

Influence of sea-salt activated chlorine and surface-mediated renoxification on the weekend effect in the South Coast Air Basin of California

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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. This phenomenon has been named the weekend effect. This study uses the University of California, Irvine-California Institute of Technology (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. Additionally, this study modifies the Caltech Atmospheric Chemistry Mechanism (CACM), used in the UCI-CIT model, by introducing new heterogeneous reactions involving nitrogen oxides and chlorine. Eight modeling scenarios that include the nitrogen oxide renoxification and heterogeneous/multiphase chlorine reactions are presented to quantify how these reactions impact the weekend effect. The renoxification reaction and chlorine chemistry are found to increase ozone levels during weekdays and weekend days. However, increases in weekdays are generally larger than these increases that occur in the weekend. As a result, renoxification and chlorine chemistry lead to a net decrease in the average weekend effect intensity. The influence of renoxification on the weekend effect depends on the reaction probability (P), and the impact on the weekend effect is significant for P larger than 0.1. 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, which produces the best agreement with observed chlorine levels in the SoCAB, leads to a basin-wide overall decrease of 29% in the weekend effect intensity with respect to the base case.

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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 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 in weekends with respect to weekdays in

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the order of 25–41% and 12–30% for nitrogen oxides (NO_x) and non-methane hydrocarbons (NMHCs), respectively. Based on these historical measurements, there are several hypotheses that could explain the nature of the weekend effect. 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 in 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 (VOCs) to NO_x ratios from 1981 to 2000, and observed that the reductions in VOC/ NO_x ratios were greater in weekdays than in weekends. Trends in 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 (SoCAB) of California, during the summer months of the years 1995–2001. Analyses on the observations showed a prominent weekend effect—more than 15 ppb increase in ozone concentration from weekdays to weekend—in downwind areas near Los Angeles. On the contrary, far downwind areas and upwind 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. Results showed 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.

This modeling study addresses several shortcomings of the preceding works by including important processes previously neglected by other researchers. Specifically, the present work focuses around two major objectives. First, it examines the effect of including a series of surface-mediated renoxification reactions that have the potential to increase the availability of NO_x and hence modify the process of ozone formation. Second, it investigates the impacts of heterogeneous chlorine chemistry on the weekend effect, particularly in coastal regions.

2. Approach to simulating the weekend effect

2.1. Model formulation

The University of California, Irvine-California Institute of Technology (UCI-CIT) atmospheric chemical transport model is used to analyze the air quality in the SoCAB of California. The computational domain, shown in Fig. 1, corresponds to an irregular region composed of 994 columns of cells. Each column corresponds to a $5 \text{ km} \times 5 \text{ km}$ region in the x, y plane and extends 1100 m in height. The columns are partitioned into five layers in the

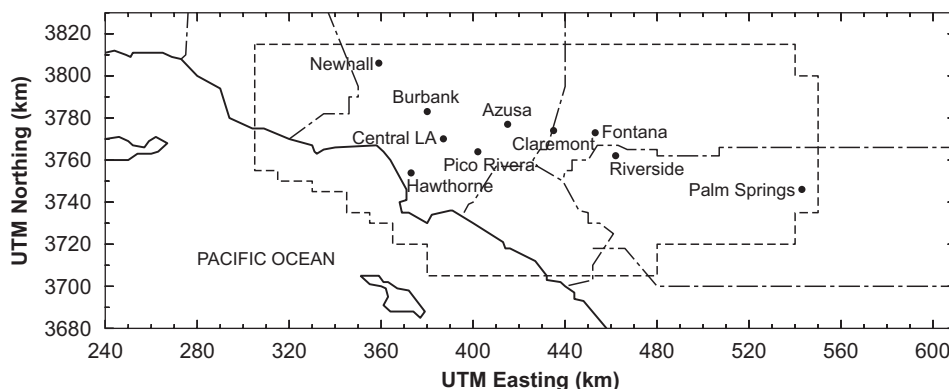


Fig. 1. Computational domain of the CIT Airshed Model that represents the South Coast Air Basin (SoCAB) of California.

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

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 (Yarwood et al., 2003). The approach in this study is to use one-day meteorology as the baseline meteorology for a period of two weeks to isolate simulation results from the effect of meteorology. The selected meteorological data correspond to August 28, 1987, which was part of the Southern California Air Quality Study (SCAQS). The SCAQS was a comprehensive campaign of atmospheric measurements in the 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, b; Pun et al., 2002; Moya et al., 2002; Knipping and Dabdub, 2002a, b). Zeldin et al. (1990) found that August 28, 1987 is representative of the meteorological conditions in the SoCAB, 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. Hence, meteorological conditions for August 28 are used here as the basis to evaluate the weekend effect.

The SCAQS episode in August 27–29, 1987 is characterized by a weak onshore pressure gradient and warming temperatures aloft. The wind flow is characterized by a sea breeze during the day and a weak land-mountain breeze at night. 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, facilitate the accumulation of pollutants over the SoCAB, which lead to high ozone concentration occurrence.

