



## RESEARCH LETTER

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## Key Points:

- The probability and area in the SoCAB affected by higher weekend O<sub>3</sub> have decreased
- The recent economic recession expedited this decrease
- Future NO<sub>x</sub> regulations will be increasingly effective at reducing O<sub>3</sub> on hot weekends

## Supporting Information:

- Supporting Information S1

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## Weakening of the weekend ozone effect over California's South Coast Air Basin

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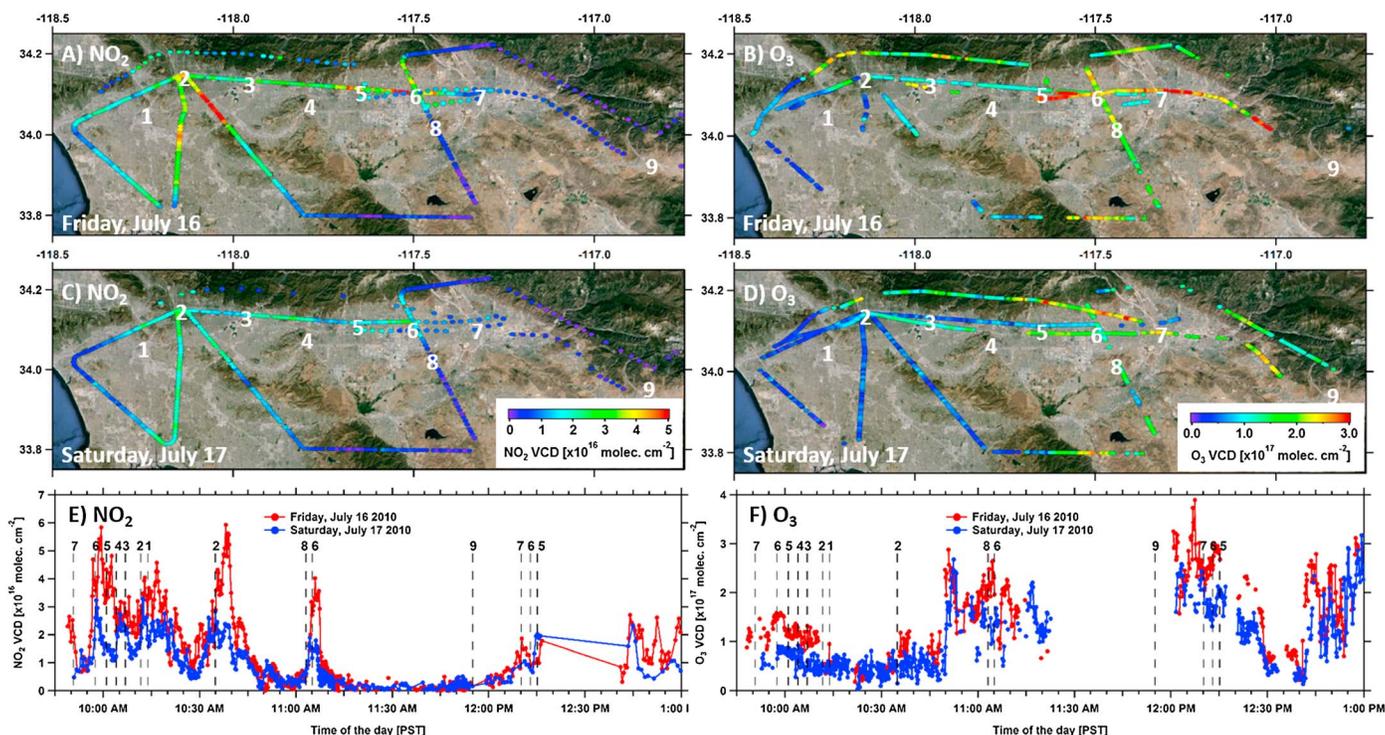
**Abstract** We have observed lower nitrogen dioxide (NO<sub>2</sub>) and ozone (O<sub>3</sub>) during a hot weekend (summer 2010) from aircraft over the entire South Coast Air Basin (SoCAB). Surface concentrations of NO<sub>2</sub>, O<sub>3</sub>, and temperature from 1996 to 2014 corroborate that this lower O<sub>3</sub> on weekends is increasingly likely in recent years. While higher surface O<sub>3</sub> on the weekends (weekend ozone effect, WO3E) remains widespread, the spatial extent and the trend in the probability of WO3E occurrences ( $P_{\text{WO3E}}$ ) have decreased significantly compared to a decade ago. This decrease is mostly the result of lower O<sub>3</sub> on hot weekends in recent years.  $P_{\text{WO3E}}$  is lowest in the eastern SoCAB. The major decrease happened during the 2008 economic recession, after which  $P_{\text{WO3E}}$  has stabilized at a 15–25% lower level throughout most of the basin. Future NO<sub>x</sub> reductions are likely to be increasingly effective at reducing O<sub>3</sub> pollution initially under hot conditions in the coming decade.

