Executive Summary

What is the ozone weekend effect?

The "ozone weekend effect" refers to the interesting observation that ozone measurements in some locations are typically higher on weekends compared to weekdays. This is somewhat surprising because smog-forming emissions mostly come from sources, such as cars, trucks, factories, and fossil-fueled power plants that could be expected to produce lower total emissions on weekends compared to weekdays.

Is the ozone weekend effect real?

Yes. In some locations, ozone concentrations are typically higher on weekends despite indications that smog-forming emissions of volatile organic compounds (VOC) and oxides of nitrogen (NO_X) are almost certainly lower on weekends (especially on Sunday) for these same locations. The ozone weekend effect is illustrated in Figure 1 and occurs when the solid line is above the dashed line in the graphs. The context of the ozone weekend effect is also illustrated in Figure 2. Note that while the number of exceedances of the California 1-hour ozone standard was greatly reduced from 1981 to 2001, the relative frequency of exceedances on weekends increased.

Measured concentrations of VOCs and NO_X in the ambient air represent the integrated impact of many sources, and these concentrations usually decrease on weekends at most monitoring sites. The decrease tends to be moderate on Saturday and more substantial on Sunday. In the SoCAB during daylight hours (6 a.m. to 8 p.m.), VOC concentrations (inferred from measured CO values) decrease about 10% on Saturday and 25% on Sunday with respect to midweek levels. Similarly, measured NO_X concentrations decrease about 25% on Saturday and 40% on Sunday. Nevertheless, ozone is now routinely higher on weekends throughout the SoCAB.

Does the ozone weekend effect occur everywhere?

No. The ozone weekend effect presently occurs at most, if not all, of the monitoring sites in the Los Angeles and San Francisco metropolitan areas, based on measurements during the ozone seasons of 1996 through 1998. However, the ozone weekend effect is absent or negligible at most sites in the Sacramento and San Joaquin Valleys.

This report primarily, but not exclusively, considers data from the Los Angeles area because data are available for analysis at many locations for many years.

How big is the ozone weekend effect?

Based on data from 1996 through 1998, typical ozone weekend effects in four major areas of California are the following:

- South Coast Air Basin – 22 ppb or 32% higher than Friday ozone
- San Francisco Bay Area Air Basin – 9 ppb or 25% higher than Friday ozone
- Sacramento Metropolitan area – 5 ppb or 8% higher than Friday ozone (not statistically significant)

- San Joaquin Valley Air Basin – 4 ppb or 6% higher than Friday ozone (not statistically significant)

(For reference purposes, regional background levels of ozone are approximately 30-40 ppb and the levels of the national and state one-hour standards for ozone are effectively 125 ppb and 95 ppb, respectively.)

Within each of these four regions, the ozone weekend effect tends to be smallest at those sites that measure the highest ozone concentrations.

Do other air pollutants exhibit a weekend effect?

Yes, but usually in the opposite direction from ozone.

Although this report emphasizes ozone, the day-of-week behavior of some other pollutants was examined (Figure 3). Analyses of recent data for nitrogen dioxide (NO_2), carbon monoxide (CO), particulate matter (PM10 and PM2.5), and six high-risk toxic air contaminants (TACs) indicate that these pollutants tend to decrease or remain the same on weekends compared to weekdays.

- Daily maximum (peak) concentrations of NO_2 (includes some additional oxidized nitrogenous compounds) and CO are lower on weekends compared to weekdays. In some locations, however, these pollutants may meet or exceed the weekday levels during some mid-day or nighttime hours.

- Concentrations of PM10 and PM2.5 are typically lower on weekends compared to weekdays. Combustion products, such as elemental and organic carbon contribute to PM. Another component of PM is particularly relevant to the issues involved with the ozone weekend effect. Particulate nitrates are secondary products of NO_X and other emissions. Analyses of ambient data for particulate nitrates in the Los Angeles metropolitan area indicate that weekend concentrations are typically lower than weekday concentrations.