Simulation of August 27–28, 1987 is used to evaluate model performance against historical observations. The emissions inventory for the SCAQS episode is described in Meng et al. (1998). The emissions inventory was obtained directly from the California Air Resources Board (CARB), and contains both gas-phase and PM speciation. Model

performance is analyzed for the baseline UCI-CIT model, as well as for the additional chemistry introduced in the chemical mechanism.

The emission inventory selected for this study to simulate the weekend effect is the August 3–7, 1997 episode used in the *Air Quality Management Plan (2003)* designed by the South Coast Air Quality Management District of California (SCAQMD). These emissions were used to validate performance of the model used in the AQMP, and include emissions from Sunday through Thursday. The approach in the current study is to run the model using emissions from a representative weekday—Wednesday—for five days (Monday through Friday), then use emissions from a representative weekend day—Sunday—for two more days (Saturday and Sunday). Total basin-wide emissions for Wednesday and Sunday are presented in Table 1.

Emissions of NO_x and VOC during weekdays follow a different temporal profile compared to weekend emissions. As shown in Fig. 2, during morning and afternoon rush hours in weekdays (6:00–8:00 a.m. and 3:00–5:00 p.m.) emissions are significantly higher than in weekends. This indicates that the main factor that contributes to the difference in emissions between weekdays and weekends is traffic activity.

2.2. Weekend effect intensity

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

$$\Delta\text{O}_3(\vec{x}) = \text{O}_{3,\text{we}}(\vec{x}) - \text{O}_{3,\text{wk}}(\vec{x}), \quad (1)$$

where $\vec{x}$ is any cell in the domain, $\text{O}_{3,\text{wk}}$ is the 24-h peak ozone concentration averaged through the week, $\text{O}_{3,\text{we}}$ is the 24-h peak ozone concentration averaged through the weekend and ΔO_3 is the weekly change in peak ozone. The weekend effect intensity, I_{we} , is defined by the criteria suggested by Qin et al. (2004) based on the weekly change in peak

Table 1
Weekday-weekend basin-wide emissions of ozone precursors in the South Coast Air Basin of California (tons/day)

	Wednesday	Sunday	Reduction (%)
NO_x	862	636	26.3
VOC	1557	1472	5.4

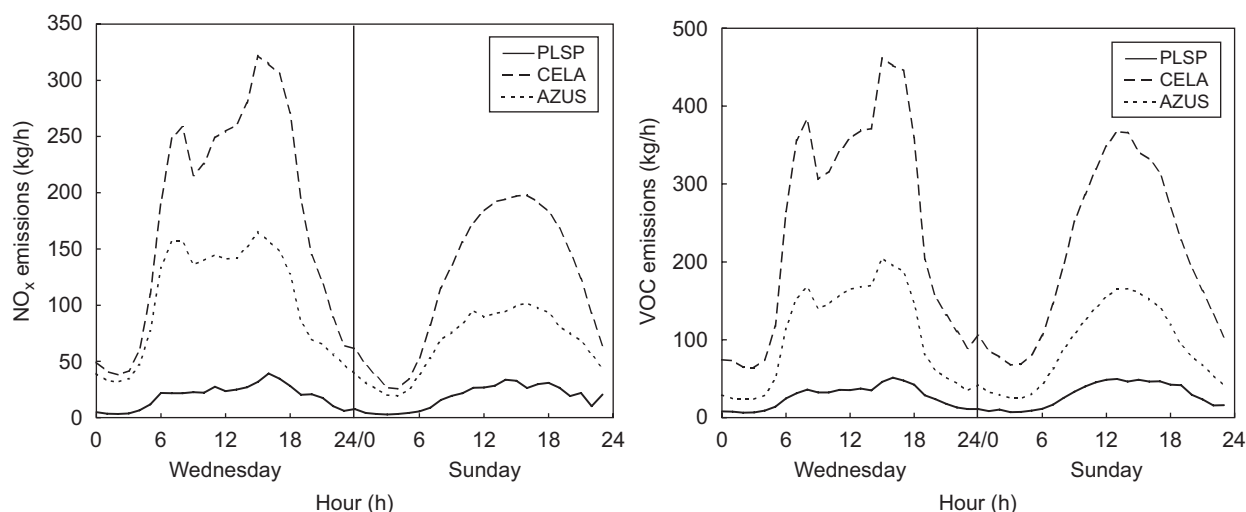


Fig. 2. (a) Baseline NO_x and (b) VOC emissions at selected locations. Solid line: Palm Springs (PLSP); dashed line: Central Los Angeles (CELA); dotted line: Azusa (AZUS). First 24 h correspond to emission estimates for Wednesday, August 6, 1997; second 24 h are emission estimates for Sunday, August 3, 1997.

Table 2

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

ΔO_3	I_{we} classification
$\Delta\text{O}_3 > 15$ ppb	Intense
$15 \text{ ppb} > \Delta\text{O}_3 > 5$ ppb	Moderate
$5 \text{ ppb} > \Delta\text{O}_3$	No effect

ozone, shown in Table 2. Analyses in this study of the weekend effect intensity concentrate on ground level cells.

