

The O₃ “Weekend Effect” and NO_x Control Strategies

Scientific and Public Health Findings and Their Regulatory Implications

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In 1999, the California Air Resources Board (CARB) formed the Weekend Effect Working Group to coordinate research activities with local, state, and federal agencies, academia, industry groups, and the public to investigate the possible causes of the weekend ozone effect in California. This article presents CARB's findings.

Ground-level ozone (O₃) is associated with increased hospital admissions for acute respiratory diseases, aggravation of asthma, and decreased lung function.¹ At one time, California had the dubious distinction of having the worst air quality in the world, with hourly average O₃ levels in Los Angeles peaking at more than 0.5 parts per million (ppm) and frequent “smog alerts.” In the early 1970s, the California Air Resources Board (CARB) initiated emissions control strategies that provided for the concurrent and continuing reductions of oxides of nitrogen (NO_x) and volatile organic compounds (VOCs) from mobile sources and, in conjunction with the local air districts, stationary and area sources.² CARB based this policy of controlling both O₃ precursors on the dual need to reduce O₃ in the urban source areas (where O₃ formation was thought to be limited by the available VOC) and the suburban downwind areas (where O₃ formation was thought to be limited by the available NO_x) where peak O₃ levels occurred.³ Over the past 25 years, this emissions control strategy reduced peak O₃ levels by more than 60% and eliminated smog alerts in Los Angeles (see Figure 1), despite a 50% increase in population and nearly a doubling of vehicle miles traveled.² While the decline in O₃ levels occurred for both weekdays (WD) and weekends (WE) in some California air basins, especially the Los Angeles and San Francisco Bay areas, O₃ levels on WE did not decrease as rapidly as they did on WD. In these urbanized areas, O₃ levels on Saturdays and Sundays are higher, on average, than those recorded during the week,⁴⁻⁶ a phenomenon commonly known as the “weekend effect.”

Because emissions and ambient levels of NO_x decline more than VOCs during the WD-to-WE transition, some automotive industry representatives presented the weekend effect as a rationale for not requiring sport utility vehicles to meet the

same emissions standards for NO_x as passenger cars in testimony at CARB hearings in 1998.⁷ CARB adopted the regulation based on the historical effectiveness of concurrent NO_x and VOC controls and research results showing that the areas in Los Angeles with the greatest improvement in peak O₃ levels generally had the greatest reduction in NO_x.⁸ In addition, CARB directed its staff to further investigate the weekend effect and its regulatory implications.⁹

In 1999, CARB formed the Weekend Effect Working Group to coordinate research activities with local, state, and federal agencies, academia, industry groups, and the public. For its part, CARB conducted data analyses¹⁰ and funded emissions research studies.¹¹ As part of the Working Group, the Coordinating Research Council (CRC)—a nonprofit research organization primarily supported by the automotive and petroleum industries—and the U.S. Department of Energy’s National Renewable Energy Laboratory (NREL) jointly sponsored research studies.¹²⁻¹⁷ The University of California at Berkeley also conducted research under U.S. Environmental Protection Agency (EPA) sponsorship.^{18,19} Several research studies are still ongoing, but most projects are complete, and many are reported in the July 2003 issue of the *Journal of the Air & Waste Management Association*.²⁰⁻²⁸ While the coordinated effort did not reach agreement on the exact causes and control implications of the weekend ozone effect, the Working Group created hypotheses to focus and refine research efforts, analyzed air quality data for Los Angeles and other areas, and began development of WE emissions inventories for air quality model applications. The focus of this article is to present CARB’s findings on the weekend effect in California. CARB staff recognize that there may be plausible alternative explanations for the causes of the weekend effect, as summarized by others.^{20,29} Furthermore, CARB thinks that ongoing research on WE emissions inventories and atmospheric chemistry will yield further insight into this complex phenomenon.

HYPOTHESES

CARB staff developed and presented six hypotheses for testing by researchers with the Weekend Effect Working Group:

1. **NO_x reduction:** Nonlinear photochemistry causes O₃ to increase on WE compared to WD, as NO_x decreases more than VOC.
2. **NO_x timing:** The shift of NO_x emissions to later in the day and further downwind from WD to WE causes NO_x to form O₃ more efficiently on WE.
3. **Carryover aloft:** Emissions of O₃ and its precursors carry over to the next day in proportion to the previous day's emissions; carryover occurs above the surface layer and these pollutants mix with the next day's emissions, contributing proportionally more to surface O₃ on WE than on WD.
4. **Carryover at ground level:** Emissions from greater nighttime activities on Fridays and Saturdays carry over near the surface to supplement fresh emissions the next day and help generate higher O₃ concentrations on WE than on WD.
5. **Increased weekend emissions:** Greater emissions from recreational, home, and lawn and garden activities on WE generate higher levels of O₃ on WE than on WD.
6. **Reduced aerosols:** Aerosol emissions reductions in the early morning and midday on WE compared to WD allows more solar radiation to reach lower levels of atmosphere and to generate more O₃ on WE than WD.