- Concentrations of benzene, 1,3-butadiene, and perchloroethylene generally decrease on weekends compared to weekdays.

- Concentrations of formaldehyde, acetaldehyde, and carbon tetrachloride did not display consistent differences between weekdays and weekends.

Figure 1. Ozone trends from 1980 through 1998 for weekdays and weekends at Azusa, L.A. - North Main St., and Riverside in the South Coast Air Basin.
The ozone weekend effect is evident when the solid (WE) line is higher than the dashed (WD) line.
Ozone trend statistic is the mean of the 2nd - 11th highest daily maximum 1-hour concentrations each year.

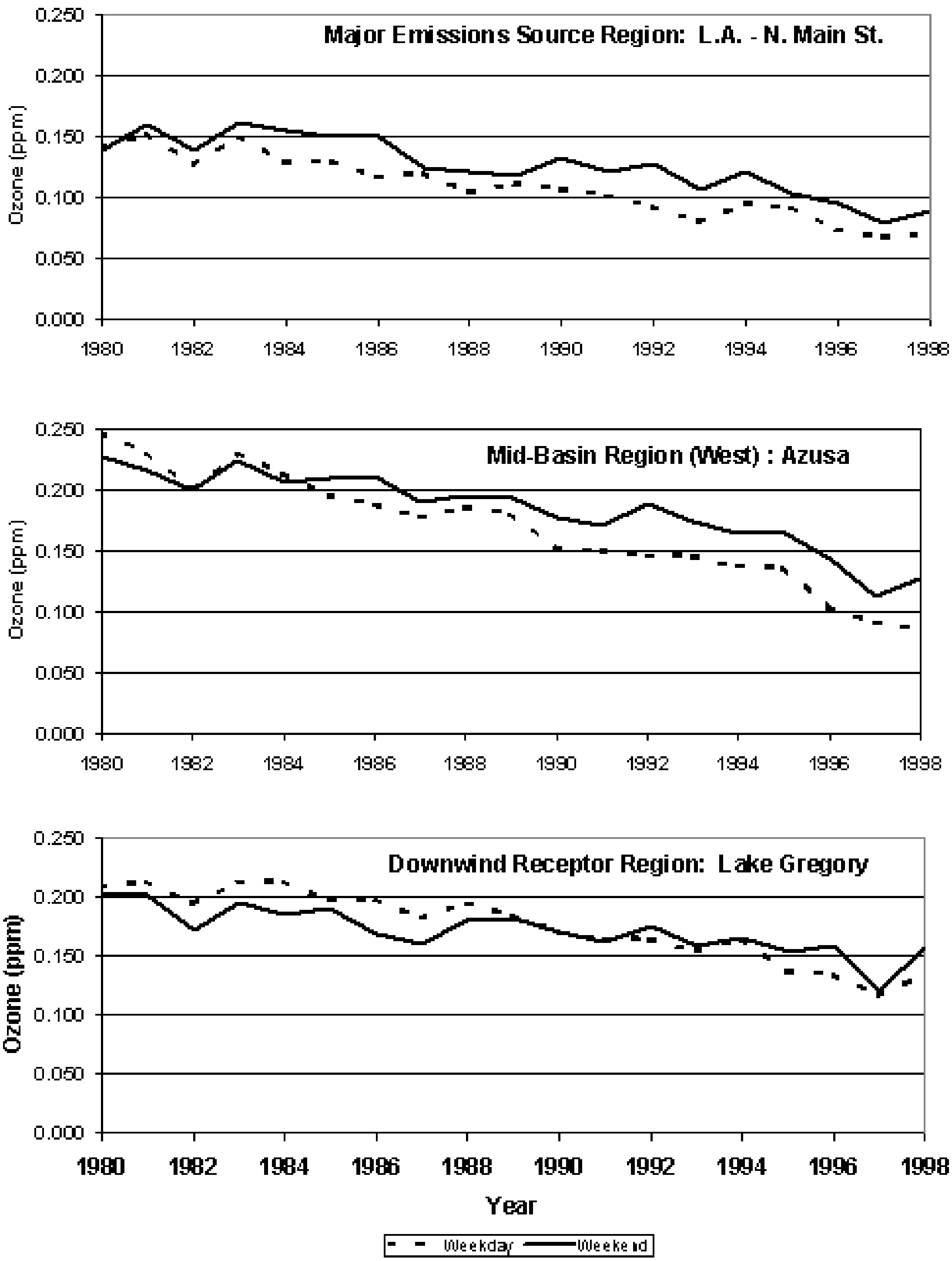
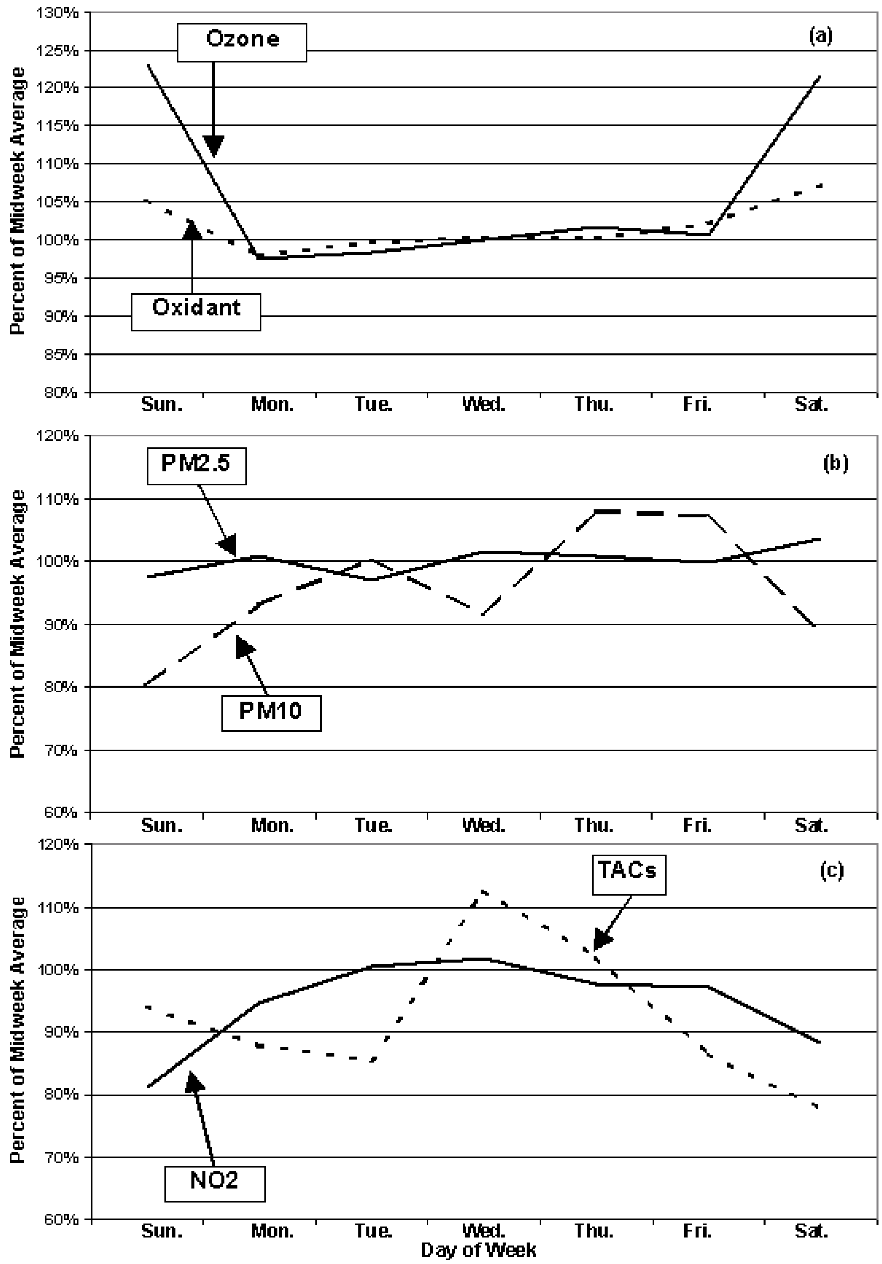


Figure 2. Changes in the number and percentage of ozone air quality standard exceedances by day of the week from 1981 to 2001 at selected sites from west to east in the South Coast Air Basin: LA – N. Main, Azusa, and Crestline (Lake Gregory).

