for Wednesday, August 6, 1997. From hour 24 to hour 48, emissions estimates for Sunday, August 3, 1997.

4 BASELINE WEEKEND EFFECT

Following the methodology proposed by Qin et al. (2004), the weekend effect is analyzed by examining the difference in peak ozone mixing ratios

$$\Delta O_3(\vec{x}) = \Delta O_{3,we}(\vec{x}) - \Delta O_{3,wk}(\vec{x}) \quad \text{(Eq. 2)}$$

where $\vec{x}$ is any cell in the domain, $O_{3,wk}$ *is* the daily 24-hour peak ozone concentration averaged through the five weekdays, $O_{3,we}$ is the daily 24-hour peak ozone concentration averaged through the two weekend days, and ΔO_3 is the weekday to weekend change in peak ozone. The weekend effect intensity, I_{we}, is defined by the criteria suggested by Qin et al. (2004) based on the weekday to weekend change in peak ozone, shown in Table 3. In the case where the weekday to weekend change in peak ozone decreases, or in other words, ΔO_3 is negative, regardless of the magnitude, it is classified as no weekend effect. The weekend effect is defined by the increase of ozone concentrations from weekdays to weekend only.

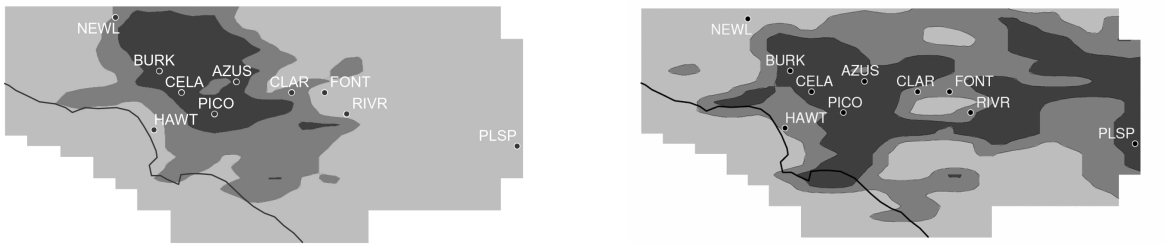
Table 3. Criteria used to quantify the intensity of the weekend effect at a given location.

ΔO_3	I_{we} Classification
ΔO_3 > 15 ppb	Intense
15 ppb > ΔO_3 > 5 ppb	Moderate
5 ppb > ΔO_3	No effect

Based on the criteria presented in Table 3, there are three monitoring stations that exhibit no weekend effect: two locations due west from the central part of the basin, Santa Clarita and Hawthorne, and one location far downwind from Los Angeles, Palm Springs. The ozone concentrations reported in Qin et al. (2004) are significantly lower than the ones reported here, because Qin et al. (2004) reported average values during seven consecutive summers. However, the results presented here showing that upwind and far downwind locations do not exhibit the ozone weekend effect are in good agreement with those historical values. Similarly, results in Table 4 show that stations located downwind of and near Los Angeles – Pico Rivera and Azusa – present an intense weekend effect, as reported in Qin et al. (2004). On the other hand, stations located in Burbank and in downtown Los Angeles also present an intensive weekend effect,

unlike historical values, which show an overall moderate weekend effect at these locations. In addition, the station located in Fontana, farther downwind than Azusa, exhibited a moderate weekend effect, which disagrees with the overall intensive magnitude reported by Qin et al. (2004). This particular disagreement found in the current work might be caused by the use of a specific meteorological episode. The episode used here probably is more stagnant than average meteorological conditions in the basin. These conditions lead to higher pollutant concentrations and hence, greater ozone formation than in the average conditions. As a result, pollutants are accumulated near a major source region of emissions – near central Los Angeles – and the weekend effect in this episode is more intensive closer to the central part of Los Angeles than in average conditions. Figure 4a show the intensity of the weekend effect in the entire SoCAB basin, based on the meteorological profile from 1987. The strongest weekend effect occurs in the north central region of the basin, around Los Angeles, Burbank, Pico Rivera and Azusa. On the other hand, most of the eastern part of the basin shows no weekend effect. Figure 4b shows the intensity of the weekend effect using another meteorological episode (September 9, 1993). This episode was characterized by higher temperatures than in the 1987 episode.

In addition, the prevailing wind on September 9, 1993 was blowing towards the east or the south-east, whereas in the 1987 episode was predominantly towards the north-east, as seen previously in Figure 2. The average magnitude of the basin wind field in 1993 episode is significantly greater than 1987 episode, which is also be seen in Figure 2. As a result, the weekend effect in the 1993 episode is stronger than in the 1987 episode. The weekend effect is also spread over a large area of the eastern part of the domain with the 1993 episode, in part due to the direction of the wind.



(a) **(b)**

Figure 4. Baseline weekend effect: (a) August 28, 1987 meteorology, (b) September 9, 1993 meteorology.

Table 4. Weekday-weekend differences in criteria pollutant concentrations simulated for one week using meteorological conditions of August 28, 1987, for the entire week, without renoxification.

Station		Morning			Afternoon		
		Weekday	Weekend	Difference (%)	Weekday	Weekend	Difference (%)
Santa Clarita							
NEWL	O_3 (ppb)	--	--	--	166	167	1
	NO_X (ppb)	46	34	-26	21	12	-45
	NMOC (ppbC)	121	120	-1	627	531	-15
	CO (ppb)	1237	1272	3	1712	1336	-22
Hawthorne							
HAWT	O_3 (ppb)	--	--	--	55	57	2
	NO_X (ppb)	331	288	-13	25	24	-2
	NMOC (ppbC)	152	153	1	197	199	1
	CO (ppb)	1110	1047	-6	378	400	6
Burbank							
BURK	O_3 (ppb)	--	--	--	92	122	32
	NOx (ppb)	181	131	-27	48	30	-38
	NMOC (ppbC)	136	140	3	518	446	-14
	CO (ppb)	1743	1934	11	1435	1198	-17
L.A. Downtown							
CELA	O_3 (ppb)	--	--	--	60	82	38
	NO_X (ppb)	269	188	-30	81	53	-35
	NMOC (ppbC)	157	161	3	451	416	-8
	CO (ppb)	2231	2458	10	1110	1025	-8
Pico Rivera							
PICO	O_3 (ppb)	--	--	--	92	120	29
	NO_X (ppb)	253	195	-23	42	26	-37
	NMOC (ppbC)	148	148	0	461	389	-16
	CO (ppb)	2101	2310	10	1271	1020	-20
Azusa							
AZUS	O_3 (ppb)	--	--	--	67	95	42
	NO_X (ppb)	236	171	-28	59	34	-42
	NMOC (ppbC)	137	141	3	415	354	-15
	CO (ppb)	2367	2526	7	1164	962	-17
Fontana							
FONT	O_3 (ppb)	--	--	--	148	156	5
	NO_X (ppb)	250	149	-40	29	21	-27
	NMOC (ppbC)	79	78	-2	305	289	-5
	CO (ppb)	1347	1342	-0	779	772	-1
Palm Springs							
PLSP	O_3 (ppb)	106	120	14	146	146	1
	NO_X (ppb)	20	7	-65	13	7	-45
	NMOC (ppbC)	32	31	-3	180	181	1
	CO (ppb)	692	648	-6	214	220	3

Table 4 shows the concentration of selected criteria pollutants in the early morning and in the afternoon at selected monitoring stations. As described in Qin et al. (2004), concentrations of NMOC and CO in the morning correspond to concentrations at 5:00 a.m. Due to the light dependency of O_3, NO_x and PM_{10}, morning concentrations of these species are those at 6:00 a.m., when light scatter data is available. Reported afternoon concentrations for NMOC, CO and PM_{10} were from 2:00 p.m.; O_3 and NO_x concentrations were reported at peak ozone hour.

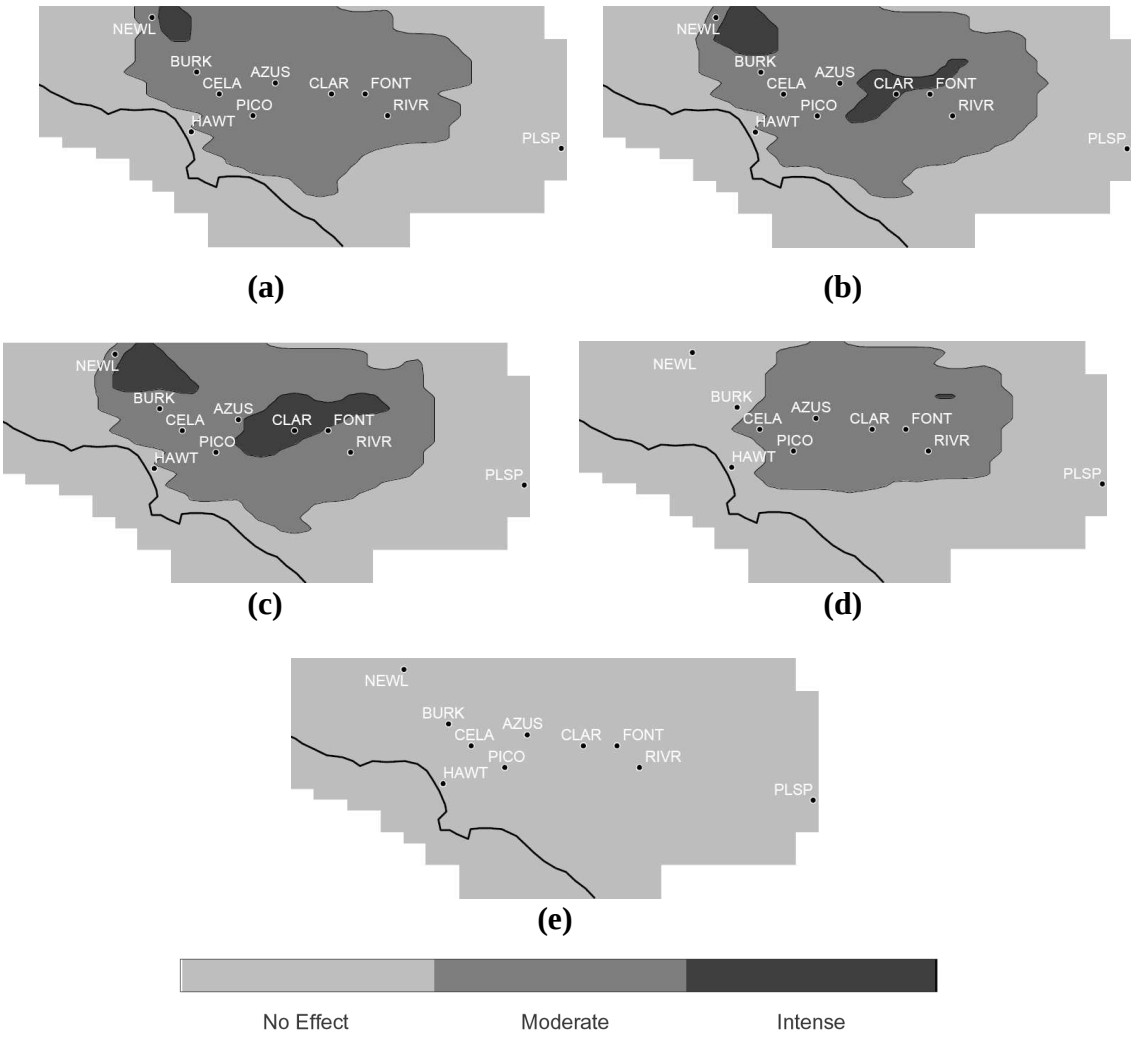


Figure 5. Weekend effect intensity in the South Coast Air Basin of California, using meteorological conditions of August 28, 1987, based on difference between the 24-hour average ozone concentration of the two weekend days and 24-hour average ozone concentration of the weekday at various height levels. (a) Ground level (0m to 38m), (b) 38m to 154m, (c) 154m to 308m, (d) 308m to 671m, (e) 671m to 1100m.

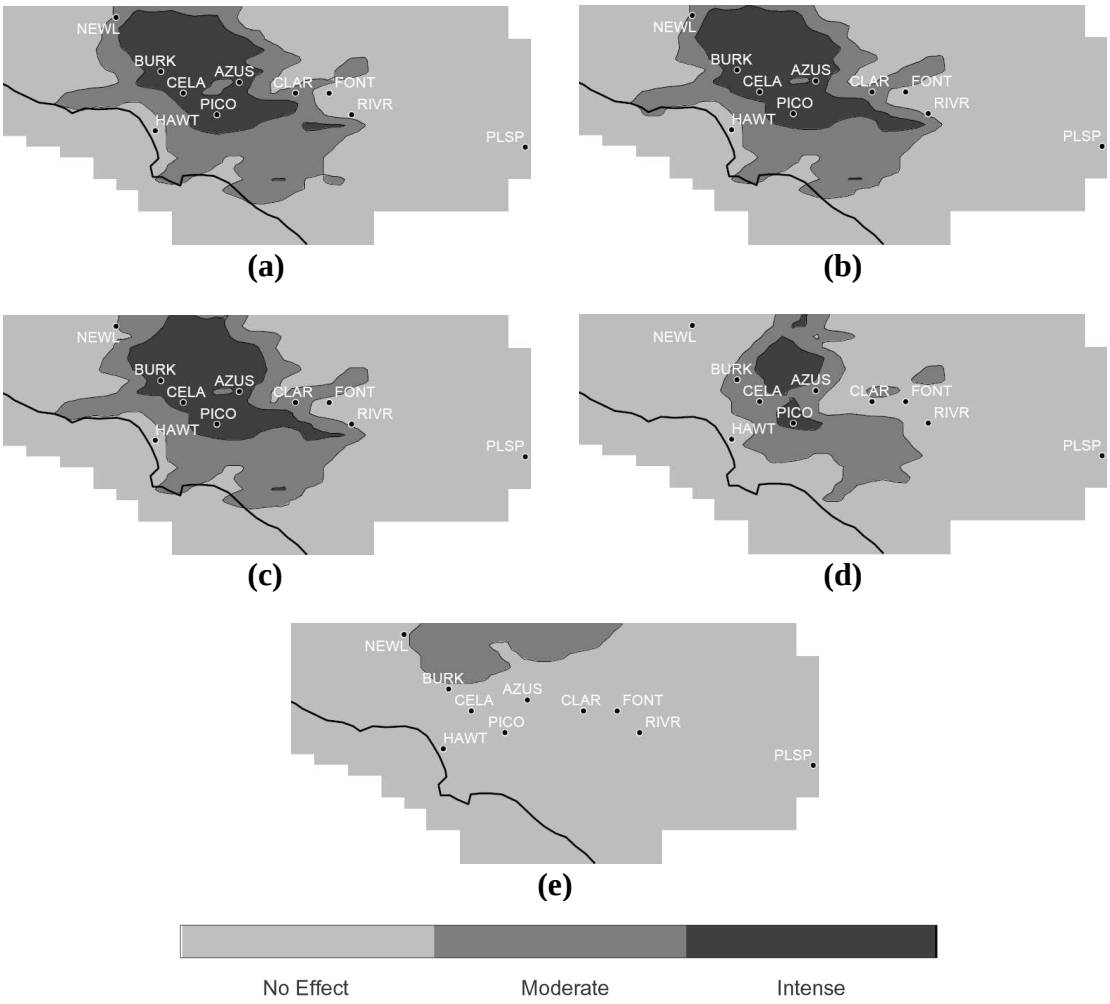


Figure 6. Weekend effect intensity in the South Coast Air Basin of California, using meteorological conditions of August 28, 1987, based on difference between the average daily-maximum ozone concentration of the two weekend days and average daily-maximum ozone concentration of the five weekdays at various height levels. (a) Ground level (0m to 38m), (b) 38m to 154m, (c) 154m to 308m, (d) 308m to 671m, (e) 671m to 1100m.

The ozone concentration at upper layers above the ground level (0 – 38m) of the base case model is analyzed to gain further insights on the possible contribution to the weekend effect by ozone aloft. Figure 5 shows the intensity of the weekend effect at five different height levels, based on the daily average ozone concentration of the weekday versus the weekend. Figure 6, on the other hand, shows the weekend effect intensity calculated by subtracting the peak concentrations of weekday from peak concentrations during the weekend. The results suggest that the weekend effect is actually more prominent in the layers immediately above the ground

level, where “intense” weekend effect is observed at greater number of locations. The overall weekend effect intensity diminishes again with the increase in height above the mid-layers of the model. This new discovery provides motivation to acquire a better understanding of the upper troposphere. A further investigation of the ozone dynamics aloft is presented in Section 8.

5 EFFECTS OF RENOXIFICATION ON THE WEEKEND EFFECT

The process of renoxificaton is the heterogeneous reaction of nitric oxide (NO) and nitric acid (HNO_3) that is deposited on surfaces

$$NO + HNO_{3,(surface)} \rightarrow NO_2 + HONO \qquad (R1)$$

The renoxification reaction increases the concentration levels of nitrogen dioxide, thus impacting the ozone formation cycle as well as the dynamics of acid rain. Furthermore, R1 produces HONO which can be a significant contributor to OH radicals during daytime.

More than five decades of laboratory studies have shown the importance of the renoxification process. Smith (1947) detected a surface reaction dependent on water vapor when studying gas-phase reactions of NO and HNO_3. Despite the long history of renoxification studies, the full details of the heterogeneous chemistry occurring at the molecular level are still not well understood.

Recent studies by Mochida and Finlayson-Pitts (2000) used transmission Fourier transform infrared (FTIR) spectroscopy at room temperature to quantify the production of NO_2 as the major product of R1. They used NO concentrations four orders of magnitude higher than in polluted atmospheres. The same techniques were repeated by Saliba et al. (2000) but using NO concentrations 2 orders of magnitude higher than in polluted atmospheres. Their findings confirm that R1 could be a significant source of HONO in the troposphere. Saliba et al. (2001) studied the impact of surface water coverage on the kinetics of R1. These studies conclude that R1 is a potentially important reaction in the urban atmosphere (due the high availability of glass surfaces) and in the free troposphere (due to the high availability of dust particles). However, Kleffmann et al. (2004) studied reaction R1 under NO concentrations lower than 10 ppm using a chemiluminescence NO_x monitor, and suggested that the contribution of R1 is insignificant. From the modeling perspective, Knipping and Dabdub (2002a) studied the influence of the renoxification reaction on urban ozone concentration levels using a three-dimensional air quality model and showed that including renoxification processes increases the predicted ozone peaks and improves the agreement with observed values.

One of the main factors that contribute to the weekend effect is the decrease in NO_x emissions that occur from weekdays to weekends. Lower NO_x concentrations in weekends, due to lower NO_x emissions, reduce ozone titration with NO, and hence do not suppress ozone concentrations as much several previous studies analyzed capability of the model to simulate the weekend effect (Marr and Harley, 2002; Yarwood et al., 2003). However, none of them considered renoxification. Since concentrations of ozone and NO_x are affected by renoxification, this study quantifies the effect of reaction (R1) in the prediction of the ozone weekend effect.

Indirectly, renoxification reactions can also affect other secondary pollutants. Meng et al. (1997) discussed the direct coupling between atmospheric ozone and PM chemistry. The mass of airborne PM is driven by gas-to-particle species conversions and depends on the NO_x and VOC gas-phase chemistry that leads to the formation of ozone. Therefore, changes in the ozone formation cycle produced by nitrogen regeneration can imply important variations in the atmospheric aerosol levels. However, these potential changes have not been thoroughly studied.

Regenerated nitrogen may increase acid nitric concentrations via reaction (R1). HNO_3 can deposit on surfaces or partition to the aerosol phase. The gas-phase conversion of HNO_3 to aerosol ammonium nitrate occurs by means of the reversible reaction:

$$NH_3 + HNO_3 \leftrightarrow NH_4NO_{3,(p)} \qquad (R2)$$

where (p) denotes particulate phase (Seinfeld and Pandis, 1999). NH_4NO_3, which can exist as a solid particle or in solution, has an affinity for dry deposition an order of magnitude lower than that of HNO_3 (Davidson and Wu, 1990). Therefore, ammonia plays an important role on the airborne lifetime of nitrate. At low NH_3 concentrations, most of the nitrate remains in the gas phase as HNO_3, where it is subject to effective dry deposition.

In contrast, at high concentrations of NH_3, most of the total nitrate is converted to the aerosol-phase, increasing the lifetime of nitrogen in the troposphere. Thus, areas with high NH_3 concentrations are more predisposed to have high nitrate aerosol peaks. The proposed renoxification mechanism might indirectly influence particulate matter nitrate levels. Reactive deposited HNO_3 regenerates nitrogen oxides, increases HNO_3 levels in gas phase and, as a

consequence, NH_4NO_3 aerosol concentrations. This work analyzes and quantifies the effect of these renoxification reactions on nitrate concentrations in the atmosphere.

Finally, this section analyzes modeled weekly variations in ozone concentration. In areas with high levels of NO_x emissions, such as the South Coast Air Basin of California, ozone concentrations on weekends is statistically higher than during weekdays, despite the decrease in daily emissions. The present work analyzes the effect of including renoxification on modeling the weekend effect.

5.1 Model Formulation

Reaction (R1) is included in the model to analyze its effect on predicted concentrations in the 1987 episode. As proposed by Knipping and Dabdub (2002), the rate of this reaction is determined by evaluating the deposition rate of gas phase nitric acid and the surface contact rate of nitric oxide. The minimum of these two processes divided by the height of the ground level layer is used as an approximation for the renoxification reaction rate. The chemical species produced by this reaction are released to the gas phase. Additional processes involving HONO has not been included in the simulation.

While Rivera-Figueroa et al. (2003) proposed a probability $P = 6 \times 10^{-9}$ for renoxification reaction (R1) on silica surfaces, Kleffmann et al. (2004) suggested that the probability of the heterogeneous reaction between deposited nitric acid and nitrogen oxides might be lower than such values. This disagreement in the scientific community about the exact value of the reaction probability shows the necessity of more experimental studies to understand this heterogeneous reaction and determine its probability on different surfaces. Rivera-Figueroa et al. (2003) suggested that sand can reach a specific surface area of 0.2-3 $\times 10^4$ cm^2 per cm^2 of cross-sectional area, which would increase the net probability of the reaction by 2,000 to 30,000 times. Future analysis of renoxification reaction between NO and deposited HNO_3 through laboratory experiments could improve our understanding of the process and provide valuable data for chemistry models.

Due to inherent uncertainties in the kinetic data, the present work considers a reaction probability ranging from P=0.001 to P=1 to analyze the effect of renoxification on ozone concentrations, as shown in Table 6. While even a reaction probability of P=0.001 may appear

to be an over estimate, many uncertainties suggest this to be a conservative implementation. Additional surfaces on urban areas and aerosols, surface roughness, land use, accumulation of deposited nitric acid and particulate nitrate are some of the unpredictable aspects in the simulation that can lead to an under prediction of the extent of renoxification. Because of the uncertainty present in the renoxification probability, this study analyses a range of probabilities to examine fully the potential impact of renoxification on the weekend effect.

5.2 Results

5.2.1 Effects of Renoxification on Ozone Concentration

The influence of the renoxification mechanism on predicted concentrations of O_3 and PM is analyzed in this work using the three-dimensional CIT Airshed model. Simulations of base case for the August 27-28th, 1987 episode are compared with results of the renoxification case. The analysis focused on three cities: Los Angeles, Claremont and Riverside. Los Angeles, situated near the coast, has a low VOC/NO_X ratio typical of polluted urban centers. In contrast, Claremont and Riverside are located inland and show a higher VOC/NO_X ratio typical of suburban areas. Differences in the emissions at those locations, their different geographical location and the transport produced by meteorological conditions dictate the different pollutant dynamics that occur in these three cities. As shown in Figure 2a, the overall wind circulation transports pollutants from Central Los Angeles towards the mountains in the northeast. The wind speed decreases at the base of the mountains accumulating pollutants in areas such as Claremont and Riverside. As a result, ozone concentrations in Claremont and Riverside are typically higher than in Central Los Angeles due to local formation and transport from upwind sources.