### 1. Introduction

The weekend ozone effect (WO3E), i.e., the occurrence of higher O<sub>3</sub> concentrations on the weekend than on weekdays, was first reported in the 1970s in New York City, Washington DC, and Los Angeles [Cleveland *et al.*, 1974; Lebron, 1975; Elkus and Wilson, 1977] and has been observed in most major urban areas in the United States [Heuss *et al.*, 2003]. The WO3E has been particularly well studied in the Los Angeles area or South Coast Air Basin (SoCAB) [Blanchard and Tanenbaum, 2003; Chinkin *et al.*, 2003; Fujita *et al.*, 2003; Pollack *et al.*, 2012, and references therein]. In the early 2000s, the California Air Resource Board (CARB) conducted a major study to better understand the WO3E. Reduced emissions of nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>) on weekends and subsequent chemical feedback are considered to be the dominant cause for the WO3E phenomenon [Marr and Harley, 2002a, 2002b; Blanchard and Tanenbaum, 2003; Fujita *et al.*, 2003; Yarwood *et al.*, 2003, 2008; Pollack *et al.*, 2012].

Ozone formation is a complex nonlinear process. Reductions in volatile organic compounds (VOC) and NO<sub>x</sub> precursors can increase, decrease, or leave the O<sub>3</sub> levels unchanged depending upon the state of the O<sub>3</sub> formation chemistry. Large reductions in heavy-duty diesel truck traffic on the weekend result in a significant decrease in NO<sub>x</sub> emissions [Marr and Harley, 2002a; Chinkin *et al.*, 2003; Harley *et al.*, 2005]. In contrast, VOC emissions are similar between weekdays and weekends [Marr and Harley, 2002a; Warneke *et al.*, 2013]. Thus, the decrease in NO<sub>x</sub> emissions from weekdays to weekends provides an inadvertent test of O<sub>3</sub> sensitivity to changes in NO<sub>x</sub> emissions. The WO3E holds key information regarding whether expected future reductions in precursor emissions due to new regulations will increase or decrease O<sub>3</sub> concentrations. Because of these implications for O<sub>3</sub> control strategies, the WO3E is of particular interest to policymakers.

Long-term trends in NO<sub>x</sub>, VOCs, and O<sub>3</sub> in the SoCAB have been extensively investigated in various studies [e.g., Warneke *et al.*, 2012; Pollack *et al.*, 2013]. However, few studies have examined multiyear changes in the WO3E. Wolff *et al.* [2013] investigated the difference in weekday and weekend O<sub>3</sub> levels to examine the changing prevalence of the WO3E in the U.S. Pusede and Cohen [2012] used a statistical analysis of O<sub>3</sub> response to NO<sub>x</sub> and VOC reactivity reduction from 1995 to 2010 to show that the O<sub>3</sub> formation chemistry in San Joaquin Valley, CA, has transitioned to NO<sub>x</sub>-limited conditions in recent years. Similarly, analysis of long-term weekly pattern of CO, NO<sub>x</sub>, and O<sub>3</sub> in Mexico City showed a changing weekday-weekend difference in O<sub>3</sub> [Stephens *et al.*, 2008]. Here we describe the changing nature of the weekday-weekend O<sub>3</sub> in the SoCAB using two



**Figure 1.** Map of South Coast Air Basin with the flight track color coded by  $\text{NO}_2$  and  $\text{O}_3$  during a weekday and a weekend: (a)  $\text{NO}_2$  vertical column measured by CU AMAX-DOAS during a research flight on Friday 16 July 2010. (b)  $\text{O}_3$  vertical column measured by NOAA TOPAZ lidar during the same flight. (c)  $\text{NO}_2$  vertical column measured on Saturday 17 July 2010. (d)  $\text{O}_3$  vertical column measured during that day. Flights on both days took place from 9:30 to 13:10 PST. The locations of the surface monitoring stations used in this study are shown and correspond to the following: (1) Los Angeles (North Main Street), (2) Pasadena, (3) Azusa, (4) Pomona, (5) Upland, (6) Fontana, (7) San Bernardino, (8) Riverside, and (9) Banning.

different data sources: (1) two NOAA Twin Otter research flights during the CalNex 2010 field campaign found evidence for lower  $\text{O}_3$  on the weekend over the entire SoCAB (inverse WO3E, or IWO3E) and (2) we use long-term data from the CARB monitoring network to provide a statistical analysis of the probability of WO3E occurrences ( $P_{\text{WO3E}}$ ) and show that the IWO3E observed by the aircraft is an increasingly likely scenario in recent years. This weakening of the WO3E is more prevalent in the eastern part of the basin, where  $\text{O}_3$  levels are highest, and at high temperatures.

