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Evolution of the Magnitude and Spatial Extent of the Weekend Ozone Effect in California's South Coast Air Basin, 1981–2000

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ABSTRACT

Since the mid-1970s, ozone (O_3) levels in portions of California's South Coast Air Basin (SoCAB) on weekends have been as high as or higher than levels on weekdays, even though emissions of O_3 precursors are lower on weekends. Analysis of the ambient data indicates that the intensity and spatial extent of the weekend O_3 effect are correlated with day-of-week variations in the extent of O_3 inhibition caused by titration with nitric oxide (NO), reaction of hydroxyl radical (OH) with nitrogen dioxide (NO_2), and rates of O_3 accumulation. Lower NO mixing ratios and higher NO_2/oxides of nitrogen (NO_x) ratios on weekend mornings allow O_3 to begin accumulating approximately an hour earlier on weekends. The weekday/weekend differences in the duration of O_3 accumulation remained relatively constant from 1981 to 2000. In contrast, the rate of O_3 accumulation decreased by one-third to one-half over the same period; the largest reductions occurred in the central basin on weekdays. Trends in mixing ratios of O_3 precursors show a transition to lower volatile organic compound (VOC)/NO_x ratios caused by greater reductions in VOC emissions. Reductions in VOC/NO_x ratios were greater on weekdays, resulting in higher VOC/NO_x ratios on weekends relative to weekdays. Trends in VOC/NO_x ratios parallel the downward trend in peak O_3 levels, a shift in the location of peak O_3 from the central to the eastern portion of the basin, and an increase in the magnitude and spatial extent of the weekend O_3 effect.

IMPLICATIONS

The decrease in weekend O_3 precursor emissions of VOC and NO_x provides a natural test case for investigating the response of O_3 levels to specific changes in precursor emissions. Our analysis demonstrates that peak O_3 will increase in the urbanized areas of the SoCAB if NO_x emissions are decreased at current levels of VOC. For this level of VOC, modeling suggests that peak O_3 will increase unless NO_x mixing ratios are decreased by approximately 90% from current weekend levels. The study also shows that weekend O_3 would be even higher were it not for concomitant weekend emission reductions of VOCs. The development of accurate day-of-week emissions inventories is required to assess the effects of current and future O_3 control regulations.

INTRODUCTION

Since the mid-1970s, many research studies have shown that ozone (O_3) levels in portions of California's South Coast Air Basin (SoCAB) are higher on weekends than on weekdays.[1–8] Higher O_3 levels occur even though the emissions of O_3 precursors, oxides of nitrogen (NO_x), and to a lesser extent, volatile organic compounds (VOC) are lower on weekends than on weekdays. San Francisco, the northeastern cities of Washington, DC; Philadelphia; and New York, and Chicago exhibit similar weekend O_3 effects.[9–11] Near-constant day-of-week O_3 levels in the face of strong weekday/weekend variations in NO_x should also be viewed as a weekend effect. By this definition, Atlanta, GA, also exhibits a weekend O_3 effect. While ambient O_3 levels have decreased substantially throughout the basin, the magnitude and spatial extent of the weekend effect have become more pronounced, especially during the past decade.[7,12] Understanding the response of O_3 mixing ratios to specific changes in VOC or NO_x emissions is fundamental to understanding the weekend O_3 effect.

The weekend O_3 effect is of special interest to policymakers because of its implications for O_3 control strategies. In November 1998, the California Air Resources Board (CARB) adopted the Low-Emission Vehicle (LEV-II) regulations, which include significant future NO_x emission reductions. The weekend O_3 effect was cited at the CARB's LEV-II hearings as evidence that further reduction of NO_x emissions at this time may be counterproductive

for O_3 attainment in the SoCAB and other coastal metropolitan areas of the state. The CARB, the U.S. Department of Energy (DOE), and the Coordinating Research Council have carried out or supported several research efforts on the weekend effect and the implications of NO_x reduction as an O_3 control strategy.[12–21]

This research was part of a larger study conducted by the Desert Research Institute (DRI) and Sonoma Technology, Inc. Measurements of O_3 and O_3 precursors collected routinely over a 20-yr period from 1981 to 2000 were analyzed. Available emissions activity data, VOC speciation, and meteorological observations in the SoCAB were reviewed to evaluate their potential effects on day-of-week variations in O_3 levels. A 9-day field study in the Los Angeles area from September 30 to October 8, 2000, was conducted to examine the relationships between emissions and air quality relevant to the weekend O_3 effect,[22] along with a concurrent effort to collect traffic data and survey emission-related activities at commercial and residential locations near ambient monitors.[23] This paper examines the evolution of the magnitude and spatial extent of the weekend O_3 effect during the study period and provides a conceptual explanation for the trends responsible for relatively higher weekend O_3 levels in the SoCAB.

APPROACH AND METHODS

Historical trends in the mean daily maximum hourly O_3 and the evolution of the magnitude and spatial extent of the weekend O_3 effect in the SoCAB were examined. The retrospective analysis of ambient data focused on day-of-week differences in the overnight carryover of O_3 precursors, the extent of inhibition of O_3 formation during the morning caused by titration with nitric oxide (NO), loss of hydroxyl radical (OH) through its reaction with nitrogen dioxide (NO_2), and the rate of O_3 accumulation from the end of the morning inhibition period to the time of peak O_3. Initially, the mean diurnal variations in O_3 and O_3 precursors at Azusa for the summers of 1995–1997 were examined to identify the parameters that would best serve as surrogates for the extent of O_3 inhibition and the rate of O_3 accumulation. The identified parameters were examined for all 12 sites analyzed.

The mean diurnal variations of O_3, NO, NO_2, and carbon monoxide (CO) at Azusa for summer 1995 are shown in Figure 1 as an example. During the carryover phase, there is little difference in the mixing ratios of NO_2 and O_3 between weekends and weekdays. NO is slightly higher on weekends, and CO is approximately 25% higher on weekends. Although carryover of O_3 precursors is higher on weekends, the differences are relatively small

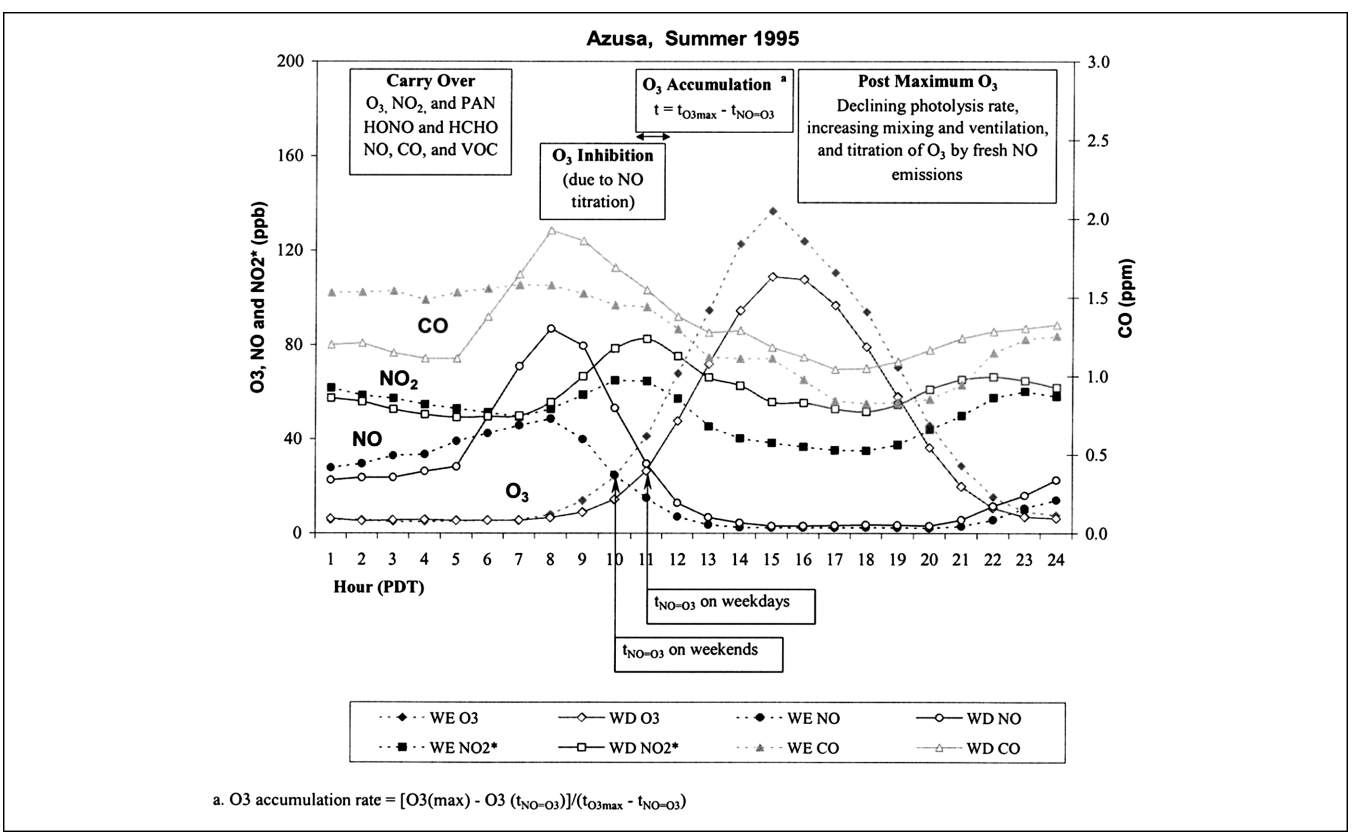

Figure 1. Mean summer 1995 diurnal variations of O_3 and NO at Azusa during the weekday and weekend. The shorter morning O_3 inhibition period and higher rate of O_3 accumulation are the main factors that result in higher O_3 on weekends. NO_2* indicates upper limits, because of interference from other reactive nitrogen oxide species such as PAN.

compared with the higher weekday mixing ratios during the morning commute periods. Fresh NO emissions during this period inhibit radical formation by titrating O_3 with NO. Ozone formation is also reduced by the reaction of OH with NO_2.[24] During this inhibition period, formaldehyde (HCHO) and, to a lesser extent, nitrous acid (HONO) are the main sources of OH radicals. The time in the morning when NO and O_3 mixing ratios cross over ($t_{NO = O3}$) was selected as a marker for the end of the morning inhibition period and the beginning of O_3 production via conversion of NO to NO_2 by the peroxy radical. Note that the NO and O_3 crossover point occurs an hour earlier on weekends.