In Figure 7, the modeled O_3 concentrations at ground level for the base case and the renoxification case are compared to observed concentrations in Central Los Angeles, Claremont and Riverside. Results show a reasonable agreement between ozone simulations and observed data. Some differences exist in the exact time when ozone concentration starts growing and decaying. In spite of these differences produced by the uncertainties in the solar radiation field and measurements, maximum concentrations are in general well-predicted.

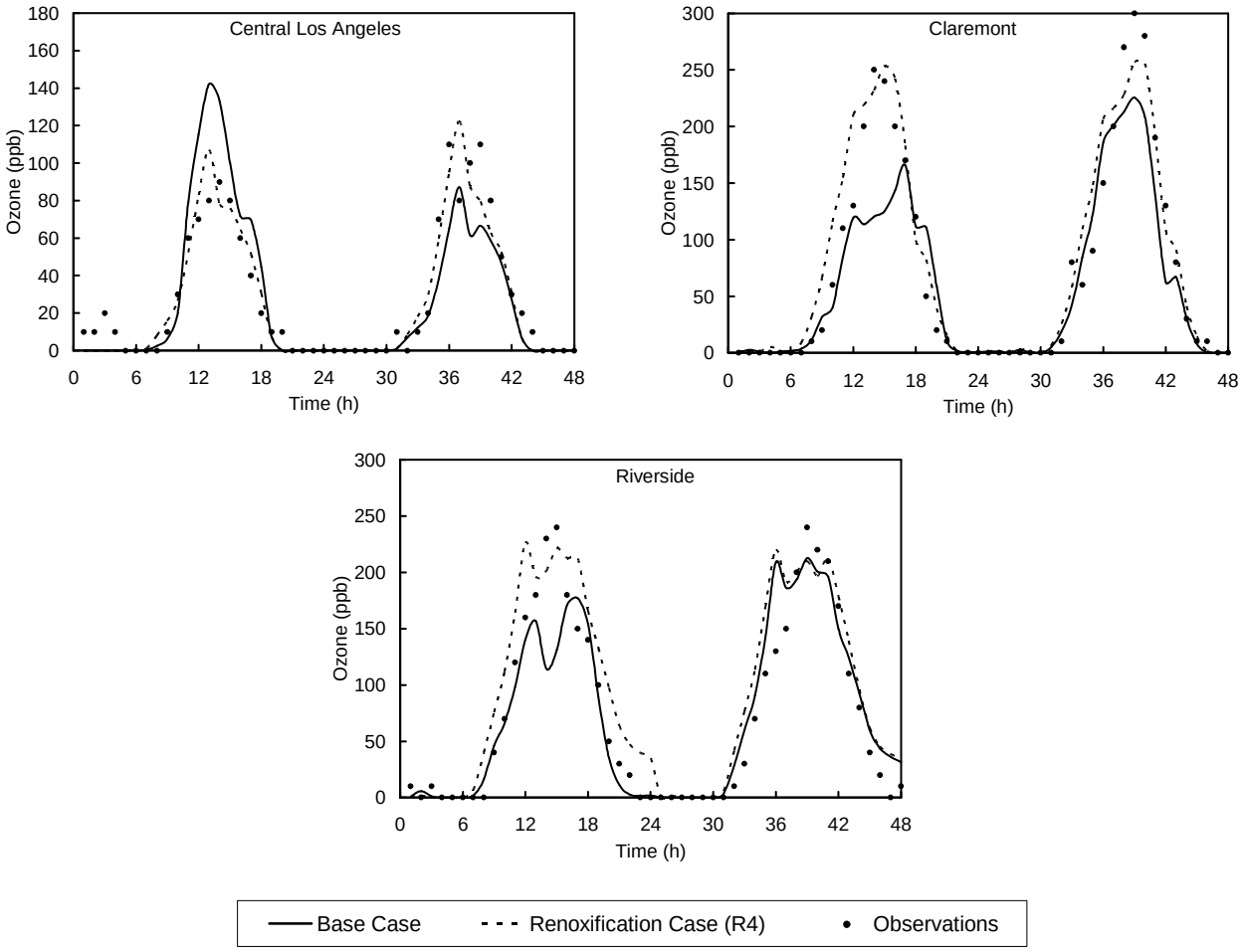


Figure 7. Observed and predicted O_3 concentrations in downtown (central) Los Angeles, Claremont and Riverside, California, for August 27-28, 1987; solid line: basecase; dashed line: renoxification; circles: observations.

Maximum O_3 concentrations in Claremont and Riverside are twice those in Central Los Angeles, significantly exceeding the California Ambient Air Quality Standard (90 ppb). Ozone peaks increase up to 30 ppb when the renoxification mechanism is included in the model. This increase improves the agreement with measurements in Los Angeles and Claremont, especially during the second day of the simulation. The intensification of the ozone formation cycle is produced by the existence of two potential new reaction routes producing NO_2: conversion of NO to NO_2 at the surface defined by reaction (R1) and photo-dissociation of nitrous acid to form NO and OH.

Table 5 shows the 1-hour average maximum predicted concentration in Riverside for different chemical species in the base case and the renoxification case with probability *P*=1. These values represent the upper bounds for the effect of renoxification on the nitrogen species. As P decreases from 1 to 0.001, the concentrations of nitrogen species tend to be closer to the values obtained from the base case without renoxification. For the case with P=0.001, concentration of O_3 and nitrogen species in Riverside are virtually the same as in the base case (with P=0), although simulation results show small differences in concentrations in other areas. Concentrations of nitrogen-containing species in the renoxification case are higher than in the base case. This is due to the limitation of HNO_3 deposition, which acts as a termination reaction for the ozone and NO_x cycle. Renoxification increases recirculation of NO_x and hence, increases concentration of nitrogen-containing species.

Table 5. Simulated maximum 1-hour concentration of selected pollutants in Riverside on August 28, 1987, for the base case and the renoxification case with reaction probability P=1.

	Maximum 1-hour Concentration (ppb)	
Species	**Base Case**	**Renoxification**
O_3	255	273
NO_2	86	88
HONO	4	10
HNO_3	15	21
N_2O_5	1	2
NO_3	$3.6\ 10^{-2}$	$4.7\ 10^{-2}$
OH	$2.3\ 10^{-4}$	$2.6\ 10^{-4}$

The difference between concentrations in renoxification and base simulations normalized by the maximum concentration in the base case is shown in Figure 8. Predicted relative differences for NO_2 concentrations exhibit limited variance. Nevertheless, the increase of ozone produced by the renoxification reaction accelerates the night-time formation of the nitrate radical (NO_3). The daytime concentration of the nitrate radical stays low because of its rapid photolysis.

However, at night, NO_3 levels reach maximum values, becoming a major contributor to the chemistry of organics in the troposphere (Finlayson-Pitts and Pitts, 2000).

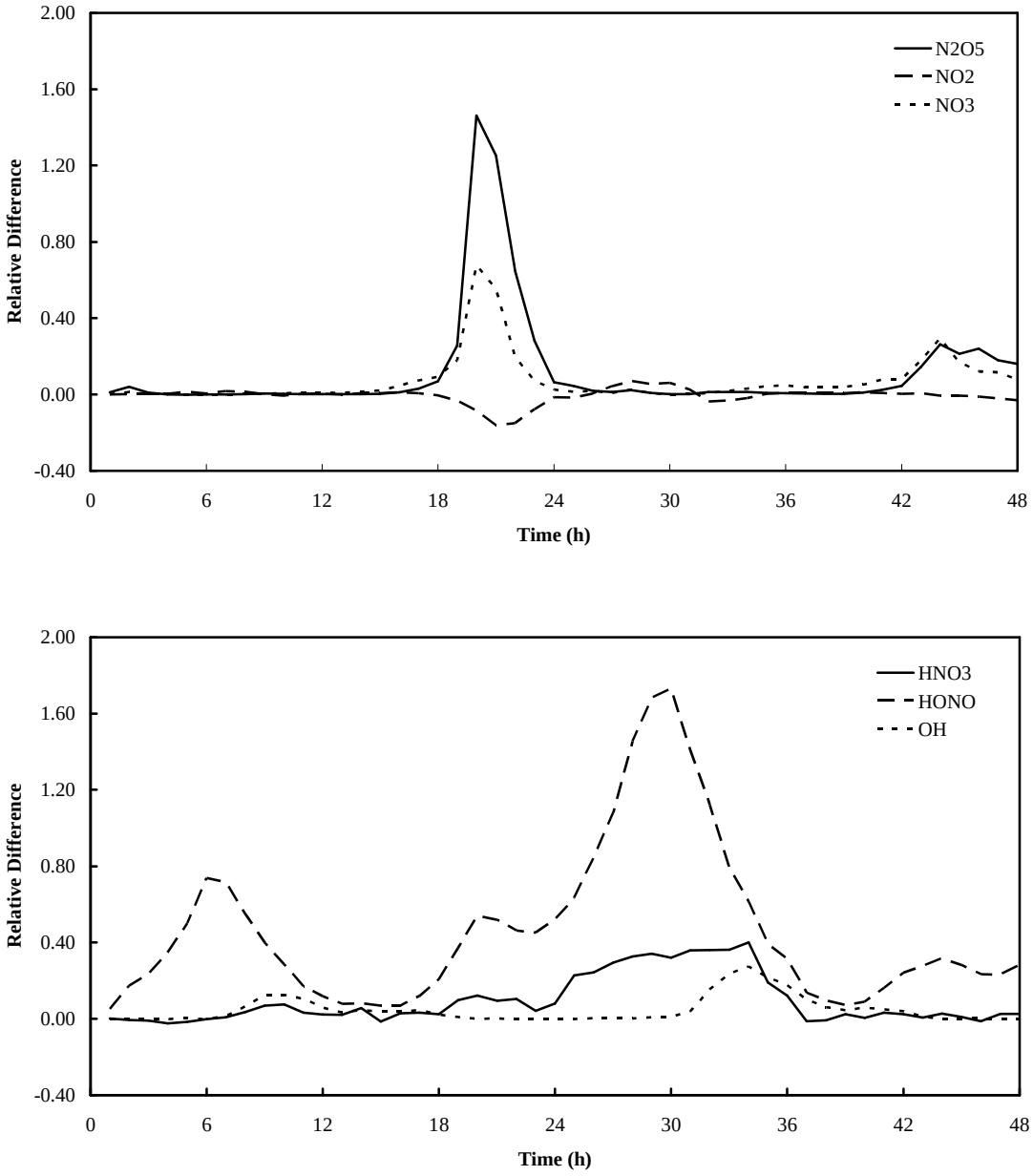


Figure 8. Relative change (RC) between renoxification and base case in Riverside, California, on August 27-28, 1987. The values (RC) are calculated with the following expression: $RC_i = (C_{i,renox} - C_{i,base})/\max(C_{i,base})$, where $C_{i,renox}$ is the concentration of species *i* in the renoxification case, $C_{i,base}$ is the concentration of species *i* in the base case, and $\max(C_{i,base})$ is the maximum concentration of species *i* in the base case.

NO_3 also reacts with NO_2 to form N_2O_5, a nighttime reservoir of reactive nitrogen. Due to these reactions, the peaks NO_3 differences occur with peaks of N_2O_5 and minimums of NO_2, as shown in Figure 8. High HONO concentrations are found in the renoxification simulation. The maximum concentrations are an order of magnitude higher than the base-case peaks. The maximum difference occurs just before sunrise time. During daylight, HONO photolyzes, producing OH and dropping to its daily minimum.

5.2.2 Effects of Renoxification on the Weekend Effect

Table 6 shows the results of the simulation of the same fictitious case as in Table 4, but including the renoxification reaction (R1) with a reaction probability of P=1. These values represent the bounds for the effect of renoxification. As P decreases from 1 to 0.001, the concentrations of nitrogen species tend to be closer to the values obtained base case without renoxification. Overall, peak ozone concentration in R1 increases at all stations on both weekdays and weekends, with respect to the base case. Only in Hawthorne is the change in peak ozone concentration smaller than 1 ppb. At the rest of monitoring stations, peak ozone concentration increases with respect to the base-case without renoxification by 10-14 ppb during weekdays and by 7-17 ppb during the weekend. Renoxification increases ozone concentrations due to reintroduction of NO_x from nitric acid deposited on surfaces. As shown in Table 6, the concentration of NO_x in the case with renoxification is slightly higher with respect to the base case at all stations, except central Los Angeles and Hawthorne. In these two locations, direct emissions of NO_x are very high and dominate over the formation of NO_x due to the chemical reactions. On the other hand, concentrations of organic compounds in the renoxification case are lower than in the base case, due to higher ozone concentrations and hence higher oxidative capacity of the urban atmosphere.

Although ozone concentrations generally increase in the basin due to the renoxification reaction, these increases occur equally during weekdays and weekends. As a result, the magnitude of the weekend effect – as measured previously as intense, moderate or non-existing – does not change significantly when the renoxification reaction is included in the chemical mechanism. As shown in Table 6, locations in Azusa, Burbank, Central Los Angeles and Pico Rivera present an extreme weekend effect whereas in Fontana, Hawthorne, Santa Clarita and

Palm Springs the increase in ozone concentration on weekends with respect to weekdays is less than 5 ppb. Overall, the simulation with a renoxification probability of *P*=1 produced a 2% decrease in ΔO_3 from the base case simulation.

Table 6. Weekday-weekend differences in criteria pollutant concentration simulated for one week using meteorological conditions of August 28, 1987, for the entire week, using renoxification with reaction probability P=1.

Station		Morning			Afternoon		
		Weekday	Weekend	Difference (%)	Weekday	Weekend	Difference (%)
NEWL	O_3 (ppb)	--	--	--	180	184	3
	NO_X (ppb)	47	34	-27	24	16	-32
	NMOC (ppbC)	121	119	-1	605	515	-15
	CO (ppb)	1237	1272	3	1710	1334	-22
HAWT	O3 (ppb)	--	--	--	56	57	2
	NO_X (ppb)	331	288	-13	25	24	-2
	NMOC (ppbC)	152	153	1	197	200	1
	CO (ppb)	1110	1047	-6	378	400	6
BURK	O_3 (ppb)	--	--	--	105	133	27
	NO_X (ppb)	180	130	-28	50	33	-33
	NMOC (ppbC)	136	140	3	506	439	-13
	CO (ppb)	1743	1934	11	1434	1198	-17
CELA	O_3 (ppb)	--	--	--	70	92	32
	NO_X (ppb)	269	188	-30	81	53	-35
	NMOC (ppbC)	157	161	3	443	410	-8
	CO (ppb)	2231	2458	10	1109	1024	-8
PICO	O_3 (ppb)	--	--	--	102	127	25
	NO_X (ppb)	252	194	-23	48	27	-44
	NMOC (ppbC)	148	148	0	453	384	-15
	CO (ppb)	2101	2310	10	1270	1019	-20
AZUS	O_3 (ppb)	--	--	--	80	109	36
	NO_X (ppb)	234	169	-28	66	41	-38
	NMOC (ppbC)	137	140	3	407	349	-14
	CO (ppb)	2367	2524	7	1163	961	-17
FONT	O_3 (ppb)	--	--	--	158	164	4
	NO_X (ppb)	248	146	-41	30	22	-26
	NMOC (ppbC)	79	77	-2	303	288	-5
	CO (ppb)	1346	1342	-0	778	771	-1
PLSP	O_3 (ppb)	113	131	16	156	160	3
	NO_X (ppb)	20	7	-66	14	8	-39
	NMOC (ppbC)	32	31	-3	180	182	1
	CO (ppb)	690	646	-6	214	220	3

Figure 9d through Figure 9g show the weekend effect intensity with reaction probability of P=0.001, 0.01, 0.1 and 1. For P=0.001 and 0.01, the renoxification reaction does not affect the overall weekend effect throughout the basin. Renoxification reaction with P=0.1 causes slight changes to the weekend effect intensity near Azusa and Fontana. Finally, including the renoxification reaction with P=1 increases the intensity of the weekend effect in locations near Azusa, Claremont, Fontana and Riverside, in addition to locations near the north eastern boundary. These increases in intensity of the weekend effect are due to the increase in NO_x concentrations due to reaction (R1), which reduces the VOC/NO_x ratio. Reducing VOC/NO_x due to the renoxification reaction produces a more VOC-limited regime than in the base case. As a result, decreases in NO_x emissions from weekdays to weekends produce larger increases in ozone concentration. However, the changes in VOC/NO_x due to renoxification are only noticeable with a reaction probability larger than 0.1.

Figure 9b shows the weekend effect intensity in the SoCAB using September 9, 1993 meteorology with renoxification reactions. The increase in weekend effect intensity due to the addition of renoxification using this meteorology – difference between Figure 9b and Figure 9a – is larger than the increase obtained with 1987 meteorology – difference between Figure 9g and Figure 9c. As stated previously, the September 9, 1993 episode was an extreme episode that led to some of the highest ozone concentrations in 1993. Temperatures in the eastern part of the domain in the 1993 episode were up to 4^{o}C higher than in the 1987 episode. Higher temperatures can lead to a more VOC-limited regime, i.e., higher NO_x/VOC ratio, due to the release of NO_x from thermal decomposition of PAN (Baertsch-Ritter et al., 2004), whereas higher NO_x/VOC ratio results in stronger weekend effect. On the other hand, higher temperatures would lead to higher biogenic emissions and higher evaporative emissions which could counteract the PAN decomposition. However, the impact of increased temperatures on increased emissions was not accounted for in this study. As a result, the weekend effect using the 1993 episode leads to a stronger weekend effect than in the case with 1987 meteorology. Moreover, the addition of renoxification with 1993 meteorology has a stronger impact on the weekend effect intensity than in the case with 1987 meteorology.

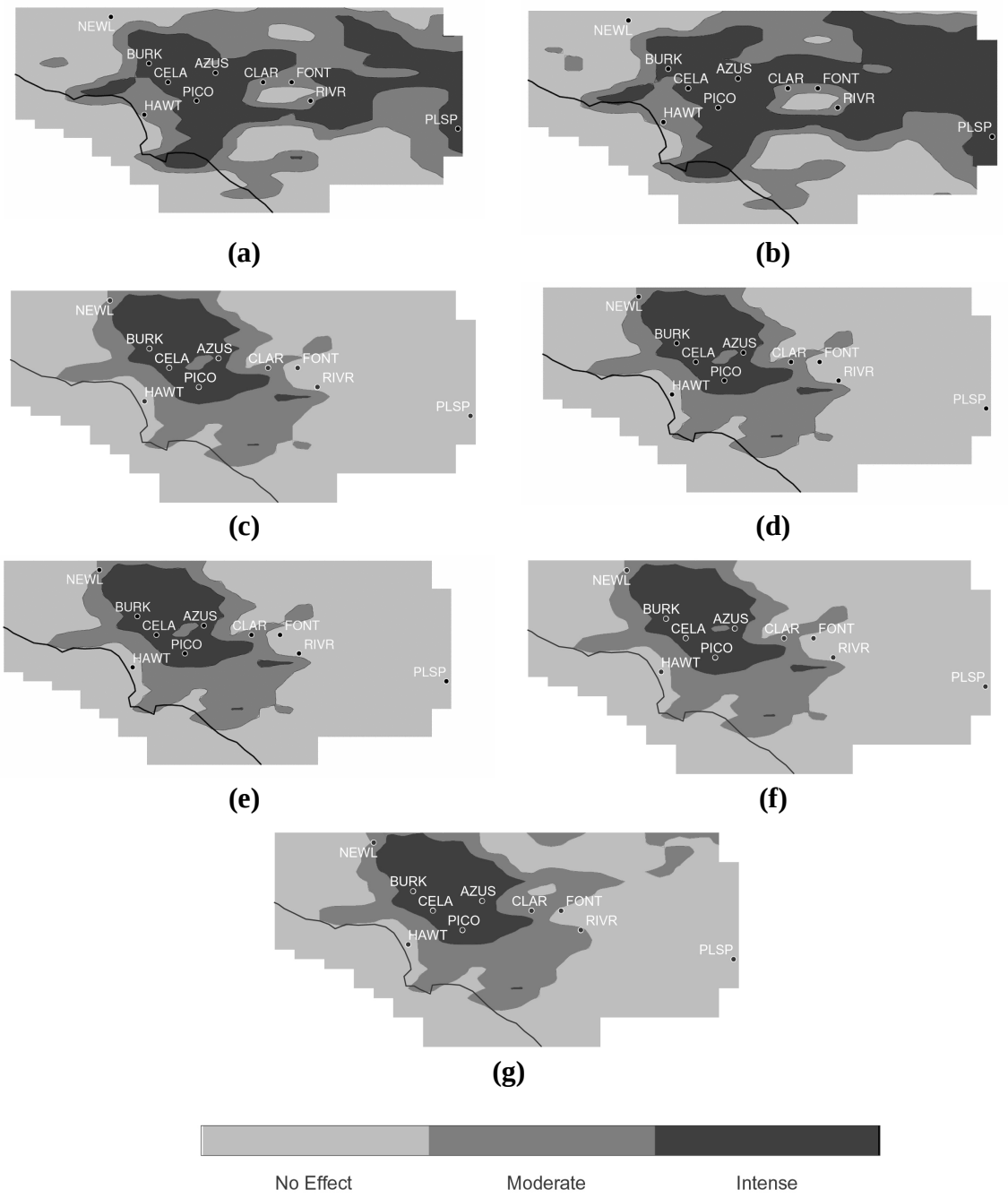


Figure 9. Weekend effect intensity in the South Coast Air Basin under various renoxification scenarios. Cases with September 9, 1993 meteorology: (a) No renoxification, (b) renoxification case renoxification reaction probability P=1; Cases with August 28, 1987 meteorology: (c) no renoxification (base case), (d) renoxification case with reaction probability P=0.001, (e) renoxification case with reaction probability P=0.01, (f) renoxification case with reaction probability P=0.1, (g) renoxification case with reaction probability P=1.

6 EFFECTS OF CHLORINE CHEMISTRY ON THE WEEKEND EFFECT

There has been important research showing the significant role chlorine plays in the chemistry of the atmosphere. Cai and Griffin (2006) studied the oxidation mechanisms of some volatile organic compounds initiated by chlorine atoms to form secondary organic aerosols (SOA). Their study found that chlorine can lead to SOA formation in marine boundary layers and coastal regions in the morning hours. Finlayson-Pitts et al. (1999) found that molecular chlorine can act as an oxidant in coastal regions.

Knipping and Dabdub (2002) conducted an investigation into the effects of adding chlorine chemistry and sources to the UCI-CIT Airshed model. They found that the addition of chlorine chemistry and sources caused an increase in ozone concentration in the morning hours and in the maximum ozone concentration. Their study focused mainly on ozone concentration levels and did not investigate weekend effects.

Finley and Saltzman (2006) reported that current air quality models often underestimate the ozone production attributed to Cl oxidation. It is clear that chlorine plays an important role in the chemistry of the troposphere, especially in coastal regions like SoCAB. This work analyzes the effect of adding chlorine reactions and sources to the UCI-CIT airshed model in relation to the weekend effect. This will be the first comprehensive analysis of chlorine's impact on the weekend effect in SoCAB using the UCI-CIT Airshed model. This report will use the most recent chlorine heterogeneous and multiphase reactions and a sea-salt particle source function to model the effects of chlorine.