## 2. Observations

### 2.1. Airborne Observations

Figure 1 shows maps of the  $\text{NO}_2$  and  $\text{O}_3$  vertical column inside the boundary layer measured by the CU Airborne Multi-Axis Differential Optical Absorption Spectroscopy (AMAX-DOAS) [Volkamer et al., 2009; Baidar et al., 2013a] and NOAA Tunable Optical Profiler for Aerosol and oZone (TOPAZ) lidar [Alvarez et al., 2011] respectively on Friday 16 July 2010 and Saturday 17 July 2010 as part of the CalNex field campaign [Ryerson et al., 2013]. Descriptions of the CU AMAX-DOAS and NOAA TOPAZ lidar measurements during CalNex can be found in Baidar et al. [2013b], and CU AMAX-DOAS has recently been further evaluated in Volkamer et al. [2015]. The maps show the horizontal distribution of vertical columns of the two pollutants inside the SoCAB on a typical summer weekday and on the following weekend. Column measurements inherently average local variations and are therefore considered to be spatially more representative. For the purpose of comparison with surface measurements, these  $\text{NO}_2$  columns were converted to surface concentrations using boundary layer heights measured along the flight track by the TOPAZ lidar. A very clear distinction was observed in the spatial distribution of the two pollutants in terms of location of their highest values. High  $\text{NO}_2$  was located mostly near downtown Los Angeles, whereas the highest  $\text{O}_3$  was seen downwind in the eastern part of the basin along the foothills.  $\text{NO}_2$  was 35% lower on the Saturday relative to the Friday, consistent with our observations on other weekends in the SoCAB and other locations over California [Oetjen et al., 2013] and other measurements during

CalNex [Pollack *et al.*, 2012]. Interestingly, despite the usual decrease in  $\text{NO}_x$ , also,  $\text{O}_3$  was found to be lower on the Saturday across the entire basin. Note that the meteorological conditions on both days were similar with clear skies and daily maximum temperatures reaching near  $40^\circ\text{C}$  (mean temperature (12:00–16:00 PST) at San Bernardino =  $38.4 \pm 0.5$  (Friday) and  $38.5 \pm 0.7$  (Saturday)). The development of the land-sea breeze was typical on both days (mean wind speed and direction (12:00–16:00 PST) at Riverside Municipal Airport =  $5.2 \pm 1.8$  m/s and  $274 \pm 9^\circ$  (Friday) and  $5.5 \pm 1.0$  m/s and  $278 \pm 11^\circ$  (Saturday)). Boundary layer height was measured by the TOPAZ lidar, and near San Bernardino at around 12:08 PST was  $1267 \pm 72$  m and  $1231 \pm 66$  m on Friday and Saturday, respectively. The flight plans were also near identical. Thus, the change in  $\text{O}_3$  between the weekday and the weekend is primarily due to  $\text{NO}_x$  reduction of the weekend. In order to put this observation of IWO3E in perspective, we have analyzed the long-term surface measurements at nine monitoring stations that were selected along our flight track, and their locations are also shown in Figure 1.