In response to peer review comments on CARB's report,¹⁰ an additional hypothesis was developed.

7. **Surface O₃ quenching by NO:** Day-of-week differences in nitric oxide (NO) emissions cause day-of-week differences in the amount of O₃ quenched ($\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$) and, therefore, allow more O₃ to be measured at the surface on WE than on WD.

Researchers analyzed air quality data in Los Angeles and other areas and concluded that the available data do not support Hypotheses 4, 5, and 6 as significant causes of the weekend effect. Although Hypotheses 1, 2, 3, and 7 are plausible, CARB considers the air quality data and modeling tools available today to be inadequate for conclusively determining their respective contributions to the weekend effect. The inability to resolve the cause(s) of the weekend effect is important because Hypotheses 2, 3, and 7 support the concurrent NO_x and VOC control policy, while Hypothesis 1 implies that NO_x control increases O₃.

CARB'S FINDINGS

The CARB report, *The Ozone Weekend Effect in California*,¹⁰ met the requirements of Section 39930 of the California Health and Safety Code for peer review of scientific studies that potentially serve as the basis for environmental regulations. Five air quality experts, under the auspices of the Office of the President of the University of California, reviewed the CARB study and provided detailed comments and suggestions

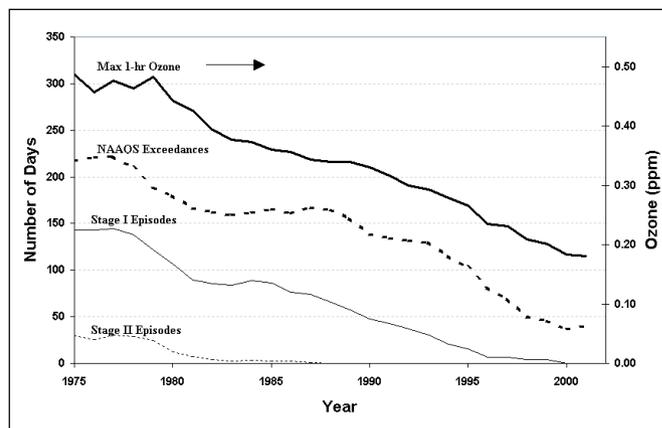


Figure 1. Changes in O₃ air quality in the Los Angeles area since 1975. Maximum 1-hr concentrations have declined 75%, exceedances of NAAQS 1-hr standard have been cut in half, and smog alerts (Stage I episode 0.20 ppm and Stage II episode 0.35 ppm) have been eliminated. Since 1975, population has increased by 50% and vehicle miles traveled (VMT) have increased by 93%. Data presented as centered 3-yr moving means.

to staff. Copies of the reports under CRC and NREL sponsorship were also provided to peer reviewers as background material for consideration during their review. Based on the weekend effect analysis, which began in 1999 and is ongoing, and the peer review comments, CARB staff came to the following conclusions:

- The weekend effect is not, as some have suggested, a “real-world” test of the O₃ air quality impact of California's NO_x control program. The major changes from WD to WE do not replicate the overall changes and impacts associated with a control program.
- The weekend effect in urban centers is larger than for those places and on those days that determine attainment of federal and state O₃ standards. In urban centers, the weekend effect may be 30%–50%. In relation to attainment of standards, however, the weekend effect is generally limited to 0%–15%.
- Ozone quenching near the surface by fresh NO ($\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$) emitted throughout the day appears to be a significant factor in the weekend effect. In the large volume of air above the surface, O₃ quenching decreases and O₃ levels are greater than at the surface. The air quality measurements routinely made at the surface do not adequately represent the conditions aloft.
- On WE, levels of NO₂, total oxidant (NO₂ + O₃), nitric acid (HNO₃), fine particulate matter (PM_{2.5}), particle nitrates, and elemental carbon tend to be similar or lower compared to WD, consistent with lower photochemical formation due to reduced NO_x and VOC emissions, and lower emissions of diesel PM. The lower levels imply significant health benefits.

- Additional NO_x reductions may be needed to help WE O₃ decline faster because the slower rate of decline in O₃ on WE than on WD occurred during a period when VOC were reduced faster (50% or more) compared to NO_x.
- Current modeling assessments of the weekend effect are not definitive because they are missing critical physical and chemical processes that would tend to reduce their sensitivity to NO_x species and potentially bias them against NO_x control.

These findings are discussed in more detail below.

Weekend Effect Not a Real-World Test of California's NO_x Program

If the weekend effect is used to represent the effect of a control strategy, the changes in emissions must be similar in all important respects. However, changes in emissions from WD to WE include differences in the composition, timing, and location of emissions sources. Control strategies often have little impact on these aspects of emissions sources. Given the demonstrable differences, the weekend effect is not a reliable basis for designing an O₃ control strategy to protect public health.