The UCI-CIT Airshed model is used to simulate a two week period from initial data obtained from ozone aloft measurements recorded in September 7, 1993. The first week of simulations is used to spin-up the model to a steady weekly cycle and the second week of simulations is used for analysis.

3. Changes to the chemical mechanism

3.1. Renoxification

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



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.

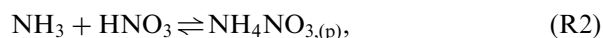
Recent studies by Mochida and Finlayson-Pitts (2000) use transmission Fourier transform infrared (FTIR) spectroscopy at room temperature to quantify the production of NO_2 as the major product of (R1). They used NO concentrations four orders of magnitude higher than in polluted atmospheres. The same techniques were repeated by Saliba et al. (2000) but using NO concentrations two 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 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 increase ozone concentrations. Previous studies analyzed model capabilities to simulate the weekend effect. 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 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:



where (p) denotes particulate phase (Seinfeld and Pandis, 1998). NH_4NO_3 , which can exist as a solid particle or in solution and 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 tropo-

sphere. Thus, areas with high NH_3 concentrations are more predisposed to exhibit high nitrate aerosol peaks. The proposed renoxification mechanism might indirectly influence PM 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.

Reaction (R1) is included in the UCI-CIT Airshed model to analyze its effect on predicted concentrations of the 1987 episode. As proposed by Knipping and Dabdub (2002a), the rate of this reaction is determined by evaluating the deposition rate of gas phase HNO_3 and the surface contact rate of NO. 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 have not been included in the simulation.

While Rivera-Figueroa et al. (2003) proposed a probability $P \geq 6 \times 10^{-9}$ for renoxification reaction (R1) on silica surfaces, Kleffmann et al. (2004) suggested that the probability of the heterogeneous reaction between deposited HNO_3 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 surfaces can reach surface areas of $0.2\text{--}3 \times 10^4 \text{ cm}^2 \text{ cm}^{-2}$ of geometric area, which would increase the net probability of the reaction by 2000–30,000 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 1 to analyze the effect of renoxification on ozone concentrations, as shown in Table 3. 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 HNO_3 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

Table 3
Renoxification scenarios and their associated renoxification probabilities

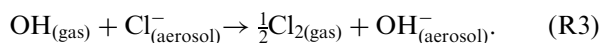
Scenario	Renoxification probability (<i>P</i>)
R1	0.001
R2	0.01
R3	0.1
R4	1

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.

3.2. Chlorine chemistry

There has been important research showing the significant role chlorine plays in the chemistry of the atmosphere (Cai and Griffin, 2006; Finlayson-Pitts et al., 1999). Knipping and Dabdub (2002b) conducted an investigation into the dynamics of chlorine chemistry. They created a modified chemistry mechanism which led to 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. This work analyzes the effect of adding chlorine reactions and sources in relation to the weekend effect. This is the first comprehensive analysis on the impact of chlorine on the weekend effect in the SoCAB. This study implements the most recent chlorine heterogeneous and multiphase reactions and a sea-salt particle source function to model the effects of chlorine.

A total of 115 chemical reactions are added to chemical mechanism: 83 of those reactions are in the gas phase and 32 are heterogeneous/multiphase reactions. See Knipping and Dabdub (2002b) for a complete list of all species and reactions added to the chemical mechanism. The most significant of these reactions is the chlorine formation from hydroxyl radical and chloride ions



Reaction (R3) occurs on the gas–liquid interface of deliquesced salt particles and is the primary source of molecular chlorine. Knipping and Dabdub (2002b) investigated reaction (R3) and determined an expression for the rate constant which is used here.

There are many sources of chlorine in the atmosphere with both anthropogenic and natural origins. The main anthropogenic sources include coal burning and pool purification. There are 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 wave 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. Monahan et al. (1986) correlated the sea-salt aerosol flux from this physical process to wind speed.

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

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

$$B = \frac{0.095 - 0.098 \log(r)}{0.65} \quad (3)$$

Notice that the sea-salt aerosol flux calculation is only dependent on the radius of the bubble and wind speed. As such, the strength of the chlorine source is highly dependent on meteorological conditions.

Knipping and Dabdub (2002b) reported that only adding marine aerosol sources clearly underestimate 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:

$$\frac{dF}{dr} = A \left(\frac{dF}{dr} \right)_0, \quad (4)$$

where A is an amplification factor and $(dF/dr)_0$ is the original sea salt aerosol source function described by Eq. (2). By amplifying the original

Table 4
Chlorine scenarios and their associated sea-salt aerosol source amplification factor

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

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 $A = 0.1$ to 100 are analyzed. Table 4 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.