6.1 Model Formulation

There are several changes in the model to account for chlorine chemistry. Twelve chemical species are added to the base case model to accommodate the new chlorine chemistry: Cl, Cl_2, ClO, HOCl, ClNO, $ClNO_2$, $ClONO_2$, OClO, ClONO, HCOCl, ClI1 and ClI2. ClI1 and ClI2 are Criegee intermediates. Introducing these new species into the model helps obtain a better understanding of the processes occurring from the chlorine model. A total of 115 chemical reactions added: 83 of those reactions are in the gas phase and 32 are heterogeneous/multiphase reactions. The most significant of these reactions is the chlorine formation from hydroxyl radical and chloride ions

$$OH_{(gas)} + Cl^-_{(aerosol)} \rightarrow \frac{1}{2} Cl_{2(gas)} + OH^-_{(aerosol)} \quad \text{(R3)}$$

Reaction (R3) takes place on the gas-liquid interface of deliquesced salt particles and is the primary source of chlorine in the model. Knipping and Dabdub (2002) investigated reaction (R3) and determined an expression for the rate constant which is used here. Other reactions include the formation of chlorine from chlorine nitrate and nitrous oxide.

$$ClONO_{2(gas)} + Cl^-_{(aerosol)} \rightarrow Cl_{2(gas)} + NO^-_{3(aerosol)} \quad \text{(R4)}$$

$$NO_{3(gas)} + Cl^-_{(aerosol)} \rightarrow \frac{1}{2} Cl_{2(gas)} + NO^-_{3(aerosol)} \quad \text{(R5)}$$

Since nitrous oxide is mostly a nighttime reactant, reaction (R4) offers insight into the differences of the nighttime chemistry which may be important in determining chlorine's impact on the weekend effect. A Sea-salt particle source function is activated, and 12 chemical species and 115 chemical reactions are added.

There are many sources of chlorine in the atmosphere from both anthropogenic and natural sources. The main anthropogenic sources include coal burning and pool purification. There are very few coal burning facilities in the SoCAB. In addition, there is almost no data available on pool purification sources. Therefore, this study focuses on natural chlorine sources in the troposphere. The main natural source of chlorine in a maritime area is from the breaking of suspended marine particles creating sea-salt aerosols.

A sea-salt particle source function is derived from the work presented by Monahan et al. (1986). This function replicates the physical process of bursting of air entrained bubbles from oceanic whitecaps along the coast. It is important to notice that this flux calculation is only dependent on the radius of the bubble and wind speed. As such, the impact of chlorine on this model is highly dependent on meteorological conditions. Monahan et al. (1986) correlated the sea-salt aerosol flux from this physical process to wind speed in the following formula:

$$\frac{dF}{dr} = 4.99 \times U^{3.41} \times r^{-2.95} \times \left(1 + 0.029 r^{1.025}\right) \times 10^{1.19 e^{-B^2}} \quad \text{(Eq. 3)}$$

where r is the radius of the bubble at formation, U is the wind speed, F is the number of particles generated per unit area per second, and B is:

$$B = \frac{0.095 - 0.098 \log(r)}{0.65} \quad \text{(Eq. 4)}$$

Knipping and Dabdub (2002b) reported that only adding marine aerosol sources clearly underestimates chlorine concentrations. Finley and Saltzman (2006) recorded molecular chlorine concentrations in Irvine, California, ranging from 2.5 to 20 ppt, while one day simulations predict molecular chlorine concentrations ranging from 0.2 to 7.2 ppt. One way to address the under prediction of chlorine is to increase the strength of the chlorine source. This is accomplished by amplifying the chlorine source function by a constant. The original chlorine sea-salt aerosol function is modified in the following fashion

$$\frac{dF}{dr} = A\left(\frac{dF}{dr}\right)_0, \qquad \text{(Eq. 5)}$$

where A is an amplification factor and $\left(\frac{dF}{dr}\right)_0$ is the original sea salt aerosol source function described by Eq. (2). By amplifying the original source function the general distribution of chlorine species retains the same structure, while the intensity of the chlorine concentration increases.

Due to uncertainties in the chlorine emissions inventories, this study examines the impact of the strength of the sea-salt source function on the weekend effect. Four scenarios with amplification factors ranging from A=0.l to A=100 are analyzed. Table 7 shows the four chlorine scenarios and their associated amplification factor. Scenarios C1 and C4 represent the extreme cases of low and high chlorine concentrations, respectively. Scenario C2 uses the original sea-salt aerosol function described by Monahan et al. (1986). Analyzing a range of chlorine source scenarios allows for a more thorough understanding of the impacts that chlorine chemistry has on the weekend effect.

Table 7. Chlorine scenarios and their associated sea-salt aerosol source amplification factor.

Scenario	Amplification Factor (*A*)
C1	0.1
C2	1
C3	10
C4	100

6.2 Results

The UCI-CIT Airshed model has been updated with the new chlorine chemistry reactions and the sea-salt particle sources. The updated model is used to simulate a two week episode in the South Coast Air Basin of California with initial conditions obtained from measured ozone aloft values recorded in September 7, 1993. Only the simulation results from the second week are used for analysis, whereas simulation of the first week is used to initialize the model and minimize the effect of initial conditions. Knipping and Dabdub (2002) found that the biggest increases in ozone concentration due to the addition of the chlorine chemistry in the model occur along the coastline. In addition, they found that adding the chlorine chemistry into the model leads to higher ozone concentration in the morning hours and to higher peak ozone concentration.

Modeling results show that the introduction of chlorine chemistry does indeed increase ozone concentrations overall. The biggest increases of ozone found in the SoCAB modeling domain are just east of Central L.A. to west of Azusa and additionally northwest of Burbank to southeast of Santa Clarita. These areas of increased ozone are slightly inland of the coast. However, there is small buffer area directly over the coast, west of Hawthorne, where there is only a small change in ozone from the base case. This small buffer area immediately over the coast is due to the sea boundary blowing clean air onto the coast which increases the advection rate and decreases local resident time.

Table 8 shows the maximum ozone concentrations averaged over the week and weekend simulated by the baseline model and by the model with chlorine chemistry. In locations near the coast, such as Hawthorne, chlorine chemistry has a low impact on ozone concentrations in both weekends and weekdays. In locations that are far from the coast, such as Palm Springs, the added chlorine chemistry produces a slight reduction in ozone concentrations. On the other hand, in locations in the central part of the SoCAB that are near downwind from natural sources the added chlorine chemistry increases ozone concentrations with respect to the base case. While the results of using amplification factors $A \leq 1$ (scenarios C1 and C2) are very similar to the base case, scenarios with larger amplification factors produce a bigger impact on the weekend effect intensity.

Table 8. Maximum ozone concentrations (ppb) averaged over the week and weekend at selected locations.

	Base Case Model			Chlorine Model (*A*=1)		
Station	**Weekday**	**Weekend**	**Intensity**	**Weekday**	**Weekend**	**Intensity**
Santa Clarita	166	167	No Effect	167	170	No Effect
Hawthorne	55	57	No Effect	55	57	No Effect
Burbank	92	122	Intense	101	123	Intense
L.A. Downtown	60	82	Intense	67	85	Intense
Pico Rivera	92	120	Intense	98	122	Intense
Azusa	67	95	Intense	76	97	Intense
Fontana	148	156	Moderate	156	158	No Effect
Palm Springs	146	146	No Effect	144	145	No Effect

Table 9 presents the weekend effect intensity of the base case and chlorine scenario C2, with *A*=1, averaged over each layer for all five layers. The results show that the inclusion of chlorine sources and reactions decreases ozone concentration and dampens the weekend effect overall. The weekend effect intensity is decreased in magnitude by 2% for the bottom 3 layers, and by 10% and 6% for layers 4 and 5, respectively.

Table 9. Weekend effect intensity (ppb) averaged for each layer, base case and chlorine scenario C2 with an amplification factor of 1.

Layer [altitude (m)]		**Base Case**	**Chlorine Case**
1	(0 - 38)	4.98	5.22
2	(38-154)	5.57	5.44
3	(154 - 308)	5.61	5.49
4	(308 - 671)	2.23	2.00
5	(671 - 1100)	-0.92	-0.98

Figure 10 shows the weekend effect intensity at the different altitude layers of the model produced from scenario C2. The chlorine model exhibits a similar weekend effect as the base case model, with the majority of the weekend effect impact concentrated in the northern middle domain. As the altitude increases the center of the weekend effect intensity migrates to the northern edge of the domain and decreases in magnitude.

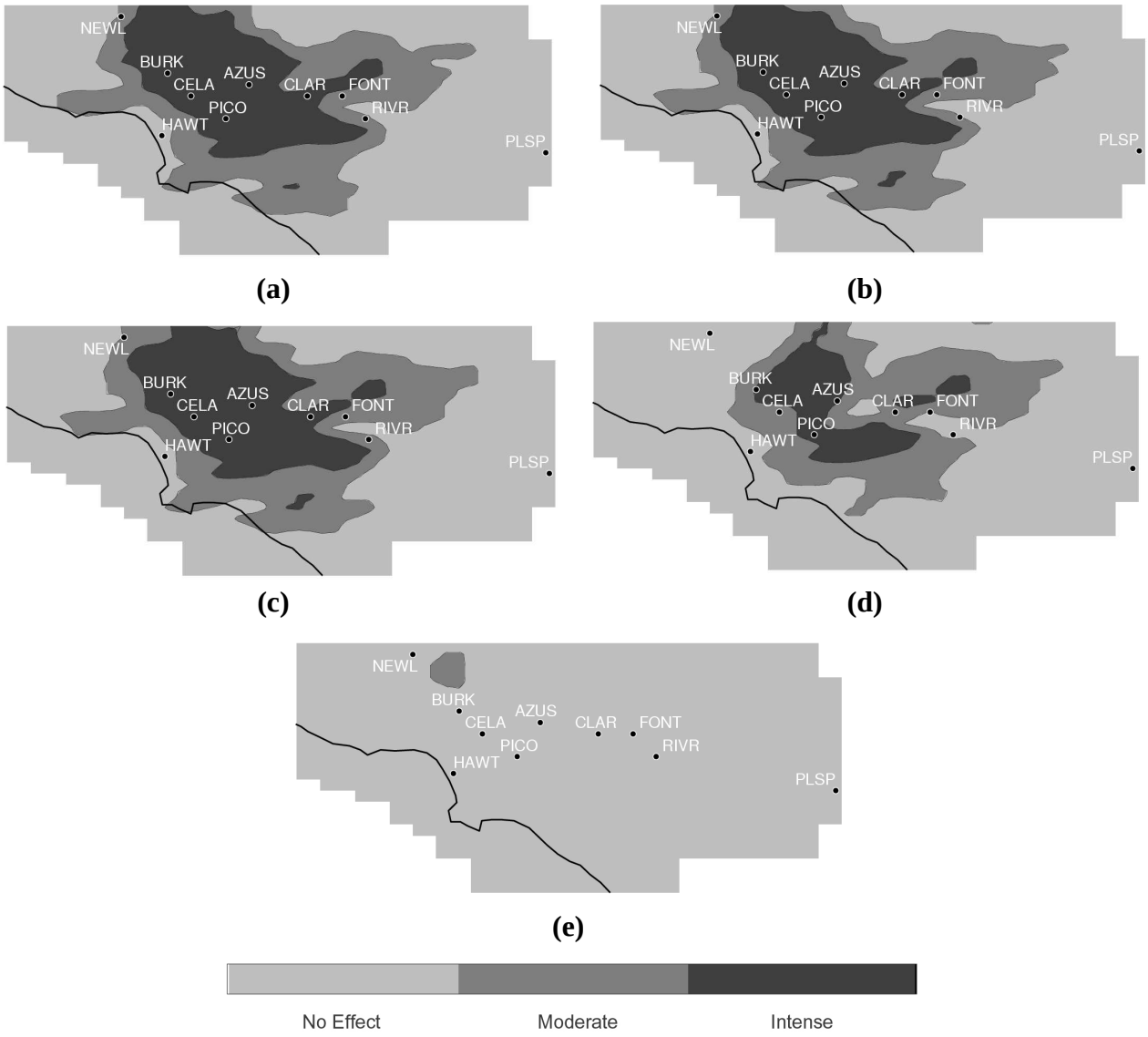


Figure 10. Weekend effect intensity in the South Coast Air Basin of California, using meteorological conditions of August 28, 1987, based on daily maximum ozone concentration at various height levels from chlorine scenario C2 using amplification factor *A*=1. (a) Ground level (0m to 38m), (b) 38m to 154m, (c) 154m to 308m, (d) 308m to 671m, (e) 671m to 1100m.

While the weekend effect intensity of chlorine scenario C2 is similar to the base case, there are some significant differences in both magnitude and spatial distribution. Figure 11 shows the difference between the weekend effect impact of the base case and the chlorine case. In coastal regions and just inland, the intensity of the weekend effect predicted in the base case is lower than the weekend effect intensity predicted in the chlorine case. On the other hand, the

weekend effect intensity in the west and north sides of the domain predicted in the base case is higher than in the chlorine case. These trends are repeated in the five layers of the computational domain.

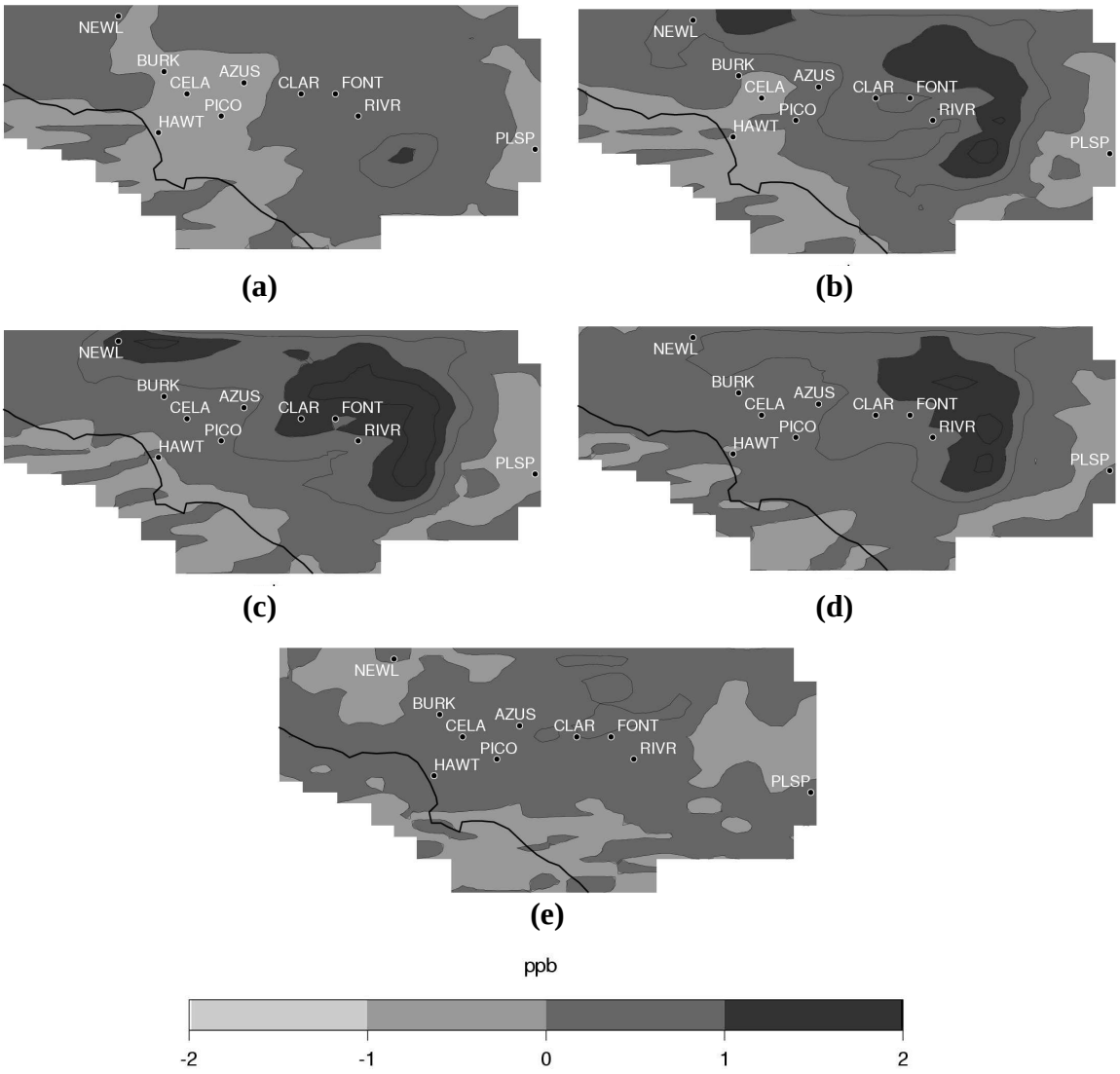


Figure 11. Weekend effect intensity difference in the South Coast Air Basin between base case model and chlorine scenario C2 using amplification factor *A*=1, using meteorological conditions of August 28, 1987. (a) Ground level (0m to 38m), (b) 38m to 154m, (c) 154m to 308m, (d) 308m to 671m, (e) 671m to 1100m.

In summary of the previous results, the addition of chlorine chemistry and sources to the UCI-CIT Airshed model has produced a more intense weekend effect near the coast as compared

to the base case. In addition, the chlorine case produces a generally less intense weekend effect over the entire domain compared with the base case.

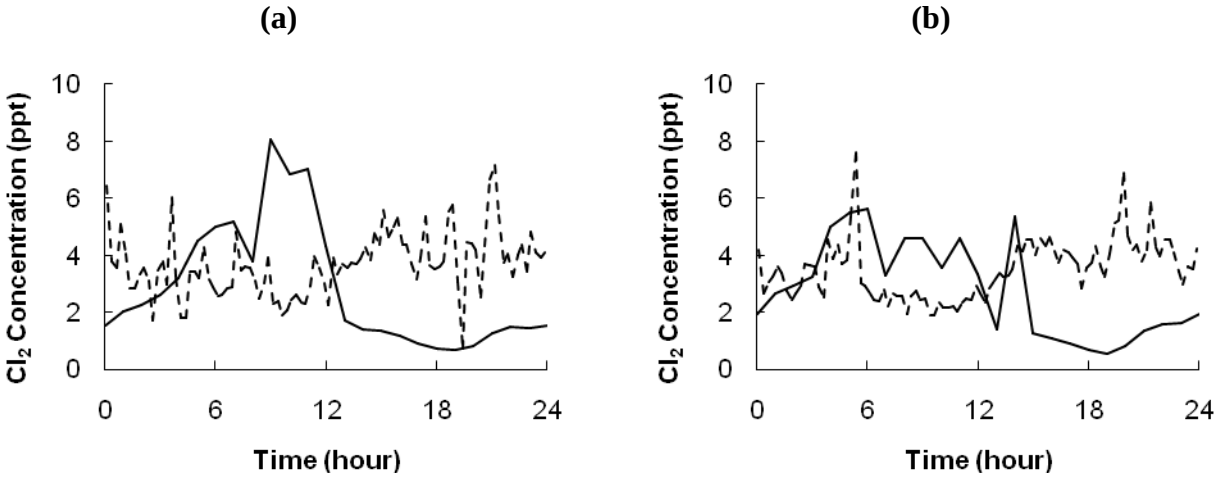


Figure 12. Cl_2 (ppt) time series for Irvine, California averaged over (a) the weekday and (b) the weekend. Dotted line is measured observations from Saltzman and Finley (2006), solid line is simulation results using chlorine scenario C3 with an amplification factor of 10.

There is reason to believe the current chlorine model underestimates the effect of chlorine on pollutant concentrations. Finley and Saltzman (2006) reported measured molecular chlorine concentrations in Irvine, California, ranging from 2.5 to 20 ppt, while modeled molecular chlorine concentrations range from 0.2 to 7.2 ppt using an amplification factor of 1. Interestingly, chlorine scenario C3 with an amplification factor of 10 is the only case able to produce chlorine levels of the same order of magnitude as the measurements from Finley and Saltzman (2006). It should be noted that there is very limited measurements of chlorine levels in southern California. The chlorine time series from the Finley and Saltzman's data is plotted with simulation results of chlorine scenario C3 in Figure 12 for both week day and weekend. Note that, the meteorology present in 2005 is inherently different than the hypothetical modeling period in 1985 used for UCI-CIT model simulations. Hence, the comparison shown in Figure 12 should be examined qualitatively. Although there is no discernible weekday-weekend pattern for Cl_2, the time series for both the weekend and weekday Cl_2 levels are shown in Figure 12 for completeness.

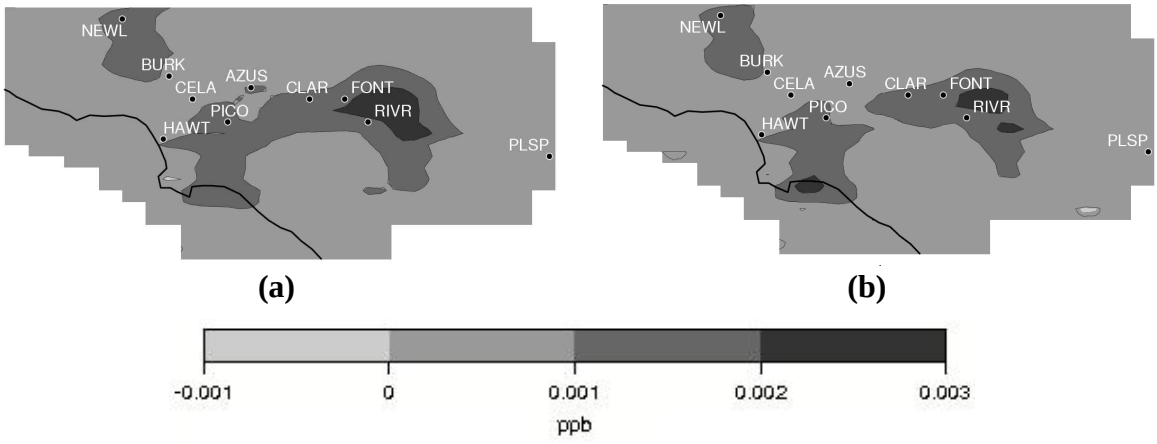


Figure 13. 24-hr averaged NO_x differecence using meteorological conditions of August 28, 1987 between base case and chlorine scenario C2 using amplification factor *A*=1 (a) Wednesday, (b) Sunday.

Figure 13 shows the 24-hr averaged NO_x difference of the base case minus the chlorine model. The results show higher NO_x concentrations in the base case than in the chlorine model, with the biggest differences located along the coast and just inland. On average, the chlorine model predicts 2% lower NO_x concentrations than the base case model. The decreased NO_x levels are mostly to due to Cl radical-NO_x reactions consuming NO_x. One possible explanation of the weekend effect is that decreased NO_x over the weekend can lead to increased ozone production in VOC-limited areas (Heuss et al., 2003). The results show higher NO_x concentrations in the base case than in the chlorine model, with the biggest differences located along the coast and just inland. The dark shaded regions in Figure 10 correspond to the light shaded areas in Figure 11a. The results show a strong correlation between a decrease in NO_x and an increase in weekend effect intensity along the coast and inland of the chlorine model.

The relation between chlorine amplification factor and peak ozone is generally positive. As Knipping and Dabdub (2002b) suggested, simulation results show that chlorine enhances the formation of ozone in the presence of NO_x. Figure 14 shows the domain averaged peak ozone of all four chlorine scenarios and the base case for both week days and weekends. In general, there is an increase in the maximum ozone concentration during weekdays and weekend days for all chlorine scenario compared to the base case. During the week days NO_x levels are higher than those during the weekend. As a result, the increase in peak ozone due to chlorine chemistry with respect to the base case is higher on the week than during the weekends. Overall, peak

ozone increases as the amplification factor is increased. However, scenarios C3 and C4 produce a minor decrease in peak ozone for Palm Springs, and scenarios C1, C2 and C3 produce a slight decrease in maximum ozone for Hawthorne. Despite these exceptions, the major trend of week and weekend peak ozone is to increase with amplification factor and the largest increases take place in Pico Rivera, Azusa, L.A. Downtown and Burbank. Scenario C4 produces an increase of 80 ppb maximum ozone during the week in L.A. Downtown and 76 ppb maximum ozone during the weekend in Azusa.