Figure 3. Day-of-week pollutant profiles for gases, particulate matter, and cancer risk (potency-weighted for six toxic air contaminants) in the South Coast Air Basin.

Notes to Figure 3:



1. Ozone and Total Oxidant (O_3 + NO_2) data are average values for 22 sites in the Los Angeles area. For O_3, daily maximum values were used. For total oxidant, the daily maximum between 10 a.m. and 6 p.m. was used. The O_3 and oxidant values for each site are the average of the daily values during the May-October O_3 seasons of 1996-1998 by day of the week.
2. Particulate matter 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 PM_{10} concentration is not known at this time. Measurements from instruments with continuous monitoring rather than filter-based sampling do not exhibit this behavior.
3. NO_2 data are average values for 22 sites in the Los Angeles area. The NO_2 values for each site are annual averages of daily maximum 1-hour 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.

Why is the ozone weekend effect of interest?

This report was written at the request of the Air Resources Board members because the ozone weekend effect has become more than an interesting scientific phenomenon. The ozone weekend effect has become a regulatory issue because this paradox has been offered by some as evidence that further reductions of NO_X emissions would be counter-productive for reducing ambient ozone levels at this time.

Before looking further into the ozone weekend effect, a little history is helpful to set the context of NO_X reductions in California's current ozone control strategy.

Are NO_X reductions a new feature of California's ozone control strategies?

No. A strategy of concurrent reductions of the major precursors of ozone, VOCs and NO_X, has been used for more than twenty-five years to reduce ozone levels in California's ambient air. Concurrent reductions of VOCs and NO_X have been very successful at reducing the high ozone levels in southern California. From the mid-1970s into the 21st century, the ozone control strategy implemented in the South Coast Air Basin (SoCAB) included reductions of both VOC emissions and NO_X emissions. Early NO_X reductions were achieved by statewide controls on emissions from motor vehicles combined with local controls on emissions from industrial sources, such as power plants and cement kilns.

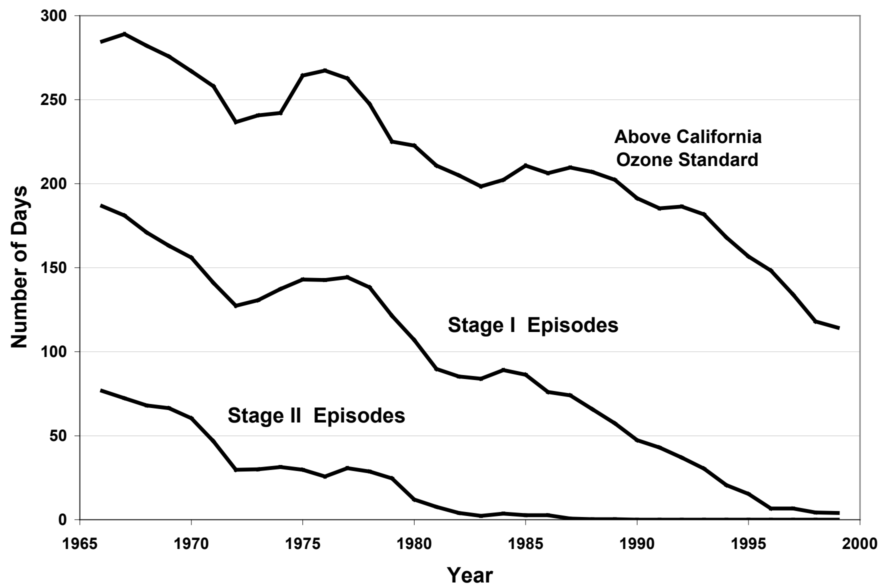
Figure 4 shows the historic success of VOC and NO_X reductions in the SoCAB. Unhealthful concentrations of ozone in the basin have been reduced dramatically, including the last two decades when VOC and NO_X have been controlled concurrently. These improvements have occurred despite rapid population growth and even faster growth in vehicle use as shown in Figure 5.