The effect of differences in the rate of O_3 accumulation during the O_3 accumulation period between weekends and weekdays for 12 air monitoring sites in the basin (Figure 2) was examined for 1981–1998 to develop a conceptual explanation that accounts for the spatial and temporal variations in the strength of the weekend effect. The duration of O_3 accumulation was estimated by the difference between time of maximum O_3 (t_{maxO3}) and $t_{NO = O3}$. The rate of O_3 accumulation (ppb/hr) is the increase in O_3 from $t_{NO = O3}$ to t_{maxO3} divided by the duration of O_3 accumulation. Weekday differences in the diurnal variations of CO, nonmethane hydrocarbons (NMHC), NO, NO_2, and NO_x were also related with variations in O_3, VOC/NO_x ratios and the ratios of O_3 to potential O_3 (defined as O_3 plus NO_2). Day-of-week variations in O_3 mixing ratios were also examined in relation to VOC reactivity, photochemical aging, and the estimated photolysis rate parameter for NO_2.

Air quality data for the summers (June 1–September 30) of 1981–1998 were obtained from the latest (February 2000) CARB ambient data compact disk. The database was validated and screened for invalid and suspicious data according to the procedures and criteria described by Fujita et al.[14] When composite means were formed by day of the week, major holidays (Independence Day and Labor Day) were removed. Table 1 shows a list of the key daily parameters of interest. Values of pollutants from 4:00 to 5:00 a.m. PDT are surrogates for carryover from the previous day. Values of pollutants from 6:00 to 9:00 a.m. represent the morning commute. The end of the O_3 inhibition period $t_{NO = O3}$ was determined by subtracting the mixing ratio of O_3 from NO and finding the hour between 7:00 a.m. and 2:00 p.m. at which this difference transitions from greater than to less than zero. The interpolation involves the intersection of the two line segments represented by the decreasing NO and the increasing O_3. Monitoring sites include North Long Beach, Anaheim, Lynwood, and Los Angeles–North Main in the western SoCAB; Reseda, Burbank, Pico Rivera, and La Habra in the central SoCAB; and Azusa, Pomona, Upland, and Rubidoux in the eastern SoCAB. The annual means were calculated for four time periods covering 1981–1984, 1985–1989, 1990–1994, and 1995–1998.

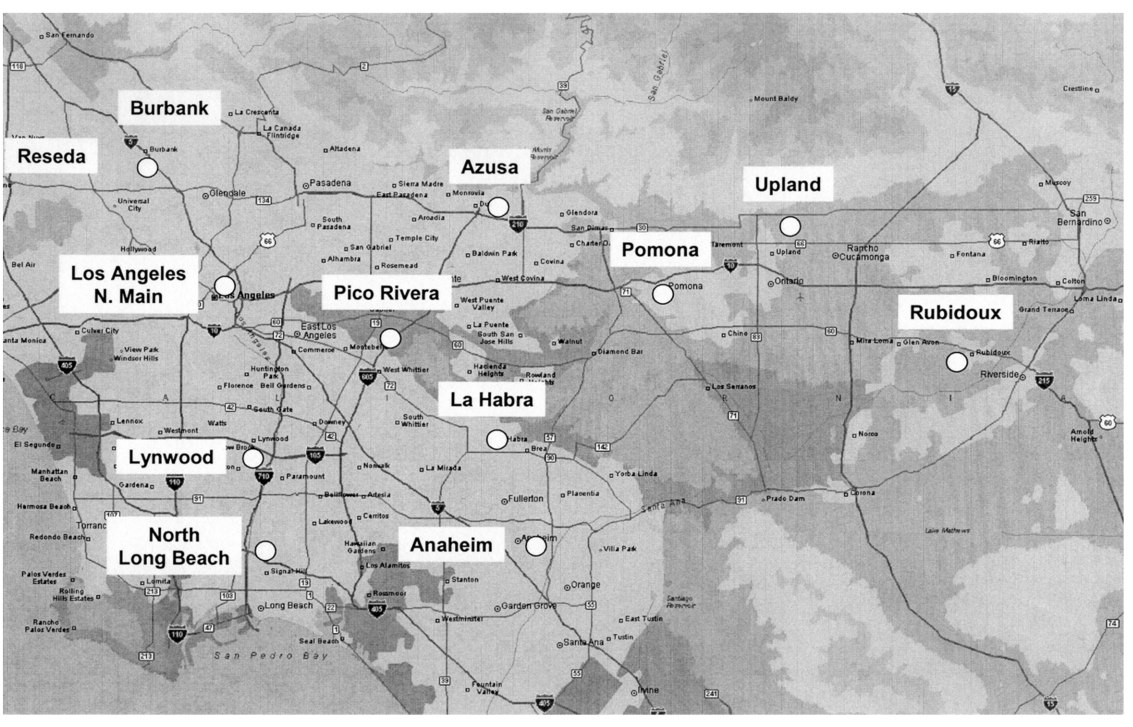

Figure 2. Map showing the locations of the 12 air quality monitoring stations in the SoCAB that are included in the retrospective analysis of the temporal and spatial evolution of the weekend O_3 effect.

Table 1. Air quality parameters for the conceptual explanation of the weekend O_3 effect.

No.	Parameter	Purpose
1	O_3 max	Weekend/weekday effect indicator
2	3:00–4:00 a.m. PST (NO)	Carryover
3	3:00–4:00 PST (NO_x)	Carryover
4	3:00–4:00 PST (NO_2)	Carryover
5	3:00–4:00 PST (O_3 + NO_2)	Potential O_3 carryover
6	3:00–4:00 PST (CO)	Surrogate for gas-powered emissions carryover
7	3:00–4:00 PST (NMHC)	Carryover (via Bendix or regression with CO)
8	6:00–7:00 a.m. PST (NO)	O_3 titration potential
9	6:00–7:00 PST (NO_2)	For NO_2–NO comparison
10	6:00–7:00 PST (CO)	Surrogate for gas-powered morning emissions
11	6:00–7:00 PST (NMHC)	Fresh emissions (peak morning commute hour)
12	5:00–8:00 a.m. PST (NO)	Morning commute
13	5:00–8:00 PST (NO_2)	Morning commute
14	5:00–8:00 PST (NO_x)	Morning commute
15	5:00–8:00 PST (CO)	Morning commute
16	5:00–8:00 PST (NMHC)	Morning commute
17	5:00–8:00 PST NMHC/NO_x	Reaction efficiency/rate for morning commute
18	$t_{NO = O3}$ (PST)	Interpolated time of morning crossover of O_3 and NO; marks end of O_3 inhibition period and start of O_3 accumulation period
19	t_{O3max} (PST)	Interpolated time of daily maximum O_3
20	$t_{O3max} - t_{NO = O3}$ (PST)	Duration of O_3 accumulation
21	$O_3(t_{NO = O3})$	O_3 concentration at morning crossover of O_3 and NO
22	O_3 rate (ppb/hr)	Rate of O_3 accumulation[a]
23	NMHC/NO_x ($t_{NO = O3}$)	Reaction efficiency/rate at $t_{NO = O3}$
24	NMHC/NO_x (t_{O3max})	Reaction efficiency/rate at t_{O3max}

[a]$(O_{3max} - O_3[t_{NO = O3}])/(t_{O3max} - t_{NO = O3})$.