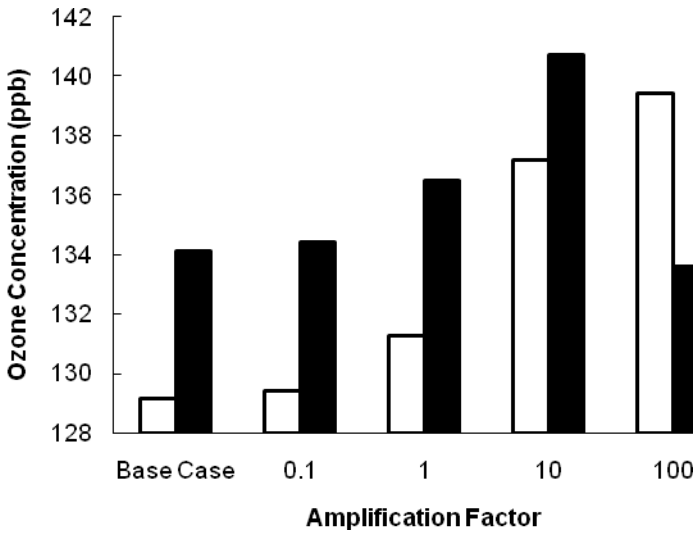


Figure 14. Domain wide averaged peak ozone (ppb) for all chlorine scenarios and the base case for the weekday (white) and weekend (black).

Like renoxification, chlorine decreases the intensity of the weekend effect. Figure 15 shows the weekend effect intensity based on the daily maximum ozone of the four chlorine scenarios. Scenarios C1 and C2 are similar to the base case weekend effect intensity, with a slight increase in the moderate intensity area and a minor decrease in the intense area. As the amplification factor increases, the weekend effect intensity decreases, specifically to the east and north of Riverside. This decrease occurs in the same general area as the Cl_2 maximum. As the chlorine amplification is increased to 10, both the moderate and intense areas of weekend effect decrease, specifically in the southern side of the domain. Scenario C4 produces a much less intense weekend effect, with a smaller area of intense weekend effect centered on Azusa and

Downtown L.A. that is surrounded by an area of moderate weekend effect intensity. Figure 15 shows the Cl_2 concentrations for the four chlorine scenarios at noon of Friday. The four chlorine scenarios produce a range of chlorine concentrations that are approximately proportional to the amplification factor. For low sea-salt source amplification ($A \leq 1$), transport of chlorine to inland locations creates a local maximum of chlorine south east of Riverside. For larger amplifications factors ($A \geq 10$), the influence of a strong sea-salt source function produces maximum chlorine concentrations located along coastal regions.

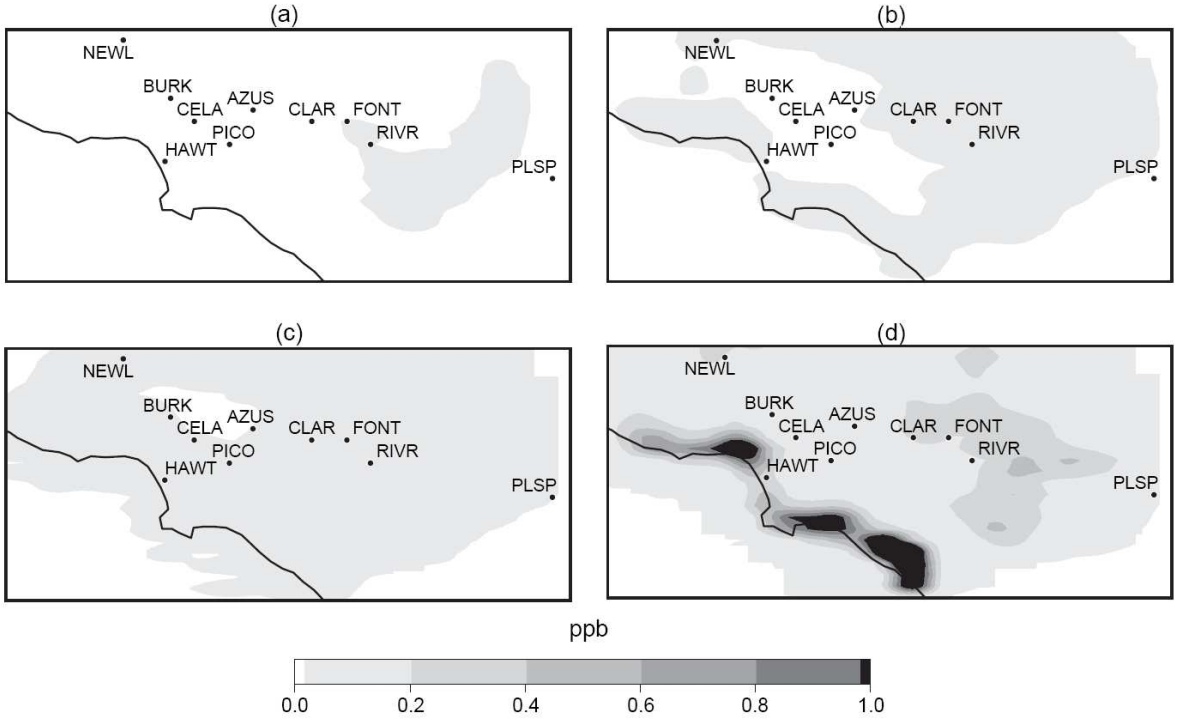


Figure 15. Cl_2 concentration (ppb) on Friday at noon predicted in the chlorine scenarios using meteorological conditions of August 28, 1987: (a) C1, A=0.1 (b) C2, A=1 (c) C3, A=10, and (d) C4, A=100.

Figure 16 shows the result of averaging the ΔO_3 over the entire domain for the nine scenarios under investigation. The basin-wide average ΔO_3 decreases rapidly with chlorine source amplification to the point that scenario C4 produces a negative ΔO_3 domain average, i.e., no net weekend effect. For the case with A=10, which leads to the best agreement with observed chlorine levels in coastal regions, the basin-wide average ΔO3 decreases by up to 29% with respect to the base case. For large amplification factors (scenarios C3 and C4), concentrations

of ozone increased from the base case during weekdays in greater extent than during the weekends. This trend results in overall lower weekend effect intensity than in the base case, but this decrease is produced by increasing weekday ozone concentrations rather than decreasing ozone concentrations over the weekends.

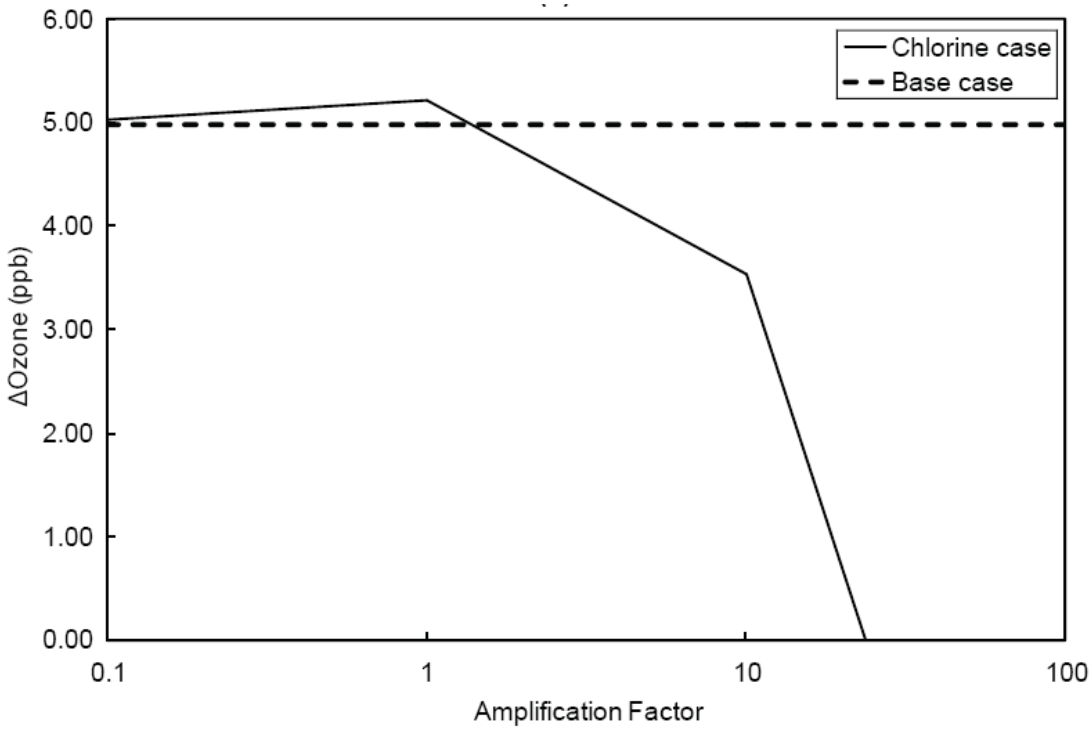


Figure 16. Domain-wide average of week-to-weekend change in peak ozone concentration, O_3 as a function of the amplification factor, A, of the sea-salt source function. Dotted line is the base case simulation, and solid line corresponds to chlorine scenarios.

7 EFFECTS OF DISTRIBUTED GENERATION ON THE WEEKEND EFFECT

Even with the most stringent emissions regulations, southern California's air quality is still among the worst in the nation. Recent energy crises have identified limitations in California's power generation and its grid infrastructure. Energy concerns and the deterioration of air quality are forcing challenging policy decisions, including the energy and environmental impacts of the distributed generation paradigm.

Distributed power generation (DG) is characterized by the sparse distribution of many stationary power generators within an urban air basin, in contrast to conventional, centralized power plants placed in remote areas, normally outside the basin. DG has the potential to meet the power demands of the near future. Deployment of DG technologies might provide additional benefits such as electrical reliability, quality, and reductions in production costs. Furthermore, power generation near the place of use minimizes electricity transmission losses.

California is currently facing an entire reorganization of its electric power industry. In 2002 more than 2000 MW could be classified as DG according to the DG strategic plan developed by the California Energy Commission (Tomashefsky and Marks, 2002). Thus California is one of the first places where DG adoption may become widespread. However, the installation of distributed generation technologies in the South Coast Air Basin (SoCAB) of California might lead to unforeseen air quality impacts and potentially alter the weekend effect.

Previous studies (Ianucci et al., 2000) have determined the total emissions produced by DG deployment for criteria pollutants during different years. Assessment of these emissions is obtained through estimates of DG market penetration, and then compared with those emissions from a case in which only central generation is considered. The conclusion reached by this study shows that no cost-effective DG technology will lower the net emissions of California's current central generation system. Fuel cells show promising benefits for air quality due to their significantly lower emissions with respect to both central and distributed sources, but high installation costs limits fuel cells to a marginal market penetration. Allison and Lents (2002) compared emissions impacts of different DG technologies and fuel types.

They concluded that even the lowest emitting DG technology is marginally competitive with combined cycle power generation. These studies, however, are limited to the evaluation of

only increasing the total amount of emissions. Also, Heath et al. (2003) considered the potential for increased human inhalation exposure to air pollutants when power plants are replaced by DG. Yet, Heath et al. (2003) restricted their work to pollutants emitted directly into the atmosphere using a simplified mass transport approach. Only recently Prof. Dabdub, in collaboration with Prof. Samuelsen's group at the National Fuel Cell Research Center (NFCRC) in the University of California, Irvine, conducted a very comprehensive and detailed modeling study to determine the potential impacts of DG installation in the SoCAB by the year 2010. The methodology and results of this study was part of a project funded by the CEC and was recently published in a peer-reviewed journal (Rodriguez et al., 2006).

7.1 Baseline Weekend Effect in the Year 2010

The analysis of the weekend effect in previous sections is based on 1997 emission estimates. This section explores the weekend effect in a future scenario in 2010 in which distributed generation (DG) is being implemented to meet part of the electricity demand in the SoCAB. The simulation of this scenario involves the use of an emissions inventory for the year 2010. This section uses the emissions inventory developed by the Southern California Air Quality Management District (AQMD) for the 2003 Air Quality Management Plan (AQMP) to demonstrate attainment of the 1-hour ozone standard. This emissions inventory includes current emission controls planned for 2010 and other measures that would reduce baseline emissions to a level at which ozone concentration would not exceed the federal 1-hour air quality standard (120 ppb). Table 10 presents a comparison between weekday-weekend emissions for the year 1997 and for the 2010 attainment scenario. Emissions in the 2010 scenario are up to 65% lower than in the 1997 emissions inventory. In addition, the weekday-weekend relative change in 2010 emissions is different than the trend in 1997. In 1997 emissions, weekday-weekend reductions in NO_x and VOC emissions are 27% and 6%, respectively. In the 2010 scenario, weekday-weekend reductions in NO_x and VOC emissions are 23% and 13%. These differences in total emissions and weekday-weekend trends between 1997 and 2010 affect concentrations of ozone precursors, which affect ozone dynamics.

Table 10. Total emissions of NO_x and VOC (in metric tons/day) estimated for weekdays and weekend, for the year 1997 and for the attainment scenario in 2010.

	1997		2010	
	Weekday	Weekend	Weekday	Weekend
NO_x	771	566	325	251
VOC	1373	1291	513	445

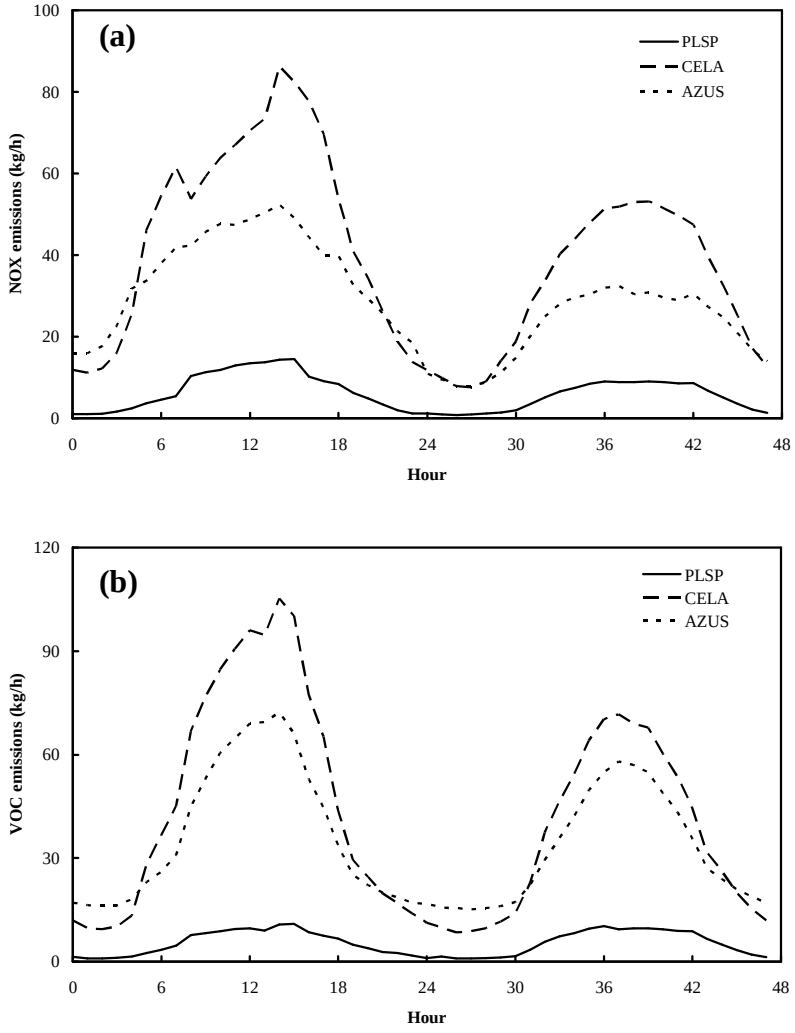


Figure 17. (a) Baseline NO_x and (b) VOC emissions at selected locations. Solid line: Palm Springs (PLSP); dotted line: Azusa (AZUS); dashed line: Central Los Angeles (CELA). First 24 hours correspond to emissions estimates for a Wednesday in the 2010 attainment inventory. From hour 24 to hour 48, emissions estimates for a Sunday in the 2010 attainment inventory.

Figure 17 shows the hourly emissions of NO_x and VOC at three different locations in a representative week day and weekend day in the 2010 scenario. As in the 1997 case (Figure 3), weekday emissions are significantly higher than in weekends within time period between the morning and evening rush hours (6 am to 6 pm). In other words, hourly trends in emissions in 2010 are similar to the trends observed in 1997. Consequently, minor changes in hourly trends from 1997 to 2010 are not considered to be a factor in the weekend effect dynamics. On the other hand, total daily emissions vary significantly from 1997 to 2010, and they are the main factor affecting ozone formation and the weekend effect.

Table 11 presents the concentration of selected criteria pollutants in the early morning and in the afternoon at selected monitoring stations. As presented in Table 4 (Section 4), concentrations of NMOC and CO in the morning correspond to concentrations at 5:00 am, whereas concentrations of O_3, NO_x and PM_{10} are those at 6:00 am. Reported concentrations in the afternoon correspond to those at 2:00 pm for NMOC, CO and PM_{10}, and at the ozone peak hour for O_3 and NO_x. The monitoring stations are listed in west-to-east order.

Compared to values simulated using 1997 emissions, ozone concentrations using 2010 emissions decrease in all the locations in both weekdays and weekends. In particular, ozone concentrations do not exceed the ozone California 1-hour air quality standard (90 ppb) in all the monitoring stations except for Santa Clarita. Concentrations of NO_x, NMOC and CO simulated using 2010 emissions are 3 to 5 times lower than in the case with 1997, as a result of the decrease in baseline emissions from 1997 to 2010.

Based on the criteria presented in Section 4, there are three monitoring stations that present no weekend effect: two locations due west from the central part of the basin, Santa Clarita and Hawthorne, and one location far downwind from Los Angeles, Palm Springs. The rest of locations present a moderate weekend effect and none of the stations presents intense weekend effect. The reduction of the weekend effect intensity in the 2010 with respect to the 1997 case is due to the significant reduction in ozone precursors.

Table 11. Weekday-weekend differences in criteria pollutant concentration simulated for one week using meteorological conditions of August 28, 1987, for the entire week, and emissions for the 2010 attainment inventory. Simulations do not include renoxification or chlorine chemistry reactions.

Station		Morning			Afternoon		
		Weekday	Weekend	Difference (%)	Weekday	Weekend	Difference (%)
Santa Clarita							
NEWL	O_3 (ppb)	--	--	--	108	99	-9
	NO_X (ppb)	15	14	-9	5	4	-32
	NMOC (ppbC)	36	33	-9	194	171	-11
	CO (ppb)	409	398	-2	645	595	-8
Hawthorne							
HAWT	O_3 (ppb)	--	--	--	45	45	-1
	NO_X (ppb)	151	136	-10	11	10	-8
	NMOC (ppbC)	33	33	-1	61	62	1
	CO (ppb)	383	302	-21	162	188	16
Burbank							
BURK	O_3 (ppb)	--	--	--	70	79	13
	NOx (ppb)	85	44	-48	14	10	-32
	NMOC (ppbC)	24	24	-4	129	112	-13
	CO (ppb)	636	602	-5	524	520	-1
L.A. Downtown							
CELA	O_3 (ppb)	--	--	--	36	42	14
	NO_X (ppb)	80	48	-40	24	17	-29
	NMOC (ppbC)	27	26	-4	104	95	-9
	CO (ppb)	649	633	-3	458	470	3
Pico Rivera							
PICO	O_3 (ppb)	--	--	--	65	72	10
	NO_X (ppb)	97	60	-38	16	11	-34
	NMOC (ppbC)	45	42	-8	144	117	-19
	CO (ppb)	783	760	-3	507	470	-7
Azusa							
AZUS	O_3 (ppb)	--	--	--	42	52	22
	NO_X (ppb)	97	53	-46	24	16	-36
	NMOC (ppbC)	49	47	-4	133	110	-18
	CO (ppb)	830	820	-1	465	439	-6
Fontana							
FONT	O_3 (ppb)	--	--	--	79	85	7
	NO_X (ppb)	77	45	-42	15	11	-28
	NMOC (ppbC)	21	21	0	122	105	-14
	CO (ppb)	755	725	-4	381	393	3
Palm Springs							
PLSP	O_3 (ppb)	66	71	9	80	79	-1
	NO_X (ppb)	8	3	-64	5	2	-49
	NMOC (ppbC)	22	22	-1	60	60	-1
	CO (ppb)	414	374	-10	130	131	1

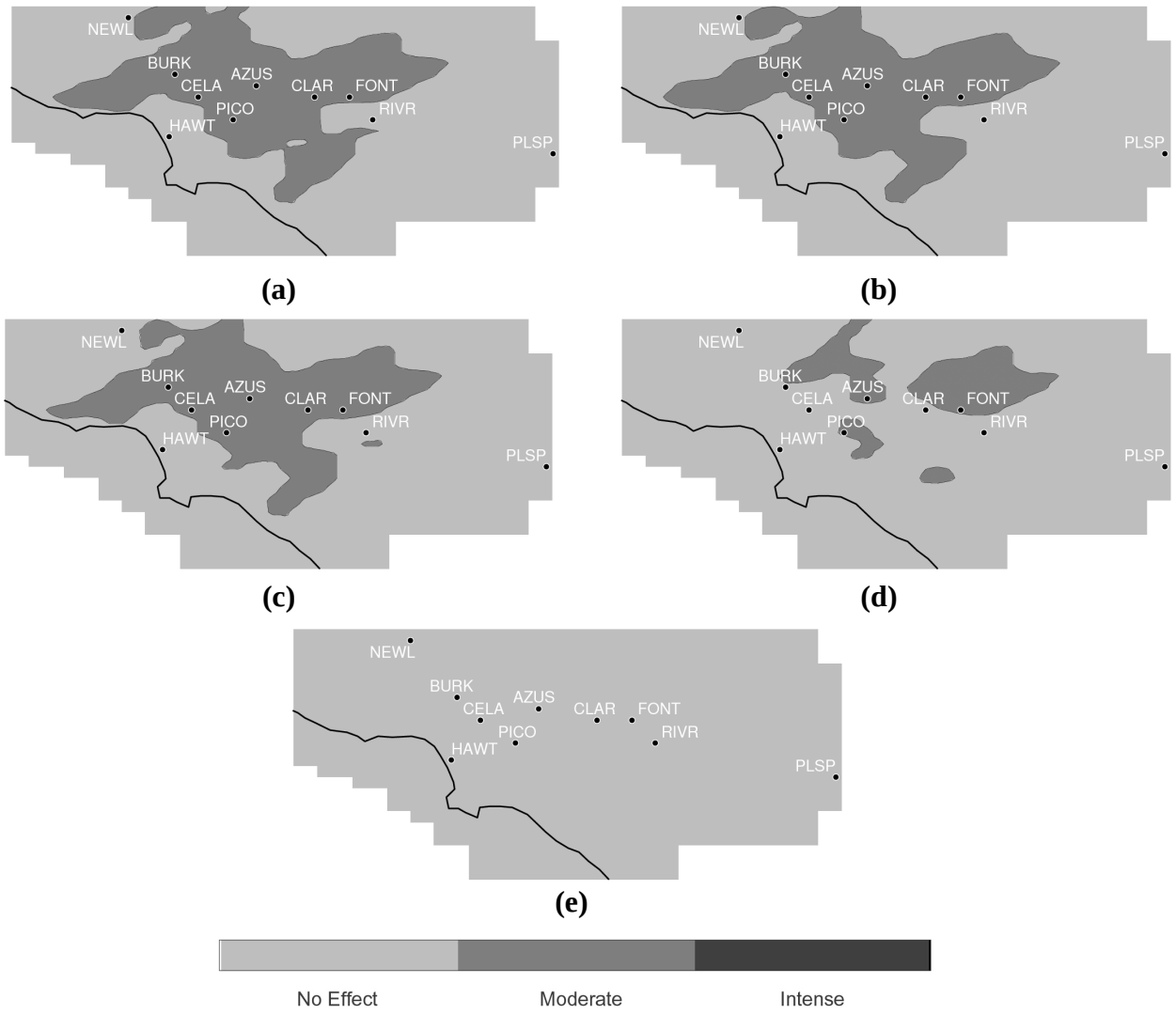


Figure 18. Weekend effect intensity in the South Coast Air Basin of California, using emissions from the 2010 attainment inventory and meteorological conditions of August 28, 1987, based on daily maximum ozone concentration at various height levels. (a) Ground level (0m to 38m), (b) 38m to 154m, (c) 154m to 308m, (d) 308m to 671m, (e) 671m to 1100m.