4. Model performance evaluation

Results from the simulations of the August 27–28, 1987 episode, which use emissions and meteorological conditions from the 1987 SCAQS episode, are compared with observations. Time series of ozone concentration at three monitoring stations, Central Los Angeles, Claremont, and Riverside, are presented in Fig. 3. The three simulations conducted consist of: (1) the baseline UCI-CIT model, (2) baseline UCI-CIT model with renoxification reaction with a probability of reaction $P = 1$ and (3) the baseline UCI-CIT with chlorine chemistry with a sea-salt source function with an amplification factor of $A = 10$. The baseline model under predicts peak ozone concentrations of the second day at all three locations. Both renoxification and chlorine chemistry increases the ozone concentrations in the second day. For the chlorine chemistry case, the increase in ozone concentrations with respect to the base case in coastal regions, such as Los Angeles, is higher than in far inland locations, such as Riverside. This is because the effect of the chlorine

chemistry is more intense in coastal locations than in far inland areas. In the case of renoxification, peak ozone concentration increases slightly more than in the chlorine case, reaching better agreement with observations of ozone concentration for August 28.

5. Results

Qin et al. (2004) explored the weekend effect by analyzing data from the California Air Resource Board. Their study examined various monitoring stations between 1995 and 2001 in the months of June through October. From these data, Qin et al. determined average maximum ozone concentrations of the week and weekend for each monitoring location. Tables 5 and 6 compare historical values reported by Qin et al. with simulation results of the episode considered herein. Table 5 shows peak ozone concentrations at all monitoring stations averaged through all weekdays and the domain-wide average peak ozone concentration during weekdays, whereas Table 6 shows the same values for the weekend.

The base case simulation predicts maximum ozone concentrations higher than historical values for six of the eight monitoring locations: Palm Springs, Pico Rivera, downtown LA, Fontana, Burbank and Santa Monica. On the other hand, there is good agreement between historical data and the base case scenario for Hawthorne and Azusa. Regarding weekend effect intensity, historical values are higher over locations to the east of the Los Angeles area, whereas in the modeling experiment the weekend effect is most intense near the central part of the basin, closer to Los Angeles. ΔO_3 is calculated from the difference between Tables 6 and 5. Out of the eight monitoring stations, four are in good agreement between base case model ΔO_3 results and data from Qin et al. (2004): Palm Springs, Hawthorne, Azusa and Santa Clarita. Differences in maximum ozone and spatial distribution of the weekend effect between historical and modeled concentrations exist because historical values correspond to average peak concentrations over a seven-year period, whereas modeled results correspond to one high-ozone episode.

Tables 5 and 6 also show modeled peak ozone concentration for the four renoxification cases and the four chlorine cases. In general, peak ozone concentrations predicted by the renoxification cases are higher than in the base case. Overall,