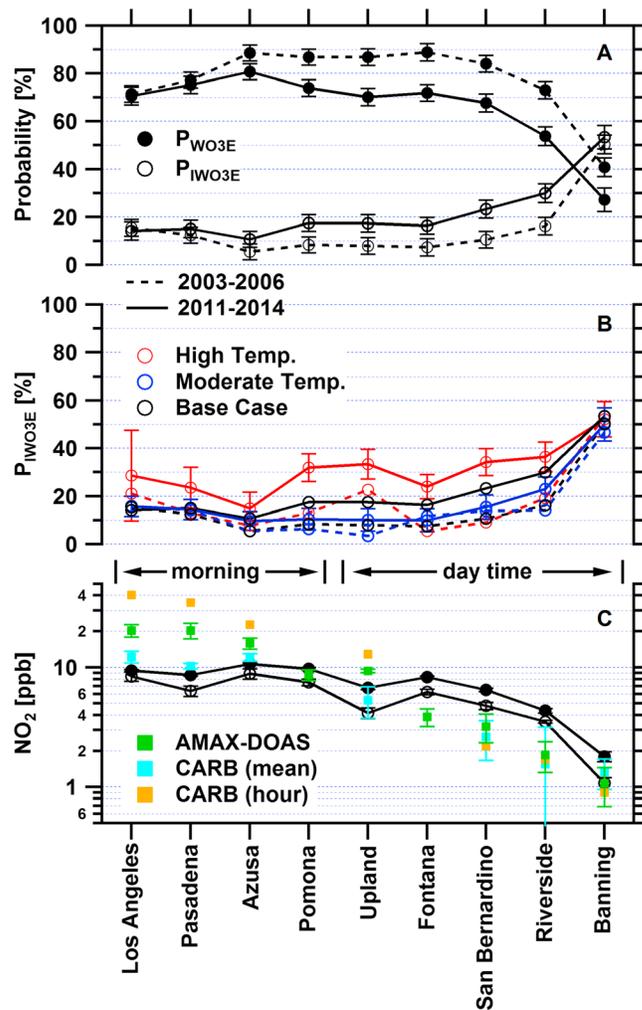
## 2.2. Surface Observations

CARB monitoring stations measure hourly  $\text{O}_3$ ,  $\text{NO}_2$ , CO, temperature, and other parameters throughout the SoCAB. Here we have analyzed data from 1996 to 2014 summer months (June–September) at nine different monitoring stations to calculate the  $P_{\text{WO3E}}$  and  $P_{\text{IWO3E}}$ , i.e., the probability that the  $\text{O}_3$  on the weekend is higher and lower, respectively, than on the weekday that it followed. We focus our analysis on probability as it captures the statistical distribution in difference in weekend to weekday  $\text{O}_3$  (see supporting information Figure S1) and better informs about the changing nature of the WO3E. Meteorology in the SoCAB is strongly influenced by the sea breeze/land breeze circulation. During daytime, a strong sea breeze flows inland from the coast as a result of uneven heating of the land and water. The sea breeze is generally well established by midmorning (11 A.M.) and last until 11 P.M. [Wagner *et al.*, 2012]. At night a weaker land breeze blows from the land to the ocean. The sea breeze helps transport pollutants from downtown Los Angeles into the eastern part of the basin during the day. While  $\text{O}_3$  produced in the upwind sites does influence the  $P_{\text{WO3E}}$  at downwind locations, we do not expect meteorological factors such as wind speed to impact  $P_{\text{WO3E}}$  changes over time as differences in meteorological conditions between years remain small and not significant (see supporting information Figure S3a). A large temperature gradient is observed within the SoCAB with lower temperature over the western part near the coast. However, there is no significant difference in temperature gradient between weekdays and weekends (see supporting information Figure S3a).

We directly compare daily mean  $\text{O}_3$  values between 12:00 and 16:00 PST for Thursday and Friday (weekday) with the corresponding Saturday and Sunday (weekend)  $\text{O}_3$  values to compute the probabilities. Saturday and Monday are often considered transition days as they are affected by the preceding weekday and weekend. Hence, the Monday–Tuesday pair was not considered for the comparison. Saturday was included to improve statistics for the weekends, but results were robust if only Sunday was considered as a weekend day (see below).

A  $\pm 3$  ppb  $\text{O}_3$  difference was defined as the threshold at which differences in weekday and weekend  $\text{O}_3$  were considered statistically significant. This threshold value is based on the  $1\sigma$  confidence interval reported for mean  $\text{O}_3$  values at the surface monitoring stations in the SoCAB for summer 2010 by Pollack *et al.* [2012]. Corresponding daily mean (12:00–16:00 PST)  $\text{NO}_2$  values were also required to be lower on the weekend compared to weekday as we were interested in the effect of  $\text{NO}_x$  reduction on the weekend on  $\text{O}_3$  levels. However, in practice, this condition only filtered  $<5\%$  of data (around 10% at downtown Los Angeles) at most sites and years, reflecting the widespread and expected  $\text{NO}_x$  reductions on the weekends (see supporting information Figure S2).

Biogenic VOC emissions (e.g., isoprene) are known to be temperature dependent [Guenther *et al.*, 1993; Steiner *et al.*, 2010]. Pusede *et al.* [2014] have recently reported a temperature-dependent component of VOC reactivity (VOCR) in the San Joaquin Valley, CA. Ambient  $\text{O}_3$  data in the SoCAB also show clear distinctions between different temperature ranges [Steiner *et al.*, 2010]. However, the temperature dependence of VOCR in the SoCAB is currently unclear. In order to account for a potential temperature dependence of biophysical or chemical feedbacks (e.g.,  $\text{NO}_x$  VOCR) in the SoCAB in our analysis, we require consecutive weekdays/weekend days to be within  $\pm 5^\circ\text{C}$  of the Friday temperature in order to be eligible for comparison. Pusede and Cohen [2012] calculated the probability of weekday and weekend  $\text{O}_3$  to exceed a certain value (70 ppb) in their study of the  $\text{O}_3$  sensitivity to  $\text{NO}_x$  and VOCR reductions in the San Joaquin Valley, CA. In their study, two classes of VOCs were reported: one that has decreased over the years and controls a larger share of VOCR at moderate temperature and a second that dominates VOCR at high temperature and has not decreased with time. In the SoCAB, the use of any