Figure 18 shows the weekend effect intensity in the SoCAB at different altitudes, obtained using the 2010 emissions and based on the daily maximum concentrations of ozone. This figure uses the methodology presented in Section 4, and is analogous to Figure 6. In general, the weekend effect intensity in the 2010 case is significantly lower than in the 1997 case.

In particular, in the 2010 case there is no region affected by an intense weekend effect, contrarily to what happens in the 1997 case. However, the size of the area affected by the weekend effect is similar in both cases. In addition, changes in the weekend effect with altitude follow a similar trend in the 1997 and 2010 cases. Namely, the area affected by the weekend effect is similar in the first three layers – from ground level to 308m – and decreases significantly in the fourth and fifth level – from 308m to 1100m.

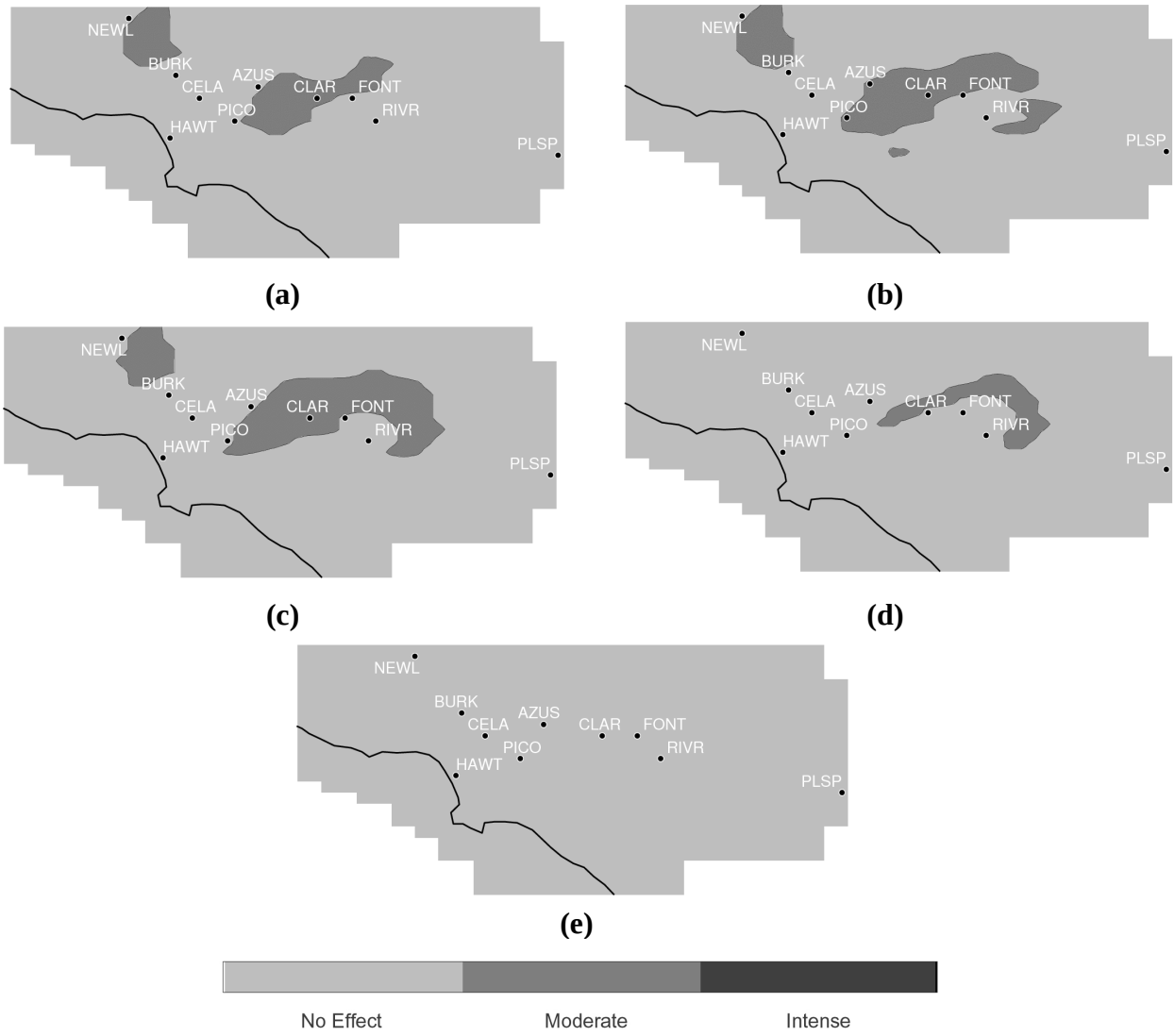


Figure 19. Weekend effect intensity in the South Coast Air Basin of California, using emissions from the 2010 attainment inventory and meteorological conditions of August 28, 1987, based on daily average ozone concentration at various height levels. (a) Ground level (0m to 38m), (b) 38m to 154m, (c) 154m to 308m, (d) 308m to 671m, (e) 671m to 1100m.

Figure 19 shows the weekend effect intensity at different altitudes, obtained using the 2010 emissions and based on the daily average concentration of ozone. This figure is analogous to Figure 5. In general, the weekend effect intensity in the 2010 case based on the daily average is significantly lower than in the 1997 case. As in the 1997 case, the weekend effect intensity in the 2010 case increases from ground level to the third level (from 154m to 308m), and then decreases to no-effect at the fifth layer. However, the weekend effect in the 2010 case based on the daily average affects a considerably smaller area than in the 1997 case. As mentioned above, the main cause of the differences in the weekend effect intensity in the 1997 and 2010 cases is the difference in emissions. Ozone precursors' emissions in 2010 are up to 3 times lower than in the 1997 case. As a result, NO_x concentrations in the 2010 case are lower than in 1997, and hence the region is not so much VOC-limited as in the 1997. Consequently, the reduction of NO_x emissions in weekends with respect to weekdays in the 2010 case leads to a milder weekend effect in comparison with the weekday-weekend trends in the 1997 case.

7.2 Development of Distributed Generation Scenarios

A distributed generation (DG) scenario is defined by a set of parameters that determine which technologies and in what manner DG is deployed in an area of interest. A fully detailed description of how a scenario is developed is included in the report 'Air Quality Impacts of Distributed Generation' prepared for the California Energy Commission by Samuelsen et al. (2005). The group of researchers limited the definition of scenario to a space of seven major parameters, each of which could be defined by a subset of secondary parameters. The list of parameters that define a DG scenario is the following:

1. **Total fraction of energy demands that are met by DG in the scenario:** The fraction of energy met by DG has a strong influence in the final air quality impacts of a DG scenario. A high penetration scenario implies that DG units meet a considerable portion of the total energy needs of the urban basin. Several research studies have investigated the potential market adoption of DG. For example, the California Energy Commission Strategic Plan for DG (Tomashefsky and Marks, 2002) forecasted adoption of DG in California for the year 2020 that could be as high as 20% of the electricity load growth. Other studies have reached similar conclusions with regard to DG market penetration (see

for example Little, 2000), but, the rate of DG adoption and amount adopted in any air basin is a matter of significant debate. As a result, the fraction of energy met by DG is uncertain, and a wide variety of DG penetration levels are recommended to span the spectrum of possible air quality impacts.

2. **Mix of DG resources to meet those demands:** In general, DG systems are comprised of a wide variety of technologies. The DG technologies that are likely to be implemented in the SoCAB include natural gas fired combustion turbines (GT) and natural gas fired reciprocating internal combustion engines (NG ICE), solar photovoltaics (PV), low temperature fuel cells (LTFC), high temperature fuel cells (HTFC), natural gas fired micro-turbine generators (MTG) and fuel cell gas turbine hybrid systems (hybrid). Diesel and petroleum distillate fueled units are not included in the current mix of DG technologies since they are usually not permitted in to run on a continual basis. These types of units are typically permitted to run as back-up generators. Each market segment predominantly uses specific types of DG technologies because the DG capacity levels and features happen to be best suited to meet the energy demands of that market segment. For example, residential applications in the range of 1-5 kW will likely favor fuel cells and photovoltaics; commercial and small industrial sectors, with capacities ranges of 25-500 kW are more suited for PV, MTGs, small ICEs and FCs; large commercial and institutional sectors, in the range of 500 kW-2 MW, might favor natural gas reciprocating engines and gas turbines; and finally the large institutional and industrial sectors with 2-50 MW capacity will be mainly served by gas turbines.

3. **Emissions associated with each DG unit type:** The technology mix considered for DG comprises from zero or near-zero emissions technologies, such as photovoltaics and fuel cells, to technologies that emit at a higher rate than central power plants. Samuelsen et al. (2005) used numerous sources that report emissions factors for the different DG technologies considered in the study. Because DG scenarios in that study are developed for the year 2010, emissions factors for DG are limited by the applicable emission standards (BACT, 2003 ARB and 2007 ARB standards).

4. **Spatial distribution of the DG within the basin:** The distribution of DG units will determine the spatial distribution of emission sources in the basin. To accurately determine a plausible spatial distribution one should conduct a detailed market study on potential DG penetration by sector. Alternatively to markets studies, socio-economic factors such as population density or land-use data can be used to determine the spatial distribution of DG.

5. **Operational duty cycle of each DG:** The duty cycle with which DG units will be operated determines the temporal variation of emissions from DG. The duty cycle for a specific DG unit depends on electricity demand, maintenance schedules and other factors. Some technologies, such as high-temperature fuel cells will probably be operated continuously due to economic factors – reduce to reasonable payback – and operational factors – high temperature requires long start-up times. Other technologies will be operated during peak demand.

6. **Emissions displaced by DG installation:** One of the benefits of most DG units is that the excess heat from the electricity generator can be used for space and water heating. In other words, DG can be used for combined heat and power (CHP) applications. The use of CHP reduces the energy needs that otherwise would be supplied by boilers. As a result, emissions from boilers can be eliminated. Displacement of emissions from boilers depends on a number of factors, such as average heat recovery factors, thermal and electricity load mismatch, and boiler efficiency (Samuelsen et al., 2005).

7. **Other estimates:** As DG technologies are emerging and evolving rapidly, there certain factors for which there is not information available. For example, emission speciation for some DG technologies is not available. In addition, there is little information on DG performance degradation with time, which can affect emissions from DG. Moreover, most DG technologies will improve due to technological advancement, increasing performance efficiency and reducing emissions. Hence, reasonable estimates or assumptions must be applied when necessary.

7.3 Sample Distributed Generation Scenarios

The air quality impacts of DG in the SoCAB were investigated in a previous study that considered a number of future scenarios estimated for the year 2010 (Samuelsen et al., 2005; Rodriguez et al., 2006). The study consisted in two main parts: (1) development of DG scenarios and (2) assessing air quality impacts of the DG scenarios developed in the first part. A systematic approach was designed to develop the DG scenarios for the first part of the study. This systematic approach was used to define the seven parameters stated above and it consisted in a 10-step methodology that used the most up-to-date data on power needs for different activity sectors in the SoCAB and estimates in DG market penetration for future years. In addition, the methodology used detailed information of geographical distribution of activity sectors in the SoCAB that allowed estimation of preferred allocation of specific DG technologies in specific activity sectors. The scenarios obtained using this methodology were labeled as 'realistic' scenarios, as they were developed using the most detailed information available at the time of the study. On the other hand, the study explored an additional set of scenarios that included parametric changes in some of the factors that defined a DG scenario. These changes intended to foresee unexpected outcomes of future DG implementation and complement realistic scenarios with alternative scenarios that allowed sensitivity analyses of the air quality impacts with respect to changes in the parameters that define DG scenarios. These alternative scenarios were labeled as 'spanning' scenarios.

In general, realistic scenarios for the year 2010 presented small air quality impacts in ozone and particulate matter (PM) concentrations. These scenarios considered a moderate DG penetration (less than 4% of the total power supplied by DG, which implies a 20% of the increase in power demand from 2002 to 2010), and hence, emissions from DG represented less than 0.5% of the total baseline emissions in the SoCAB. Overall, air quality impacts of realistic DG scenarios were small.

Most spanning scenarios considered that DG would supply 4% of the total power demand in 2010. An additional spanning scenario considered a DG penetration of 20% of the total power to determine the sensitivity of air quality impacts of DG with respect to DG penetration. Different spatial distributions of DG implementation were analyzed, and results showed that air quality impacts from DG use are affected by the geographical location of DG units. In

particular, results suggested that if DG is to be widely used in the basin, then it should not be concentrated in a small area. Different temporal distributions of DG emissions were also explored. Results showed that an amount of DG emissions concentrated during a 6-hour period (peak duty cycle) produced a larger impact in air quality than the same amount emitted during 24 hours (base load duty cycle).

Since realistic DG scenarios presented only minor impacts on air quality, this study focuses on spanning DG scenarios to evaluate the effect of DG on the weekend effect. In particular, two DG scenarios are considered for this study. The parameters that define each DG scenario are as follow:

(a) Population-Weighted (PW2010):

1) DG penetration: 20% of the increased electricity demand from 2002 to 2010 – increased electricity demand in the SoCAB is 5.3 GW – is met by DG
2) DG technology mix: 30% GT, 30% ICE, 25% MTG, 7% FC, 8% PV
3) Emissions factors: compiled by Samuelsen et al. 2005
4) Spatial distribution: DG is distributed proportionally to population density in 2010
5) Duty cycle: all units operate base-loaded
6) Emission displacement: no CHP is considered
7) Other estimates: No performance degradation is considered, and 98% of the units are installed after 2007

(b) Extra-High DG Penetration (EHP):

1) DG penetration: 20% of the total electricity demand in 2010 – electricity demand in 2010 in the SoCAB is 29 GW – is met by DG
2) DG technology mix: 30% GT, 30% ICE, 25% MTG, 7% FC, 8% PV
3) Emissions factors: compiled by Samuelsen et al. 2005
4) Spatial distribution: DG is distributed proportionally to population density in 2010
5) Duty cycle: all units operate base-loaded

6) Emission displacement: no CHP is considered
7) Other estimates: No performance degradation is considered, and 98% of the units are installed after 2007

In Samuelsen et al. (2005) no consideration was made on how DG operation would change from weekdays to weekends. There is little work produced on this regard. Sidiqqi et al. (2003) developed a model to evaluate a microgrid of DG units in terms of performance and economic factors. They suggested that customers would prefer to fully use DG units and use the grid to complement the need for electricity demand. Hence, this study assumes that DG units are operated constantly during the entire week.

Daily emissions of the two scenarios are presented in Table 12. Emissions from scenario PW2010 correspond to less than 1% of total weekly emissions in the 2010 baseline emissions. Samuelsen et al. (2005) reported that scenario PW2010 would increase ozone concentration by up to 4 ppb in some areas of the SoCAB, although these increases occur typically when ozone concentrations are not at the peak. Scenario EHP, which assumes approximately 5.5 times the DG penetration in scenario PW2010, produces an increase of 4.3% in NO_x emissions and 0.8% in VOC emissions, with respect to baseline weekday emissions, and of 5.5% in NO_x emissions and 1.0% in VOC emissions, with respect to baseline weekend emissions. Samuelsen et al. (2005) reported that scenario EHP leads to an increase in the peak ozone concentration of 1 ppb. In addition, ozone concentration increases by up to 3 ppb in some areas of the SoCAB in the afternoon, when ozone concentrations are typically high.

Table 12. Daily criteria pollutant emissions from DG in two sample DG scenarios in the South Coast Air Basin of California

DG Scenario Name	CO	NO_x	VOC	NH_3	SO_X
In tons/day					
PW2010	8.2	2.5	0.8	0.3	0.1
EHP	44.4	13.8	4.3	1.4	0.5
In % relative to baseline 2010 weekday emissions					
PW2010	0.3	0.8	0.2	0.2	0.3
EHP	1.8	4.3	0.8	0.8	1.3
In % relative to baseline 2010 weekend emissions					
PW2010	0.3	1.0	0.2	0.2	0.3
EHP	1.5	5.5	1.0	0.8	1.3

7.4 Impact of distributed generation on the weekend effect

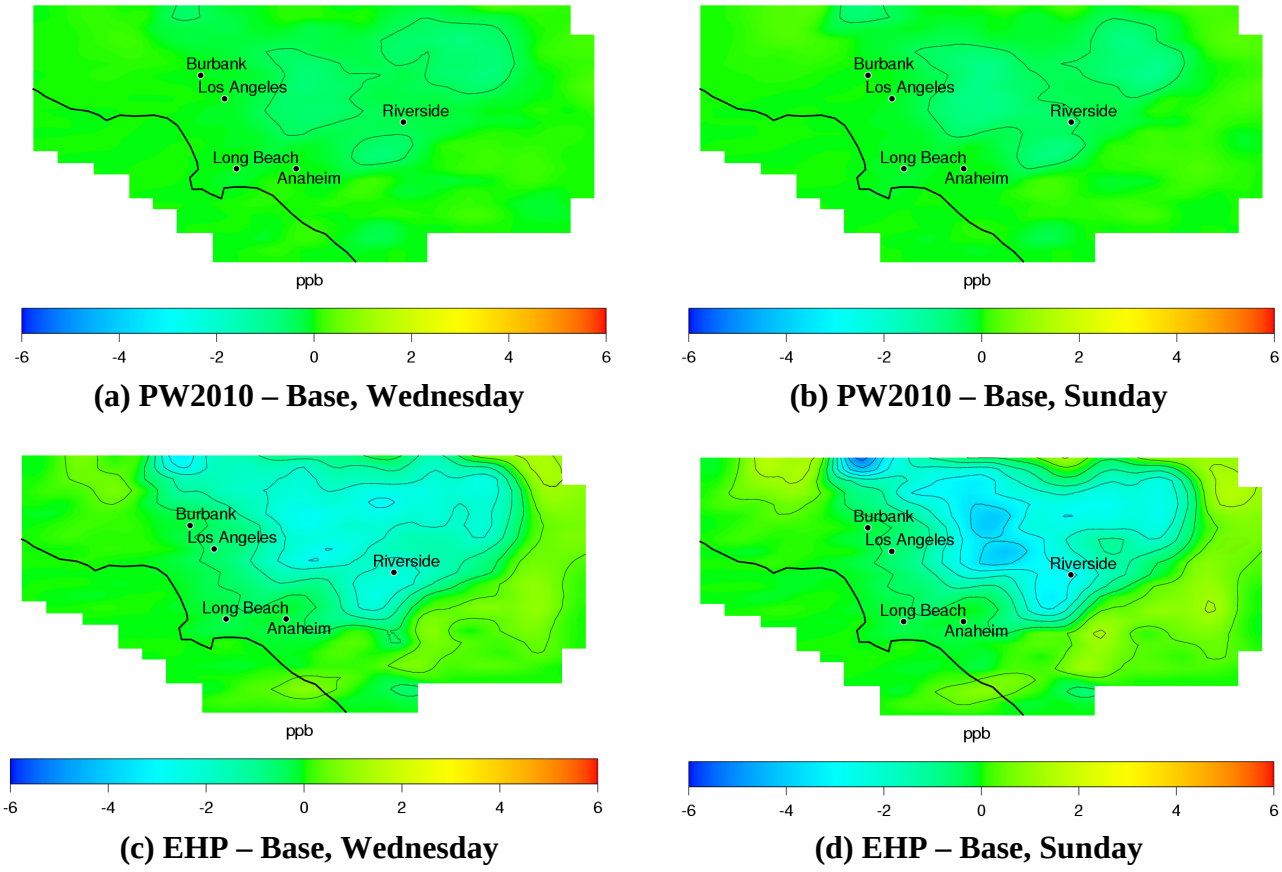
Understanding how introducing new emissions from DG affects the weekend effect requires that one first understands how DG affects the air quality in a representative weekday and in a representative weekend day. Figure 20 shows the differences in ozone concentration at hour 16:00 between the scenarios PW2010 and EHP, and the 2010 base case. Differences are shown for Wednesday and for Sunday, which are considered representative days for a weekday and a weekend day. Results show that the addition of emissions from DG leads to a reduction of ozone concentration at the time of the ozone peak (hour 16:00) in the central part of the basin, with respect to the base case. In scenario EHP, in which DG emissions are up to 5.5 times the emissions in PW2010, ozone concentrations increase in downwind locations in the eastern part of the domain, leading to a 1 ppb increase in the basin-wide ozone peak concentration. This suggests that the emissions in 2010, even though they are significantly lower than in 1997, still produce a VOC-limited regime in the central part of the domain. Consequently, small increases in NO_x emissions due to implementation of DG lead to decreases in ozone concentrations.

As shown in Figure 20a and Figure 20b, impacts on ozone concentrations in scenario PW2010 are small and similar along the entire week. As a result, DG implementation in scenario PW2010 does not produce any significant changes in the distribution and intensity of the weekend effect (See Figure 21).

Figure 21 shows the weekend effect intensity in the entire SoCAB for the base case, scenario PW2010 and scenario EHP. The weekend effect intensity based on the daily maximum for scenario PW2010 (Figure 21a) is exactly the same as the base case (Figure 21c). In addition, differences in weekend effect intensity based on the daily average between scenario PW2010 (Figure 21b) and the base case (Figure 21d) are small. Overall, the emissions levels introduced by scenario PW2010 do not affect significantly the weekend effect.

As shown in Figure 20c and Figure 20d, impacts on ozone concentrations in scenario EHP are larger than impacts produced by scenario PW2010. In addition, changes in ozone concentration over the weekend are larger than the changes during weekdays. This occurs because the relative contribution of DG emissions to total emissions is larger in the weekend than during the week. Ozone concentrations on Wednesday in the central part of the domain in scenario EHP are up to 3 ppb lower than ozone concentrations in the base case. On Sunday,

ozone concentrations in scenario EHP are up to 6 ppb lower than ozone concentrations in the base case. As a result, implementation of scenario EHP reduces the differences in ozone concentration between weekdays and weekends in the central part of the domain, dampening the weekend effect. However, differences in weekend effect intensity as defined in Section 4 between scenario EHP and the base case are small, regardless of whether the intensity is determined by the ozone daily peak concentration or by the ozone daily average concentration.



(a) PW2010 – Base, Wednesday

(b) PW2010 – Base, Sunday

(c) EHP – Base, Wednesday

(d) EHP – Base, Sunday

Figure 20. Differences in ozone concentration between two DG scenarios and the 2010 base case, at hour 16:00, of a representative week day and a representative weekend day.