NMHC were estimated from CO using an empirical relationship between NMHC and CO in canister samples collected by DRI at three sites in the SoCAB during the summers of 1995 and 1996.[25] DRI collected canister and 2,4-dinitrophenylhydrazine (DNPH) cartridge samples twice daily (6:00–9:00 a.m. and 1:00–4:00 p.m. PDT) at downtown Los Angeles, Burbank, and Azusa during six 7-day periods during each summer (504 samples). The canister samples were analyzed for methane, CO, carbon dioxide (CO_2), and speciated C_2–C_{12} hydrocarbons. CO correlates well with NMHC for each of the three sampling sites with the R^2 of the regression ranging from 0.84 to 0.93. NMHC is predicted from the following empirical relationship derived from the combined regression of data from all three sites:

$$\text{NMHC} = (305 \pm 5) \times \text{CO} + (82 \pm 8), \quad R^2 = 0.89, \text{ and } n = 491 \tag{1}$$

NMHC and CO are in units of ppbC and ppm, respectively, and uncertainties are standard errors. The resulting estimates of NMHC are reasonably valid for determining day-of-week variations in NMHC mixing ratios and NMHC/NO_x ratios for any year within the 18-yr period of interest. However, they are probably not valid for establishing long-term trends in NMHC and NMHC/NO_x ratios because the slope of the regression between CO and NMHC may have changed over time with changing emission control technology.

Ambient 1999 and 2000 summer data from the Photochemical Assessment Monitoring Stations (PAMS) at Azusa, Pico Rivera, and Upland and from the CARB O_3 precursor trends site in downtown Los Angeles–North Main[18] were used in the second phase of the analysis. The PAMS O_3 precursor monitoring is conducted annually in California during the peak O_3 season (July 1–September 30). U.S. Environmental Protection Agency (EPA) methods TO-14[26] and TO-11[27] are used in PAMS for sampling and analysis of speciated hydrocarbons[26] and carbonyl compounds, respectively. The database consists of 55 individual hydrocarbons, total nonmethane organic carbons (NMOC), and three carbonyl compounds (HCHO, acetaldehyde, and acetone). CARB collects one 3-hr sample every third day at Los Angeles–North Main beginning at 6:00 a.m. Eight consecutive 3-hr hydrocarbon samples are collected daily (beginning at midnight) at Type 2 PAMS sites and every third day at all other PAMS sites. In addition, one 24-hr sample is required every sixth day year-round at Type 2 sites and during the summer monitoring period at all other sites.

Several terms are used that represent subsets of VOC. These terms are operational definitions and reflect the sensitivity and selectivity of the analytical methods. NMHC are defined as C_2–C_{11} hydrocarbons collected in stainless-steel canisters and measured by gas chromatography with flame ionization detection by EPA method TO-14. Known halocarbons and oxygenated compounds (e.g., aldehydes, ketones, ethers, and alcohols) are excluded from NMHC. Carbonyl compounds are aldehydes and ketones, the most common being HCHO, acetaldehyde, and acetone. Carbonyl compounds are operationally defined as C_1–C_7 oxygenated compounds measured by collection on acidified DNPH-impregnated C_{18} or silica gel cartridges and analyzed by high-performance liquid chromatography with UV detection. PAMS carbonyl data normally include only HCHO, acetaldehyde, and acetone. Total NMOC are the sum of quantifiable peaks by EPA method TO-14A, including unidentified hydrocarbons but excluding halocarbons. NMOC also refers to the sum of NMHC plus carbonyl compounds by TO-11.

The NO_2 mixing ratios used in the analysis were determined by the difference of NO_x and NO measured by chemiluminescence analyzers. In addition to NO_2, analyzers that are commonly used at air quality monitoring stations also convert other reactive nitrogen oxide species such as peroxyacetyl nitrate (PAN), organic nitrates, and nitric acid (HNO_3) vapor to NO, thereby causing interference. Particulate nitrate and HNO_3 are also potential interferents but are removed by the inlet system. NO_2 reported by these instruments must be considered upper limits, but the magnitude of the interference is relatively small in urban areas where NO sources are large.

The Regional Acid Deposition Model, version 2,[28] was used in a chemical box model to calculate O_3 isopleths. Simulations were performed over a range of observed NO_x and VOC mixing ratios. To calculate the O_3 isopleths, more than 650 simulations for a range of initial mixing ratios of NO_x and anthropogenic NMHC were performed. A detailed discussion of the conditions used in these simulations is given in Stockwell et al.[29] The photolysis rates of 21 species were varied over the diurnal cycle representative of conditions near sea level throughout a typical midsummer day. The simulations were initialized for a range of NO_x and VOC concentrations. There were no more emissions throughout the simulation period nor was afternoon ventilation included. For these simulation conditions, the O_3 concentrations peaked near midday, and these concentrations were plotted as an O_3 isopleth diagram. The box model simulations reasonably depict the O_3 formation from a particular mixture of VOC and NO_x. Current weekday and weekend observations of the VOC and NO_x mixing ratios were superimposed on the O_3 isopleth plot along with similar observations from the 1987 Southern California Air Quality Study (SCAQS).[30]

RESULTS

Southern California has historically experienced the most severe O_3 pollution in the United States. Before emission reduction measures were implemented, hourly mean O_3 mixing ratios approaching 0.70 ppm were reported in the SoCAB, and Stage III episodes (O_3 exceeding 0.50 ppm) were relatively frequent events in the 1960s. Large reductions in O_3 levels have occurred in the past 20 years, especially during the 1990s. The basin recorded 167 days exceeding the National Ambient Air Quality Standard of 0.12 ppm maximum hourly mean for O_3 in 1980, 158 days in 1985, 130 days in 1990, 98 days in 1995, and 33 days in 2000.[31] The maximum hourly mean mixing ratios of O_3 in the basin declined during this period from 0.45 ppm to 0.18 ppm. The highest levels of O_3 now occur on weekends throughout the basin, although peak levels of O_3 have dropped sharply (Figure 3).

The current weekend O_3 phenomenon has evolved over time. Between 1981 and 1984, peak O_3 levels were higher on weekdays in most of the central and eastern parts of the basin (see Figure 3). However, most monitoring sites in the western basin showed slightly higher weekend O_3 mixing ratios. By 1990–1994, O_3 mixing ratios were higher on weekends throughout the basin, and the weekend effect continued to strengthen after 1995. The 12-site mean Sunday/Wednesday ratios in peak O_3 and standard errors of the mean ratios for 1981–1984, 1985–1989, 1990–1994, and 1995–1998 are 1.02 ± 0.02, 1.05 ± 0.03, 1.20 ± 0.03, and 1.25 ± 0.02, respectively. The corresponding Saturday/Wednesday ratios are 1.04 ±

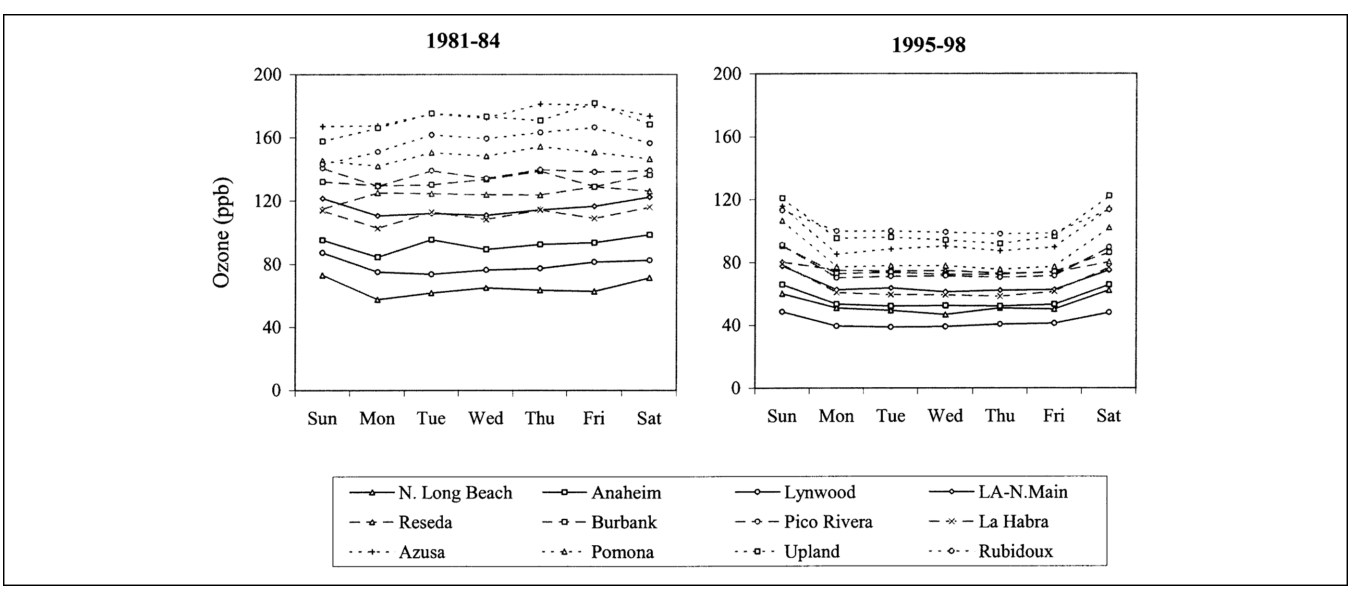

Figure 3. Mean maximum 1-hr mixing ratios of O_3 during summers (June 1–September 30) of 1981–1984 and 1995–1998 in the SoCAB. Sites in the western, northern and central, and central to eastern basin are denoted by solid, dashed, and dotted lines, respectively.