**Figure 2.** Four year probability of WO<sub>3E</sub> occurrences ( $P_{WO3E}$ ); probability that weekend O<sub>3</sub> is lower than weekday ( $P_{IWO3E}$ ) and mean weekend NO<sub>2</sub> values (12:00–16:00 PST) at different sites in the SoCAB. (a)  $P_{WO3E}$  for 2003–2006 (dashed, solid circle) and 2011–2014 (solid, solid circle); open circles represent  $P_{IWO3E}$  for the same years (all base case), and error bars represent uncertainty in the counting statistics. (b) Temperature dependence of  $P_{IWO3E}$  is observed only in recent years (solid lines) and hot conditions (red); base case (black lines) shown in Figure 2a; high-temperature conditions (34–45°C) (red); moderate-temperature conditions (25–33°C) (blue). (c) Mean weekend NO<sub>2</sub> (2011–2014) is lower under conditions when weekend O<sub>3</sub> is lower than weekday (identical symbols as in Figure 2a); the error bars represent standard error of the mean. CU AMAX-DOAS NO<sub>2</sub> VCDs (green) from 17 July 2010 at/close to the measurement sites were converted into mixing ratio using boundary layer height measured by NOAA TOPAZ lidar; the error bars represent standard deviation. Mean NO<sub>2</sub> surface concentration (12:00–16:00 PST) for 17 July 2010 (turquoise) and at the hour nearby the CU AMAX-DOAS measurement (before 11:00 PST is marked “morning,” and after 11:00 PST “daytime”) (orange).

single (fixed) O<sub>3</sub> threshold value is not really practicable, because of the large variability of O<sub>3</sub> from the coast to the inland locations. We have investigated the temperature sensitivity of  $P_{WO3E}$  within the SoCAB by requiring Friday temperature to be within (1) a high-temperature bin (34–45°C) and (2) a moderate-temperature bin (25–33°C) and compare with (3) the base case (18–45°C). We used temperature (daily maximum between 12:00–16:00 PST) measured at the respective monitoring station when available. Temperature data from closest monitoring station were used for Pasadena (Azusa), Pomona (Upland), and Fontana (San Bernardino). For the years 2003, 2012, and 2013, temperature measured at USC downtown campus station was used for the downtown Los Angeles site as data from the North Main Street are limited for those years. The 34–45°C bin was chosen as it accounts for around half the summer weekdays-weekends pair in San Bernardino and showed sufficient difference in  $P_{WO3E}$ . Coincidentally, it is also the high-temperature regime in *Pusede and Cohen* [2012]. By constraining the temperature dependence of VOCR between the weekday and weekend, the changes in O<sub>3</sub> and hence  $P_{WO3E}$  and  $P_{IWO3E}$  of the high- and moderate-temperature intervals can be attributed to changes in NO<sub>x</sub>.

Sensitivity studies were performed that varied the following parameters: (i) only considering Sunday as a weekend day, (ii) changing the difference O<sub>3</sub> threshold value from 3 ppb by ±1 ppb, (iii) changing the temperature range to ±10°C, (iv) changing the temperature range to ±3°C, (v) changing the time period for daily mean O<sub>3</sub> calculation from 12:00–16:00 PST to 11:00–17:00 PST, and (vi) changing the statistical parameter from mean O<sub>3</sub> to maximum O<sub>3</sub>. These tests indicated consistently that the results were robust regardless of the parameters chosen; i.e., changing

the parameters had a negligible effect on the  $P_{WO3E}$  across the SoCAB. Excluding Saturday from the weekend only had the effect of worsening the statistics (i.e., half of the data points are not eligible for comparison), but the results remained the same (see supporting information Figure S4). Results from sensitivity studies are compared to the base case in Figures S4 to S8 in the supporting information.