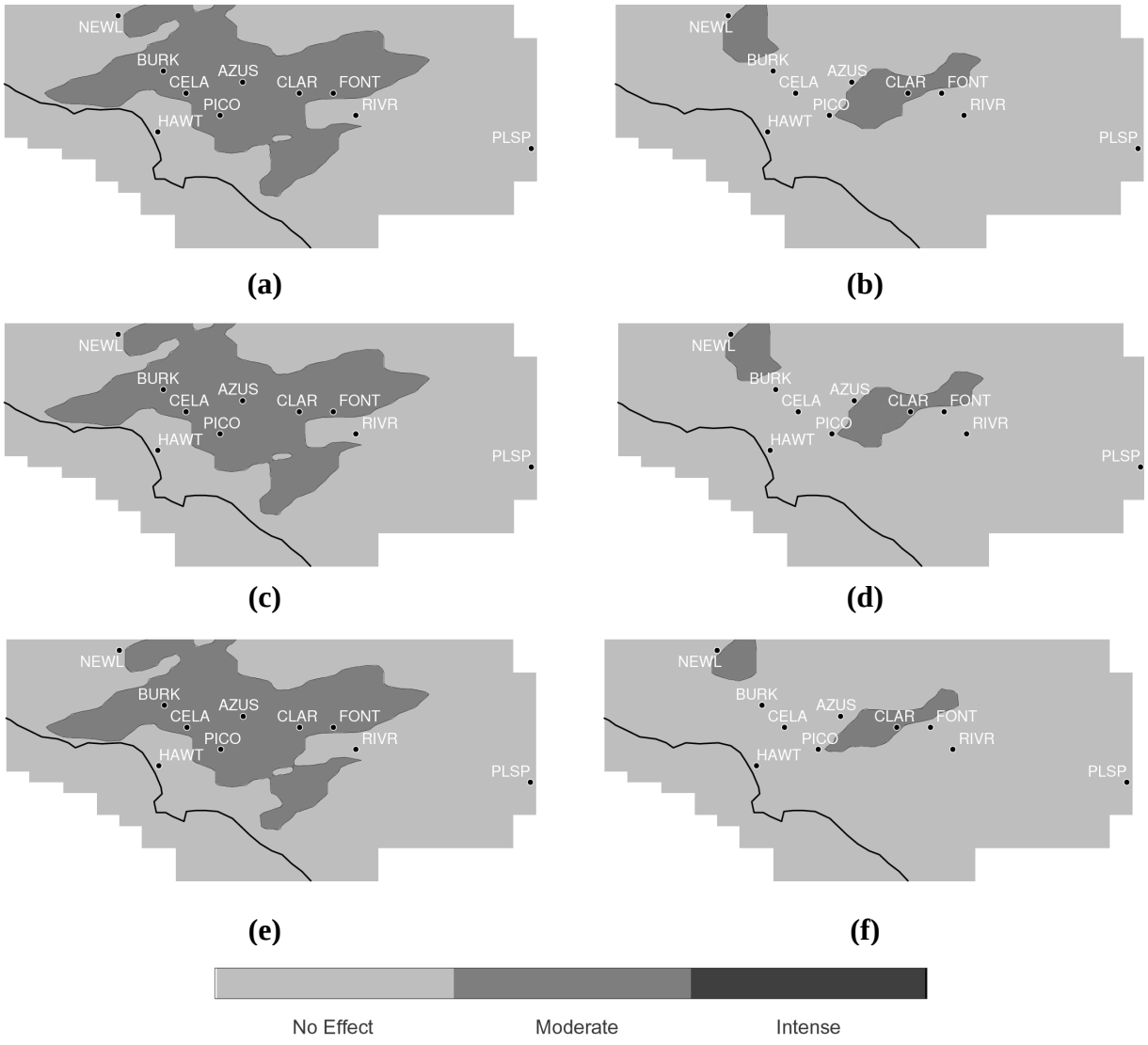


Figure 21. Weekend effect intensity in the South Coast Air Basin of California, using meteorological conditions of August 28, 1987, under different scenarios: (a) 2010 baseline weekend effect intensity based on maximum ozone concentration, (b) 2010 baseline weekend effect intensity based on 24-hour average, (c) PW2010 scenario weekend effect intensity based on maximum ozone concentration, (d) PW2010 scenario weekend effect intensity based on 24-hour average, (e) EHP2010 scenario weekend effect intensity based on maximum ozone concentration, (f) EHP2010 scenario weekend effect intensity based on 24-hour average.

8 EFFECTS OF OZONE ALOFT ON THE WEEKEND EFFECT

One of the hypotheses to explain the weekend effect is that pollutants are carried over above the nocturnal boundary layer, and may exert a greater influence on weekends than on weekdays for surface O_3 concentrations. To study the existence of pollutant reservoirs that are carried over from weekdays to weekends, this study analyzed the vertical profiles of pollutant concentration at altitudes up to 1100m.

Originally, the UCI-CIT Airshed model was designed to output pollutant concentrations from the ground level layer only. Consequently, to study how the concentration of ozone is affected aloft, the model is modified to output the concentrations of pollutants above the ground level of 38m, up to the height of 1100m. The model utilizes the mixing height prescribed by data estimated by CALMET, which influences the vertical mixing of the pollutants.

8.1 Effects of NO_x emissions on the weekend effect

A set of simulations were conducted to analyze the effect of reducing NO_x emissions on ozone concentrations aloft. The weekday emissions were kept the same as in the base case, whereas weekend emissions were scaled by factors of 0.8, 0.6, 0.4, 0.2 and 0. Results are evaluated for the ground level layer and upper levels. Figure 22 shows the effect of changing NO_x emissions on peak ozone concentration at different vertical levels at a specific location in the basin (Azusa).

It is important to note the effect of reducing NO_x emissions by 20% because it is equivalent to weekday-weekend changes in emissions: on the weekends, emissions of VOC decrease by approximately 6% and emissions of NO_x decrease by approximately 27% compared to mid-week. Hence, the VOC/NO_x ratio on weekends is about (1-0.06)/(1-0.27) = 1.29 times the mid-week VOC/NO_x ratio. If one only changes NO_x emissions – as in Figure 22 – to analyze the weekday-weekend trends, the weekend NO_x emissions should be 0.78 times the midweek NO_x emissions to maintain the same relation in the VOC/NO_x ratio between weekdays and weekends. Namely, if NO_x emissions in weekends are 22% lower than in weekdays and VOC emissions remain constant, the VOC/NO_x ratio on weekends is about 1.00/0.78 = 1.29 times the mid-week VOC/NO_x ratio, which is equivalent to the relation between weekday and weekend actual emissions. Figure 22 shows that when NO_x emissions are reduced by 20%, Saturday peak ozone

is smaller than Sunday peak ozone in all four layers of the atmosphere shown. In the SoCAB, Sunday peak ozone is typically higher than Saturday peak ozone. Hence, simulation results agree qualitatively well with the relative Saturday and Sunday peaks observed from ambient data.

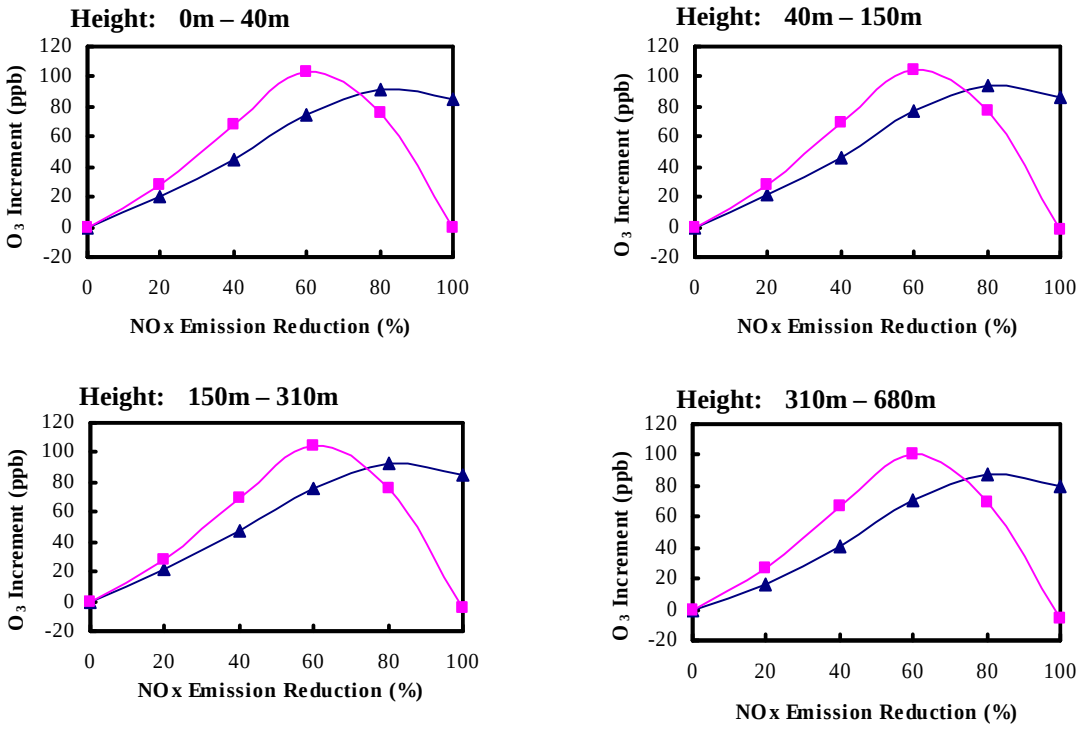


Figure 22. Effect of changing NO_x emissions on peak ozone concentration at different heights. Peak ozone on Saturday (▲); Peak ozone on Sunday (■).

8.2 Effects of ozone concentration aloft on the weekend effect

The concentration profiles of NO_x and ozone at various heights are compared at specific times and locations. In order to verify the validity of the model results, predicted values are compared with measurements from Southern California Ozone Study 1997 (SCOS-97). Figure 23 shows that the measured and predicted ozone vertical profiles at 8:00 a.m. and 2:00 p.m. in Central Los Angeles, Pomona, and Riverside display similar trends. Simulation results show good agreement with measurements in the first three layers of the modeling domain (0m to 308m). The most drastic weekend effect intensity occurs, as modeling results show, in the first three layers of the domain (0m to 308). More specifically, the greatest weekend effect intensity is

shown to be in layers two and three (38m to 308m), which is the focus of this study. The fourth (308m to 671m) and fifth (671m to 1100m) layer of the domain have the some discrepancies in ozone concentrations with the SCOS-97 data. In fact, the model tends to over-predict the ozone concentration. Comparing the morning and afternoon ozone vertical profile at the three locations mentioned, the afternoon shows a better agreement between the predicted and measured value. This may be attributed by the presence of the inversion layer which is dependent on the meteorology. One must note that the model simulations are performed using SCAQS-87 meteorology episode, which was a comparatively intense set of meteorological conditions; on the other hand, SCOS-97 is notorious for having mild meteorological conditions. Hence, there is no reason to compare the two quantitatively, but only qualitatively.

There is little information on observations of NO_x vertical profiles that can be used to evaluate model performance. Roberts et al. (1993) presented vertical profiles of ozone and NO_x concentrations obtained by aircraft spiral measurements in El Monte, CA, which is approximately 20 km from Central Los Angeles. Vertical profiles were obtained from ground level through 1500m in the morning, midday and afternoon of June 25, 1987. Aircraft measurements show qualitatively good agreement with the model predictions obtained for Central Los Angeles. Measured NO_x concentration at ground level is high in the morning and decreases dramatically at 1000m, which matches model results. The observed vertical gradient of NO_x concentrations at around noon is less steep than in the morning, and in the afternoon hours NO_x concentrations observed at ground level increase with respect to the ones at midday. All these features are observed qualitatively in Claremont, which is located 30 km eastwards from El Monte. Nevertheless, more measurements on vertical distribution of ozone precursors would be necessary to better assess model performance that could be used to study the hypothesis of ozone aloft as a cause of the weekend effect.

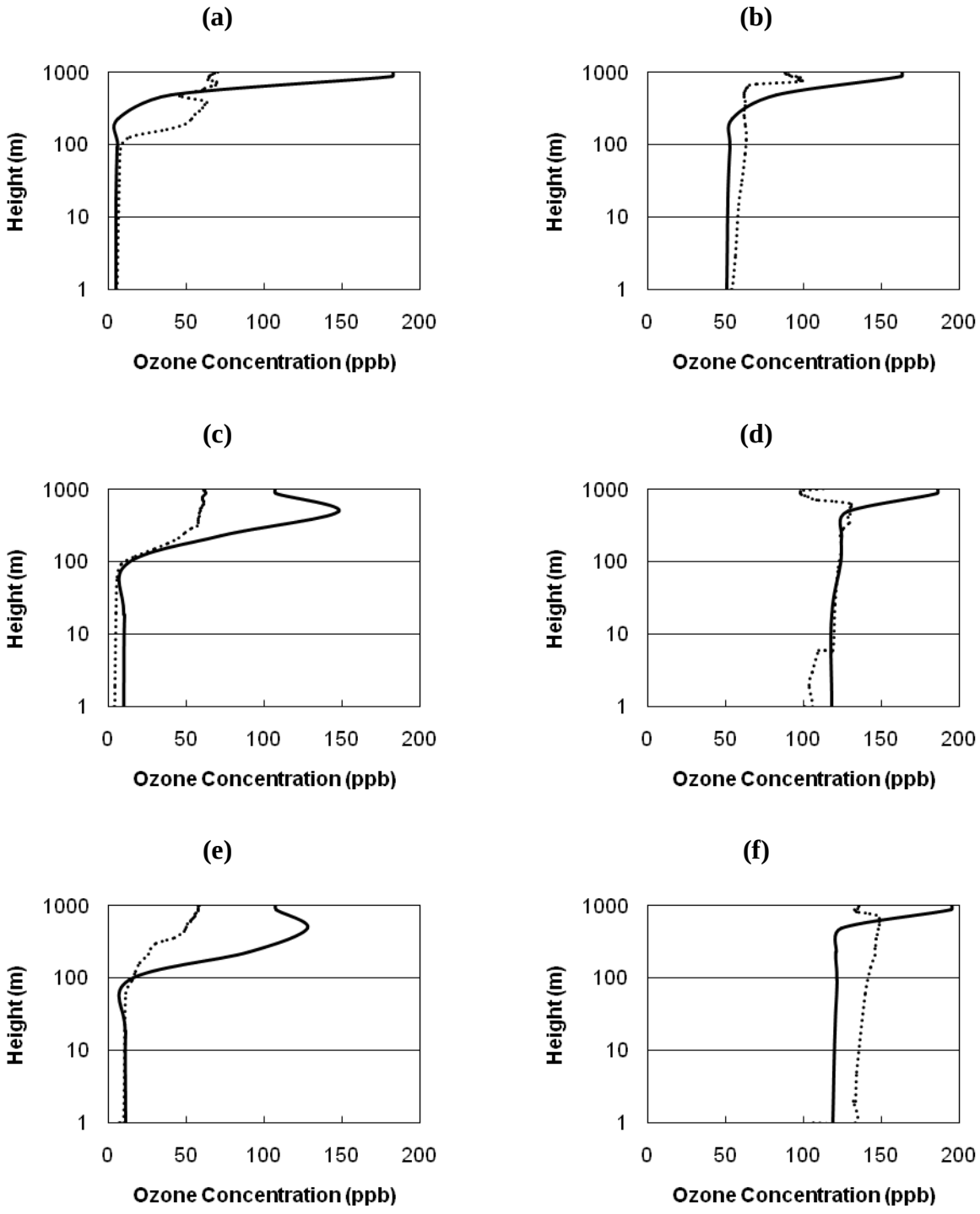


Figure 23. Southern California Ozone Study 1997 (SCOS-97) measurements (dashed line) and model predictions (solid line) of ozone concentrations versus height for August 6, 1997: (a) Central Los Angeles at 8:00 a.m., (b) Central Los Angeles at 2:00 p.m., (c) Pomona at 8:00 a.m., (d) Pomona at 2:00 p.m., (e) Riverside at 8:00 a.m., (f) Riverside at 2:00 p.m.

Figure 24 and Figure 25 show ozone and NO_x vertical profiles at hours 7:00 a.m., 1:00 p.m. and 5:00 p.m., in Claremont and Central Los Angeles, respectively. These two figures show an inverse relationship between the increase in ozone and the decrease in NO_x concentration from weekdays to weekends. Using the weekday results as a baseline, ozone concentration at the surface in Central Los Angeles increased about 33% on the weekends. This is consistent with weekend effect analysis of ambient measurements at the L.A.-North Main monitoring site. Also, the amount of ozone sequestered in the air at 7:00 a.m. can be expressed as 48,750 ppb-meters (area of the triangle aloft). This is the same for both weekdays and weekends, which is appropriate for assessing the effect of lower NO_x and VOC on weekends compared to weekdays. The amount of total ozone in the air at 1:00 p.m. is about 93,000 ppb-m on weekdays and 104,500 ppb-m on weekends. This indicates an increase of 11,500 ppb-m in total ozone or a 12% increase. Therefore, the same ozone carryover from the day before yields 12% more ozone in general, but 33% more ozone recorded at ground level.

Figure 25 indicates that total NO_x on the weekend dropped by 40% compared to the weekday amount. The total difference in NO_x was approximately 19,200 ppb-m. So, a decrease of 19,200 ppb-m NO_x yielded an increase of 11,500 ppb-m ozone, perhaps due entirely to a decrease in surface-level destruction of O_3 by fresh NO. This is what is meant by the ozone that carries over aloft is allowed a disproportionate effect on weekends compared to weekdays. A 40% decrease in NO_x yielded a 12% increase in total ozone and a 33% increase in ozone measured at the surface. The 12% increase in total ozone is the only aspect of these quantities that is difficult to corroborate with measured data, due to the scarcity of measurements aloft.

The above discussion links the carryover aloft hypothesis with the surface O_3 quenching hypothesis. That is, the presence of large amounts of fresh NO emitted at the surface on weekends prevents the expression of both carryover ozone and newly created ozone at the surface. On weekends, the large decrease in fresh NO emitted at the surface allows more of the total ozone, half of which is carryover, to be expressed at the surface.

Figure 24 representing Claremont differs in a few ways from Central Los Angeles. At 7:00 a.m., the initial ozone reservoir aloft is greater for the weekend than it is for the weekdays. The way the modeling was set up, the reservoir should be the same before sunrise, when vertical mixing and photochemistry begin. So, one must assume that convective mixing from the surface

is already starting to erode the nighttime surface-based inversion, which is consistent with some field observations. Also, one must entertain the possibility that the mixture of ingredients aloft generates additional ozone before vertical mixing reaches it. Such phenomenon was observed in the surface-based Light Detection and Ranging (LIDAR) for remote observation of ozone aloft during the SCOS-97 field study. The ozone LIDAR was set up at the El Monte Airport, and ozone concentrations were monitored up to two kilometers up to two kilometers with the differential absorption LIDAR (DIAL). The field-study report shows that new ozone is created from 500m to 1500m aloft, between the hours of 7 and 8 a.m., well before convective mixing would reach that high. Our model results show similar patterns as the LIDAR measurement of higher ozone concentration aloft compared with the ground level during the morning hours.

Rough calculations using Figure 24 indicate a 10% increase in total ozone at 1:00 p.m. on the weekend compared to the weekdays with a 26% increase in ozone. A 10% increase in total ozone delivered a 26% increase in the surface-based weekend effect. Figure 24c shows an even higher peak on the weekend for a 35% weekend effect. At 1:00 p.m., a drop of 13,500 ppb-m in total NO_x represents a 45% reduction in NO_x that resulted in a 26% increase in ozone concentration from weekdays to weekend.

A basic question is this: why did the 12% increase in total ozone at Central Los Angeles and the 10% increase in total ozone at Claremont occur? Of course, it is possible that non-linear ozone chemistry, such as VOC/NO_x ratio hypothesis, plays a significant role in producing the apparent results. However, an alternative explanation is available here as well.

The reduced amount of fresh NO on weekends is carried aloft by convective mixing where it encounters O_3 and organic radicals fumigating downward from the reservoir that was sequestered aloft over night, where NO flashes to NO_2 immediately. This NO_2 is in the presence of aged VOC's and, presumably, organic radicals that also carried over aloft. Therefore, the new NO_2 immediately enters a system prepared to generate new ozone efficiently. As demonstrated in Figure 28, the VOC/NO_x ratios in the carryover system aloft are quite high, and the set a necessary numerical limit of 50; actual ratios can be significantly higher. Each new NO molecule would destroy one O_3 but then help generate multiple O_3 molecules. In that case, the VOC/NO_x ratio of fresh emissions is not the main culprit; instead, the interaction of fresh NO with ozone that carries over from the previous day makes ozone production more efficient.

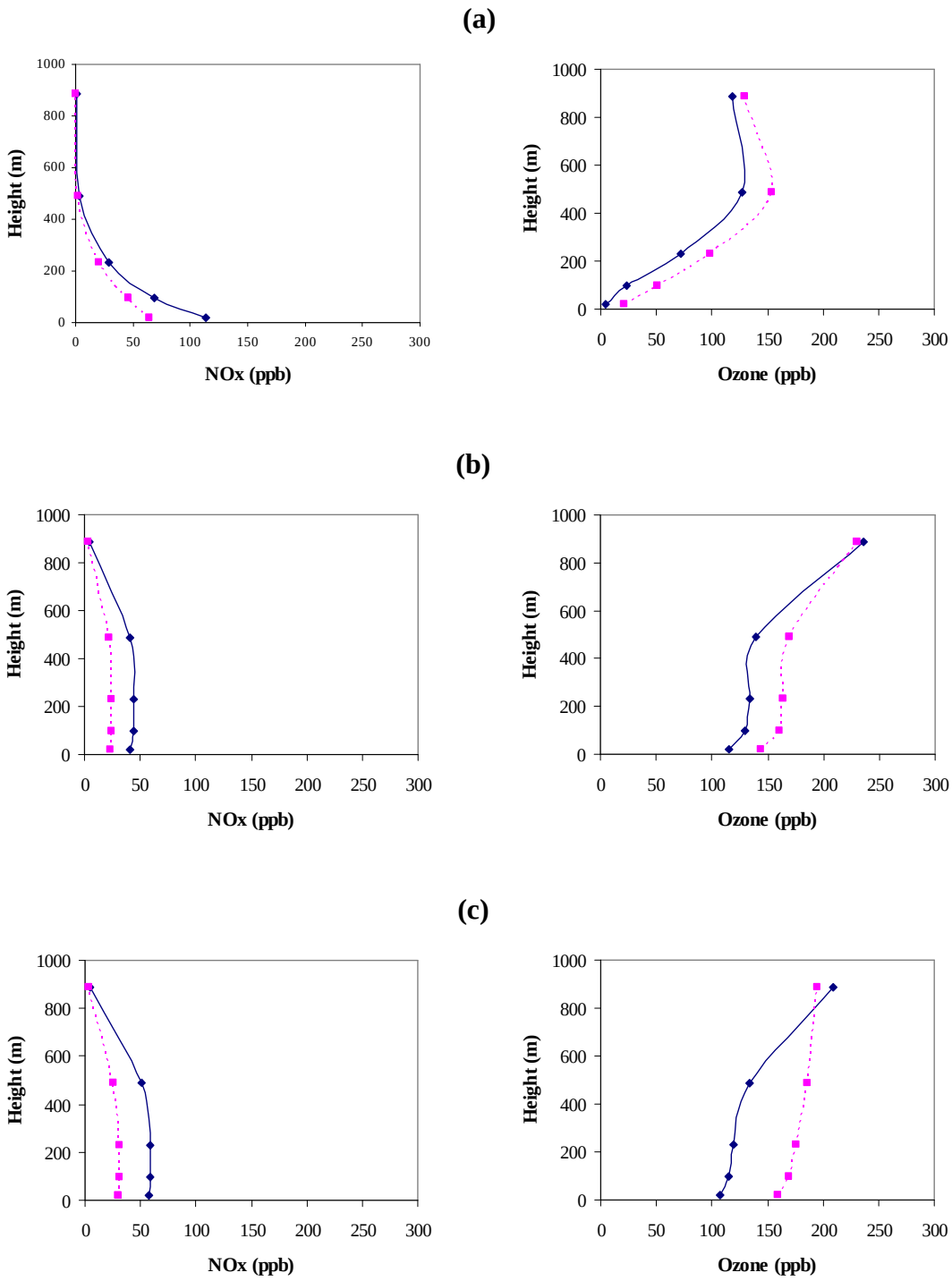


Figure 24. Weekday (♦ solid line) and weekend (■ dashed line) ozone and NO_x concentrations versus various height levels at Claremont, (a) 7:00 a.m., (b) 1:00 p.m., and (c) 5:00 p.m.