0.01, 1.05 ± 0.02, 1.17 ± 0.02, and 1.24 ± 0.02, respectively. Ozone mixing ratios in 1995–1998 expressed as ratios of the 1981–1984 values range from 0.54 to 0.59 for weekdays (Monday–Friday), 0.67 on Saturdays, and 0.70 on Sundays. The larger reductions in peak O_3 mixing ratios on weekdays have been accompanied by a shift in the location of peak O_3 levels from the central portion of the basin to the eastern basin and mountain locations. In the western basin, represented by Los Angeles–North Main, the current (1999–2000) mean peak O_3 levels are approximately 60 ppb lower than levels in 1980–1985 for all days of the week. In contrast, decreases in peak O_3 in the central basin (Azusa and Upland) have been greater on weekdays (~100–110 ppb) than on Saturdays (~70–90 ppb) or Sundays (60–70 ppb).

The current weekend O_3 effect in the SoCAB is illustrated by the correlations in Figure 4 for summer 1999–2000. The mean hourly O_3 mixing ratios at Azusa during midweek (Tuesday–Thursday) are correlated with the corresponding hourly O_3 mixing ratios on Monday, Friday, Saturday, and Sunday for each daylight hour between 6:00 a.m. and 9:00 p.m. The analogous plots for NO are also shown in each panel. NO mixing ratios are lower on weekends relative to midweek at Azusa by approximately the same ratio for all daylight hours. Conversely, O_3 is higher on weekends relative to midweek by a constant ratio for all daylight hours. The corresponding plots for Los Angeles–North Main, Pico Rivera, and Upland (not shown) show similar correlations. The Saturday/midweek ratios for O_3 during the daylight hours were 1.26–1.32 at the four sites, with a mean of 1.28. The corresponding ratios for NO were 0.51–0.69, with a mean of 0.61. The Sunday/midweek ratios for O_3 during daylight hours were 1.44–1.55, with a mean of 1.50. The ratios for NO were 0.29–0.43, with a mean of 0.35. The correlations yield an R^2 of 0.98 or better. As expected, correlations of the midweek hourly NO and O_3 mixing ratios with the corresponding hourly values on Monday and Friday show little

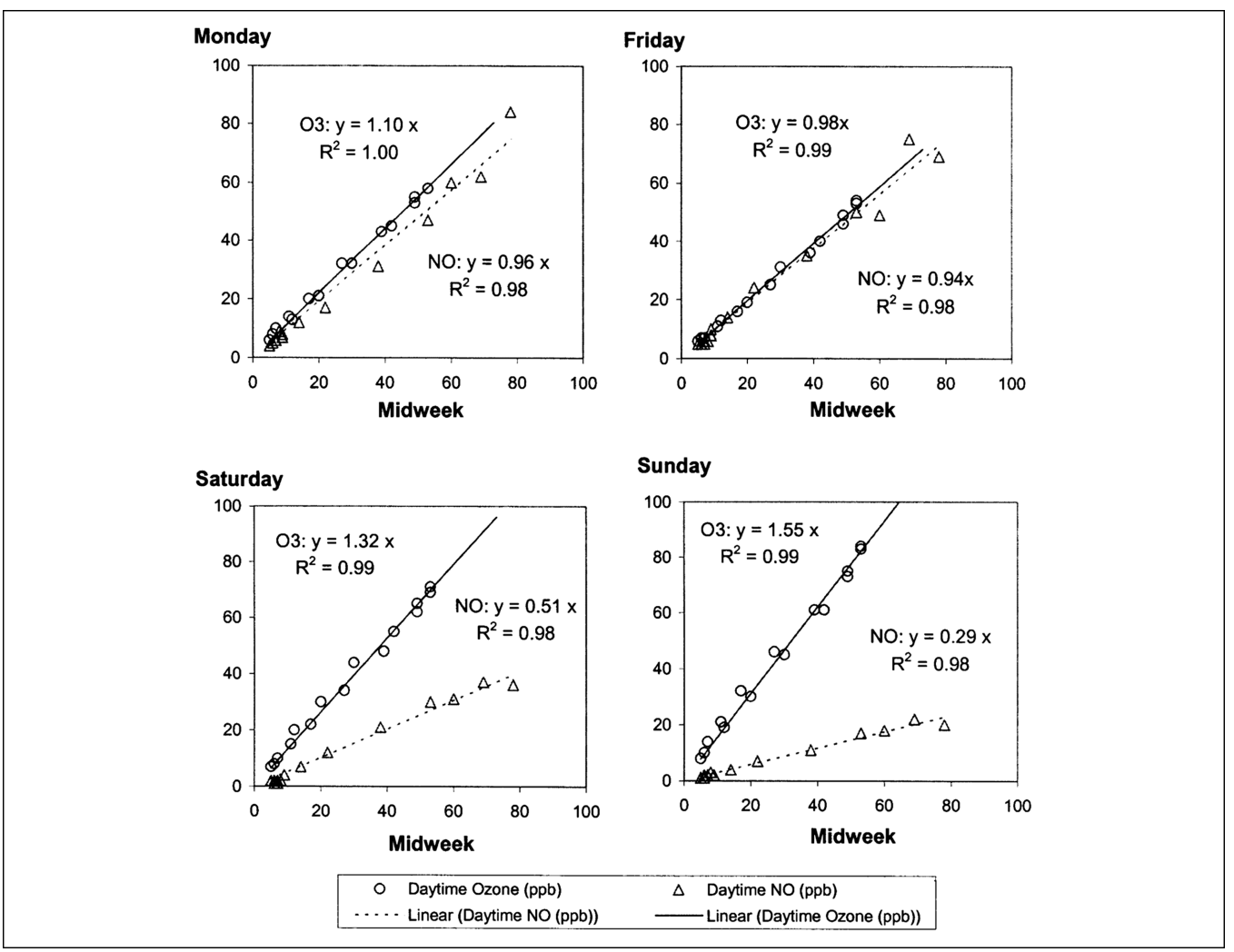

Figure 4. Correlation plots of summer 1999–2000 mean hourly O_3 mixing ratios at Azusa during midweek (Tuesday–Thursday) vs. the corresponding mean hourly O_3 mixing ratios on Monday, Friday, Saturday, and Sunday for each daylight hour between 6:00 a.m. and 9:00 p.m. Analogous plots for NO are also shown in each panel.

variance with one another. These results indicate that each of the sites examined has its own relative O_3 pattern that is fixed for all days of the week and that the Sunday/midweek ratio is a multiplicative constant, which differentiates weekdays from weekends. These results suggest that the weekday-weekend differences in the diurnal pattern of NO and O_3 are established early in the morning, and the influence of the chemical factors (either emissions or rate and efficiency of O_3 formation) related to this "constant" is maintained throughout the daylight hours.

The plots in Figure 5 show the trends in mean NO, NO_2, NO_x, and NHMC (estimated) mixing ratios at 4:00–5:00 a.m. and 7:00–8:00 a.m. by day of week. The overnight carryover of NO is 10–20% lower on Sundays and Mondays relative to midweek and approximately 10–15% higher on Friday and Saturday mornings. NO_2 carryover shows no significant day-of-week differences. The magnitude of the carryover of NO and NO_2 has decreased approximately 20% over the past 18 years. Overnight carryover of NMHC is greatest on Saturday and Sunday mornings, with ratios to Wednesday of 1.20 and 1.12, respectively, and least on Monday mornings. Higher carryover of NMHC on Sunday relative to Wednesday, coupled with lower relative carryover of NO, suggests that the carryover of NO and NMHC emissions is driven by different sources.

Initially, O_3 formation is inhibited by high mixing ratios of NO, which inhibit radical formation by titrating O_3. The O_3 inhibition period ends earlier on weekends than on weekdays because NO mixing ratios during the morning, especially from 6:00 to 9:00 a.m., are substantially lower on weekends. Mean 7:00–8:00 a.m. NO mixing ratios on Saturday and Sunday are 55–70% and 33–39% of the mean weekday mixing ratios, respectively (see Figure 5). The mean NO_2/NO_x ratios at 7:00–8:00 a.m. are approximately 0.4 on weekdays, approximately 0.5 on Saturdays, and close to 0.6 on Sundays (Figure 6). The morning crossover of NO and O_3 indicates the end of the inhibition period and the beginning of O_3 accumulation via conversion of NO to NO_2 by peroxy radical. The O_3 inhibition period ends 0.5–0.7 hr earlier on Saturdays and approximately 1.1–1.3 hr earlier on Sundays. In general, O_3 inhibition ends earlier in downwind areas and later in areas with the highest amounts of fresh NO emissions. Under the typical summer transport pattern in the basin, less time is available near the coast for O_3 to accumulate before ventilation occurs. However, the delay in the start of O_3 accumulation caused by inhibition on weekdays

