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A Process-Analysis Based Study of the Ozone Weekend Effect

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Notation:**CMAQ:** Community Multiscale Air Quality (model)**CCOS:** Central California Ozone Study **Δ or Δ_{ED} :** Indicates weekend minus weekday difference of a quantity**HO_x:** Sum of OH and HO₂**IRR:** Integrated Reaction Rate**MM5:** Mesoscale Meteorological model version 5**NO_x:** Nitrogen oxides. Defined as the sum of NO and NO₂**O_x:** Odd oxygen. Defined as the sum of O₃ and NO₂**ppm:** parts per million by volume**ppb:** parts per billion (10⁹) by volume**PA:** Process Analysis**SAPRC99:** Statewide Air Pollution Research Center chemical mechanism (1999 version)**VOC:** Volatile Organic Compound**[X]:** Concentration of species X**1. Introduction**

Urbanized regions have been observed to have higher ozone concentrations on weekends than on weekdays, a phenomenon known as the Ozone Weekend Effect. Since the NO_x emissions that lead to ozone formation are usually lower on weekends this appears counter-intuitive. However, the chemistry of ozone production is complicated, ultimately depending on a combination of the concentration and time profiles of ozone precursors (NO_x and VOCs), their relative ratios, solar UV intensity, water vapor concentration, and meteorological conditions. The weekend effect was first observed in the 1970s (Cleveland et al., 1974; Lebron, 1975) and since then in many parts of the US and world. The statistical significance of the effect using a variety of statistical methods and surface ozone observations has been evaluated for all California (Marr and Harley, 2002a), for the California South Coast Air Basin (Blanchard and Tanenbaum, 2003), and for several (non-California) cities around the US, (Pun et al, 2003). A recent study near Sacramento (Murphy et al., 2006) studies an urban plume as it advects downstream. The weekend

effect has also been investigated with photochemical modeling (Marr and Harley, 2002b, Yarwood et al., 2008), and a combination of the modeling and observations (Fujita et al., 2003). A review by Heuss et al. (2003) discusses the magnitudes, geographical locations where it is observed, and possible causes of the weekend ozone effect. Several hypotheses have been proposed to explain the weekend effect: reductions in the mass of emitted NO_x , changes in the timing of NO_x emissions; carryover of O_3 from the previous day; increases in VOC emissions on weekends; and increases in photolysis rates due to weekend decreases in soot emissions. Most studies of this issue conclude that reduction in the mass of emitted NO_x on weekends is the dominant cause of the ozone weekend effect (Marr and Harley, 2002a; Heuss et al., 2003; Jimenez et al., 2005). In this study, we use process analysis to explore this hypothesis further and focus on analyzing chemical pathways to improve our understanding of the underlying reasons for the weekend effect.

In this study the weekend effect is examined using a 3-D photochemical air quality model, CMAQ v4.5 (Byun and Schere, 2006). We compare results from a multi-day simulation that includes a complete weekend to two hypothetical cases in which the emissions of the two weekend days are replaced by weekday emissions. Process analysis is used to understand differences between species concentrations and chemical Integrated Reaction Rates (IRRs) in the simulations, partitioning the weekend effect into its most influential components to provide an indication of their relative importance.

Section 2 contains a description of the details of model setup and emissions for the two simulations, and an overview of process analysis. Section 3 contains simulation results showing a weekend effect, followed by a review of odd oxygen production chemistry, and a quantitative analysis of weekday-weekend differences in the chemistry. Discussion and conclusions are presented in section 4.

2. Methods

2.1 Modeling System

Model simulations use CMAQ version 4.5 with the SAPRC99 gas-phase chemical mechanism (Carter, 2000). The mechanism includes a total of 72 species and >200 reactions. VOC species are either represented explicitly or lumped into one of several alkane, olefin, aromatic and other organic classes. The modeling domain over Central California is shown in Figure 1. The authors have applied CMAQ to this domain previously, as described with more simulation details and measures of the model performance in Harley et al. (2006), and Steiner et al. (2006); we present only a brief summary. The horizontal extent of the study domain is 384 km east to west, and 468 km north to south, with a horizontal grid resolution of 4 km. The vertical extent is from the surface to approximately 16 km above sea level (100 mbar pressure). Meteorological fields were developed by Bao et al. (2006) using the MM5 meteorological model. Boundary conditions are taken from the literature, as reported by Jin et al. (2008).



Figure 1: Central California modeling domain used in this study

Emissions are classified as area, point, biogenic and motor vehicle. With the exception of biogenics, typical weekday vs. weekend emissions are different. For example the motor vehicle emission inventory represents four distinct traffic activity patterns: weekday (Mon-Thu), Friday, Saturday, and Sunday. Friday emissions differ from the other weekdays due to increased traffic and a broader afternoon peak traffic period. Motor vehicle emission timings are shifted on weekends due to the absence of morning commuter traffic, but still indicate a substantial amount of activity (Harley et al., 2005). Diesel truck traffic and associated NO_x emissions decrease significantly on weekends. The area and point source inventories also exhibit differences between weekday and weekend emissions but do not draw distinctions between Fridays and other weekdays, or

between Saturdays and Sundays. Biogenic emissions, which are temperature and light sensitive, are determined by applying the meteorology of the actual day to a seasonally adjusted estimate of leaf cover. Hence there are day-to-day differences in our biogenic inventory but no specific weekday-weekend difference

To study weekend-weekday differences we compare the results of a 7-day simulation (25th-31st July 2000, Julian days 207-213), to a second, hypothetical simulation in which emissions for Saturday and Sunday (from area, motor vehicle and point categories only) have been replaced by weekday emissions. We note that in the CARB inventory, VOC and CO emissions are higher on weekends due mostly to changes in area source emissions. Similar concerns about emissions in Southern California were raised by Chinkin et al, (2003) in a study of precursor emissions. Acknowledging that a higher level of weekend VOC and CO emissions is not typical around the country and to ascertain what effect this might have on the weekend effect, we have conducted a third simulation with a hybrid scenario in which the NO_x emissions are those of a weekend but the VOC and CO emissions are those of a weekday. Most of the results presented focus on differences between the first two scenarios; the results from the hybrid scenario are discussed mainly in section 3.3.