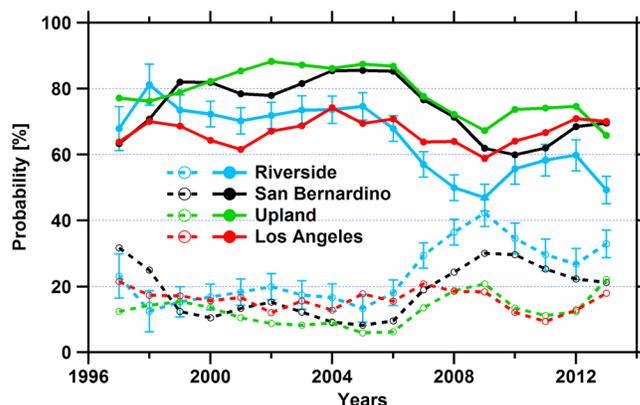
### 3. Results and Discussion

The aircraft data show a reduction in  $\text{NO}_2$  and  $\text{O}_3$  on the weekend that affected the entire SoCAB during the CalNex case study (Figure 1). Analysis of surface monitoring data corroborates this finding and shows that the likelihood of such events occurring ( $P_{\text{WO3E}}$ ) is increasing in recent years. Figure 2a shows the 4 year average  $P_{\text{WO3E}}$  and  $P_{\text{IWO3E}}$  at the nine surface monitoring sites for the years 2003–2006 and 2011–2014. The uncertainty is calculated as counting error ( $0.5/N^{1/2}$ ) where  $N$  is number of points that qualify the temperature,  $\text{NO}_2$ , and  $\text{O}_3$  criteria for comparison.  $N$  at San Bernardino is 180, 79, and 97 and 207, 130, and 65 for the base case, high-, and moderate-temperature cases in 2011–2014 and 2003–2006, respectively. For the base case during 2003–2006, the  $P_{\text{WO3E}}$  was around 80–90% across the basin from Azusa to San Bernardino in the east. The  $P_{\text{WO3E}}$  for the most recent 4 year period is 15–25% lower across most of the basin except for the western part where the decrease is smaller (Azusa, Pasadena, and downtown Los Angeles). More importantly,  $P_{\text{IWO3E}}$  is increasing in the recent period indicating that  $\text{O}_3$  is lower on increasingly more weekends.

A more detailed analysis of temperature reveals that the recent increase in  $P_{\text{IWO3E}}$  is larger during hot conditions. Figure 2b shows the 4 year average  $P_{\text{IWO3E}}$  for the base case, high-, and moderate-temperature cases during 2003–2006 and 2011–2014. The highest  $P_{\text{IWO3E}}$  is observed for the high-temperature cases throughout the SoCAB.  $P_{\text{IWO3E}}$  did not depend on temperature a decade ago, and no significant change is observed at moderate temperatures in recent years. However, there is a highly significant split between  $P_{\text{IWO3E}}$  during hot and moderate temperature conditions in recent years. Indeed, the change in the  $P_{\text{IWO3E}}$  (and  $P_{\text{WO3E}}$ ) base case in recent years is driven by these high-temperature days. The aircraft case study during CalNex falls in the high-temperature category. The analysis of the surface measurements thus confirms that the lower weekend  $\text{O}_3$  during the case study is not a curiosity but is increasingly likely to occur in recent years. In recent years  $P_{\text{IWO3E}}$  has increased disproportionately over most of the basin. The eastern part of the basin has higher temperatures, lower  $\text{NO}_x$  levels, and experienced a larger increase in  $P_{\text{IWO3E}}$  (and larger decrease in  $P_{\text{WO3E}}$ ) compared to the western part. This disproportionate increase in  $P_{\text{IWO3E}}$  indicates not only the weakening of the WO3E in the SoCAB but also a tendency toward gradual shrinking of the area where  $\text{NO}_x$  reductions cause higher  $\text{O}_3$  on the weekends. This gradual shrinking of the area affected by the WO3E is in sharp contrast to a decade ago, when Fujita *et al.* [2003] reported an eastward expansion of the WO3E.

The WO3E is caused by the combination of (i) decreased  $\text{O}_3$  titration in the morning due to lower  $\text{NO}_x$  emission on the weekends resulting in higher  $\text{O}_3$  from the previous day to start with and (ii) increased photochemical production in the afternoon. The VOC/ $\text{NO}_x$  ratio plays a critical role for the photochemical  $\text{O}_3$  formation chemistry. At low VOC/ $\text{NO}_x$  ratios typically seen over urban areas, VOC is generally the limiting reactant. This represents VOC-limited or  $\text{NO}_x$ -saturated chemical conditions for  $\text{O}_3$  formation, and a further decrease in  $\text{NO}_x$  emissions results in more efficient  $\text{O}_3$  production. This is considered to be the dominant cause for the WO3E in the SoCAB [Pollack *et al.*, 2012]. At high VOC/ $\text{NO}_x$  ratios,  $\text{NO}_x$  becomes the limiting reactant and less  $\text{O}_3$  is formed upon further decreasing  $\text{NO}_x$  emissions. This is known as  $\text{NO}_x$ -limited conditions for  $\text{O}_3$  formation [Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 2006]. Figure 2a shows that the  $\text{NO}_x$ -saturated conditions typical of the WO3E remain dominant in most of the SoCAB also in recent years. However, conditions when  $P_{\text{WO3E}}$  is equal to  $P_{\text{IWO3E}}$  are sufficient to indicate an overall shift in  $\text{O}_3$  formation chemistry ( $P_{\text{WO3E}}$  does not need to equal zero). While decreased  $\text{NO}_x$  titration on weekends always results in higher  $\text{O}_3$  at the start of the weekend compared to the weekday, photochemical production of  $\text{O}_3$  depends upon the  $\text{O}_3$  formation chemistry condition. In our analysis of  $P_{\text{WO3E}}$  and  $P_{\text{IWO3E}}$ , we required the  $\text{NO}_2$  to be lower on the weekend and hence can safely assume that the  $\text{O}_3$  on the weekends were higher in the morning to begin with. Interestingly, despite starting with higher  $\text{O}_3$  in the morning,  $\text{O}_3$  is lower in the weekend afternoons on an increasingly larger number of weekends (Figure 2b). This can only be explained by lower photochemical  $\text{O}_3$  production in the weekend afternoon compared to weekday afternoon. Since our analysis was constrained by temperature as a proxy for VOCR (the VOCR is similar for weekday and weekend), the decreasing trend in  $P_{\text{WO3E}}$  (and increasing  $P_{\text{IWO3E}}$ ) indicates that under hot conditions an increasing number of weekends show  $\text{O}_3$  production chemistry shift to  $\text{NO}_x$ -limited conditions in recent years.