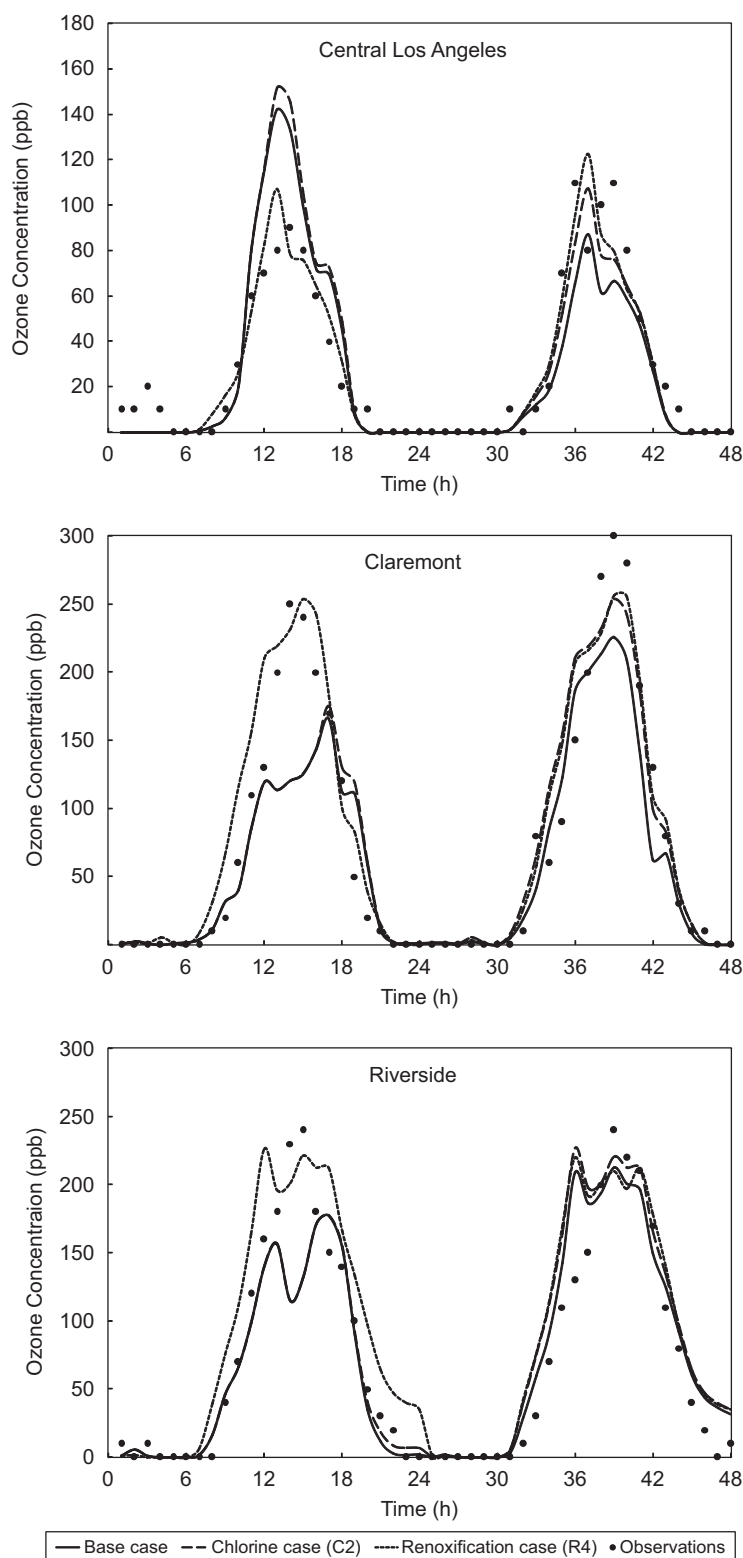


Fig. 3. Observed and predicted ozone concentrations for August 27–28, 1987 in downtown (central) Los Angeles, Claremont and Riverside, California; solid line: base case; dotted line: simulation with renoxification reaction probability, P , of 1; dashed line: simulation with sea-salt source function with an amplification factor, A , of 10; circles: observations.

Table 5

Modeled and historical values of ozone peak concentration (ppb) during weekdays at selected sites in the South Coast Air Basin of California

Station	Historical peak O ₃ concentrations	Simulated peak O ₃ concentrations								
		Base case	R1	R2	R3	R4	C1	C2	C3	C4
Santa Clarita	78 ± 30	167	167	167	168	183	167	171	191	217
Burbank	64 ± 24	96	96	96	97	109	97	102	116	163
Azusa	74 ± 31	75	75	75	76	93	75	78	101	156
Fontana	78 ± 33	150	150	150	151	159	150	153	171	176
Downtown LA	58 ± 21	64	64	64	65	75	65	69	90	144
Pico Rivera	62 ± 23	100	100	100	101	111	101	106	126	175
Hawthorne	52 ± 14	52	52	52	52	52	52	52	51	51
Palm springs	77 ± 24	146	146	146	147	156	146	147	145	138
Domain average	–	129	129	129	130	140	129	131	137	139

Historical values are obtained from [Qin et al. \(2004\)](#) and are average values obtained during June–October in the period 1995–2001. Modeled values correspond to one-week data.

Table 6

Modeled and historical values of ozone peak concentration (ppb) during the weekend at selected sites in the South Coast Air Basin of California

Station	Historical peak O ₃ concentrations	Simulated peak O ₃ concentrations								
		Base case	R1	R2	R3	R4	C1	C2	C3	C4
Santa Clarita	85 ± 27	170	170	170	172	191	171	182	217	211
Burbank	79 ± 28	125	125	125	126	136	126	129	142	176
Azusa	100 ± 38	102	102	103	103	119	103	107	138	178
Fontana	101 ± 37	158	157	158	158	166	158	162	177	177
Downtown LA	70 ± 24	86	87	87	88	97	88	94	120	154
Pico Rivera	79 ± 29	127	127	127	128	135	128	135	153	183
Hawthorne	57 ± 15	54	54	54	54	54	54	53	53	54
Palm springs	79 ± 23	146	146	146	147	160	146	146	140	125
Domain average	–	134	134	134	135	145	134	136	141	134

Historical values are obtained from [Qin et al. \(2004\)](#) and are average values obtained during June–October in the period 1995–2001. Modeled values correspond to one-week data.

renoxification increases ozone concentration due to reintroduction of NO_x from HNO₃ deposited in surfaces. Concentration of NO_x in the renoxification cases is slightly higher with respect to the base case, except near central Los Angeles and Hawthorne. In these two locations, direct emissions of NO_x are high and dominate the formation of NO_x. On the other hand, concentrations of organic compounds in the renoxification cases are lower than in the base case, due to higher ozone concentrations and hence higher oxidative capacity of the urban atmosphere. Increasing renoxification probability generally increases peak ozone concentrations. For cases with probability of reaction smaller than 0.1, increases in peak ozone are equal to or smaller than 1 ppb. Increase in reaction probability has a minimal impact in Hawthorne for

both week and weekend maximum ozone. In contrast, Azusa and Santa Clarita show the biggest increase in peak ozone from the renoxification scenarios. Scenario (R4) produces an increase of 17 ppb maximum ozone during the week in Azusa and 20 ppb maximum ozone during the weekend in Santa Clarita, compared with the base case.

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. In general, there is an increase in the maximum ozone concentration during weekdays and weekend days, due to the addition of chlorine chemistry and the sea-salt source function. 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, LA. Downtown and Burbank. Scenario C4 produces an increase of 80 ppb maximum ozone during the week in LA. Downtown and 76 ppb maximum ozone during the weekend in Azusa.