In summary the emissions scenarios for the three simulation scenarios are:

1. Weekend scenario: Tue Wed Thu Fri Sat Sun Mon
2. Weekday scenario: Tue Wed Thu Fri Mon Mon Mon
3. Hybrid scenario: NO_x: Tue Wed Thu Fri Sat Sun Mon; VOC/CO: Tue Wed Thu Fri Mon Mon Mon

All emission scenarios are identical for the first 96 hours, additionally the biogenic emissions are identical for the whole period, as are solar intensity and initial, boundary, and meteorological conditions. The first 72 hours of the simulations are treated as a spinup period to diminish the influence of initial conditions; we focus on comparing the underlined days (Julian days 211 and 212) above. Model outputs consist of hourly average concentrations, and integrated reaction rates calculated using process analysis tools. Figure 2 shows time series of VOC and NO_x emissions for the first two scenarios,

summed over all categories, for a region east of San Francisco Bay where there is a demonstrable weekend effect. The lower weekend NO_x emissions are largely attributable to reduced diesel engine emissions from both on-road and off-road mobile sources.

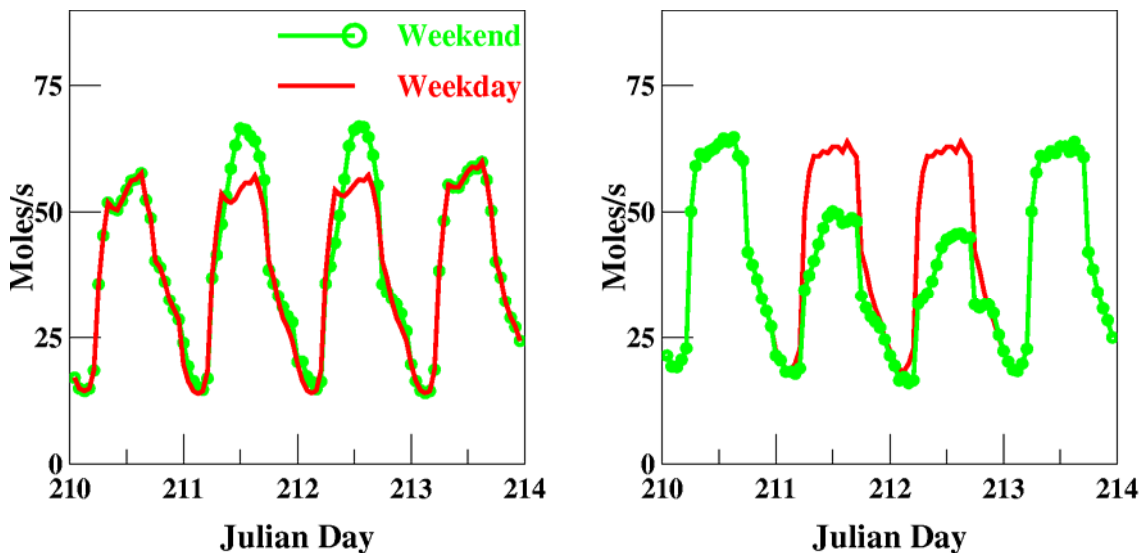


Figure 2: VOC (left) and NO_x (right) emission profiles for the first two scenarios, from Friday (Julian Day 210) through midnight on Monday (Julian Day 214), summed over a $64 \text{ km} \times 64 \text{ km}$ region east of San Francisco Bay. At times when only one color is seen the two curves overlap exactly.

2.2 Process Analysis

Process analysis (PA) is a means of quantifying the contributions made by individual physical processes and chemical reactions to the concentrations of chemical species (Jeffries and Tonnesen, 1994; Tonnesen and Dennis, 2000; Reynolds et al, 2003). In a multi-dimensional air quality model, the concentrations of all chemical species are determined by applying continuity equations and chemical reaction rates to form systems of differential equations that specify the time rate of change in species concentration caused by the different chemical and physical processes. The resulting concentration fields reveal only the net effects of all processes. For short-lived intermediate radicals, a concentration is less revealing than a measure of species fluxes in and out of the radical pool. PA quantifies contributions of individual processes: chemical reactivity, diffusion, convection, emissions, and deposition to the net production of a species. It can be used to

provide a fundamental explanation of the reasons for a model's predictions and quantifies the relative importance of each process.

The implementation of PA in CMAQ (Gipson, 1999) provides at the end of each hourly timestep, the change in concentration of desired species due to various user-selected physical and chemical processes. Our study focuses on using PA to track concentration changes caused by chemical reactions, which it does by integrating the chemical reaction rates as they are determined in the calculation. It is possible to track individual reactions, linear combinations of reactions, all reactions involving production or loss of a particular species, etc. One can also group species together and track changes that affect groups as a whole in a similar fashion. This approach is useful when dealing with a group of species involved in fast exchange reactions that occur at high, nearly equal rates in the forward and reverse directions with net effects that are much smaller than rates in either direction. IRRs calculated by PA represent concentration changes of a species (or species group) in ppm h^{-1} attributable to a particular reaction or set of reactions

3. Results

3.1 Spatial Occurrence of the Weekend Effect

All simulations are identical until midnight between day 210 (Friday) and day 211 (Saturday) at which time they begin to differ in area, motor vehicle and point emissions. Effects on secondary pollutants such as ozone are apparent beginning early on Saturday. Figure 3 shows maps of ΔO_3 (Weekend O_3 – Weekday O_3) at the surface at 8 am, 12 noon and 3 pm PDT. Over most of the domain weekend O_3 is comparable (differences are within a few ppb of zero) to weekday O_3 , but increases in weekend ozone are seen for the urbanized San Francisco Bay and Sacramento areas, consistent with observations reported elsewhere (Marr and Harley, 2002a; Murphy et al., 2007). A similar effect is seen on the following day, Sunday. The squares in the rightmost panel of Figure 3 indicate five $64 \text{ km} \times 64 \text{ km}$ regions that will be the subject of further study (clockwise from top left): (1) east of the SF Bay area, in which O_3 concentrations are higher on weekends, (2) northeast of Fresno, in which the weekend concentrations are lower, (3)

southeast of Fresno, similar to the previous region, (4) east of San Luis Obispo characterized by very low emissions, and (5) over the ocean.

Results shown will be averaged (or summed in the case of emissions) over the whole 64 km × 64 km region. regions extend vertically from the surface to a height of 4 vertical layers (≈100m) to reduce the sensitivity of the results to vertical diffusion.