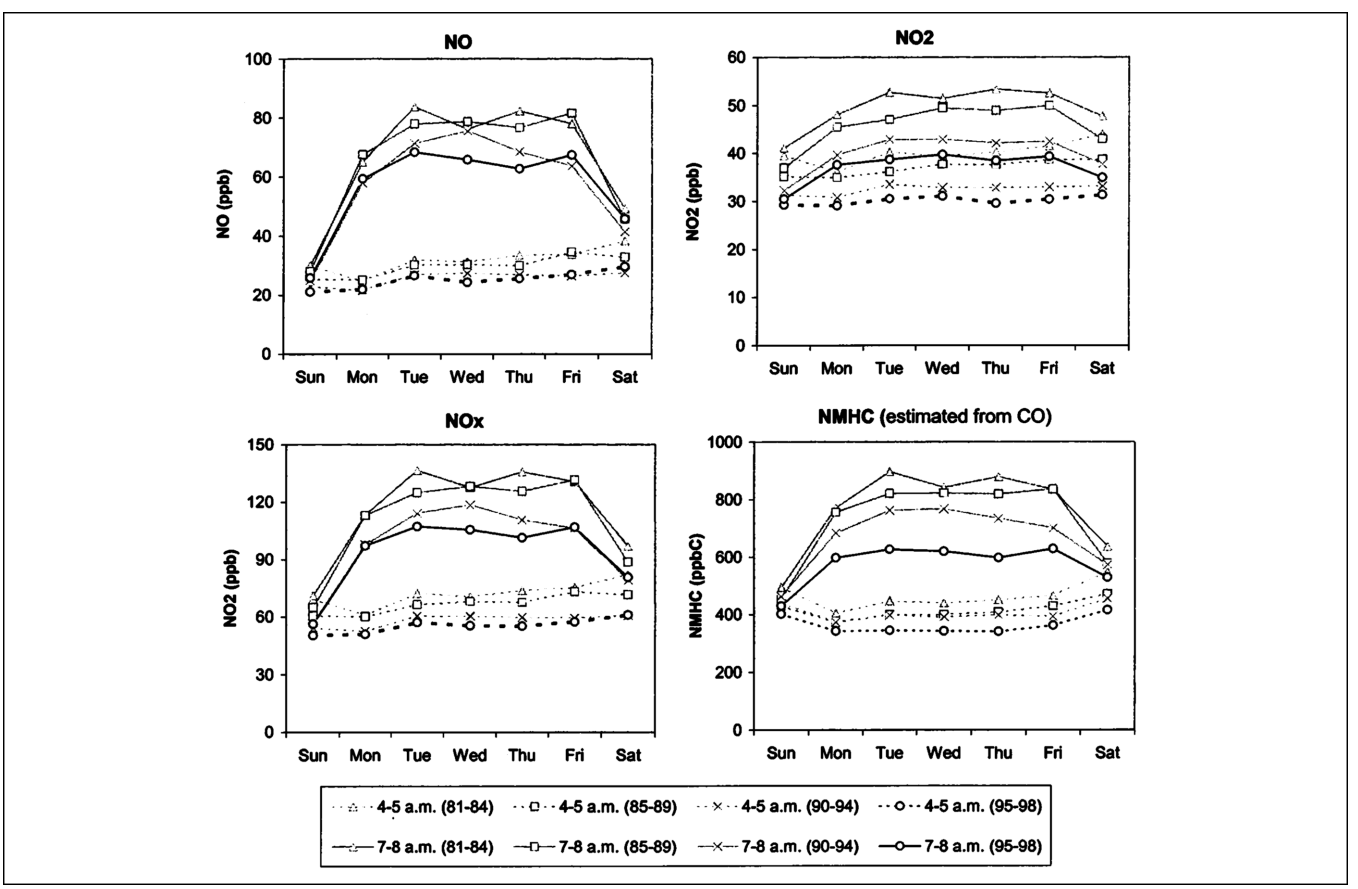

Figure 5. Historic changes in day-of-week patterns of NO and NMHC mixing ratios; 12-site mean NO and NMHC (estimated from CO) at 4:00–5:00 a.m. and 7:00–8:00 a.m. PDT by day of the week in the SoCAB during 1981–1998.

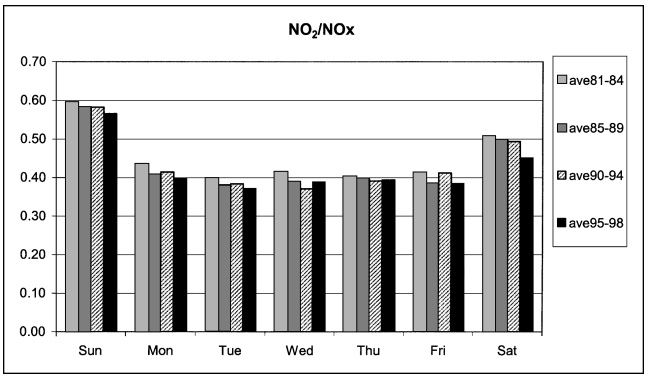

Figure 6. 12-site mean NO_2/NO_x ratios at 7:00–8:00 a.m. PDT by day of the week.

relative to weekends has changed very little in 18 years, as shown in Table 2. Although this relative difference in the duration of O_3 accumulation may be an important factor in producing a weekend effect, the observed long-term changes in the magnitude and spatial extent of the weekend effect are not caused by the changes in the duration of O_3 accumulation.

In contrast to the duration of O_3 accumulation, which has remained relatively constant from 1981–1998, O_3 accumulation rates were cut in half and a third on weekdays and Sundays, respectively, during the 18-yr period. The largest reductions occurred in the central basin. Table 2 shows that O_3 accumulation rates were lower on weekends than on weekdays through most of the 1980s but became higher on weekends during the 1990s. The transition from lower to higher O_3 accumulation rates on weekends relative to weekdays coincides with increases in the magnitude and spatial extent of the weekend effect in the SoCAB. This also coincides with a steeper decline in O_3 during the 1990s, especially in the western and central parts of the basin.

Figure 7 shows the trends in the differences between Sunday and Wednesday O_3 accumulation rates as 3-yr running means for western, central, and eastern SoCAB sites. Changes in emissions from weekdays to weekends in the early 1980s resulted in little change in the O_3 accumulation rate at western sites and generally lower weekend rates at central and eastern sites. The lower weekend O_3 accumulation rate offsets the shorter O_3 inhibition period on weekends at central and eastern locations, resulting in either no change or slightly lower O_3 mixing ratios on weekends (i.e., a small weekend effect). The weekend O_3 effect in the western basin during the early 1980s was largely caused by decreased O_3 inhibition. The transition to higher weekend O_3 accumulation rates occurred in the mid-1980s in the western basin and in the late 1980s in the central basin. Ozone accumulation rates have been approximately equal on weekdays and weekends since the early 1990s in the eastern basin. Coupled with the shorter inhibition period, O_3 mixing ratios were consistently higher on weekends during the 1990s, with the strongest weekend effect occurring in the central basin on an absolute and relative basis. The spatial evolution in the weekend effect parallels the shift in peak O_3 levels from the western to the eastern portion of the basin.

Trends in mixing ratios of O_3 precursors over the past 20 years show a gradual transition in the SoCAB to lower VOC/NO_x ratios in much of the basin. The data show that differences between weekday and weekend VOC/NO_x ratios have steadily increased over time. The ratios of the mean 6:00–9:00 a.m. $NMHC/NO_x$ ratio on Saturdays to those on Wednesdays were 1.05, 1.06, 1.17, and 1.18 for 1981–1984, 1985–1989, 1990–1994, and 1995–1998, respectively. The corresponding Sunday/Wednesday ratios are 1.10, 1.17, 1.27, and 1.42. Consequently, O_3 formation has become less VOC-limited on weekends relative to weekdays. This transition parallels the downward trend in peak O_3 levels, a shift in the location of peak O_3 levels from the central to the eastern portion of the basin, and an increase in the magnitude and spatial extent of the weekend O_3 effect in the SoCAB.

Current (1999–2000) $NMHC/NO_x$ ratios in the SoCAB are approximately half those observed during the 1987 SCAQS.[32] The mean $NMHC/NO_x$ ratios (of Los Angeles–North Main, Pico Rivera, Azusa, and Upland) from 6:00–9:00 a.m. were 31–59% higher on Sundays (mean of 46%) and 20–39% higher on Saturdays (mean of 29%), as shown in Figure 8. The mean 6:00–9:00 a.m. $NMHC/NO_x$ ratios (ppbC/ppbv) are 4.9 and 5.5 on Saturdays and Sundays, respectively, and increases to a high of 6.7 and 7.5 during the period of peak O_3 (12:00–3:00 p.m.). The mean $NMHC/NO_x$ ratio is 4.6 on Mondays and

Table 2. Trends in duration and rate of O_3 accumulation in the SoCAB on Sunday, Wednesday, and Sunday Minus Wednesday, 1981–1999.

	Duration of O_3 Accumulation (hr)			O_3 Accumulation Rate (ppb/hr)		
	Sunday	Wednesday	Sunday−Wednesday Differences	Sunday	Wednesday	Sunday−Wednesday Differences
1981–1984	5.5 ± 0.2	4.2 ± 0.3	1.3 ± 0.2	21.3 ± 1	24.3 ± 1.2	−3.1 ± 0.8
1984–1989	5.3 ± 0.3	4.2 ± 0.3	1.1 ± 0.1	19.5 ± 1.2	20.6 ± 1.6	−11 ± 0.8
1990–1994	5.2 ± 0.3	4.4 ± 0.3	0.8 ± 0.1	18.2 ± 0.9	16.3 ± 1	1.9 ± 0.6
1995–1998	5.8 ± 0.3	4.5 ± 0.2	1.3 ± 0.2	13.8 ± 0.9	12.2 ± 0.9	1.6 ± 0.5

Note: These figures are 12-site means and standard errors of the means.