First, emissions changes associated with the weekend effect in the Los Angeles area include greater reductions in NO_x (perhaps twice as much as VOC due to reduced activity of heavy-duty diesel trucks),^{10,19,24} while historical emissions trends show that VOC reductions were twice as great as NO_x reductions.² Projections of emissions from the present to 2010 show approximately equal NO_x and VOC reductions.² This difference between the relative reductions of the O₃ precursors on WE and over the years would likely influence the photochemistry of the air mixture by changing the VOC/NO_x ratio and causing a different photochemical regime for O₃ formation.

Second, temporal changes on WE differ from those associated with most control measures. Control measures reduce emissions over the time those emissions sources are active. Temporal changes in emissions associated with the transition from WD to WE include (1) the transition from bi-modal (morning and evening) traffic peaks to a uni-modal (midday) peak, and (2) more evening activities on Fridays and Saturdays (see Figure 2).^{10,19,24} Hence, much of the emissions are put into a different physical and chemical environment on WE than on WD.

Third, the spatial distribution of emissions is different on WD than WE. Traffic data indicate a shift in activity from the urban business zones toward residential and recreational areas.^{10,19} Furthermore, the activity of heavy-duty vehicles is likely to decline more in the central basin than near the entry points to the basin.^{10,24} Emissions control measures tend to reduce emissions where they occur rather than redistributing them.

Fourth, emissions and meteorology on any given day influence the atmospheric loading of O₃, O₃ precursors, and reaction

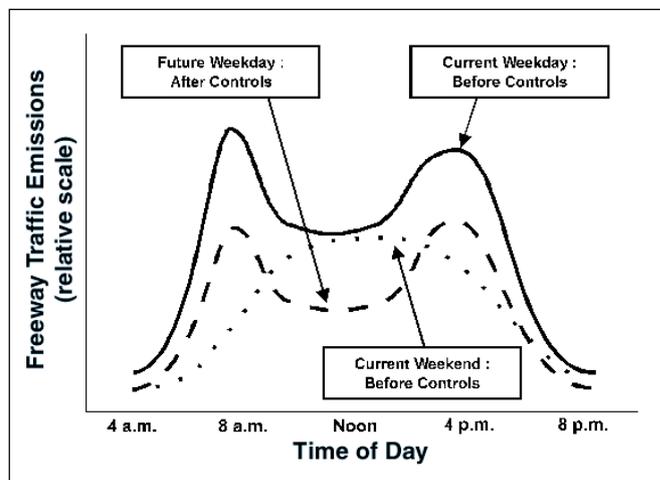


Figure 2. Comparison of the diurnal distributions of weekday freeway emissions, before and after a hypothetical light-duty motor vehicle control measure, with weekend freeway emissions.

products that carry over to the following day. In other words, air quality “today” depends, in part, on pollutants that persist from “yesterday.” Daily emissions of O₃ precursors, particularly NO_x, decrease from Friday to Saturday to Sunday and increase again on Monday. Because the potential for carryover is proportional to daily emissions, the fresh emissions on Saturday and Sunday occur in an environment influenced by the higher emissions on the preceding day. Similarly, the emissions on Monday occur in a context established by lower emissions on Sunday. This may explain why average O₃ levels on Mondays have typically been the lowest of all WD, although there may have been a shift to Wednesdays in recent years (see Table 1). Future NO_x reductions associated with a control program would affect emissions on all days continuously rather than intermittently (i.e., every seventh day). In Los Angeles, this carryover occurs in the large reservoir of O₃ and O₃ precursors extending hundreds of meters above the surface layer, and is not captured by routine surface-based measurements.³⁰

For these reasons, the weekend ozone effect has limited and uncertain application toward predicting the impacts of future emissions controls.

Weekend Effect is Smaller for Peak O₃ Areas

The weekend effect may be best characterized by its magnitude in those areas and on those days with the most unhealthy O₃ levels, namely, those days that determine whether regions attain the federal and state O₃ standards (i.e., the so-called “design sites” on “design days”). In such cases, the WE O₃ increase is only one-fourth to one-half of its typical magnitude in urban centers¹⁰ (see Figure 3). The magnitude of the weekend effect is sometimes presented in terms that reflect the most extreme experience at one or two central urban locations that measure relatively low O₃ levels. The dramatic differences,

Table 1. Frequency and percent of site-years with which different days of the week recorded the lowest mean of daily maximum O₃ measurements during the May–October O₃ season in the Los Angeles area.