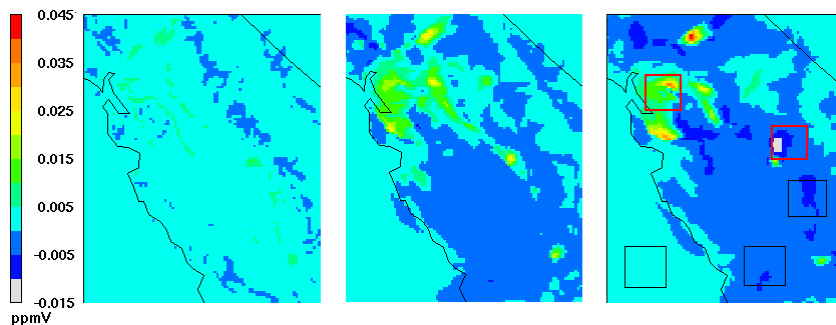


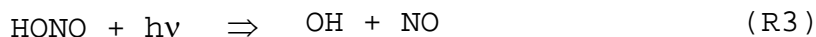
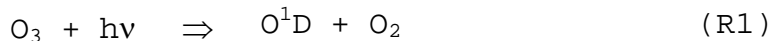
Figure 3: Difference in surface [O₃] on Day 211 (i.e. between a Saturday and a weekday) at 8 am PDT (left panel), 12 pm (center) and 3 pm (right). The red squares on the rightmost panel indicate regions: SF Bay area (shows weekend effect) and NE of Fresno (no weekend effect) for which further analysis is provided. The black squares indicate three other regions for which ozone differences are also examined.

3.2 O_x Production

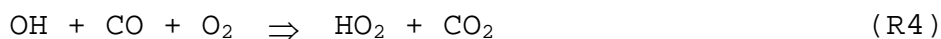
Before discussing differences between weekend and weekday simulations we first discuss a simplified picture of O_x production. Tonnesen and Jeffries (1994) provide a more detailed description to which we direct the reader. Additionally they suggest that the reactivity of a system can be designated by the production of odd oxygen (O_x), defined as the sum of the concentrations of all species that are atomic oxygen, readily release atomic oxygen, or are the further oxidation products of such species. We adopt a simpler definition using only the two major components, O₃ and NO₂, which account for greater than 99% of daytime O_x, with no loss of utility.

O_x production is initiated by the production of OH radicals (termed “new OH”) from several sources. PA reveals that at mid-day, OH originating from the reaction of O¹D

with H₂O (R2) after O₃ photolysis (reaction R1) produces O¹D accounts for most (75%) of the OH production. Another significant contributor to new OH is nitrous acid photolysis, R3 (13%), with the remainder coming from 15 other reactions.



New OH proceeds to oxidize CO and VOC via R4 and R5, forming either hydroperoxy radicals (HO₂) or one of several peroxy radicals (including methyl peroxy, peroxyacetyl and peroxypropionyl) that are collectively called RO₂.



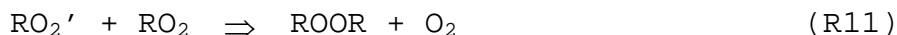
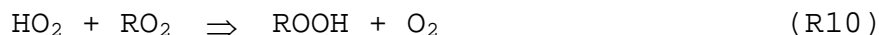
Many of the oxygenated organic products of reactions R5 (e.g. aldehydes and ketones) undergo further reactions with OH or aldehyde photolysis to form more HO₂/RO₂. R5 is shorthand for about eighty SAPRC99 reactions involving directly emitted VOC or their oxygenated products. Since CO in R4 reacts similarly to a VOC in R5, we refer to them collectively as “OH+(VOC or CO).” On average during daylight hours about 1.4 HO₂ molecules and 1 RO₂ molecule ultimately are produced per OH+(VOC or CO) reaction that occurred earlier, with very little variation over the day between 8 am and 4 pm.

The actual production of O_x occurs when HO₂ or RO₂ oxidize NO to NO₂ in R6 and R7. On average during daylight hours ultimately about 2.2 molecules of NO₂ are formed per OH+(VOC or CO) reaction.



In addition to producing O_x, R6 also produces OH which then reacts with VOC to continue the cycle. On average during daylight hours ultimately about 1.25 OH are formed from R6 per the OH+(VOC or CO) reactions that took place earlier. If the number of OH formed per circuit is ≥1 this cycle would continue indefinitely, resulting in a rapid increase in O_x limited only by the availability of raw material CO, VOC and NO.

Fortunately the cycle is damped by termination reactions in which both OH and HO₂/RO₂ participate.



The OH radical terminates mainly through R8, where it reacts with NO₂ to form nitric acid, which effectively removes both HO_x and NO_x from further participation in O₃ chemistry. HO₂ and RO₂ self-terminate through reactions R9-R11 to form peroxides. These termination reactions provide the necessary damping of the OH-HO₂ cycle, and reduce the cycling probability of radicals, Pr[OH], so that the average HO_x cycles only a few times before terminating. This mean number of cycles, calculated by summing the probabilities of a HO_x making 1,2,3...∞ circuits, i.e. 1 / (1 – Pr[OH]), is generally known as the OH chain length and can be thought of as an amplification factor of new OH. Higher values result in higher O_x production by increasing the amount of cycling HO_x. Even the simplified picture we have presented has complications. The cycle is “leaky”, in the form of sources and sinks. HO₂ and RO₂ are also produced on a smaller scale by oxidation of VOC by O₃ (15 reactions), and NO₃ (27 reactions). Some HO₂ is created directly, such as from photolysis of formaldehyde (R12),



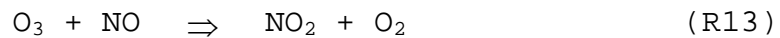
which can occur as a primary emission species, although it is mostly produced in R5. There are fast exchange reactions which lock up a fraction of HO₂/RO₂ for short amounts of time. There are also reactions which store HO_x, RO₂ and NO_x in nighttime reservoir compounds (like NO₃, N₂O₅ and PAN) and release them the next day through photolytic reactions. While these complications make it difficult to achieve complete chemical accounting in PA, it is still possible to obtain reasonable estimates of species fluxes as they go through the complex reaction pathways.

3.3 Titration and O_x Production in the Bay Area

The region just east of San Francisco Bay (Figure 3 right panel) is one in which our simulations (and the observations of Marr and Harley, 2002a) show a weekend effect.

Table 1 contains a summary of weekend and weekday emissions, concentrations and IRRs at 8 am, 12 pm and 3 pm for the Bay Area, for comparisons of weekend and weekday quantities. (Table S1 in the Supplemental information section contains hourly interval data for selected rows from Table 1.) As shown in Table 1 line E1, weekend NO_x emissions are approximately 25% lower than weekday emissions. We also noted that in this region both weekend and weekday NO_x and VOC emissions were large compared to other parts of the domain as can be seen by comparing with Table 2 and Table S3 which cover different regions.