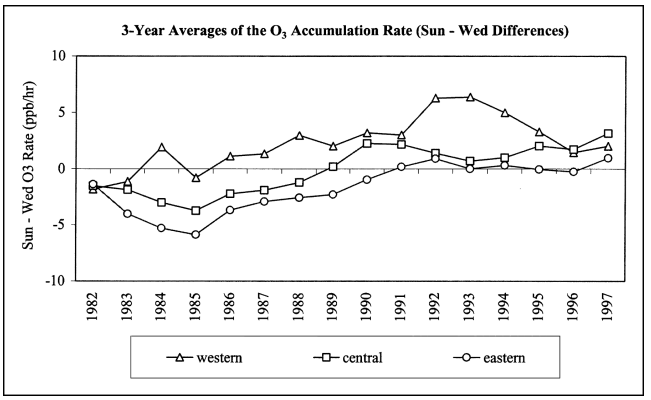

Figure 7. 3-yr running means of the Sunday minus Wednesday differences in the rates of O_3 accumulation for 1982–1997.

ranges from 3.7 to 3.9 for other weekdays. The mean midday NMHC/NO_x ratios do not exceed 7. The long-term trends shown in Figure 5 for NO and NMHC indicate that the downward trend in weekday NMHC/NO_x is caused by reductions in hydrocarbon emissions to a greater extent than NO_x emissions.

Along with a decrease in the rate of O_3 accumulation, weekday peak O_3 mixing ratios have steadily decreased relative to its maximum potential (sum of O_3 and NO_2), as shown in Figure 9. In contrast, peak O_3 on Sundays has remained constant relative to its maximum potential. The ratios of peak to maximum potential O_3 on Saturdays were similar to Sundays during the 1980s through mid-1990s but have since decreased. The decrease in the O_3 accumulation rates and higher ratio of peak O_3 to maximum potential O_3 on weekends relative to weekdays in the western and central basin, coupled with lower weekend mixing ratios of NO_x and higher weekend VOC/NO_x ratios, indicates that O_3 formation in the SoCAB has become increasingly VOC-limited overall but less VOC-limited on weekends relative to weekdays.

In addition to VOC/NO_x ratios, the reactivity of individual organic species with OH radical also affects the rate of O_3 formation. Carter's maximum incremental reactivity (MIR) values[33] were used to calculate the total MIR of the 55 PAMS target species, and it is slightly lower on weekends. Formaldehyde is slightly higher during weekends in the afternoon. With the addition of carbonyl compounds in the MIR calculations, weekend MIRs are equal to weekday MIRs during the morning and slightly higher during the afternoons. These results are consistent with Franzwa and Pasek.[34] Although the reactivity of the VOCs is comparable or slightly lower on weekends, higher ratios of HCHO to the sum of PAMS and lower ratios of more reactive species to less reactive species (i.e., xylenes/benzene) indicate that on weekends, the VOC mixture is relatively older with less fresh emissions.

Theoretical analysis shows why VOC control measures undertaken between 1987 and 2000 have been effective in reducing O_3, as depicted in Figures 10 and 11. Ozone mixing ratios estimated from the isopleth diagram are predicted to have been reduced from 200 ppb to a mean near 100 ppb during this period, which is in reasonable agreement with observations. The current mixing ratios of VOC and NO_x are in the VOC-limited portion of the O_3 isopleth diagram for weekends and weekdays. The diagram shows that the decrease in NO_x leads to an increase in O_3 mixing ratios of approximately 40 ppb between weekdays and weekends, and this is consistent with observations. The modeling analysis suggests that an O_3 disbenefit will result if NO_x emissions are decreased at current levels of VOC until the NO_x mixing ratios are decreased from current weekday levels by approximately 90% to approximately 10–12 ppb where O_3 production becomes NO_x-limited.

The simulations in Figure 11 show that the VOC/NO_x ratio decreased from a mean near 7.5 during 1987 to 3–5 during 1999–2000. On weekends, the VOC/NO_x ratio increases to 4–7 and may reach 10 or 12. The shift in the VOC/NO_x ratio increases the mean O_3 production efficiency (the number of O_3 molecules produced per NO_x molecule converted to unreactive HNO_3 or organic nitrates, $\Delta[O_3]/(\Delta[HNO_3] + \Delta[\text{organic nitrates}])$) from less than 4 to 4–6. The simulations also show that for current conditions, the OH mixing ratios increase with decreasing NO_x mixing ratios; daytime HNO_3 production has decreased between 1987 and 2000 because of the decrease in VOC mixing ratios; and currently the production of HNO_3 is lower by approximately 9 ppb between weekends

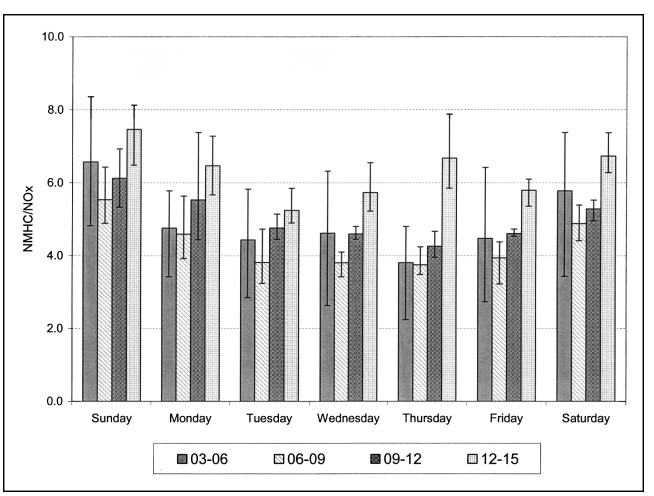

Figure 8. Day-of-week variations in the mean NMHC/NO_x ratios during carryover (3:00–6:00 a.m. PDT), O_3 inhibition (6:00–9:00 a.m.), O_3 accumulation (9:00 a.m.–12:00 p.m.), and O_3 peak (12:00–3:00 p.m.) at Los Angeles–North Main, Azusa, Pico Rivera, and Upland during the summers (July–September) of 1999 and 2000. Error bars denote maximum and minimum ratios among the four sites. *Note*: Data for Los Angeles were available only for the inhibition period.

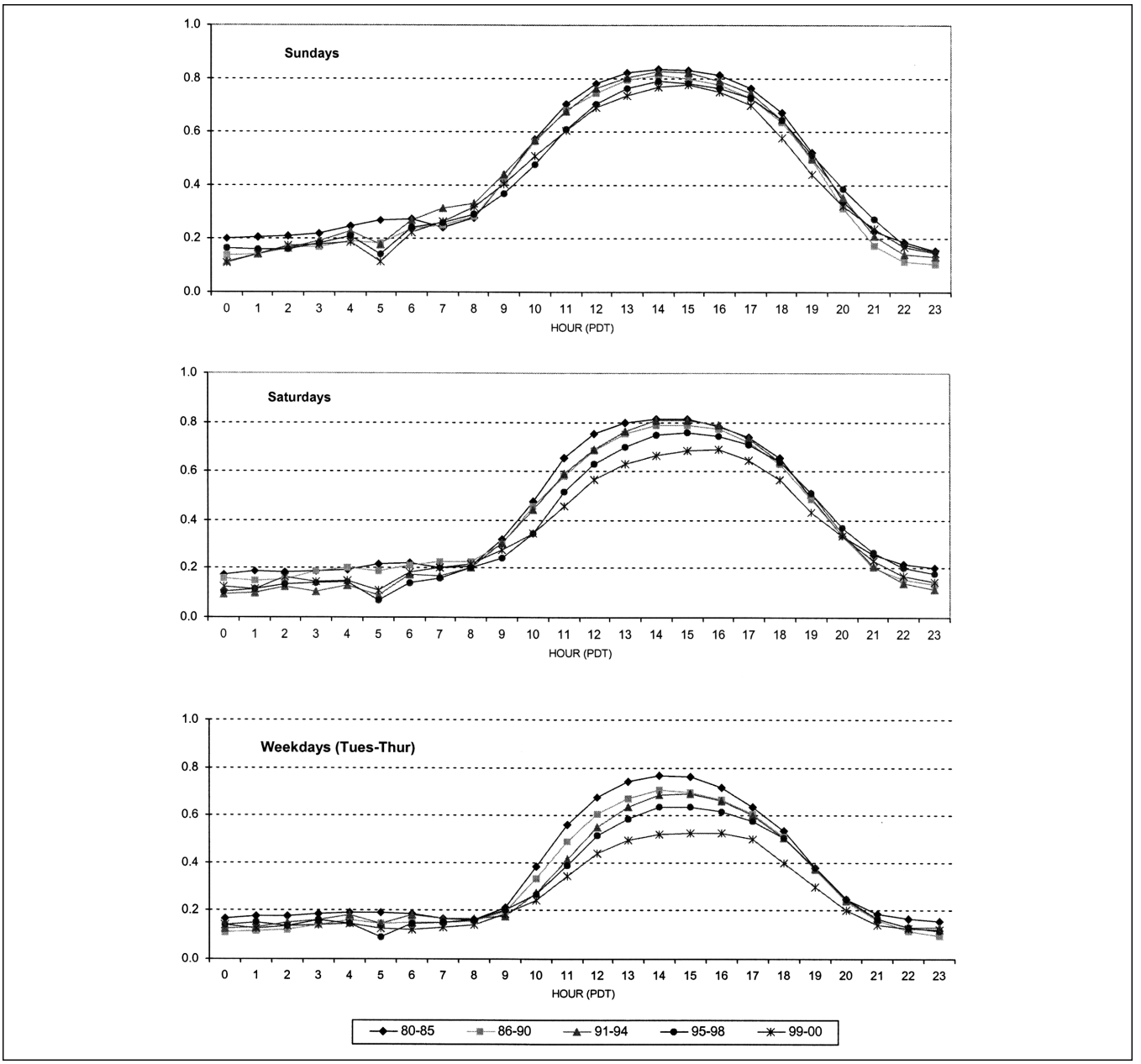

Figure 9. Diurnal variations in the ratios of O_3 to potential O_3 (O_3 + NO_2) on Sundays, Saturdays, and weekdays at Azusa for 1980–1985, 1986–1990, 1991–1994, 1995–1998, and 1999–2000.

and weekdays. Predicted PAN, HCHO, aldehydes, and organic nitrates are reduced by reductions in VOC mixing ratios, but their mixing ratios are not strongly affected by the NO_x at current mixing ratios. A weekend effect is not expected for these species.