The weekend effect intensity contours are shown in Fig. 4 for the base case, renoxification and chlorine scenarios. The base case weekend effect intensity is characterized by an intense region near the Los Angeles and Burbank area that extends to the west of Riverside. The Riverside and Fontana area shows a moderate weekend effect intensity that continues to the south. Far inland around Palm Springs there is no predicted weekend effect.

With the inclusion of renoxification, the area with intense weekend effect near Los Angeles and Burbank shrinks. Fig. 3a–d show the weekend effect intensity of renoxification scenarios (R1), (R2), (R3) and (R4) which have renoxification reaction probabilities P of 0.001, 0.01, 0.1 and 1, respectively. Renoxification increases the oxidative capacity of the environment by enhancing NO_x concentrations. This leads to an increase of ozone production. Near high NO_x sources like Burbank and Riverside, the addition of renoxification causes ozone production to increase more during the week than during the weekend. Hence, the weekend effect intensity decreases as the renoxification probability is increased. Downwind in the SoCAB, to the eastern side of the domain, there are significantly fewer NO_x sources. Here the weekend effect intensity increases with increasing renoxification probability due to a shift in the VOC to NO_x ratio. Between scenarios (R1) and (R2) there is a slight increase in moderate weekend effect intensity area to the north of Riverside and south of Hawthorne along the coast. As the renoxification probability is further increased, the areas of intense and moderate weekend effect continue to shrink. While there is only a slight change in weekend effect intensity between renoxification probabilities of 0.01 and 0.1,

the difference between renoxification probabilities of 0.1 and 1 is more apparent. Scenario (R4) produces a weekend effect intensity that is shifted towards the coast and has a reduced intense and moderate area compared with the base case.

Like renoxification, chlorine decreases the intensity of the weekend effect. Fig. 3e–h 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 LA. that is surrounded by an area of moderate weekend effect intensity. Fig. 5 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. Finley and Saltzman (2006) measured Cl_2 in Irvine, California, and found the concentrations of Cl_2 to range between 2.5 and 20 ppt in the months of August through November. These measurements correspond best with an amplification factor of $A = 10$.

Fig. 6 shows the result of averaging the ΔO_3 over the entire domain for the nine scenarios under investigation. Results show that renoxification has a minor influence on the overall basin-wide weekend effect. Only with renoxification probability of $P = 1$ there is a significant change in average ΔO_3 from the base case, which is a decrease of 2% with respect to the basin-wide average intensity in the base case. On the other hand, 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.