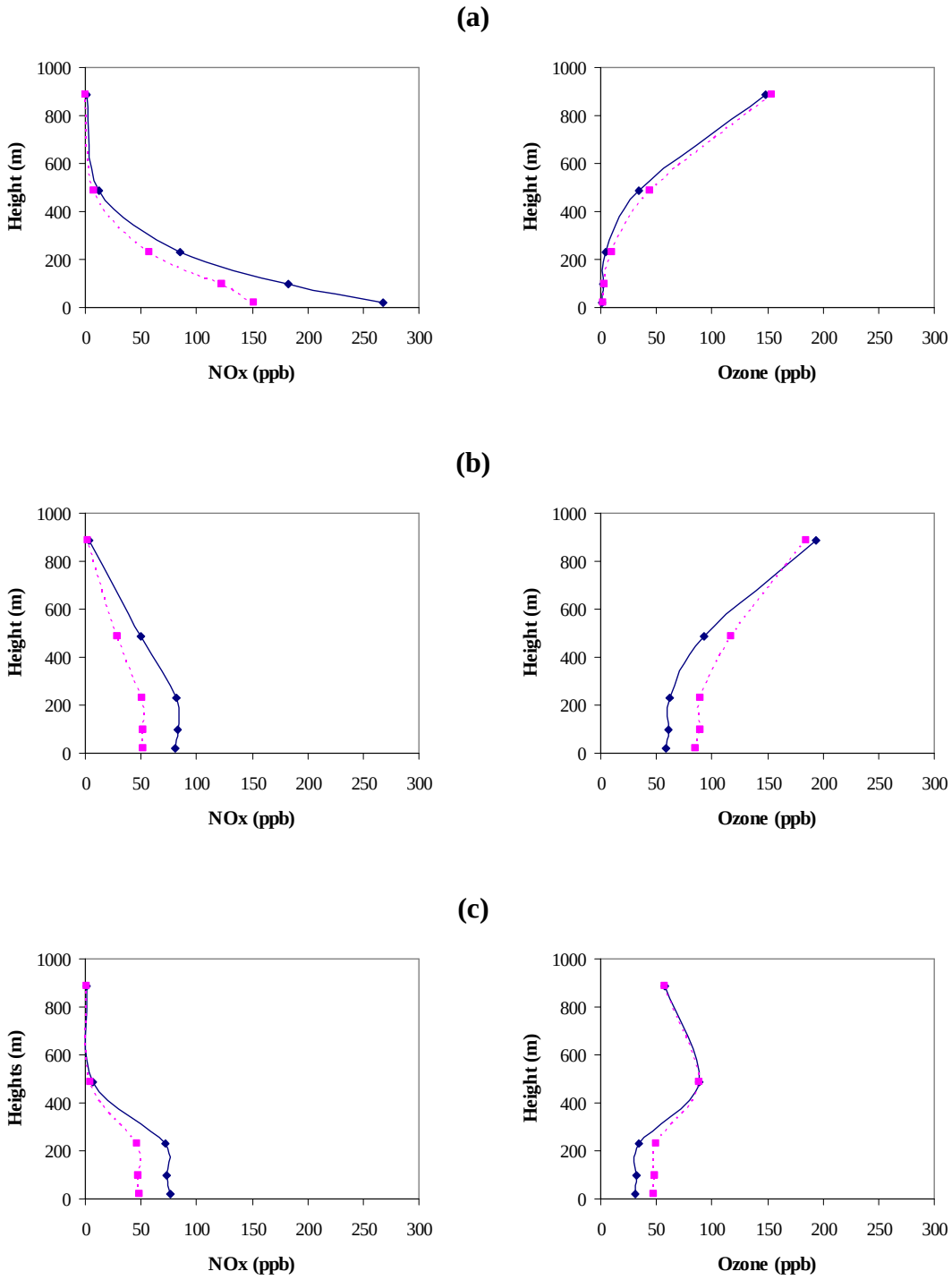


Figure 25. Weekday (◆—solid line) and weekend (■ dashed line) ozone and NO_x concentrations versus various height levels at Central Los Angeles, (a) 7:00 a.m., (b) 1:00 p.m., and (c) 5:00 p.m.

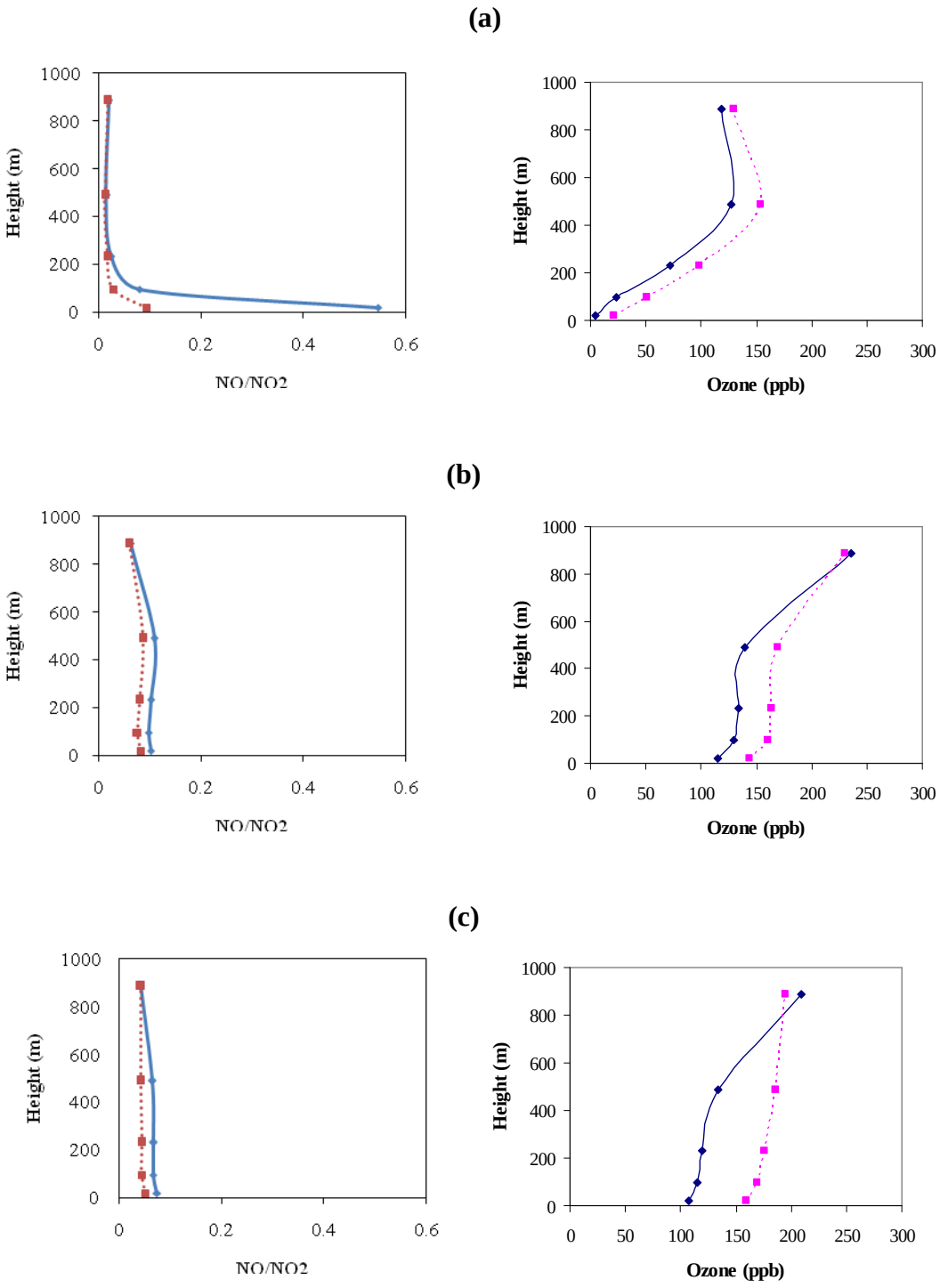


Figure 26. Weekday (solid line) and weekend (dashed line) NO/NO_2 ratio and ozone concentration versus height levels at Claremont, (a) 7:00 a.m., (b) 1:00 p.m., and (c) 5:00 p.m.

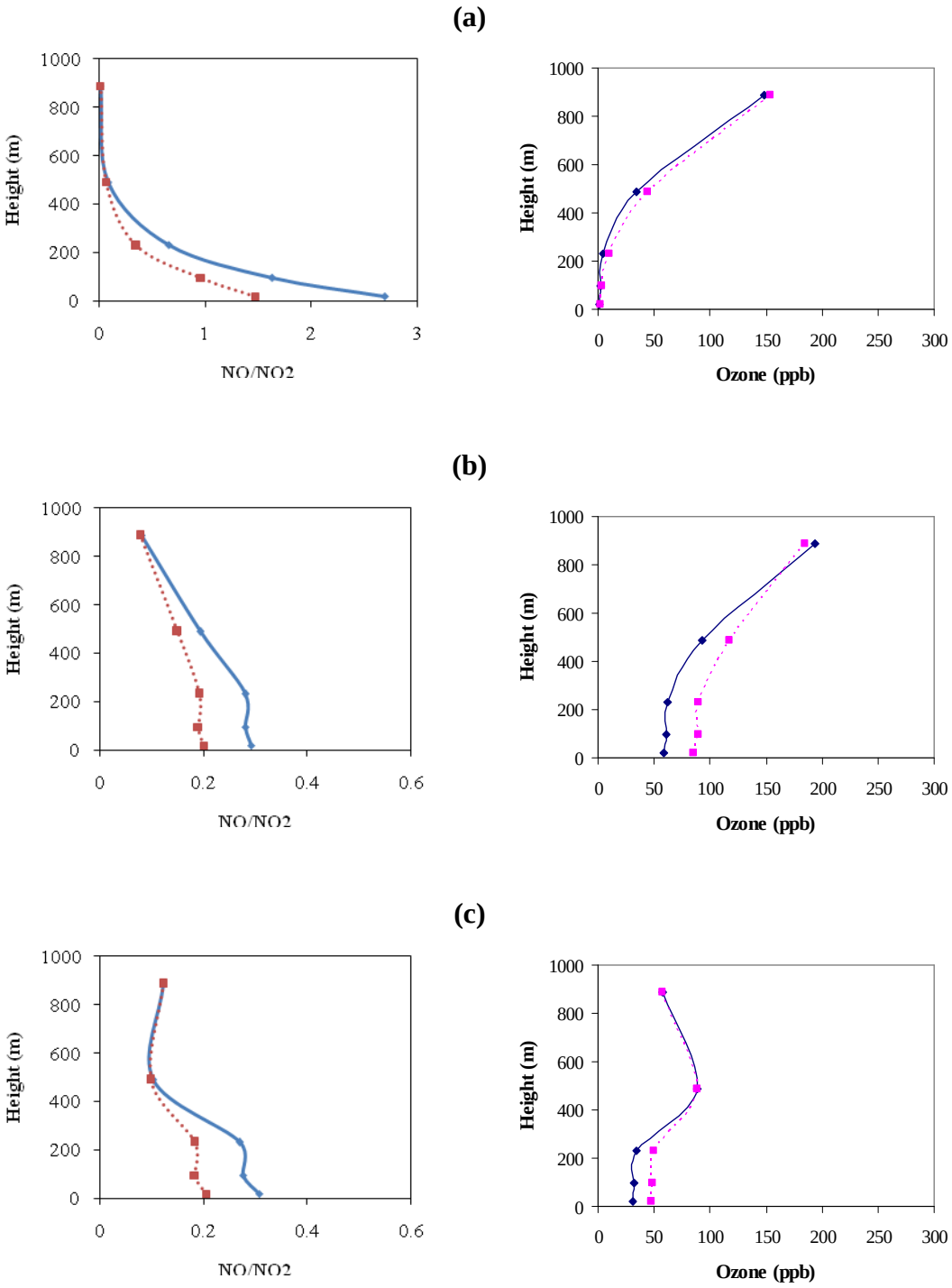


Figure 27. Weekday (solid line) and weekend (dashed line) NO/NO_2 ratio and ozone concentration versus height levels at Central Los Angeles, (a) 7:00 a.m., (b) 1:00 p.m., and (c) 5:00 p.m.

Rarely have smog chamber studies been performed with initial conditions that already have a large mass of gases with 50 to 100 ppb ozone followed by gradual introduction of smaller amounts of gas containing fresh NO. Data from one such experiment found that a fresh infusion of NO did not cause ozone to drop perceptibly. Instead, ozone was produced rapidly, and the system quickly reached a new, substantially higher ozone peak (Hess et al., 1992).

Figure 26 and Figure 27 show the vertical profiles of NO/NO_2 ratio at hours 7:00 a.m., 1:00 p.m. and 5:00 p.m., in Claremont and Central Los Angeles, respectively. A decrease in NO/NO_2 ratio from weekdays to weekends also has an inverse relationship with the increase in ozone weekdays to weekends. A trend of higher ozone concentrations at upper levels coincide with the decrease in NO/NO_2 ratio, which is explained by the decrease in ozone titration due to the virtual elimination of NO with altitude, and the increase in ozone production by the increase in NO_2.

To quantify the effects of NO_x aloft in the modeling domain, the ratios of VOC to NO_x concentrations at each of the five modeling layers are examined individually. The analysis consists in comparing the weekday/weekend 24-hour average VOC/NO_x ratio at each of the five height domains. In order to avoid invalid values resulted from zero NO_x concentrations, the maximum VOC/NO_x ratio is set at 50. Figure 28 shows the daily average VOC/NO_x ratio for weekdays and weekends at the five vertical levels of the modeling domain. Note that the VOC/NO_X ratios are generally smaller in the weekdays (denoted by a darker color). Figure 29 shows the difference in the VOC/NO_x ratio between weekends and weekdays. The model results show that ground level VOC/NO_x on the weekend is higher than on weekdays, because the decrease in NO_x emissions is greater than the decrease in VOC emissions from weekdays to weekends. At upper levels of the model domain, namely between 38m and 154m above the ground level, higher differences in VOC/NO_x from weekdays to weekend are actually observed in the central part of the domain. The increase of VOC/NO_x at this layer could explain why there is a more intense weekend effect at this layer than at the ground. The weekday-weekend VOC/NO_x ratio differences at heights between 154m and 671m follow a similar trend, where greater differences are observed at locations southeast of Pico Rivera and northwest of Central Los Angeles. Finally, maximum differences in the VOC/NO_x ratios between weekdays and weekends at the uppermost layer – from 671m to 1100m – occur in the central part of the

domain, which differs from what happens at lower levels. This indicates the significance of the ozone aloft dynamics in contributing to the weekend effect, as previously observed in Figure 5. At locations where no weekend effect was observed, such as Hawthorne, the changes in VOC/NO_x ratio throughout the week are minimal.

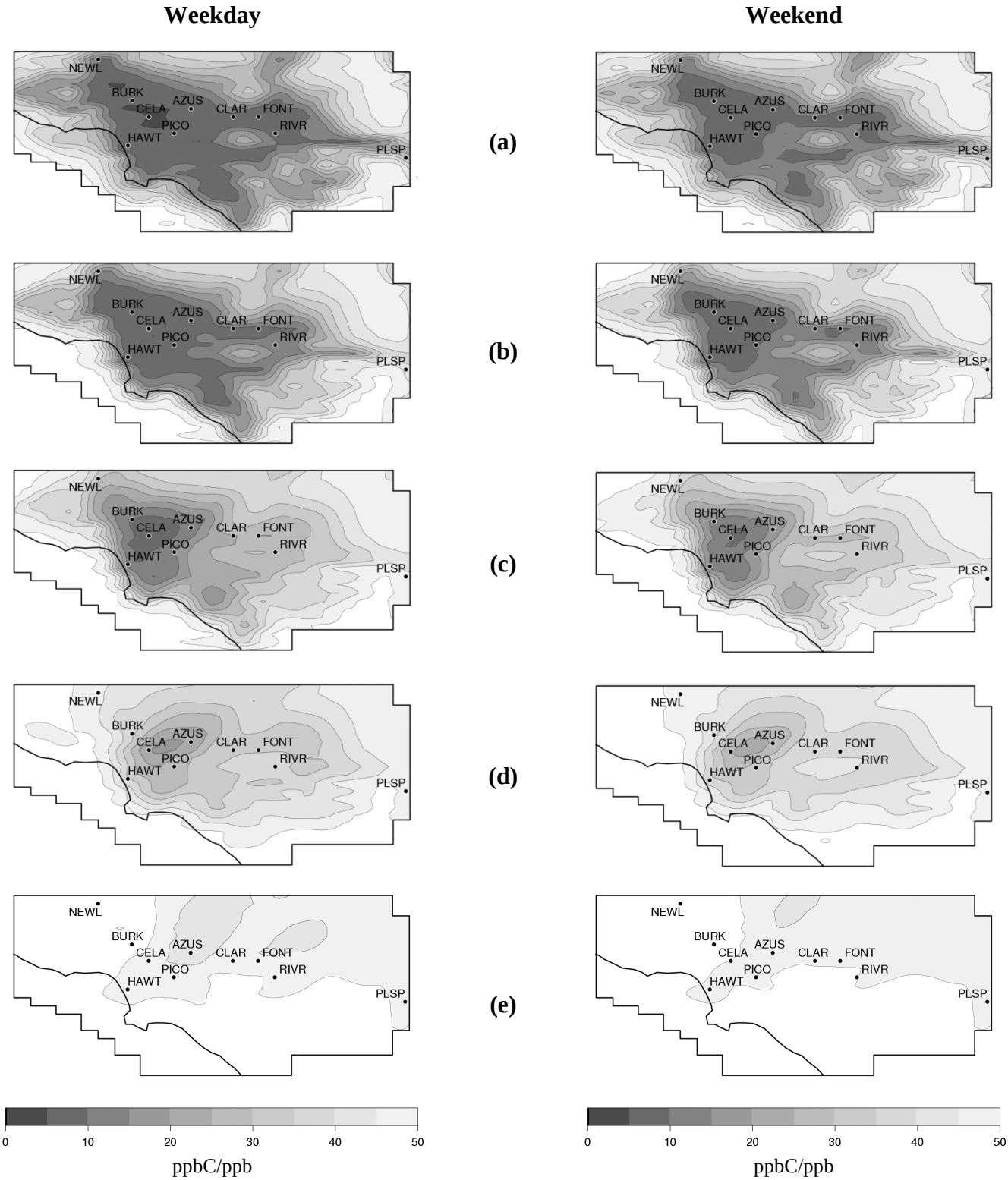


Figure 28. Daily average VOC/NO_X ratios (ppbC/ppb) for weekdays and weekends of the 1997 base case using meteorology from August 28, 1987 at: (a) 0m to 38m, (b) 38m to 154m, (c) 154m to 308m, (d) 308m to 671m, (e) 671m to 1100m.

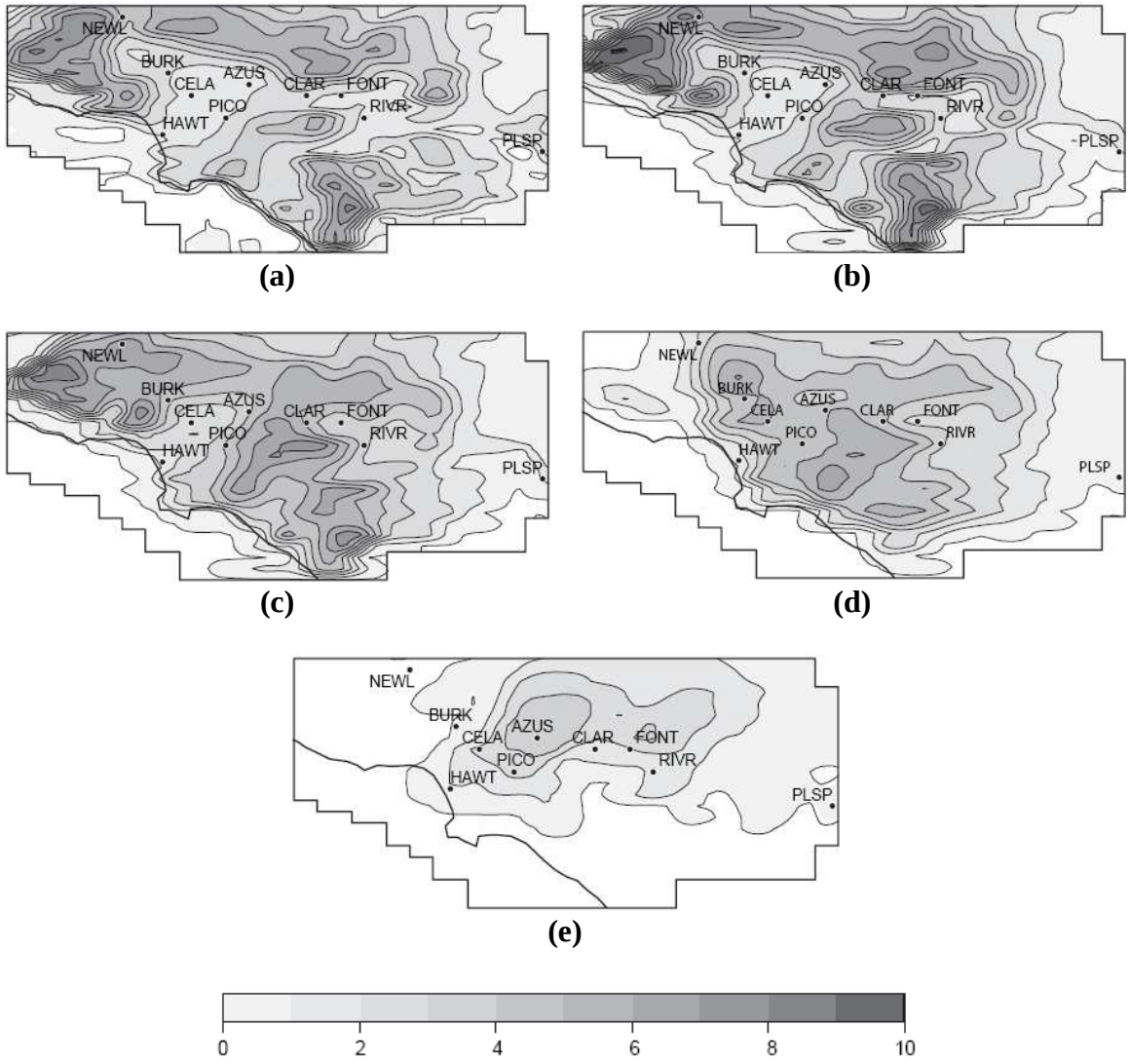


Figure 29. Weekend to weekday VOC/NO_X (ppbC/ppb) ratio differences in the South Coast Air Basin in California using meteorology from August 28, 1987 at: (a) 0m to 38m, (b) 38m to 154m, (c) 154m to 308m, (d) 308m to 671m, (e) 671m to 1100m.