Area	Period	Summary for Site/Years ^a	Day of Week							
			Sun	Mon	Tue	Wed	Thu	Fri	Sat	
Coastal:										
15 sites	1981–1985	Average (ppm)	0.113	0.102	0.106	0.109	0.109	0.111	0.117	
		% lowest	1	51	8	7	25	6	1	
	1986–1990	Average (ppm)	0.103	0.092	0.096	0.095	0.094	0.095	0.102	
		% lowest	3	33	13	19	23	9	0	
	1991–1995	Average (ppm)	0.095	0.076	0.076	0.077	0.078	0.080	0.092	
		% lowest	0	43	11	13	15	19	0	
	1996–2000	Average (ppm)	0.076	0.059	0.057	0.058	0.056	0.060	0.072	
		% lowest	0	13	24	30	18	15	0	
	Inland:									
	5 sites	1981–1985	Average (ppm)	0.130	0.130	0.135	0.140	0.138	0.141	0.139
			% lowest	33	38	0	4	17	4	4
		1986–1990	Average (ppm)	0.123	0.124	0.130	0.130	0.132	0.131	0.128
% lowest			36	24	8	12	12	0	8	
1991–1995		Average (ppm)	0.119	0.106	0.106	0.107	0.108	0.111	0.124	
		% lowest	4	48	8	12	16	12	0	
1996–2000		Average (ppm)	0.096	0.080	0.079	0.081	0.079	0.079	0.093	
		% lowest	0	20	20	28	16	16	0	

^aThe maximum number of "site-years" possible is the product of the number of sites and the number of years in the period. For each site in each year, the day of week with the lowest average for daily maximum O₃ was identified and tallied. The frequency for each day of the week is expressed as a percent of the total number of site-years available.

such as 40% or even 50%, that can occur are misleading. Based on daily maximum O₃ levels from 1998 through 2000, WE O₃ increases in downwind areas, where the highest O₃ levels tend to occur, were approximately 20% in the Los Angeles and San Francisco Bay areas and 5% in California's Central Valley. On days with high O₃-forming potential in the Los Angeles area, the weekend effect was even smaller (i.e., O₃ levels were 10%–15% higher on WE than on WD).¹⁰

Local O₃ Quenching May Explain Weekend Effect

Nitric oxide destroys or "quenches" O₃ to produce NO₂ and O₂. Because NO_x is emitted primarily as NO (90%–95%), this reaction destroys O₃ near NO_x sources and immediately forms NO₂. Subsequent photolysis of NO₂ is the only known source of the oxygen atom necessary for creating O₃ in the lower atmosphere.³ O₃ quenching is particularly active near the surface, due to the proximity of mobile sources responsible for approximately 90% of all regional NO_x emissions. Quenching, however, is a temporary effect because the NO₂ that is produced will participate in additional photochemical reactions above the surface. These reactions can form various products, including O₃, peroxyacetylnitrate (PAN), HNO₃, and particle nitrates, all of which have adverse health effects.

On WD, emissions of NO are probably greater throughout

the day compared to WE. An analysis of hourly ambient NO_x levels in the Los Angeles area showed that typical midday levels of NO are at least 20%–30% lower on Saturdays and 35%–55% lower on Sundays compared to WD levels.¹⁰ Thus, NO emissions destroy much more ground-level O₃ on WD than on WE.

An analysis of data from ozonesondes (i.e., weather balloons that measure oxidant levels, primarily O₃) during the 1997 Southern California Ozone Study indicates that surface O₃ quenching at 2:00 p.m. PDT is greater on WD than on WE.¹⁰ At Riverside, WD O₃ levels at the surface averaged 20% lower than the O₃ levels 100 m above ground. On WE, however, the average difference was only 9%. These results are important because Riverside is in the downwind region of Los Angeles, where the highest O₃ levels are frequently recorded. The limited number of ozonesondes prevents broad conclusions from these data, but the direction is consistent with the following broad-based analysis.

Quenching of O₃ by NO emissions near the surface seems to be a major factor in the weekend effect because total oxidant (NO₂ + O₃) on WE is similar to total oxidant on WD. An analysis of total oxidant at 22 locations monitoring both pollutants in the Los Angeles area during the O₃ seasons (May–October) for 1998 through 2000 found the largest weekend effect for total oxidant was 9% and the basinwide average was