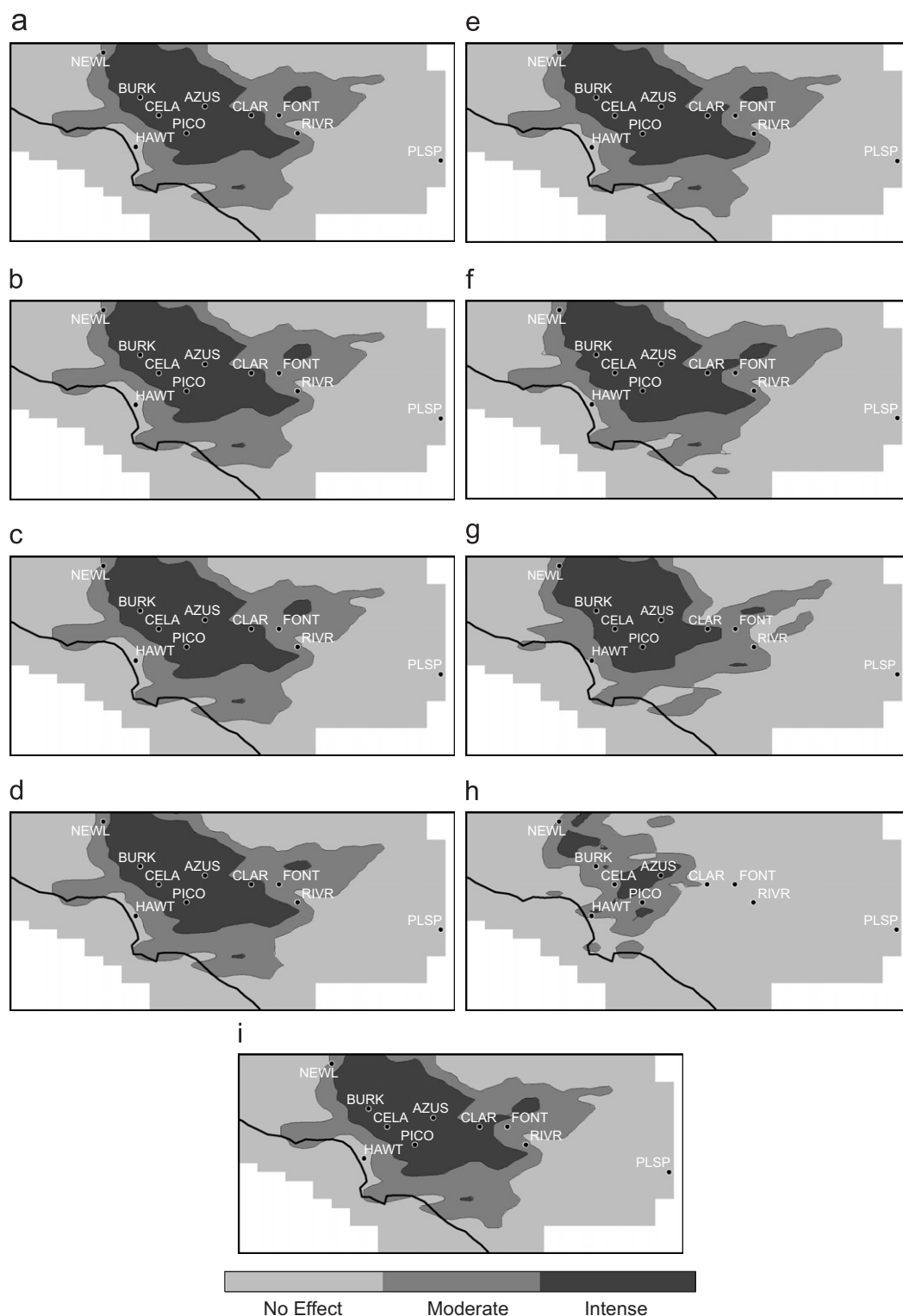


Fig. 4. Weekend effect intensity: (a) renoxification scenario (R1), $P = 0.001$, (b) renoxification scenario (R2), $P = 0.01$, (c) renoxification scenario (R3), $P = 0.1$, (d) renoxification scenario (R4), $P = 1$, (e) chlorine scenario C1, $A = 0.1$, (f) chlorine scenario C2, $A = 1$, (g) chlorine scenario C3, $A = 10$, (h) chlorine scenario C4, $A = 100$, and (i) base case simulation. Selected locations shown: Azusa (AZUS), Banning (BANN), Burbank (BURK), LA. Downtown (CELA), Fontana (FONT), Hawthorne (HAWT), Santa Clarita (NEWL), Pico Rivera (PICO), Palm Springs (PLSP), Upland (UPLA).

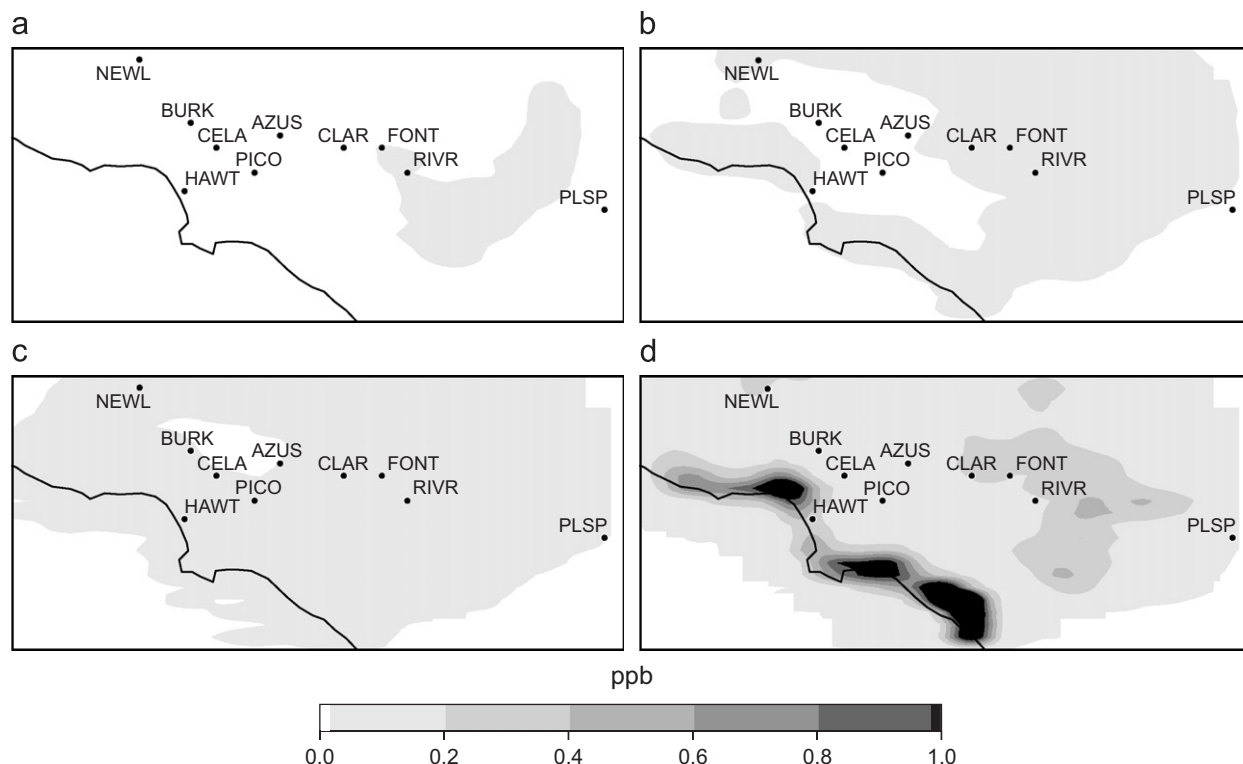


Fig. 5. Cl_2 concentration (ppb) on Friday at noon predicted in the chlorine scenarios: (a) C1, $A = 0.1$, (b) C2, $A = 1$, (c) C3, $A = 10$, and (d) C4, $A = 100$.