A similar analysis is performed with VOC/NO_x ratios for the year 2010. As presented before, emissions of NO_x and VOC in 2010 are significantly lower than the emissions for 1997. Since the decrease in NO_X emissions from 1997 to 2010 is smaller than the decrease in VOC emissions for the same period, the VOC/NO_x ratio in 2010 is generally lower than in 1997. Having low VOC/NO_x ratio is thought to provide VOC-limited conditions that favor the weekend effect. However, simulation results show that ozone concentrations and the weekend effect intensity in 2010 are lower than in 1997. This does not correspond to what has been

observed from 1980 to 2000 in the South Coast Air Basin of California. Emissions of NO_x and VOC and the daily maximum concentrations of ozone – 1-hr or 8-hr – decreased on both weekdays and weekends throughout the SoCAB. However, ozone concentrations in weekdays improved more rapidly than it did in weekends. As a result, a gap between weekends and weekdays emerged and widened as the years progressed. The ozone weekend effect increased in absolute magnitude (O_3 ppb difference between weekends and weekdays) and increased even as emissions decreased and ozone concentrations decreased. The shift in the weekend effect intensity trends from the periods 1980-2000 and 2000-2010 could be explained partly by the significant decrease in VOC and NO_x emissions assumed by the 2010 emissions inventory with respect to the 1997 emissions inventory. In addition, weekend effect intensity in 2010 could be lower than in 1997 because VOC emission reduction from weekdays to weekend in 2010 is 13%, more than twice the weekday-to-weekend reduction in VOC emissions in 1997 (see Table 13). In a VOC-limited region as the SoCAB, a decrease in VOC tends to reduce ozone concentration. As the relative weekday-weekend reduction in VOC emissions in 2010 is larger than in 1997, the weekend effect intensity in 2010 is dampened with respect to 1997, even though the VOC/NO_x ratios present in 2010 – shown in Figure 30 – are smaller than in the year 1997. In addition, the differences in VOC/NO_x ratios from weekday to weekend in 2010 (see Figure 31) are smaller than the ones occurred in 1997, and supports the fact that lower differences in VOC/NO_x from weekday to weekends leads to lower weekend effect intensity. This is the first study that considers a future weekend effect episode, and further research is needed to confirm if there is an inflection point in the weekend effect intensity as the emissions are reduced in the future.

Table 13. Weekday and weekend emissions of NO_x and VOC (tons per day) in the South Coast Air Basin of California and the percentage reduction in emissions from weekdays to weekends for the years 1997 and 2010

	August 3-7, 1997			**August 3-7, 2010**		
	Weekday (tons/day)	**Weekend (tons/day)**	**Weekday-weekend decrease (%)**	**Weekday (tons/day)**	**Weekend (tons/day)**	**Weekday-weekend decrease (%)**
NO_x	771	566	27	325	251	23
VOC	1373	1291	6	513	445	13

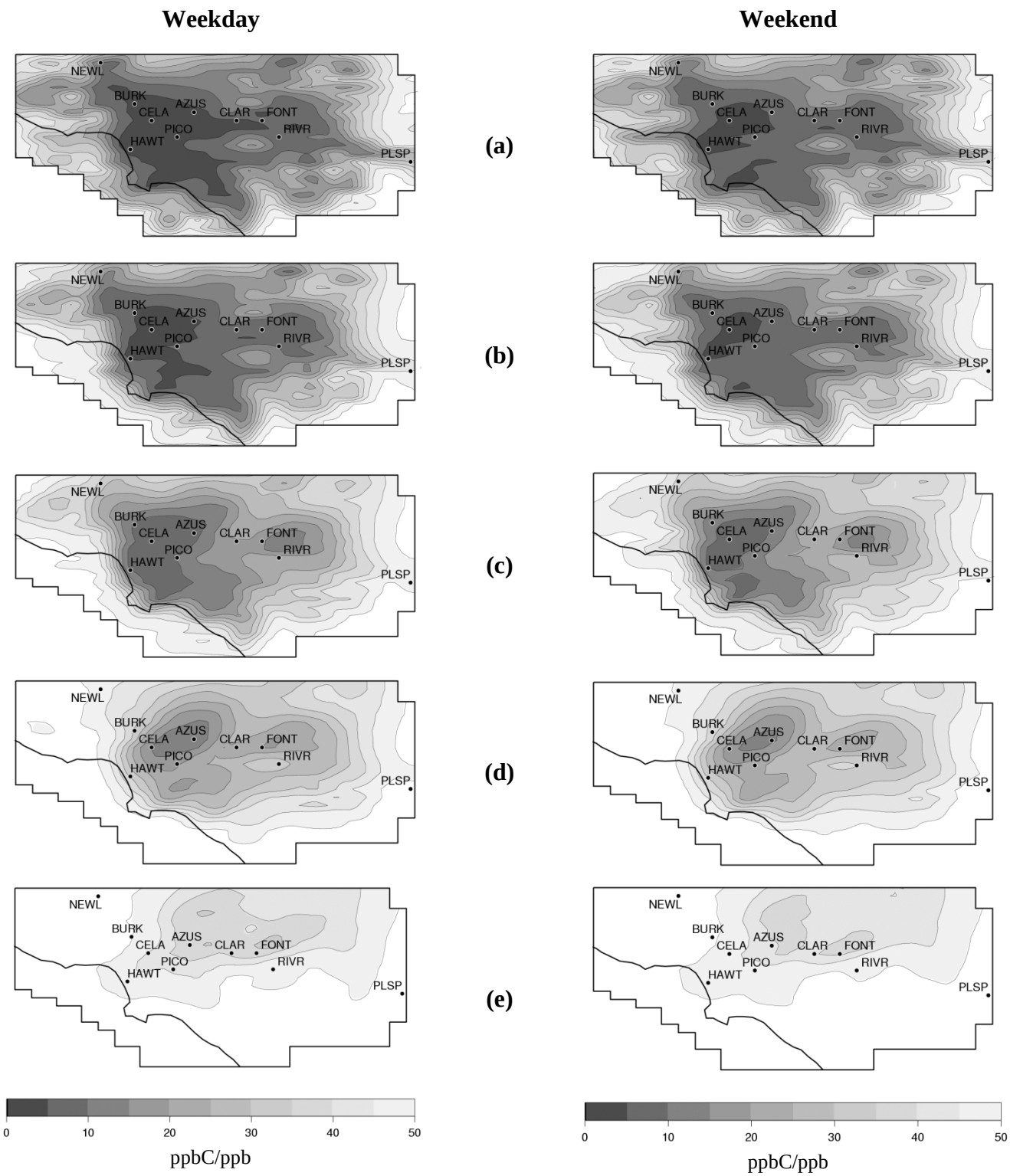


Figure 30. Daily average VOC/NO_x ratios (ppbC/ppb) for weekdays and weekends of the 2010 base case using meteorology from August 28, 1987 at: (a) 0m to 38m, (b) 38m to 154m, (c) 154m to 308m, (d) 308m to 671m, (e) 671m to 1100m.

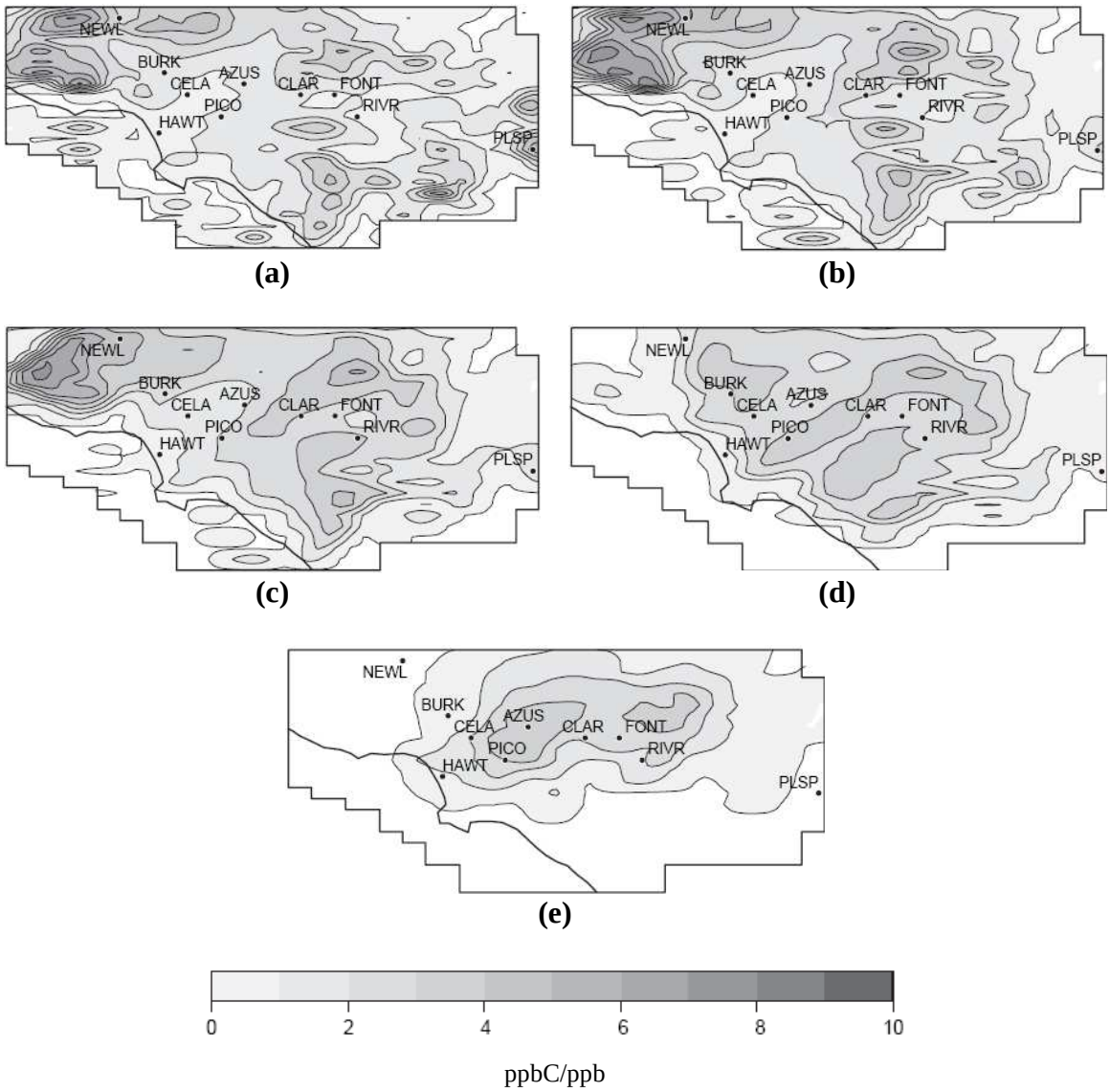


Figure 31. Weekend to weekday VOC/NO_X (ppbC/ppb) ratio difference in the South Coast Air Basin in California at various height levels for the year 2010. (a) 0m to 38m, (b) 38m to 154m, (c) 154m to 308m, (d) 308m to 671m, (e) 671m to 1100m.

9 SAPRC-07 CONSIDERATION

Carter (2007) describes recent developments in atmospheric chemical mechanisms and updates to the SAPRC mechanism. The new version, SAPRC-07, prompted a reevaluation of the chemical mechanism used in the UCI-CIT model, CACM. The scientific revisions implemented in SAPRC-07 from SAPRC-99 include: 1) updated of reactions and their rate constants based on recent scientific findings and evaluations; 2) reformulated method to represent peroxy reactions that is more appropriate for modeling secondary organic aerosol formation; 3) improved representations for several VOCs; and 4) new species and reactions of chlorine chemistry. The new features of the SAPRC-07 mechanisms and their relevance to CACM were examined.

SAPRC-07 has updated the base mechanism, the portion of the mechanism that represents the reactions of the inorganic species, the common organic products, and the intermediate radicals leading to these products. Most of the rate constant changes, however, as commented by Carter (2007), are relatively small. This was confirmed by a thorough examination of every rate constant and reaction in CACM. A few errors that were identified in SAPRC-99 are corrected in SAPRC-07, but none of which are present in CACM.

SAPRC-07 has also included the addition of lumped higher organic species that are closely associated with the formation of secondary organic aerosols (SOA), and their corresponding reactions, all of which are present already in CACM with finer lumping mechanisms. A detailed development of SOA mechanisms, however, was beyond the scope of SAPRC-07 project, so it is simplified in many respects. The UCI-CIT model utilizes a module based on inorganic gas-aerosol equilibrium named Simulating the Composition of Atmospheric Particles at Equilibrium 2 (SCAPE2) and the Model to Predict the Multiphase Partitioning of Organics (MPMPO) Mechanisms (Griffin et al., 2005).

Finally, SAPRC-07 has added chlorine chemistry into the box model as an optional capability. The effect of the addition of chlorine chemistry to the UCI-CIT model was studied in this project. The chlorine model presented in this study includes more species than SAPRC-07. It also considers heterogeneous and multiphase chlorine chemistry, which allows it to depict the effects of chlorine emissions using a very fundamental approach.

Overall, the current version of CACM implemented in the UCI-CIT model is not significantly affected by the development of SAPRC-07 mechanism. The changes in reactions

and rate constants in SAPRC-07 are relatively small, and most of the additional lumping mechanisms are already present in CACM. The improvement in SOA precursors in SAPRC-07 are already accounted for in the UCI-CIT model (Griffin et al., 2005). Finally, the addition of the chlorine chemistry mechanisms into SAPRC-07 is shown to be comparable to the chlorine chemistry mechanisms described by Knipping and Dabdub (2002). Therefore, the updates presented by Carter (2007) do not have any significant impact on the results of this study.

10 SUMMARY AND CONCLUSIONS

This study is the first to include new heterogeneous reactions involving renoxification and chlorine chemistry in a modeling analysis of the weekend effect. In addition, this effort explores the weekend effect in future emissions scenarios that include emissions from distributed generation in the SoCAB. Finally, this study analyzes the dynamics of ozone formation and weekly differences at upper levels of the urban air shed. All the input parameters used in the various case studies of this report are summarized in Table 14.

Table 14. Summary of the different inputs used in the main sections presented in this study.

	Chemistry			Emission Episode	
Sections	**CACM**	**Renoxification Reaction (R1)**	**Cl Chemical Reactions**	**1997**	**2010**
Base Case	Yes	No	No	Yes	No
Heterogeneous Renoxification Process	Yes	Reaction Probability (P)[a]	No	Yes	No
Sea-salt Activated Chlorine Chemistry	Yes	No	Amplification Factor (A)[b]	Yes	No
Distributed Generation (DG)	Yes	No	No	No	DG Emissions
NO_x Reduction	Yes	No	No	Weekend emission reduction	No

[a] P = 0.001, 0.01, 0.1, and 1.0
[b] A = 0.1, 1, 10, and 100

While in remote atmospheres there is a clear relationship among NO_x, VOCs and ozone, this relationship tends to breakdown in the urban atmosphere. In polluted air, the processes by which NO_x and VOCs create ozone begin to compete with each other and the relationship among ozone, NO_x and VOC concentrations becomes complex and nonlinear. A result of increasing

NO_x can lead to a decrease or increase of ozone depending on the local VOC concentrations. Table 15 summarizes the impacts that chlorine, renoxification, and distributed generation have on NO_x, ozone and the weekend effect. Notice that relationship among NO_x ozone and the weekend effect is not always very clear.

Table 15. Summary of the change in NO_x and ozone concentrations, as well as the weekend effect intensity, from the base case with the introduction of renoxification process, chlorine chemistry, and distributed generation.

	NO_x Impact	**O_3 Impact**	**Weekend Effect Impact**
Heterogeneous Renoxification Process	Increases NO_x recirculation while conserving NO_x mass	Increases O_3 production from newly available NO_x	Little difference in weekend effect intensity (minor decrease)
Sea-salt Activated Chlorine Chemistry	Decreases NO_x through NO_x reservoir species abstraction	Increases O_3 production in the presence of NO_x	Moderate decrease in weekend effect intensity
Distributed Generation (DG)	Increases NO_x due to direct emissions	Increases O_3 production downwind. Decreases O_3 near emission sources	No effect, less than 5 ppb change in ΔO_3 over base case

This study shows that the UCI-CIT Airshed model is capable of reproducing the weekend effect. The model uses different representative emissions for weekdays and weekends to create weekly fluctuations. Results of the base case simulation have shown good agreement with observations from Qin et al. (2004) who measured ozone concentrations during a period of seven summers. Modeling results show a weekend effect intensity that is generally higher than averaged historical values, as model results only represent one particular episode. Results show there is a significant weekend effect produced from variations in NO_x emissions. Nevertheless, the 1987 meteorological episode used in the simulations discussed is representative of the synoptic conditions in the SoCAB.

The renoxification reaction increases ambient concentrations of NO_x by releasing back NO_2 and HONO from the heterogeneous reaction of NO with HNO_3 in aerosols present on surfaces. The recirculation of NO_x back to the gas phase leads to an increase in ozone concentration with respect to the base case. Increases in ozone concentration due to renoxification occur on weekdays and weekends. However, increases in ozone concentration near strong NO_x sources during weekdays are larger than the increases that occur during weekends, resulting in a net decrease in the weekend effect intensity in areas around central LA. The influence of renoxification on the weekend effect depends on the renoxification reaction probability (*P*). Simulation results show that a renoxification probability less than 0.1 has a minimal impact on the weekend effect. Conversely, a renoxification probability of 1 leads to a basin-wide overall decrease in ΔO_3 of 2%. Earlier studies based on chamber experiments suggested that *P* could be on the order of 10^{-8}, and with the effect of high specific surface area, *P* could increase up to 10^{-4}. Another important factor that is yet unaccounted for in the renoxification probability is the specific area. Many urban environments have specific surface areas that are significantly larger than 1. A large specific surface area increases the available surface area renoxification can occur on and therefore can increase the renoxification probability. The effect of specific area on renoxification needs to be studied in more detail through measurements and experimentation. As a result, the impact of renoxification might still be under estimated due to the role of specific surface area. .

Results show that the addition of chlorine chemistry and a sea-salt aerosol source causes an increase in the maximum ozone concentration in the presence of NO_x, as suggested by Knipping and Dabdub (2002b). Chlorine leads to higher ozone production during the week days than during the weekend. Hence, the chlorine cases produce a less intense weekend effect compared to the base case. This trend continues as more chlorine is introduced into the system. An amplification factor of A=10 leads to the best agreement with observed chlorine levels in coastal areas and produces an overall basin-wide decrease in the weekend effect intensity of 29% compared to the base case.

There have been several studies focusing on the control of ambient ozone levels in California (Winner et al., 1995; Nguyen and Dabdub, 2002; Kelly and Gunst, 1990). Winner et al. (1995) examined the effects of changing the boundary conditions on ozone isopleths of Los

Angeles. Nguyen and Dabdub (2002) focused on the effects that control strategies have on particulate matter. Kelly and Gunst (1990) examined an outdoor smog chamber while varying initial contaminant concentrations. Results from all of these studies indicate that control of NO_x in the absence of VOC control is not enough to reduce ozone levels. The current study supports such a conclusion by providing modeling evidence of a weekend effect produced through weekly variations in emissions such as NO_x. In fact, lower NO_x emissions are capable of increasing ozone formation (e.g. Table 4).

The present study analyzed for the first time potential weekend effect in a future scenario in 2010. In addition, this study considers future emissions from distributed generation of power in the SoCAB and their impact on the weekend effect. In general, the weekend effect intensity in the year 2010 is milder than the baseline weekend effect simulated for the year 1997. The reduction of the weekend effect from 1997 to 2010 is mainly due to lower emissions of NO_x and VOC. The contribution of emissions from distributed generation to the total baseline emissions is less than 5% even for a high DG penetration scenario, and as a result, emissions from DG have a limited influence on the weekend effect.

Weekend effect levels are impacted by renoxification as well as chlorine chemistry. This work provides modeling evidence that indicates the observed weekend effect intensity in the SoCAB would be even greater in the absence of renoxification. In summary, renoxification leads to 2% average basin-wide decrease in the weekend effect magnitude in the SoCAB. Tables 4 and 6 show that at locations with large differences between weekday and weekend levels of ozone (those larger than 2%), the differences are even greater when renoxification is not considered. Namely, the values of ozone differences presented in the right-most column of Table 4 tend to be greater than the corresponding values in Table 6. More dramatically, realistic scenario of chlorine chemistry (A=10) leads to a 29% average basin-wide decrease. Therefore, it is highly recommended that future weekend effect studies incorporate at least chlorine dynamics.

This study reports for the first time results on weekend effect at upper layers of an urban air shed. In highly polluted areas, where NO_x emissions are high and the weekend effect intensity at ground level is strong, ozone concentrations at ground level are generally low due to titration of ozone by fresh NO. However, concentrations of ozone aloft are significantly higher than concentrations at ground level. The increase of ozone concentrations from ground level to

upper layers generally coincides with a decrease from high NO_x concentrations at ground level to low NO_x concentrations at upper levels. This supports the hypothesis that the weekend effect is mainly caused by the decrease in NO_x emissions from weekdays to weekends, which reduces the O_3-titration capacity of highly polluted areas, and hence high O_3 concentrations in the weekends. Parametric reductions of NO_x emissions lead to an increase in peak ozone concentrations in locations in the center part of the SoCAB at all vertical levels. Only very drastic reductions in NO_x emissions (close to 100%) lead to a reduction of ozone in all five layers of the computational domain after two days of simulation. VOC/NO_x ratios in the weekdays are lower than in weekends for the first four layers, in areas where the weekend effect is present. Only in the uppermost layer there is no significant weekend effect (in which there is no difference in VOC/NO_x between weekdays and weekends). In conclusion, the weekend effect occurs at ground level as well as at altitudes up to 670m, and is mainly due to the decrease in NO_x emissions and the increase in the VOC/NO_x ratios from weekdays to weekends.

RECOMMENDATIONS

This modeling study assesses the dynamic response of the weekend effect to the addition of the renoxification process and the incorporation of chlorine chemistry into air quality models. The results also show the influence of distributed generation on the weekend effect in future scenarios. Furthermore, this study focuses on the impact of pollutants aloft. Based on the results from the work presented, the following list of recommendations should be considered:

- More accurate accounting of anthropogenic chlorine sources is needed to better determine the distribution and concentration levels of chlorine in the SoCAB. This information combined with the sea-salt aerosol source should provide a better picture of the true weekend effect.

- The renoxification probability is inherently dependent upon ground roughness, specific area and land use. An empirical relationship among these parameters and the renoxification probability would allow for better modeling of the renoxification process and its subsequent impact on the weekend effect.

- Weekend episodes should be included in the analysis of air pollution control strategies. Simulation results of future scenarios in the year 2010 suggest that even with low NO_x and VOC emissions that could lead to attainment of the ozone air quality standards, there is a weekend effect. These findings imply that the SoCAB will be under VOC-limited conditions, which cause an increase in ozone concentrations due to decreases in NO_x emissions, as it generally happens from weekdays to weekends. Hence, weekend episodes are likely to pose more problems with the ability of the SoCAB to attain the ozone standards than weekday episodes.

- Although the influence of DG emissions to the weekend effect proved to be minor, DG emissions should be included in the emissions inventory to account for all sources in the SoCAB. Emissions from distributed generation could contribute to approximately 1% to the total basin-wide emissions in 2010. In future years the contribution of DG could be up to 5% if high penetration is achieved.

- Modeling studies indicate that the weekend effect intensity at heights from 40m to 300m is greater than at ground level. However; most measurement campaigns concentrate on ground level. It is recommended to also collect field data aloft to corroborate this modeling insight.

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