Figure 4a shows a time series of ΔO₃, the weekend minus weekday [O₃] difference in the Bay area. The weekend O₃ excess begins early on day 211 (Saturday), soon after midnight, at which time weekend and weekday emissions begin to differ



O₃ titration IRRs are much lower on weekends (Table 1, P1). . At early times, when there is no photolysis, reduced titration of O₃ by reaction R13 must be the sole reason for higher weekend O₃.

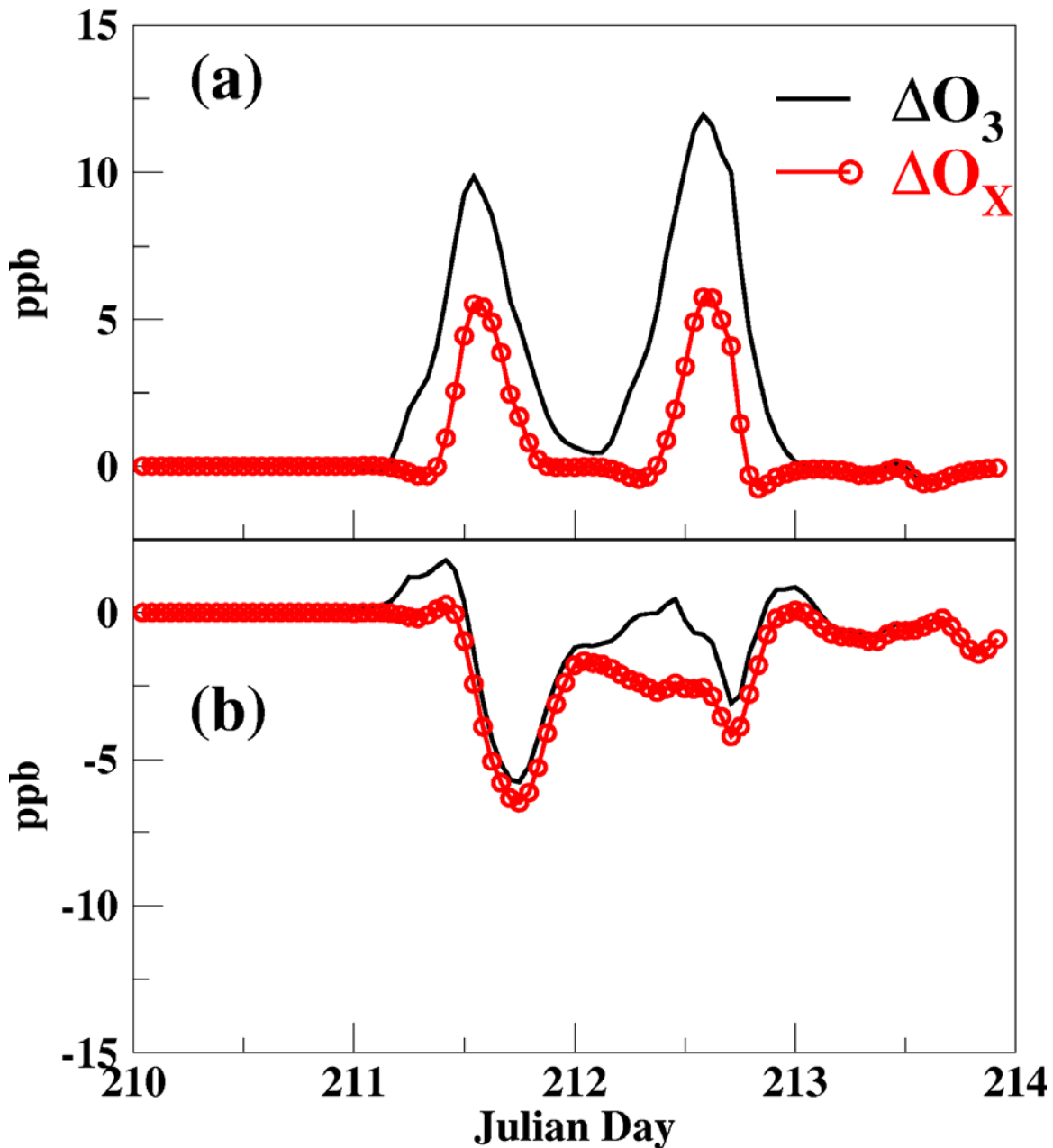


Figure 4: Weekend minus weekday O_3 and O_x averaged over (a) the Bay area and (b) NE Fresno regions.

The red curve in Figure 4a shows ΔO_x . In the early morning this curve is close to zero indicating that O_x is conserved and titration is responsible for the entire O_3 difference. Later, as the red curve rises, the role of titration difference decreases but it is still significant throughout the day. ΔO_x begins to rise significantly after 10 am, and at its peak accounts for about half of ΔO_3 . We shall show that the O_x difference occurs as a

result of the weekend-weekday differences of (1) precursor concentrations, (2) the production and fate of OH radicals, and (3) the production and fate of peroxy radicals. The trends for day 212 (Sunday) are similar to those of day 211. Figure 4b shows the corresponding ΔO_3 and ΔO_x for the NE Fresno region, and will be discussed in section 3.4.

OH Production and Fate: OH production comes from both new OH and cycled OH. Examining Table 1, P1-P3, overall new OH production on weekends is slightly higher than weekdays. A larger weekend-weekday difference of OH production comes from OH that is cycling (Table 1, P4). There is also a lower OH removal rate through termination reaction R8 (Table 1 P6) because of the lower NO_2 concentrations on weekends (Table 1, C2). Finally, VOC emissions are higher on weekends around noon and afternoon (Table 1, E2). As a consequence of these last three factors, there is a 20-30% higher weekend rate of OH reacting with VOC or CO (Table 1 P7). This is shown in Figure 5a for daylight hours.