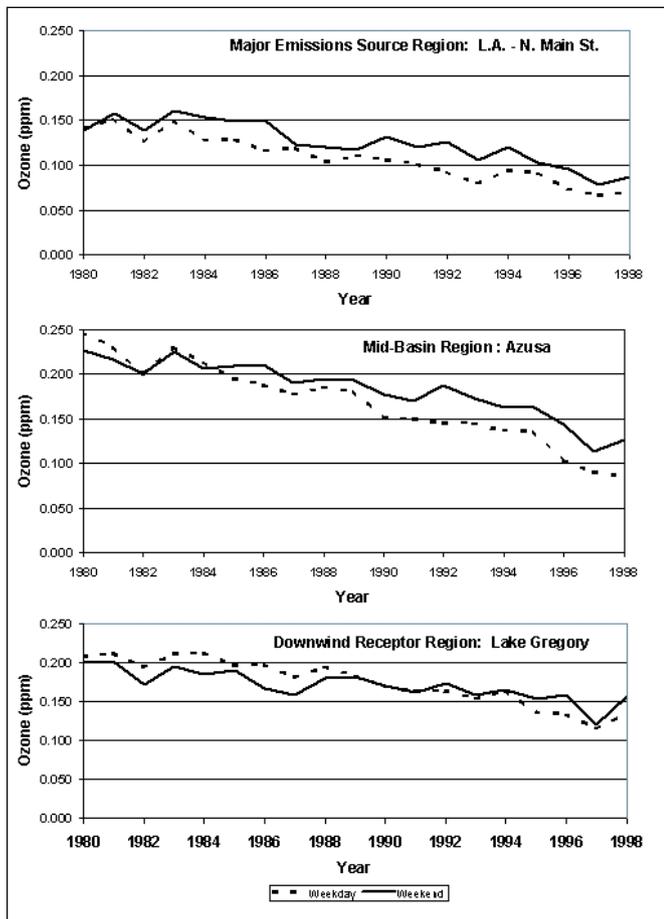


Figure 3. O₃ trends from 1980 through 1998 for weekdays and weekends at three sites across the Los Angeles area. O₃ is the mean of the 2nd–11th highest daily maximum levels each year.

5%.¹⁰ These are much smaller than the values in the same areas for the weekend effect, for which the largest increase was 43% and the average increase was 20%.

Day-of-week patterns in other pollutants are consistent with the theory that higher O₃ on WE does not necessarily imply increased photochemical activity (see Figure 4). Levels of HNO₃, PM₁₀, PM_{2.5}, particle nitrates, and elemental carbon tend to be similar or lower compared to WD, again consistent with lower photochemical activity (relative to the O₃ increase) due to reduced NO_x and VOC emissions and lower emissions of diesel PM.^{10,14,23,28}

Potential Need for More NO_x Control to Reduce Weekend O₃

In California during the past 20 years, VOC emissions decreased by almost twice as much as NO_x emissions (60% and 37%, respectively).² During this period, O₃ decreased faster on WD than on WE, and the highest O₃ levels are now experienced on WE. Since an emphasis on VOC reductions has reduced WE O₃ at a slower rate than WD, one must consider whether greater NO_x reductions might accelerate O₃ improvements on WE.