For the case with $A = 10$, which leads to the best agreement with observed chlorine levels in coastal regions, the basin-wide average ΔO_3 decreases by up to 28% with respect to the base case.

6. Conclusion

This study shows that the UCI-CIT Airshed model is capable of reproducing the weekend effect. The model uses representative emissions for weekdays and weekends, and shows good agreement with 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 weekly variations in NO_x emissions. Nevertheless, the meteorological episode is representative of the synoptic conditions in the SoCAB, and trends presented in the modeling results are in agreement with historical values averaged amongst seven consecutive summers.

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 in 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 of the order of 10^{-8} , and with the effect of high specific surface area, P could increase up to 10^{-4} . However, this value could be larger as the specific area of an

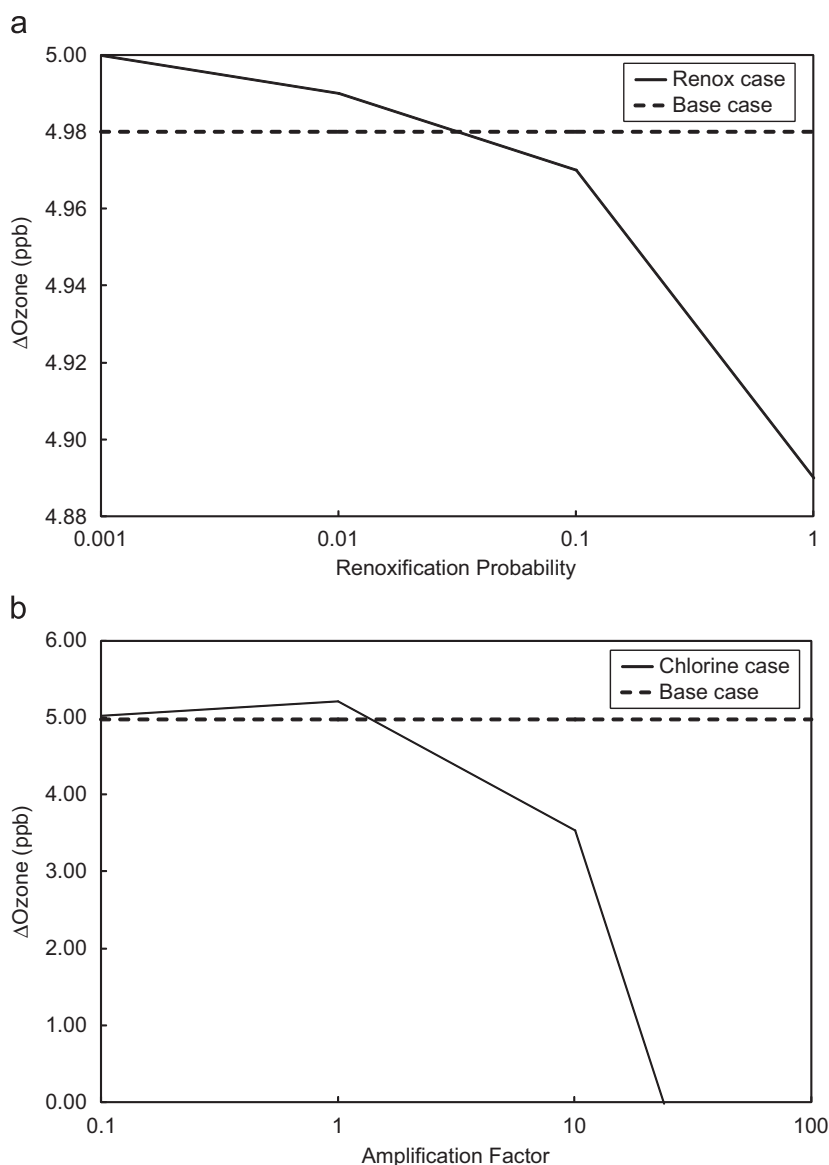


Fig. 6. Domain-wide average of week-to-weekend change in peak ozone concentration, ΔO_3 : (a) as a function of the renoxification reaction probability P . Dotted line is the base case simulation, and solid line corresponds to renoxification scenarios and (b) as a function of the amplification factor, A , of the sea-salt source function. Dotted line is the base case simulation, and solid line corresponds to chlorine scenarios.

urban environment could be significantly larger than 1.

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 PM. 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 suggesting that NO_x emissions reductions from week days to weekends can lead to higher ozone concentrations.

This work provides modeling evidence that indicates that observed weekend effect intensity in the SoCAB would be even greater in the absence of renoxification and/or chlorine chemistry. In summary, renoxification leads to 2% average basin-wide decrease in the weekend effect magnitude in the SoCAB. More dramatically, the most realistic scenario of chlorine chemistry leads to a 29% average basin-wide decrease. Therefore, it is highly recommended that future weekend effect studies incorporate at least chlorine dynamics.

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