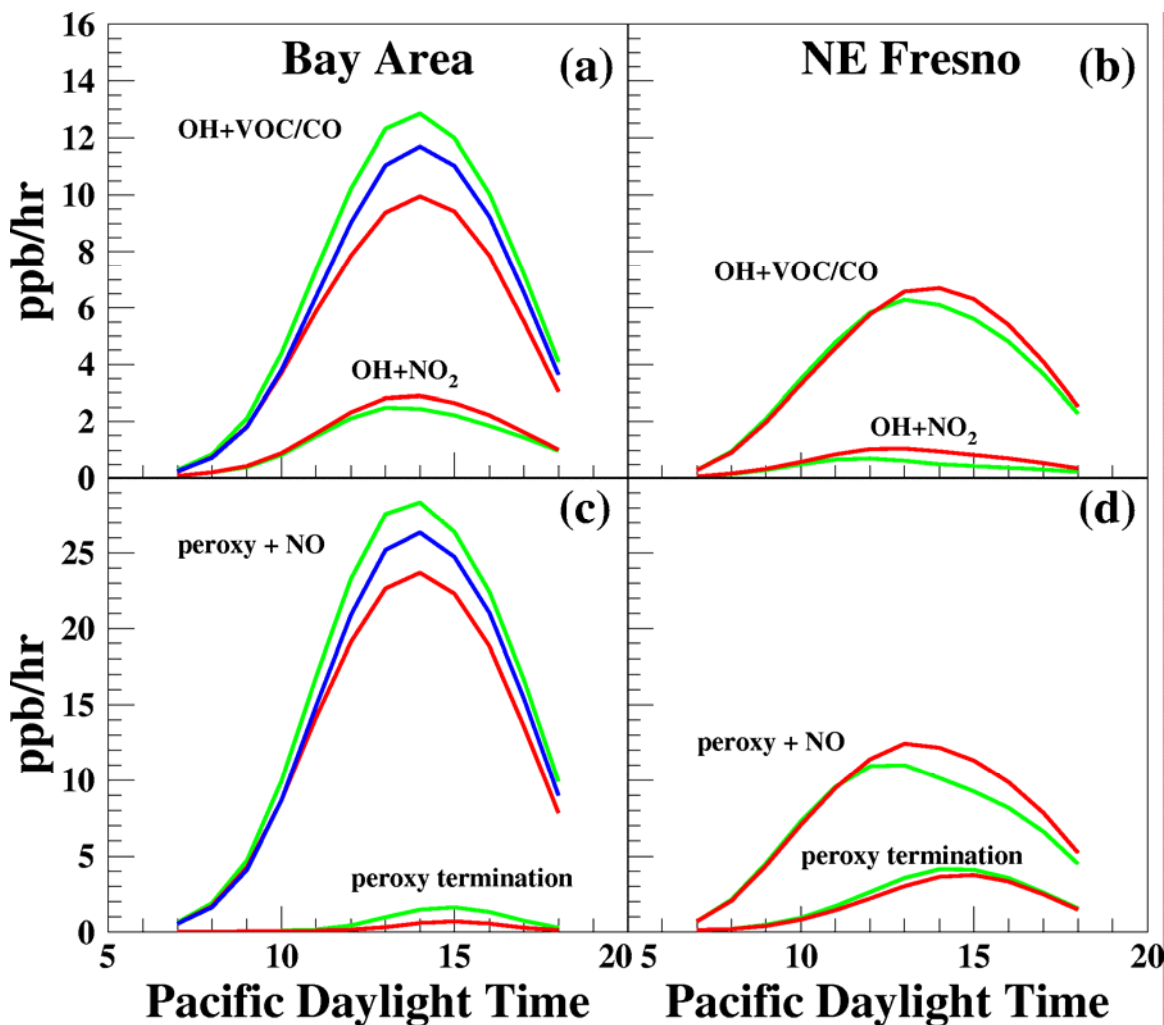


Figure 5: Comparison of Weekend (green), Weekday (red) and where available Hybrid (blue) IRRs during daylight hours on Saturday (Day 211). (a) IRRs of OH reactions in the Bay region. The upper curves show the rate of OH+(VOC or CO) to form peroxy radicals. The lower curves show the rate of the nitric acid-forming termination reaction. (b) Same plot for the NE Fresno region (c) IRRs of peroxy reactions in the Bay region. The upper curves show the rate for oxidizing NO to NO₂ while the lower curves show the termination reactions between peroxy radicals to form peroxides. (d) Same plot for the NE Fresno region.

Peroxy Radical Fate: Peroxy radicals react mainly through reactions (R6 and R7) with NO to form O_x or through termination reactions (R9-R11). Figure 5c shows that the weekend rate of reactions R6 and R7 is larger than the weekday rate even though [NO] is lower on weekends by approximately a factor of two (Table 1, C1). This occurs because

in order to maintain equilibrium where peroxy formation equals peroxy removal the weekend peroxy radical concentrations increase (Table 1 C8) by a compensating factor of two. A further consequence of this rise in peroxy concentration is an increase in the rates of termination reactions R9-R11 on weekends. However even on weekends termination rates are so much lower than the peroxy+NO rates that they do not impact them in a significant way (Table 1 P11, P12, and Figure 5c) and so the rates of peroxy+NO are quite NO_x-insensitive.

To determine the effect of higher weekend VOC and CO emissions in our simulations, we conducted a hybrid simulation of a weekend in which the NO_x emissions are those of a weekend but the VOC and CO emissions are those of a weekday. The data for the hybrid scenario lie between those of the other two scenarios, as expected, but are closer to the weekend case than to the weekday case. This can be seen by comparing [O₃] and several IRRs (Table 1 C5b, P7b, P9b, P10b) to the corresponding data from the weekend and weekday scenarios. (Table 1 C5, P7, P9, P10). . While higher weekend VOC and CO emissions contribute, the results indicate that a weekend effect can occur without them.

Table 1: Comparison of Weekend (WE) and Weekday (WD) simulations over the region east of San Francisco Bay at 3 times of day: 8am, 12 pm and 3 pm PDT. Emissions are summed, and Concentrations and IRRs are averaged from height 0-100m. The emissions are presented as the change in ppb/hr which they induce and also more traditionally as moles/s in parenthesis. Selected results from the hybrid scenario which uses weekday VOC and CO emissions (see sub-section 3.3) are suffixed with a “b”.