Have concurrent reductions of VOCs and NO_X been effective only on weekdays?

No. Concurrent reductions of VOCs and NO_X have been effective at reducing ozone levels on all days of the week, including weekends. Figure 1 shows trends for weekdays and for weekends at three locations in the SoCAB. Both weekdays and weekends show substantial improvements at all three locations. On average however, ozone concentrations have declined slightly more slowly on weekends than on weekdays. The trends for other sites in the SoCAB show similar results.

Figure 4. Trends for the number of days per year when the California Ambient Air Quality Standard for ozone was exceeded * and when Stage I ** and Stage II *** ozone episodes occurred within the South Coast Air Basin.

Notes: Early ozone values represent "total oxidant" adjusted to "ozone equivalent". Trends are 3-year



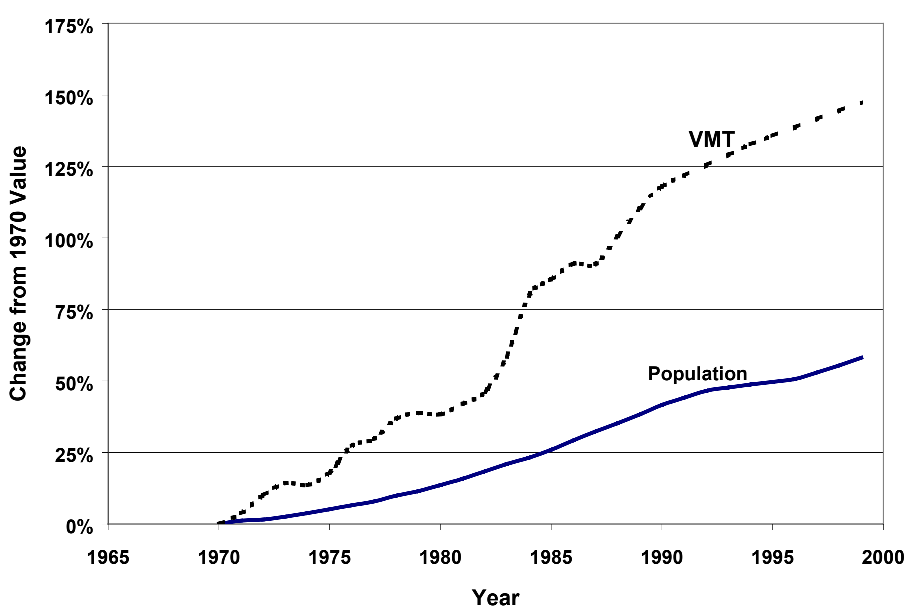
moving averages based on annual values for 1965 - 2000.

* Exceedances of the CA hourly ozone standard (95 ppb or more) decreased more than 60 percent.

** Stage I episodes, max-hour ozone of 200 ppb or more, last occurred in 1998.

*** Stage II episodes, max-hour ozone 350 ppb or more, were eliminated in 1989.

Figure 5. Percent growth in population and vehicle miles traveled from 1970 to 1999 in the South Coast Air Basin.



Are NO_X emission reductions only relevant to ozone?

No. Secondary products of NO_X emissions contribute to ambient levels of several pollutants in addition to ozone. Some of these pollutants, such as fine particulate matter (PM10 and PM2.5), nitrogen dioxide (NO_2), nitric acid, peroxyacetylnitrates (PANs), and some mutagenic nitro-polycyclic aromatic hydrocarbons are known to be detrimental to human beings, to the environment, or to both.