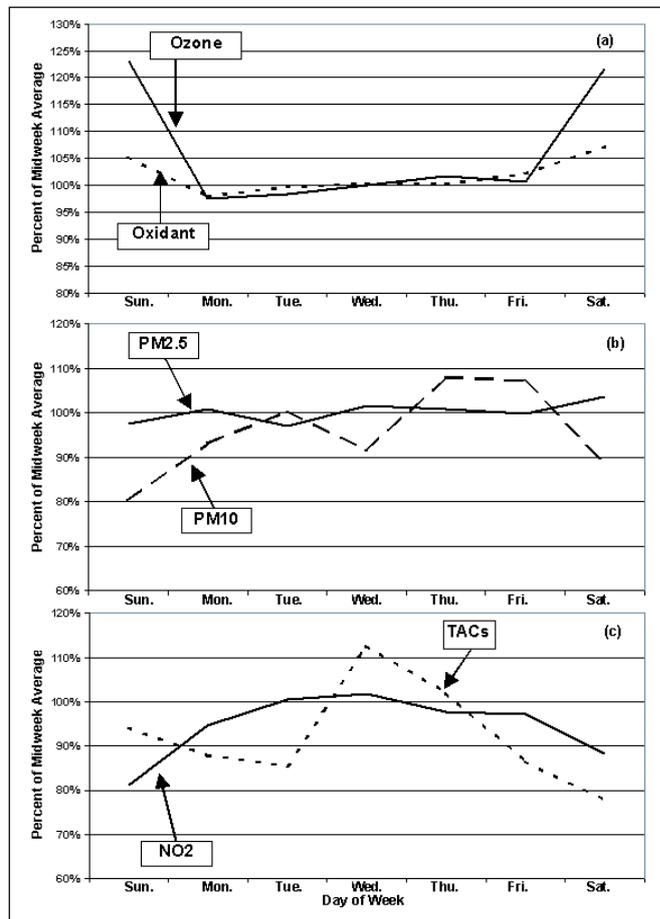


Figure 4. Day-of-week profiles for O₃, total oxidant (O₃+NO₂), PM, NO₂, and cancer risk (potency-weighted) for six toxic air contaminants in the Los Angeles area. (a) O₃ and total oxidant data are average values for 22 sites in the Los Angeles area (daily maximum values were used for O₃, the daily maximum between 10:00 a.m. and 6:00 p.m. was used for total oxidant); the O₃ and oxidant values for each site are the average of the daily values during the May–October O₃ seasons of 1996–1998 by day of the week. (b) PM data are average values for 17 sites in the Los Angeles area; the value for each site is the average of all values during 1996–1998 by day of the week; the cause of the Wednesday dip in the PM₁₀ concentration is not known at this time. (c) NO₂ data are average values for 22 sites in the Los Angeles area; the NO₂ values for each site are annual averages of daily maximum 1-hr concentrations; the TAC values are total cancer risk estimates for six TACs (benzene, 1,3-butadiene, formaldehyde, acetaldehyde, perchloroethylene, and carbon tetrachloride) using average values for 1996–1998.

An emphasis on VOC emissions reductions has led to an expanded weekend effect. This pattern was also found by an analysis of the weekend effect in the Los Angeles, San Francisco Bay, and Sacramento areas before and after the introduction of California's Phase 2 reformulated gasoline (CaRFG2) in 1996.⁶ Emissions inventories indicate that CaRFG2 reduced total VOC emissions 50% more than it reduced NO_x emissions.³¹ In each of the three air basins, O₃ was reduced on all days of the week, however, immediately

following the introduction of CaRFG2, the magnitude of the weekend effect increased significantly, and Sunday emerged as the day-of-week with the highest O₃ levels.

Evidence of the regional O₃ levels being positively associated with NO_x levels rather than negatively associated as in the weekend effect is presented in Figure 5. In particular, note the flat trend in the 1980s and the declining trend in the 1990s. These NO_x trends correspond very well, in timing, direction, and magnitude, with the O₃ trends presented in Figure 1. The correspondence of these trends suggests that O₃ levels for the Los Angeles area are positively associated with NO_x controls and that the weekend effect is a complex perturbation that occurs on a weekly cycle. Unfortunately, quality-assured VOC data are not available for the same period.

Air Quality Models Limited in Ability to Evaluate Causes of Weekend Effect

While air quality models in use today are quite advanced, incomplete data and current limitations for characterizing several important physical, chemical, and meteorological processes inhibit their ability to realistically evaluate the weekend effect. For example, data are limited regarding air quality and meteorological conditions aloft; modeling costs force the use of vertical layers often larger than homogeneous layers observed; and potentially significant NO_x reactions are missing (see Table 2). For these and other reasons (e.g., emissions inventory uncertainties and uncertainties in chemistry under low-NO_x conditions), models have traditionally had a difficult time properly recreating precursor and O₃ levels at the surface and especially aloft.

In the past, the formation of HNO₃ from NO₂ in the atmosphere was considered to provide a sink for NO_x because of the efficient deposition of HNO₃ at the earth's surface. However, recent experimental studies have shown that HNO₃ on silica surfaces reacts with NO to generate nitrous acid (HONO) and NO₂.³²⁻³⁴ While the detailed mechanism and kinetics remain to be fully elucidated, such "renoxification" of HNO₃ back into photochemically active forms that can then regenerate O₃ and other secondary air pollutants may have significant ramifications for air quality model predictions. The incorporation of a renoxification process into an air quality modeling application appears to resolve two long-standing discrepancies between model estimates and observations.³⁵ The first is the occurrence of two O₃ peaks often observed on high O₃ days at downwind locations in the Los Angeles area, such as Riverside and San Bernardino. Air quality models that do not include the renoxification reaction only estimate a single peak. The second improvement in model estimates with renoxification is much better agreement with the observed peak O₃ in the central Los Angeles area; historically, models underestimated O₃ in this region by a significant amount. While the improvement between model estimates and field

Table 2. Major physical and chemical processes missing from many current air quality models and the effect on peak modeled O₃ levels for the Los Angeles area.^{35,40,44,45}

Atmospheric Process	Peak Modeled O ₃ Change for Los Angeles Area
• Renoxification: HNO _{3(surface)} + NO _(g) → HONO, NO ₂ , others	0.02 ppm increase (20 µg/m ³) particulate nitrate increase
• Cl ⁻ from sea-salt aerosols	0.004 ppm increase (0.012 ppm coastal)
• NO ₂ + OH → HNO ₃ rate constant uncertainty	0.035 ppm uncertainty
• Radiative transfer model	0.02–0.10 ppm increase

observations is intriguing and suggestive of renoxification, it is clear that this is an area that warrants further experimental and theoretical work, as well as probing the implications for control strategy development.