		8am		12 pm		3 pm	
		WE	WD	WE	WD	WE	WD
Emissions(ppb/hr and (moles/s))							
E1	NO_x	5.8 (40)	9.7 (61)	7.5 (50)	10.0 (63)	7.3 (48)	10.0 (64)
E2	All VOC	7.6 (48)	8.6 (53)	11.7 (66)	9.2 (55)	11.7 (64)	9.8 (57)
E3	Anthro. VOC	6.6 (41)	7.6 (47)	9.3 (54)	6.8 (42)	9.2 (52)	7.3 (45)
E4	CO	81 (471)	89 (501)	124 (663)	78 (415)	123 (642)	86 (482)
Concentrations (ppb)							

C1	[NO]	5.6	10.2		3.2	6.3		2.1	3.9
C2	[NO ₂]	8.9	12.3		9.7	14.5		7.5	11.2
C3	[NO _x]	14.5	22.6		12.9	20.8		9.7	15.0
C4	[VOC]	26.0	29.0		33.5	33.3		29.5	28.3
C5	[O ₃]	24	21		63	54		76	67
C5b	[O ₃]	24	--		60	--		73	--
C6	[CO]	248	270		365	329		349	305
C7	10 ³ × [OH]	.07	.05		.45	.36		.40	.35
C8	10 ³ × [HO ₂]	1.6	1.1		13.0	6.0		16.5	9.1
C9	H ₂ O ₂	.2	.2		.3	.25		.8	.6
C10	HNO ₃	.5	.5		3.1	3.5		3.3	3.9
Process Analysis IRRs (ppb/hr)									
P1	O ₃ +NO titr.	88	117		305	467		226	354
P2	All new OH	.2	.2		2.1	2.1		2.9	2.6
P3	New OH (O ₃ photolysis)	.04	.03		1.3	1.1		2.0	1.8
P4	Cycled OH	1.0	.9		12.6	10.3		14.2	12.1
P5	OH ch. len. (unitless)	5.8	4.9		7.0	6.0		6.1	5.6
P6	OH+NO ₂ →HNO ₃	.2	.2		2.1	2.3		2.2	2.7
P7	OH+(VOC/CO)	.8	.7		10.2	7.9		12.0	9.4
P7b	OH+(VOC/CO)	.7	--		9.0	--		11.0	--
P8	HO ₂ prod	1.0	.9		13.0	10.4		15.8	12.8
P9	HO ₂ +NO	1.0	.9		12.6	10.3		14.2	12.1
P9b	HO ₂ +NO	0.9	--		11.3	--		13.4	--
P10	RO ₂ +NO	0.9	0.8		10.7	8.9		12.2	10.2
P10b	RO ₂ +NO	0.8	--		9.6	--		11.4	--
P11	HO ₂ term.	0.02	0.02		.4	.1		1.3	.6
P12	RO ₂ term.	0	0		.06	.01		.3	.1

3.4 Titration and O₃ Production Northeast of Fresno

For the region northeast of Fresno (see Figure 3) in the San Joaquin Valley we present the results in Table 2 and Figure 5b,d, analogous to Table 1 and Figure 5a,c respectively. (Table S2 in the Supplemental information section contains hourly interval data for selected rows from Table 2.) In the Fresno region, as in the Bay area and many parts of the domain, weekend emissions of NO_x are significantly lower. Weekend emissions of VOC and CO are higher (Table 2 E1-E4), though not as much as in the Bay area. It would seem that a weekend effect should also occur here. Indeed a small titration-induced O₃ excess does occur early in the day, (Figure 4b and Table 2 C5) however by 12 pm this is dominated by extra weekday O₃ from O_x production. Why does the weekend

effect end like this in Fresno but not in the Bay area? In the Fresno region the overall concentration of NO is low on both weekends and weekdays compared to the Bay area. This causes a peroxy radical buildup in order to maintain equilibrium values where the peroxy removal and formation rates are equal. Unlike the Bay area this buildup is significant enough that the peroxy termination reactions R9-R11 begin to compete with the peroxy+NO reactions R6 and R7 with the result that R6 and R7 account for a smaller fraction of the total peroxy radical reactions (Figure 5d), and their rates acquire a positive sensitivity to [NO_x]. In the high-NO_x Bay area, peroxy termination reaction rates are relatively low so that they do not impact the peroxy+NO reaction rates significantly which makes the peroxy+NO rates more or less independent of [NO_x]. The positive sensitivity in the Fresno region results in a larger impedance of the flux of HO₂ through the HO_x cycle on weekends. We even have a data point where this causes a sign change: in Fresno at 12 pm, (Table 2 lines P7-P10), the weekend OH+(VOC or CO) rate is slightly higher than the weekday rate, but the peroxy+NO reaction rate ends up slightly lower, whereas in the Bay area the latter rate follows the former faithfully. This ability to not impede the cycling flux of HO_x is one of the key factors required for a weekend ozone effect.

Table 2: Comparison of Weekend (WE) and Weekday (WD) simulations over the NE Fresno region at 3 times of day: 8am, 12pm and 3pm PDT. Emissions are summed, and Concentrations and IRRs are averaged from height 0-100m. . The emissions are presented as the change in ppb/hr which they induce and also more traditionally as moles/s in parenthesis. Selected results from the hybrid scenario which uses weekday VOC and CO emissions (see sub-section 3.3) are suffixed with a “b”.

		8am		12 pm		3 pm	
		WE	WD	WE	WD	WE	WD
Emissions (ppb/hr and (moles/s))							
E1	NO_x	1.9 (10)	3.7 (20)	2.2 (12)	4.0 (20)	2.2 (11)	3.9 (19)
E2	All VOC	4.1 (22)	4.9 (26)	6.5 (32)	6.1 (30)	6.6 (31)	6.5 (31)
E3	Anthro. VOC	2.3 (14)	3.1 (19)	3.3 (18)	3.0 (16)	3.3 (18)	3.3 (18)
E4	CO	27 (151)	36 (196)	42 (212)	33 (164)	42 (207)	36 (187)