For some of these compounds, data are scarce and specific changes attributable to reductions in NO_X emissions are difficult to identify. However, routine measurements of NO_2 show that annual maximum concentrations at 15 sites in the SoCAB were reduced by 32% to 64% from 1980 to 1998. The Basin did not attain the federal annual average air quality standard for NO_2 until the mid-1990s. In addition to NO_2, particulate nitrate, nitric acid, PAN, and other secondary products of NO_X emissions have declined in the last 20 years in the SoCAB.

Because multiple pollutants are affected by NO_X reductions, they must be considered as part of an overall strategy for attaining all air quality standards and reducing air toxics exposures. Nevertheless, the remainder of this summary primarily considers the ozone weekend effect and its relevance to NO_X reductions as an ozone control measure.

Why do some believe the ozone weekend effect implies that major reductions of NO_X emissions will be counter-productive for reducing ozone?

Despite the long-term record of success for concurrent reductions of VOCs and NO_X in California, some people assert that further, significant NO_X reductions will be counter-productive for controlling ozone. That is, they believe greater success will be achieved with only VOC reductions. Their reasoning, called the **NO_X-reduction hypothesis** in this report, includes three points.

First, smog chamber experiments show that NO_X sometimes promotes and sometimes restricts ozone formation depending on the relative abundance of VOCs. The abundance of VOCs relative to NO_X is characterized by the VOC/NO_X ratio. In experiments where the VOC/NO_X ratio is less than 8 to 10, reducing NO_X tends to increase ozone formation. However, when the VOC/NO_X ratio is higher than 8 to 10, reducing NO_X tends to decrease ozone formation.

Second, VOC/NO_X ratios at ground level average less than 8 to 10 in most of the SoCAB. However, the ratio varies spatially and temporally. If ozone formation in this complex air basin is similar to that in a smog chamber, then reducing NO_X emissions should (hypothetically) promote increased ozone formation until the VOC/NO_X ratio shifts toward a NO_X-limited ozone formation regime. On weekends, NO_X emissions are reduced substantially, along with smaller reductions of VOC emissions. With lower NO_X and higher ozone on weekends, the real world and the laboratory appear to be consistent.

Finally, the short lifetime of NO_X relative to VOC emissions and the limited residence time of air masses on an urban scale leads opponents of NO_X-reducing regulations to propose that the <u>steady</u> NO_X reductions from strategic regulations mimic the <u>periodic</u> NO_X reductions on weekends. Because the periodic NO_X reductions are associated with ozone increases, they assert that strategic NO_X reductions would slow the rate of progress that would otherwise be earned through VOC reductions alone.

Although CARB staff agrees that NO_X reductions can cause ozone concentrations to increase temporarily via ozone quenching and VOC-limited chemistry, staff contends that NO_X reductions are not counter-productive for attaining ambient air quality standards.

Are there other possible causes of the ozone weekend effect?

Yes. The NO_X-reduction hypothesis is only one possible explanation of the ozone weekend effect. This report explores the NO_X-reduction hypothesis along with several alternative hypotheses concerning the cause or causes of the ozone weekend effect. Contrary to the NO_X reduction hypothesis (which predicts an ozone disbenefit (i.e., increase) with reduced NO_X in a VOC-limited ozone formation regime), the alternative hypotheses do not imply that strategic NO_X reductions would be counter-productive for reducing ozone concentrations in the long term. In fact, ozone air quality has improved most when NO_X air quality has also improved (compare Figures 4 and 6).

The various hypotheses are not mutually exclusive; each could explain a large or small part of the overall effect. Each additional hypothesis is described below in hypothetical terms only. Later in this summary, each hypothesis is evaluated in light of the available data.

- **NO_X-timing hypothesis**: This hypothesis assumes that the timing of NO_X emissions on weekends is different from weekdays. The total NO_X emissions on weekends may be the same or less than on weekdays, but the timing is assumed to make the weekend emissions more efficient at producing ozone, leading to higher observed ozone concentrations on weekends.