Analysis of  $\text{NO}_2$  levels (i) when weekend  $\text{O}_3$  is higher than weekday  $\text{O}_3$  and (ii) when weekend  $\text{O}_3$  is lower showed that  $\text{NO}_2$  levels are consistently lower for (ii) than (i) at all sites. Figure 2c shows the mean weekend  $\text{NO}_2$  values for the last 4 years (2011–2014) for the two cases. There is no temperature dependence in  $\text{NO}_2$  in



**Figure 3.** Time series of  $P_{WO3E}$  (solid line) and  $P_{IW03E}$  (dashed line) from 1996 to 2014 (3 year running mean) for downtown Los Angeles (red), Upland (green), Riverside (blue), and San Bernardino (black) monitoring stations in the SoCAB.

to  $NO_x$ -limited conditions resulting in lower  $O_3$  on the weekends. This transition is more likely to occur when ambient temperatures are high.  $NO_2$  concentrations measured by the AMAX-DOAS on Saturday 17 July 2010 in the eastern part of the SoCAB are lower than the average  $NO_2$  typical of the  $NO_x$ -limited  $O_3$  formation conditions based on the surface monitoring data (see Figure 2c). Thus, this large decrease in  $NO_2$  is likely the driver for the lower  $O_3$  observed by the TOPAZ lidar for the high-temperature case study shown in Figure 1. Higher  $NO_2$  values were observed over the western part of the basin during morning rush hour and are consistent between AMAX-DOAS and the monitoring network (Figure 2c). A recent study by Hong *et al.* [2015] showed that additional reduction of vehicular traffic due to a freeway closure in the western SoCAB popularly known as “Carmageddon” resulted in lower  $O_3$  on the weekend. An average reduction of 14% in vehicular traffic due to the closure resulted in 16% lower  $O_3$  compared to nonclosure weekends. The ambient temperature during Hong *et al.*'s [2015] case study was around 20°C which is near the bottom of our temperature ranges and further highlights the difference in  $O_3$  formation chemistry in the western and eastern SoCAB.  $NO_x$  emission in the SoCAB has been decreasing over the last five decades [Pollack *et al.*, 2013].  $NO_x$  is expected to continue to decrease in the SoCAB in the coming years [Millstein and Harley, 2010] as a result of the new stringent emission regulations for both heavy-duty diesel vehicles as well as cars and light-duty trucks that are already in place [California Code of Regulations, 2008, 2012]. With the  $O_3$  formation chemistry already near its peak, and/or even in  $NO_x$ -limited conditions for an increasing number of hot weekends, these regulations aimed at reducing  $NO_x$  emission are likely to be progressively more effective at reducing  $O_3$  pollution on hot days in the SoCAB in the decade ahead.

The apparent temperature dependence of  $P_{IW03E}$  in recent years is in stark contrast to a decade ago, when neither  $P_{WO3E}$  nor  $P_{IW03E}$  showed any obvious dependence on temperature. Given the lack of an apparent temperature dependence of  $NO_x$ , and the dominance of primary CO sources (masking any possible temperature effect from secondary CO), our analysis indeed can only be explained if there was a temperature dependence of VOCR in the eastern SoCAB. No clear conclusion can be drawn in the western SoCAB in particular downtown Los Angeles from our data. Pusede *et al.* [2014] showed that VOCR in the San Joaquin Valley has a temperature-independent component and a temperature-dependent component that increases exponentially with temperature. Any temperature-dependent VOCR contribution that is dominant at high temperature and has not changed over the years could help explain the observation of a larger increase in  $P_{IW03E}$  at high temperature (Figure 2b). In such a scenario, the  $NO_x$  decrease over time results in an increasing VOC/ $NO_x$  ratio over the years. A relatively larger  $NO_x$  decrease on select weekends then increases the VOC/ $NO_x$  ratios sufficiently to shift  $O_3$  formation chemistry to  $NO_x$ -limited conditions. VOC emissions from motor vehicles, which are a major component of the temperature-independent VOCR fraction that dominates at moderate temperatures [Pusede *et al.*, 2014], have decreased within the SoCAB over the years along with  $NO_x$  (see Figures S2 and S3). At moderate temperatures, the VOC/ $NO_x$  ratio changes over time are