Concentrations (ppb)							
C1	[NO]	1.3	2.3	.3	.7	.2	.3
C2	[NO ₂]	3.5	4.9	1.4	2.7	1.1	1.8
C3	[NO _x]	4.8	7.2	1.6	3.4	1.2	2.1
C4	[VOC]	24.3	24.7	21.0	21.5	19.3	19.5
C5	[O ₃]	44.2	42.9	73.8	73.4	87.7	92.0
C5b	[O ₃]	44.1	--	73.7	--	87.7	--
C6	[CO]	173	179	184	185	190	191
C7	10 ³ × [OH]	.1	.1	.5	.5	.4	.5
C8	10 ³ × [HO ₂]	8.9	8.1	32.3	28.4	33.5	32.5
C9	H ₂ O ₂	.7	.7	1.5	1.3	2.3	2.0
C10	HNO ₃	1.1	1.2	2.7	3.4	3.0	4.3
Process Analysis IRRs (ppb/hr)							
P1	O ₃ +NO titr.	40	56	49	97	26	52
P2	All new OH	.24	.24	2.9	2.8	3.9	4.0
P3	New OH (O ₃ photolysis)	.08	.08	2.2	2.1	2.9	3.0
P4	Cycled OH	1.0	1.0	5.6	5.9	4.3	5.6
P5	OH ch. len. (unitless)	5.5	5.3	3.0	3.2	2.2	2.5
P6	OH+NO ₂ →HNO ₃	.15	.17	.7	1.0	.4	.8
P7	OH+(VOC/CO)	.9	.9	5.9	5.8	5.6	6.3
P7b	OH+(VOC/CO)	.9	--	5.8	--	5.6	--
P8	HO ₂ prod	1.2	1.2	7.7	7.6	7.6	8.5
P9	HO ₂ +NO	1.0	1.0	5.6	5.9	4.3	5.6
P9b	HO ₂ +NO	1.0	--	5.6	--	4.3	--
P10	RO ₂ +NO	1.1	1.0	5.3	5.5	5.0	5.7
P10b	RO ₂ +NO	1.0	--	5.3	--	5.0	--
P11	HO ₂ term.	.2	.1	1.9	1.6	3.0	2.7
P12	RO ₂ term.	.05	.05	.7	.6	1.1	1.0

3.5 Titration and O_x Production in other regions

Three additional regions (Figure 3) in other parts of the domain are also examined. (1) A region southeast of Fresno has similar emission patterns to the region lying to the northeast, and shows similar weekend-weekday differences. (2) The region east of San Luis Obispo is characterized by very low emissions on weekends and on weekdays, with weekend NO_x slightly lower. The underlying reason for lack of a weekend effect is the same as for NE of Fresno. (3) Over the ocean there are negligible emissions so a weekend effect is not expected. Supplemental Table S3 contains emissions, concentrations and IRRs for the first two of these regions.

4. Summary & Discussion

Summarizing the results of Section 3:

1. Weekend O₃ excess observed in early morning hours is caused by reduced O₃+NO titration which occurs as a result of lower NO_x emissions.
2. The excess untitrated O₃ increases the formation of new OH through a higher rate of O₃ photolysis.
3. Increased weekend VOC and CO emissions contribute to an increased rate of peroxy formation through OH+(VOC or CO) but are not a necessary component of a weekend effect.
4. Radical termination in NO_x-rich areas is primarily through nitric acid formation which decreases with decreasing NO_x, and contributes toward a weekend effect. In NO_x-poor areas peroxy-peroxy termination is more significant. This increases with decreasing NO_x and works against a weekend effect.
5. From the increased rate of peroxy formation through OH+(VOC or CO) in the previous items we get in NO_x-rich areas a corresponding increase in O_x formation almost independent of the NO concentration. In NO_x-poor areas any gains in peroxy formation through OH+(VOC or CO) are not passed on to result in increased O_x formation, which exhibits a positive sensitivity to NO concentration.

The weekend effect has a titration component and an O_x component, each contributing about half of the excess weekend O₃. In terms of VOC-sensitivity and NO_x-sensitivity on an ozone isopleth plot, the titration component of the weekend effect is possible in either a NO_x or VOC-sensitive region, provided that weekend NO_x is lower. We see this in both the Bay Area and Fresno regions. From our simulation it appears that the O_x component of the effect occurs in VOC-sensitive regions provided that weekend NO_x is lower (the Bay Area), but does not occur in the NO_x sensitive regions (Fresno). Even here it is not the VOC-sensitivity *per se* that is responsible, but the negative sensitivity to NO_x. Using PA we can investigate in more detail just why this happens. The titration component clearly requires just one ingredient: (1) lower weekend NO_x emissions. This sets the stage for the O_x component which requires two additional ingredients: (2) A higher weekend rate of OH+(VOC or CO) to cause higher peroxy formation and (3) sufficiently high NO concentration (even on weekends) to propagate that higher peroxy formation back to higher weekend OH formation. Ingredient 2 has contributions from lower weekend nitric acid formation, higher weekend new OH formation from, say, O₃ photolysis, and higher weekend VOC emissions. Ingredient 3 implies that there is a critical value of [NO] above which a weekend effect would occur. The O_x production contour plot from Tonnesen and

Dennis(2000) (which shows O_x production as a function of VOC and NO_x concentrations) provides guidance on the location of this. If both weekend and weekday NO_x values are above (or below) it a weekend effect would (or would not) occur. If they straddle the ridge of maximum O_x production the outcome is not clear. In terms of PA the condition for the Ingredient 3 is satisfied when the ratio of the rates of peroxy+NO to peroxy termination are sufficiently high that peroxy+NO remains the dominant mode of peroxy removal even with, say, a factor of two reduction in NO_x concentration. If this ratio is not sufficiently high then termination reactions remove significantly more peroxy on the (lower NO_x) weekends, wiping out any imbalance from Ingredient 2 and ruling out a weekend effect.

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Figure Captions

Figure 1: Central California modeling domain used in this study

Figure 2: VOC (left) and NO_x (right) emission profiles for the first two scenarios, from Friday (Julian Day 210) through midnight on Monday (Julian Day 214), summed over a 64 km × 64 km region east of San Francisco Bay. At times when only one color is seen the two curves overlap exactly.

Figure 3: Difference in surface [O₃] on Day 211 (i.e. between a Saturday and a weekday) at 8 am PDT (left panel), 12 pm (center) and 3 pm (right). The red squares on the rightmost panel indicate regions: SF Bay area (shows weekend effect) and NE of Fresno (no weekend effect) for which further analysis is provided. The black squares indicate three other regions for which ozone differences are also examined.

Figure 4: Weekend minus weekday O₃ and O_x averaged over (a) the Bay area and (b) NE Fresno regions.

Figure 5: Comparison of Weekend (green), Weekday (red) and where available Hybrid (blue) IRRs during daylight hours on Saturday (Day 211). (a) IRRs of OH reactions in the Bay region. The upper curves show the rate of OH+(VOC or CO) to form peroxy radicals. The lower curves show the rate of the nitric acid-forming termination reaction. (b) Same plot for the NE Fresno region (c) IRRs of peroxy reactions in the Bay region. The upper curves show the rate for oxidizing NO to NO₂ while the lower curves show the termination reactions between peroxy radicals to form peroxides. (d) Same plot for the NE Fresno region.