- **Carryover near the ground hypothesis**: This hypothesis assumes that the volume of traffic is greater on Friday and Saturday nights compared to other nights of the week. This extra traffic is assumed to emit more VOCs and NO_X during the nighttime hours between Friday and Saturday and between Saturday and Sunday. The additional emissions are assumed to remain near the ground and help form extra ozone during the daylight hours on Saturday and Sunday.

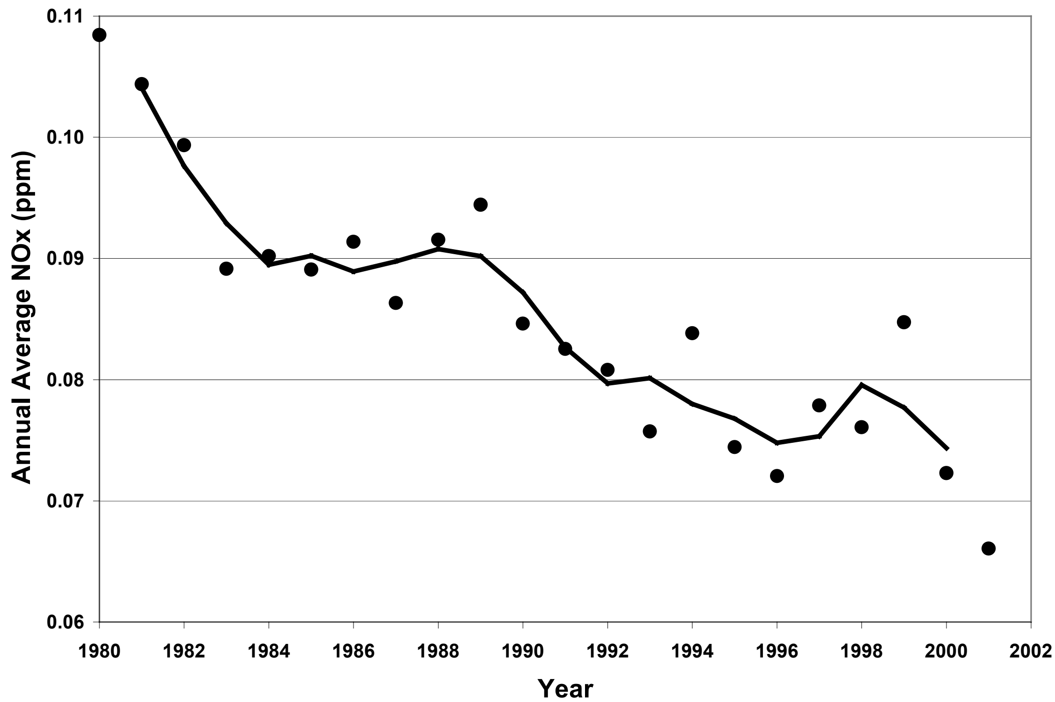
- **Carryover aloft hypothesis**: This hypothesis assumes that large amounts of ozone and ozone-forming pollutants commonly persist overnight above the cool layer of air near the surface. On the following day, these pollutants are assumed to mix down to the ground as the Earth is warmed by sunlight. The pollutants that mix down from aloft are assumed to interact with fresh surface emissions in such a way that ozone measured at the surface on weekends is greater than the ozone measured at the surface on weekdays. As the meteorological setting becomes more stable and conducive for increased ozone concentrations over a period of days, the ozone and ozone precursors can accumulate from day to day aloft. With the shorter lifetime of NO_X emissions than VOC emissions, VOC/NO_X ratios aloft should be higher than at the surface and ozone formation aloft should be highly sensitive to NO_X emissions. Being more sensitive to NO_X emissions, ozone concentrations aloft may likely have decreased even faster than surface ozone concentrations have declined during the last two decades. In addition, if the increased activities of Friday and Saturday evenings occur while vertical mixing is still occurring to some extent, these extra ozone precursors may be available to support additional ozone formation the following day.