the eastern SoCAB (see supporting information Figures S7 and S8). The lower  $NO_2$  observed when the weekend  $O_3$  is lower is thus primarily caused by lower  $NO_x$  emissions on the weekend. Faster photochemical  $NO_x$  removal can provide a positive feedback to the significant  $NO_x$  reduction during weekends but likely plays a secondary role as is further corroborated by the rather small decrease (if significant) of CO on weekends (see supporting information Texts S2 and S3 and Figures S3, S7, and S8). Thus, depending upon the extent of  $NO_x$  decrease on the weekend, the  $O_3$  formation chemistry remains either  $NO_x$  saturated on the weekends (increasing weekend  $O_3$ ) or transitions

thus likely small compared to hot temperatures, which is consistent with the lack of a change in  $P_{\text{WO3E}}$  we find at moderate temperatures in recent years compared to a decade ago. A temperature sensitivity of VOC/ $\text{NO}_x$  ratios is very likely also the reason for the observation of a small change in  $P_{\text{IWO3E}}$  in the western part of the basin, where temperature is lowest, and usually in the moderate temperature range.

### 3.1. Effect of the Economic Recession

Figure 3 shows the time series (3 year running mean) of  $P_{\text{WO3E}}$  for four sites in the SoCAB. The probability over the downtown Los Angeles has remained the same for the last two decades. For Upland, Riverside, and San Bernardino, the probability remained fairly constant between 70 and 90% for a decade from 1997 to 2006. A very sharp decrease is observed between 2007 and 2010, which coincides with the period of the economic recession. The  $P_{\text{WO3E}}$  and  $P_{\text{IWO3E}}$  are almost equal in 2009 indicating that the WO3E was not a dominant phenomenon in Riverside for the years 2008–2010. It increased slightly and then settled to a new (overall lower) probability level in recent years. Four other sites in the middle of the basin (not shown here) also follow a similar trend with a sharp decrease around 2008. Satellite observations have shown a much larger than average decrease in  $\text{NO}_x$  in many parts of the world during the economic slowdown [Castellanos and Boersma, 2012; Russell et al., 2012]. Russell et al. [2012] reported around 15% per year, 3 times faster than usual,  $\text{NO}_x$  reduction in Los Angeles for the period 2007–2009 based on Ozone Monitoring Instrument observations from space. Similarly, fuel sales data for diesel fuel and on-road diesel  $\text{NO}_x$  emission in the SoCAB showed a 17–20% decrease between 2007 and 2009 [McDonald et al., 2012]. Before 2007 fuel sales data for diesel fuel and on-road diesel  $\text{NO}_x$  emissions showed a gradually increasing trend. Satellite observations also show a much slower decrease in  $\text{NO}_x$  after the recession (~2% per year from 2009 to 2011) [Russell et al., 2012]. The decrease observed for diesel fuel sales and on-road diesel  $\text{NO}_x$  emission also stopped after 2009 [McDonald et al., 2012]. In context of these observations, our analysis shows that the economic recession not only had an impact on  $\text{NO}_x$  emissions, but this sharp decrease very likely has also expedited the reduction in  $P_{\text{WO3E}}$ . More importantly, the more recent value of the  $P_{\text{WO3E}}$  is significantly different than what it was a decade ago.

## 4. Conclusions

For a hot weekend during summer 2010, we have observed that the usual decrease in  $\text{NO}_x$  was accompanied by a widespread decrease of  $\text{O}_3$  in the SoCAB. This observation from research aircraft was found to be spatially representative also of the surface measurement networks inside the SoCAB. Analysis of  $P_{\text{WO3E}}$  and  $P_{\text{IWO3E}}$  at nine different CARB surface monitoring stations along our flight track suggests that photochemical  $\text{O}_3$  formation is more frequently  $\text{NO}_x$  limited on hot weekends in recent years and supports that the observations during the CalNex case study are representative and increasingly likely to occur in recent years. We find that the  $\text{O}_3$  formation chemistry on hot weekends is markedly different than at moderate temperatures and at its peak in the SoCAB. Larger  $\text{NO}_x$  reductions on weekends shift photochemical  $\text{O}_3$  formation toward  $\text{NO}_x$ -limited conditions on increasingly more weekends in recent years. While  $\text{NO}_x$ -saturated conditions still dominate, the area affected by the WO3E is slowly shrinking. The eastern part of the basin has higher temperatures, and lower  $\text{NO}_x$ , and is more likely to experience lower  $\text{O}_3$  on weekends under hot conditions in the future. Our results suggest that a temperature-dependent component to VOCR exists in the SoCAB that is increasingly relevant under hot conditions and needed to explain the temperature dependence of  $P_{\text{WO3E}}$  and  $P_{\text{IWO3E}}$  in recent years. Future regulations aimed at reducing  $\text{NO}_x$  emissions are likely to be more effective at decreasing  $\text{O}_3$  pollution especially on hot weekends in the coming decade.

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