CONCLUSIONS

The causes of the weekend O_3 effect are weekend/weekday differences in emissions,[18,19] the complex nonlinear photochemistry of O_3 in which the rate of O_3 formation is a complicated function of the mixture of VOC and NO_x, and the timing of the onset of formation. The O_3 isopleth diagram (see Figure 10) illustrates the dependence of O_3 production on the initial amounts of VOC and NO_x. The O_3 ridge in the isopleth diagrams corresponds to the maximum O_3 mixing ratio that can be achieved at a given combination of VOC and NO_x. The OH radical chain length reaches a maximum at VOC/NO_x ratios about the ridgeline in the O_3 isopleth. The ridgeline corresponds to the VOC/NO_x ratio at which O_3 is most efficiently formed. Above the ridgeline, a reduction of NO_x lowers the rate at which OH and NO_2 are removed by formation of HNO_3 and leads to an increase in maximum O_3. This region is commonly described as VOC-limited (i.e., lowering VOC most effectively reduces O_3). NO_x disbenefit refers to a situation when NO_x reduction leads to an

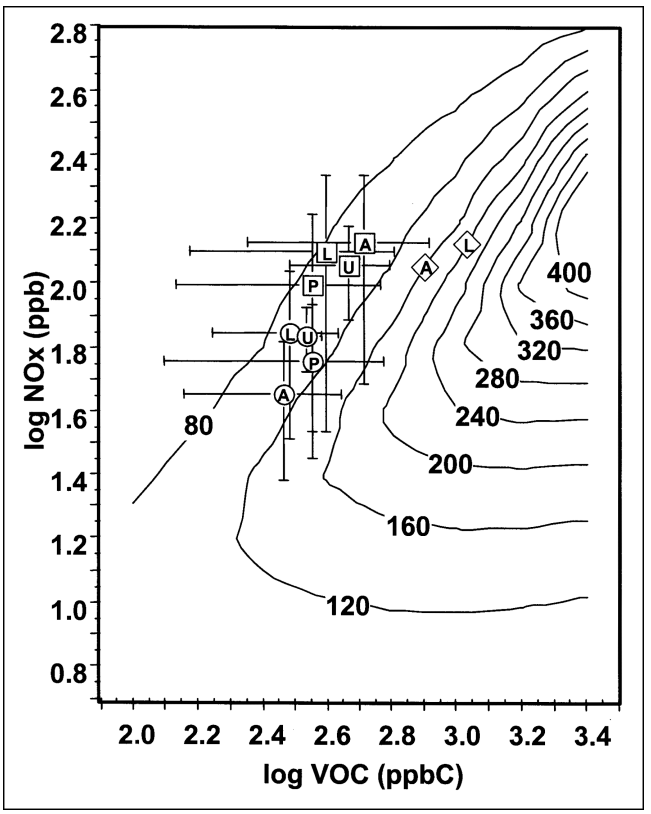

Figure 10. Ozone isopleth plot. Mixing ratios for NO_x and NMHC during the summers of 1999 and 2000 with error bars representing 1 standard deviation from the mean with the labels (A) representing Azusa, (L) representing Los Angeles–North Main, (P) representing Pico, and (U) representing Upland. The squares represent Wednesday and the circles represent Sunday. The error bars are not symmetrical because of the logarithmic scale. The two white dots labeled (L) and (A) represent the mean conditions for Los Angeles–North Main and Azusa during 1987, respectively. The simulation conditions are given by Stockwell et al.[28]

increase in O_3. This disbenefit occurs only in the VOC-limited region. Below the ridgeline at low NO_x mixing ratios, there is a large region where lowering NO_x most effectively reduces O_3 and large reductions in VOC have practically no effect on maximum O_3. This region is described as NO_x-limited. A decrease in NO_x above the ridgeline increases O_3; a decrease in NO_x below the ridgeline decreases O_3. Reduction in both NO_x and VOC simultaneously is most effective along the ridgeline.

The nonlinearity of O_3 photochemistry imposes two necessary conditions for a reduction in NO_x on the weekend to result in higher production of O_3. The first condition is that O_3 formation be VOC-limited. Removing NO_x from a VOC-limited system reduces the removal of OH radical by reaction with NO_2 to form HNO_3, thereby increasing the efficiency and rate of O_3 formation. The weekend effect is greatest where the O_3 formation is more VOC-limited during the weekday and less VOC-limited during the weekends. The evolution in the magnitude and spatial extend of the O_3 effect over the past 20 years is consistent with greater reduction in VOC mixing ratios relative to NO_x and higher weekend VOC/NO_x ratios relative to weekday ratios.

The second condition is that the peak O_3 level on weekdays does not reach its maximum potential so that time is a limiting factor in O_3 production. Analysis of the ambient air quality data shows that this is the case in the SoCAB. Consequently, peak O_3 is determined by the duration of O_3 accumulation, which is a function of the extent of O_3 inhibition caused by NO emission, and the rate of O_3 accumulation, which depends on the VOC/NO_x ratio. Although the amount of O_3 that can potentially form on weekdays is greater, peak O_3 levels are higher on weekends because the duration of O_3 accumulation is longer and the rate of O_3 formation is greater on weekends.

NO typically exists in excess of O_3 in the urban center overnight and suppresses the mixing ratio of O_3 to zero or near zero in the surface layer. Fresh NO emissions during the morning commute prolong the inhibition of O_3 accumulation after sunrise. During this inhibition period, the photolysis of carbonyl compounds and smaller contributions of HONO and other radical precursors are the primary source of OH radicals until a sufficient amount of NO has been converted to NO_2. Ozone carried over aloft from the previous day can mix down in the morning and contribute O_3 and radicals to the developing surface O_3 chemistry. The length of the morning O_3 inhibition period is largely determined by the mixing ratio of NO and NO_2/NO_x ratios. Lower NO_x emissions on weekends decrease NO titration of the O_3 newly formed at the surface and the O_3 transported from aloft. Lower NO mixing ratios and higher NO_2/NO_x ratios during weekend mornings decrease the removal of O_3 by titration with NO, thereby allowing O_3 to accumulate approximately an hour earlier on weekends compared with weekdays. This advance in timing of O_3 accumulation on weekends is similar throughout the basin, and it has remained relatively constant from 1981 to 1999. Ozone formation is also inhibited by the reaction of OH with NO_2; the magnitudes of the O_3 concentration sensitivity coefficients for the OH + NO_2 and the NO + O_3 reactions are large and within a similar range, and their signs are negative.[24] The relatively lower NO_2 concentrations on weekends result in less OH radical loss and more O_3 formation.

Under the typical summer transport pattern in the basin, less time is available near the coast for O_3 to accumulate before ventilation occurs. The O_3 accumulation period is approximately 3 hr near the coast and increases to approximately 6 hr in the eastern part of the basin. During transport to the east side of the basin, VOC/NO_x ratios increase because NO_x is removed more rapidly than VOC, which results in increased rates of O_3 formation.