Other heterogeneous chemistry that occurs on surfaces in the boundary layer may be very important. For example, the generation of HONO, which is the major source of hydroxyl (OH) radical at dawn (and even when averaged over 24 hr) involves reactions at the earth's surface. Thus, the highest HONO/NO_x ratios are observed immediately at the surface and decrease with altitude in the boundary layer.³⁶ While the mechanism is not yet well-established, it likely involves surface species, such as N₂O₄ and NO₂⁺, and molecular nitric acid on surfaces.³⁷ Despite the fact that HONO drives the chemistry at dawn through production of the OH radical, its generation at the earth's surface is not well-represented in current models.

These comments do not imply that the models are fundamentally flawed, but rather that the uncertainties in chemistry preclude an accurate representation of such heterogeneous processes in models at the present time. This is an important area for future research because heterogeneous chemistry of NO_x, and likely other species, occurs in the region closest to the earth's surface where many field measurements are made for model testing and where the influence of such surface reactions is likely to be maximized.

Many urban regions in California are located near the coast where significant levels of sea salt exist. A variety of experimental data show that chloride and bromide in sea salt react in air to generate chlorine- and bromine-based O₃ precursors³⁸ and, indeed, molecular chlorine (Cl₂) has been measured in a coastal area in the eastern United States.³⁹ Recent modeling studies for Los Angeles suggest that the generation of chlorine atoms from such species may lead to significant increases in model-estimated O₃, up to 12 ppb in some areas.⁴⁰ Although

bromine is a minor component of sea salt (i.e., molar ratio Br/Cl is approximately 1:650), there is some evidence supporting a contribution of bromine atoms to O₃ destruction at sunrise in a number of coastal locations such as in Japan.⁴¹ There is increasing evidence that halogen chemistry affects O₃ levels in coastal urban areas, but it has not been included in airshed modeling applications for control strategy development. There is a need for measurement of halogen atom precursors in such areas, and elucidation of the kinetics and mechanisms of their formation so these processes can be accurately included in the models.

Reaction with NO₂ to form HNO₃ is the major sink for the OH radical, the key species driving the oxidation of VOC in the O₃ formation process. There is disagreement about the best estimates for the rate of this reaction, with recommended rates differing approximately a factor of two for atmospheric conditions.^{42,43} Uncertainties in the rate of reaction have significant impacts on the issue of NO_x versus VOC limitation for O₃, HNO₃, and particulate nitrate formed in air quality model simulations.⁴⁴

In photochemical models, radiative transfer theory can be used to predict actinic fluxes and, therefore, photolysis rates throughout the modeling domain. However, there is considerable uncertainty in these calculated rates.⁴⁵ These uncertainties stem from inaccuracies in the models themselves, as well as uncertainties in the input data required by the models. Although these uncertainties can be theoretically approximated, it is still not known how well radiative transfer models predict actual actinic fluxes. This issue can be resolved by simultaneous measurements of the optical properties of the atmosphere (which serve as input to the radiative transfer model), surface albedo, and actinic flux. Without such data, the assignment of uncertainty limits to calculated photolysis rates remains problematic.

In addition, simulations of the weekend effect should evaluate the model's ability to produce realistic daytime and nighttime pollutant levels, especially the distribution of NO_x species, from the surface through the mixed layer of air. Emissions and meteorology each day determine the initial conditions throughout the domain for the following day. Such initial conditions may significantly influence the O₃ levels reached each day. Empirical data needed to evaluate such model performance are limited at this time.

PUBLIC HEALTH FINDINGS AND REGULATORY IMPLICATIONS

Unlike O₃, most pollutant levels do not increase on WE. Emissions and ambient levels of primary (i.e., emitted directly from the source) pollutants decline at almost all locations on WE. Other pollutants that are a mixture of direct emissions and secondary formation also tend to decline on WE. Formaldehyde and acetaldehyde are distinctly lower on Sundays and slightly lower on Saturdays and Wednesdays, although the

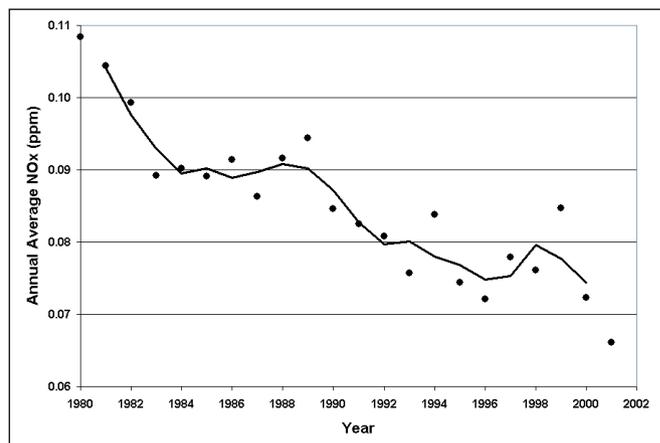


Figure 5. Trend in ambient NO_x in the Los Angeles area; composite of daily average NO_x measurements at 18 monitoring sites.