Table Captions

Table 1: Comparison of Weekend (WE) and Weekday (WD) simulations over the region east of San Francisco Bay at 3 times of day: 8am, 12 pm and 3 pm PDT. Emissions are summed, and Concentrations and IRRs are averaged from height 0-100m. The emissions are presented as the change in ppb/hr which they induce and also more traditionally as moles/s in parenthesis. Selected results from the hybrid scenario which uses weekday VOC and CO emissions (see sub-section 3.3) are suffixed with a “b”.

Table 2: Comparison of Weekend (WE) and Weekday (WD) simulations over the NE Fresno region at 3 times of day: 8am, 12pm and 3pm PDT. Emissions are summed, and Concentrations and IRRs are averaged from height 0-100m. . The emissions are presented as the change in ppb/hr which they induce and also more traditionally as moles/s in parenthesis. Selected results from the hybrid scenario which uses weekday VOC and CO emissions (see sub-section 3.3) are suffixed with a “b”.

Supplemental Material

Table S3: Comparison of selected emissions, concentrations and IRRs from Weekend and Weekday simulations (separated by “/”) over the region east of San Francisco Bay at hourly intervals from 8am to 4pm PDT. Emissions (in moles/s) are summed, concentrations and IRRs are averaged from height 0-100m.

Time	8am	9am	10am	11am	12pm	1pm	2pm	3pm	4pm
Emissions (moles/s)									
E1 (NO _x)	40/61	43/61	47/62	49/62	50/63	50/63	48/62	48/64	49/62
E2 (all VOC)	48/53	53/52	59/52	63/53	67/55	66/56	65/56	64/57	61/55
Concentrations (ppb)									
C3 [NO _x]	15/23	16/25	16/26	15/24	13/21	11/18	10/16	10/15	11/16
C4 [VOC]	26/29	30/34	33/36	34/35	33/33	32/31	31/29	30/28	29/28
C5 [O ₃]	24/21	29/24	37/31	50/42	63/54	73/63	77/68	76/67	67/59
Process Analysis IRRs (ppb/hr)									
P2(All new OH)	.2/.2	.4/.5	.8/.9	1.4/1.5	2.1/2.1	2.7/2.6	3.0/2.8	2.9/2.6	2.3/2.1
P6 OH+NO ₂ → HNO ₃)	.2/.2	.4/.4	.8/.9	1.5/1.6	2.1/2.3	2.5/2.8	2.5/2.9	2.2/2.7	1.9/2.2
P7(OH+ (VOC/CO))	.9/.7	2.1/1.8	4.4/3.7	7.4/5.9	10.2/7.9	12.3/9.4	12.9/10.0	12.0/9.4	10.0/7.9
P9+P10 (H/RO ₂ +NO)	1.9/1.7	4.7/4.3	9.9/8.7	16.8/14.2	23.3/19.1	27.6/22.7	28.4/23.7	26.4/22.3	22.4/18.8
P11+P12(H /RO ₂ term)	.02/.02	.05/.03	.09/.05	.17/.07	.45/.15	.96/.32	1.5/.57	1.6/.70	1.3/.56

Table S4: Comparison of selected emissions, concentrations and IRRs from Weekend and Weekday simulations (separated by “/”) over the region northeast of Fresno at hourly intervals from 8am to 4pm PDT. Emissions (in moles/s) are summed, and concentrations and IRRs are averaged from height 0-100m.

Time	8am	9am	10am	11am	12pm	1pm	2pm	3pm	4pm
Emissions (moles/s)									
E1 (NO _x)	10/20	11/20	11/20	11/20	12/20	11/20	11/19	11/19	11/18
E2 (all VOC)	22/26	25/27	28/28	30/29	32/30	33/31	32/31	31/31	28/29
Concentrations (ppb)									
C3 [NO _x]	4.8/7.2	4.3/6.8	3.3/5.7	2.3/4.4	1.7/3.4	1.3/2.6	1.2/2.2	1.2/2.1	1.3/2.1
C4 [VOC]	24/25	24/25	23/24	22/22	21/21	20/21	20/20	19/20	19/19
C5 [O ₃]	44/43	49/47	57/55	66/64	74/73	80/81	84/87	88/92	90/95
Process Analysis IRRs (ppb/hr)									
P2(All new OH)	.2/.2	.6/.6	1.1/1.1	2.0/2.0	2.9/2.8	3.6/3.6	4.0/4.1	3.9/4.0	3.3/3.4
P6 OH+NO ₂ → HNO ₃)	.1/.2	.3/.3	.5/.6	.7/.8	.7/1.0	.6/1.1	.5/1.0	.4/.8	.4/.7
P7(OH+(VOC/CO))	.9/.9	2.1/2.0	3.5/3.3	4.8/4.6	5.8/5.8	6.3/6.6	6.1/6.7	5.6/6.3	4.8/5.4
P9+P10 (H/RO ₂ +NO)	2.1/2.1	4.5/4.3	7.3/7.1	9.6/9.5	10.9/11.4	11.0/12.4	10.1/12.2	9.3/11.3	8.2/9.9
P11+P12(H /RO ₂ term)	.2/.2	.5/.4	.9/.8	1.7/1.4	2.6/2.2	3.6/3.0	4.1/3.6	4.1/3.8	3.5/3.3

Table S3: Comparison of Weekend (WE) and Weekday (WD) simulations for the regions SE of Fresno and east of San Luis Obispo at 12pm PDT. Emissions are summed, and Concentrations and IRRs are averaged from height 0-100m.

		SE Fresno		East SLO	
		WE	WD	WE	WD
Emissions (moles/s)					
E1	NO_x	11.0	16.6	2.6	3.3
E2	All VOC	28.8	26.6	8.8	8.9
E3	Anthro. VOC	22.2	20.1	2.3	2.3
E4	CO	143	87	8	6
Concentrations (ppb)					
C3	[NO_x]	1.3	1.8	.8	.9
C4	[VOC]	24.8	24.6	14.2	14.1
C5	[O₃]	80.1	82.3	79.8	80.4
C6	[CO]	190	180	169	166
Process Analysis IRRs (ppb/hr)					
P6	OH+NO₂→HNO₃	0.6	1.0	.3	.4
P7	OH+(VOC/CO)	6.4	6.8	4.3	4.5
P9+P10	HO₂/RO₂+NO	11.3	12.9	6.7	7.2
P11+P12	HO₂/RO₂ term.	3.2	2.6	3.2	3.1