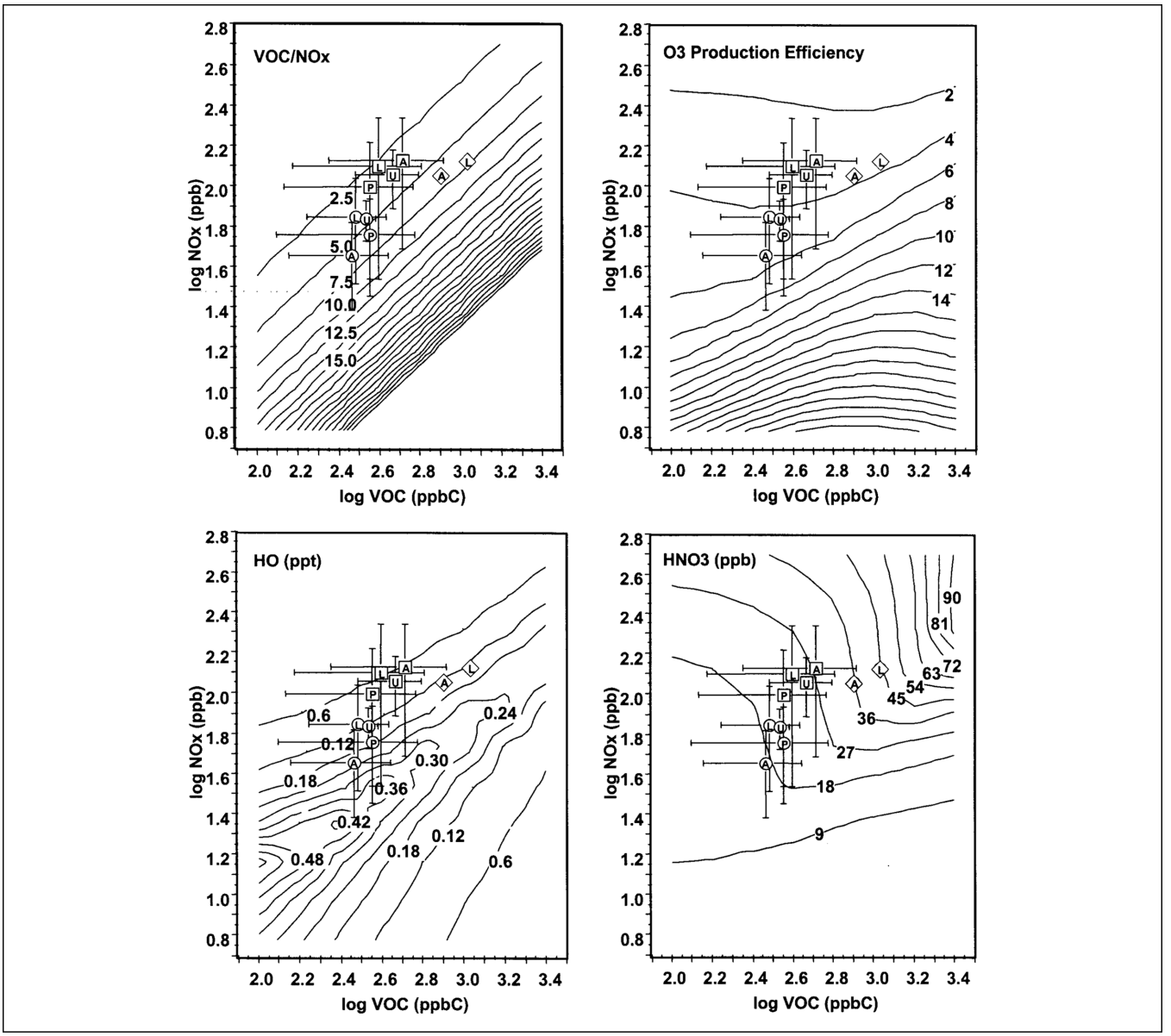

Figure 11. Plots of VOC/NO_x ratio, O_3 production efficiency ($\Delta[O_3]/(\Delta[HNO_3] + \Delta$[organic nitrates]), OH, and HNO_3. Also plotted are mixing ratios for NO_x and NMHC during the summers of 1999 and 2000 with error bars representing 1 standard deviation from the mean with the labels (A) representing Azusa, (L) representing Los Angeles–North Main, (P) representing Pico Rivera, and (U) representing Upland. The squares represent Wednesday and the circles represent Sunday. The error bars are not symmetrical because of the logarithmic scale. The two diamonds labeled (L) and (A) represent the mean conditions for Los Angeles–North Main and Azusa during 1987, respectively.

Addition of dispersed NO_x sources in downwind suburban areas may extend the area of VOC limitation further downwind, and increases in the rate of O_3 formation caused by increasing VOC/NO_x ratios during transport may be offset by dilution in the absence of fresh emissions. Near the coastline, the day-of-week differences in the VOC/NO_x ratios have greater influence on weekday versus weekend differences in peak O_3 mixing ratios because of the shorter time for O_3 accumulation. In the eastern basin, day-of-week differences in the initial VOC/NO_x ratios and the resulting differences in O_3 formation rates have less effect on weekday versus weekend peak O_3 mixing ratios because of the longer O_3 accumulation times, which allow O_3 formation to proceed closer to completion. Thus, the weekend O_3 effect reaches maximum intensity in the central basin because of the competing factors of O_3 accumulation time and rate of O_3 formation. Day-of-week differences in these air quality parameters arise from changes in the spatial and temporal distribution of VOC and NO_x emissions caused by changes in activity patterns between weekdays and weekends.[18,19]

VOC/NO_x ratios affect the rate and efficiency of O_3 production. Photochemical reactivity of the VOC mixture

also affects the rate of O_3 formation, but reactivity of the VOC is lower on weekends and does not account for the higher O_3 formation rates on weekends.[34] Analysis shows that the weekend effect is greatest where the O_3 formation is more VOC-limited during weekdays and less VOC-limited during weekends. VOC/NO_x ratios have decreased by half over the past 15 years.[32] The relative increase in the VOC/NO_x ratio on weekends caused by a greater decrease in NO emissions than VOC emissions is consistent with the observed evolution of the weekend effect in the SoCAB over the past two decades and current diurnal and day-of-week variations in O_3 relative to VOC, NO, and NO_2 mixing ratios and NO_2/NO_x and VOC/NO_x ratios.

This transition parallels the downward trend in peak O_3 levels, a shift in the location of peak O_3 levels from the central part of the basin (e.g., Pasadena to Azusa) to the eastern part of the basin (e.g., Lake Gregory), and an increase in the magnitude and spatial extent of the weekend O_3 effect in the SoCAB. The rate of O_3 accumulation from the end of O_3 inhibition to the time of O_3 maximum on weekdays decreased by half over the same time period, with the largest reductions occurring in the central basin on a relative and absolute basis.[14] Rates of O_3 accumulation were consistently lower on weekends than weekdays through most of the 1980s but became consistently higher on weekends during the 1990s (see Figure 7). Central and eastern parts of the basin showed either no change or slightly lower O_3 mixing ratios on weekends (i.e., no weekend effect) in the 1980s because the shorter O_3 inhibition periods were offset by the lower rates of O_3 accumulation. A transition to higher weekend O_3 accumulation rates in the 1990s, coupled with a shorter inhibition period, resulted in higher weekend O_3 mixing ratios during the 1990s and a strengthening of the weekend O_3 effect within the basin.

Although projecting emission inventories into the future is quite uncertain, application of the day-of-week patterns developed in this study to published projected emissions permits speculation on future-year emissions ratios and future-year O_3 mixing ratios by day-of-week. Chinkin et al.[20,23] applied the day-of-week patterns developed in this study to emission forecasts by CARB for 2010 and obtained predicted O_3 precursor emissions on weekdays in 2010 that are comparable to those on weekends in 2000. Precise predictions of O_3 mixing ratios from emissions changes are not possible without the use of comprehensive photochemical models. Because of high levels of NO_x emissions in the SoCAB, O_3 production is hydrocarbon-limited even when NO_x emissions decrease on the weekends. Under these hydrocarbon-limited conditions, O_3 production efficiency is a function of the VOC/NO_x ratio, and, under the same meteorological conditions, O_3 mixing ratios would be expected to increase as the VOC/NO_x ratio increases. Thus, higher VOC/NO_x ratios on weekends result in higher O_3 mixing ratios, even though the total mass of emissions decreases. The forecast of higher VOC/NO_x ratios in 2010 suggests that weekday and weekend O_3 mixing ratios could be even higher in future years unless the levels of NO_x control are large enough to change the atmosphere in the SoCAB to a NO_x-limited regime.

Based on these results, we conclude that the weekend/weekday O_3 effect is caused by reduced NO_x emissions on weekends. Weekend O_3 levels would be even higher were it not for significant decreases in weekend VOC emissions.[19,20] The weekend NO_x reduction hypothesis is most consistent with the observed spatial and temporal variations in available ambient air quality and emission activity data and long-term trends in the magnitude and spatial extent of the weekend O_3 effect. During the summers of 1999 and 2000, the NMHC/NO_x ratios at the four SoCAB PAMS sites were 4–8 from sunrise to the time of peak O_3 so that O_3 formation is VOC-limited throughout this period. Blanchard and Tanenbaum[21,35] concluded (based on their estimates of the extent of reaction) that most monitoring sites in the SoCAB are VOC-limited. Application of day-of-week patterns to future-year published emission inventories suggests that because of predicted increases of the VOC/NO_x ratio in emissions caused by greater NO_x control relative to VOC in the future, O_3 concentrations may not decline despite predicted decreases in emissions.

This study shows that there are substantial changes in air quality resulting from variations in emissions by both day of week and location within the SoCAB. The impact of the spatial and temporal variations in emissions on O_3 mixing ratios should be better quantified. The analysis of ambient observations to determine O_3 and its precursor trends and relationships (as done in this paper), along with the development of accurate, temporally and spatially resolved day-of-week emission inventories (including separate inventories for Saturdays and Sundays) can provide insights as to how photochemical air quality simulation models can be used to quantify weekend O_3 effects both now and for future control scenarios. This is especially critical for air quality management strategies, because in many urban U.S. locations, weekend O_3 is as high as or higher than on weekdays.

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