pattern is not strongly marked.²⁸ In addition, HNO₃ and particle nitrates tend to be similar or lower compared to WD, consistent with less photochemical activity due to reduced emissions of NO_x and VOC. Reduced levels of both primary and secondary pollutants, such as PM₁₀, PM_{2.5}, diesel PM, NO₂, and HNO₃, have important public health benefits. California recently adopted new standards for PM_{2.5} and altered its annual standard for PM₁₀.⁴⁶ The health benefits from attaining the new PM standards would be substantial: It is estimated that 6500 premature deaths, 340,000 asthma attacks, and 2.8 million lost work days could be avoided each year.⁴⁶ Estimates indicate that diesel PM is responsible for approximately 70% of the cancer risk from airborne toxics in California.⁴⁷ Recent controlled exposure studies suggest that NO₂ may enhance the response of allergic asthmatics to airborne allergens, even when exposure levels are quite close to the existing ambient air quality standard; California is currently reviewing its NO₂ standard.⁴⁸ In addition, NO₂, HNO₃, and PM have been associated with reduced lung function growth of 1% per year in children who live in polluted communities in southern California.⁴⁹

Recent findings from the Southern California Children's Health Study raise additional health concerns for children that play outdoors during the peak O₃ periods in the afternoon. When 10:00 a.m.–6:00 p.m. O₃ levels increased by 0.02 ppm, a fairly common day-to-day variation, school absences due to respiratory illnesses increased by 63%.⁵⁰ A three-fold increase in the development of asthma occurred in children who live in high O₃ communities and play three sports.⁵¹ Both EPA and CARB currently are reviewing their ambient air quality standards for O₃.

Although the weekend effect was first observed in the mid-1960s and early 1970s in Los Angeles,^{4,5} O₃ levels have declined continuously in response to the combined NO_x and VOC control policy (see Figure 1). The concern that the weekend effect is becoming more widespread, while VOC/NO_x ratios are decreasing, is partially mitigated by the observation that O₃ levels have decreased strongly on both WD and WE.

In a 1991 report, the National Research Council recommended that "to substantially reduce O₃ concentrations in many urban, suburban, and rural areas of the United States, the control of NO_x emissions will probably be necessary, in addition to, or instead of, the control of VOCs."⁵² The observation that the period with the greatest NO_x decline corresponds to the greatest improvement in peak O₃ levels in Los Angeles (see Figure 5), and the large health benefits from reductions in other NO_x-related pollutants, indicate that the strategy of concurrent control of NO_x and VOC is still valid.

CONCLUSIONS

The weekend effect is not a reliable indication that NO_x control is detrimental to attaining the ambient air quality standards for O₃. Emissions of O₃ precursors shift in relative proportions, time, and space from WD to WE in ways that do not mimic a NO_x control policy. Still, it is important to understand the weekend effect and its relationship to long-term trends that indicate California's O₃ control program has been effective on all days of the week, though more so on WD than on WE. The weekend effect plays a limited role when considering strategies for attaining federal and state O₃ standards because it is relatively small in the peak O₃ areas on days with the highest meteorological potential to form O₃. In these circumstances, which have the greatest regulatory and health effects significance, the weekend effect is a fraction of its magnitude in other areas or on days with lower meteorological potential to form O₃.

Differences in WD and WE quenching of O₃ by fresh NO emissions may explain a significant portion of the weekend effect. Several observations support this conclusion, including the similarity of total oxidant (NO₂ + O₃) levels on WD and WE. In addition, the absence of a weekend effect for PM_{2.5} and particle nitrates on WE is consistent with the theory that the O₃ quenching effect is a temporary, near-surface phenomenon that does not counter the need for continuing NO_x control. In carrying out their regulatory responsibilities, CARB and local air pollution control districts must consider the control of NO_x emissions from mobile and stationary sources in the overall context of NO_x reaction products and their impacts on humans and the environment.

With the evolution of the weekend effect to more areas of California, the highest O₃ concentrations now tend to occur on WE. Thus, the focus of O₃ control policies must now begin shifting from the traditional analysis and modeling of WD to WE. Research efforts need to acquire the fundamental information and data necessary to address the plausible causes of the weekend effect. For example, studies of atmospheric conditions and processes hundreds of meters above the surface are needed because routine surface measurements are overwhelmed by fresh emissions and do not necessarily represent conditions in the larger mass of air above where O₃ concentrations are typically higher.

Concurrent research must be undertaken to improve air quality models by developing more accurate day-of-week emissions

inventories of pertinent species. Including pertinent physical parameterizations and chemical reactions in the models will help elucidate the causes and implications of the weekend effect. These research efforts must be comprehensive to guide the emissions control strategies that will continue to reduce O₃ on all days of the week and particularly on the days of the week with the highest O₃ levels and the greatest health implications.

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