- **Increased weekend emissions hypothesis**: This hypothesis assumes that the total emissions of VOCs and the total emissions of NO_X from all sources (human activities and natural) are actually greater on weekends compared to weekdays. Therefore, the higher concentrations of ozone observed on weekends are assumed to reflect the greater emissions of ozone precursors, or more reactive VOC emissions.

- **Aerosol and ultraviolet (UV) radiation hypothesis**: This hypothesis assumes that there are more aerosols and soot particles in the atmosphere on weekdays than on weekends. Aerosols scatter UV radiation (some back toward space) and some (e.g., organics and soot) can absorb the ultraviolet sunlight that drives ozone-forming reactions in the atmosphere. Therefore, it is assumed that the ultraviolet solar radiation needed to initiate the ozone forming reactions is absorbed on weekdays more than on weekends. The larger amount of available ultraviolet radiation near ground level on weekends is assumed to contribute to the formation of higher ozone concentrations on weekends.

- **Ozone quenching hypothesis**: This hypothesis assumes that NO emissions during the morning are greater on weekdays than on weekends and that they destroy more of the available ozone in the layer of air near the ground where air monitoring instruments are located. Thus, ozone is suppressed more and ozone formation is retarded more on weekdays compared to weekends, leading to the weekend effect.

Figure 6. Trend in ambient NO_X concentration in the South Coast Air Basin.
(composite of daily average NO_X measurements at 18 monitoring sites)



Do the available data demonstrate which hypotheses are correct?

No. Despite California's ambitious programs in air quality monitoring, emissions inventories, and atmospheric research, crucial gaps in the available data must be filled before definitive conclusions can be reached in this regard.

Existing data are not sufficient because ongoing programs and special studies are usually designed to address typical days or extreme "episode" days. In general, these programs have not been designed to explain why ozone concentrations might differ (as they do) on different days of the week.

Current air monitoring data are sufficient to demonstrate that the ozone weekend effect is real and to suggest possible causes. However, this study shows that additional data are needed before the cause or causes of the ozone weekend effect can be determined.

Do the available data indicate which hypotheses are plausible?

Yes. Analyses of the available data indicate that several hypotheses are plausible and each may explain a significant portion of the ozone weekend effect. A plausible hypothesis, however, is not sufficient to determine California's long-term ozone control strategy.

- The **NO_X-reduction hypothesis** is plausible. Although the VOC/NO_X ratio is not an ideal indicator of ozone formation regimes and the measurements are biased low by 40 percent or more (due to under-reporting of VOC and over-reporting of NO_X), the VOC/NO_X ratios from surface measurements appear to generally be in the "VOC-limited" range. Ambient air quality data indicate that NO_X emissions are reduced on weekends proportionally more than VOC emissions. Therefore, higher ozone on weekends compared to weekdays could be a direct result of lower NO_X emissions in a VOC-limited ozone formation regime. In such an ozone formation regime, NO_X reductions can cause an ozone disbenefit, i.e., peak ozone concentrations increase.

- The **NO_X-timing hypothesis** is plausible. Traffic is the single largest source of NO_X emissions in the South Coast Air Basin. On weekday mornings, rush-hour traffic produces large amounts of NO_X, leading to daily-maximum concentrations of NO_X between 6 a.m. and 9 a.m. On weekends, however, the morning traffic is much lighter; NO_X emissions and peak concentrations between 6 a.m. and 9 a.m. are substantially lower on weekends. By mid-day, however, traffic volumes and both NO_X and VOC emissions are closer to weekday levels.

  This timing difference is potentially important because laboratory experiments and computer models indicate that NO_X emitted later in the day can produce ozone more efficiently. Higher ozone concentrations on weekends may result from differences in the timing of NO_X emissions. As a result of these weekend timing effects, the ozone response to lower NO_X emissions on the weekend might not accurately predict the ozone response to additional NO_X reductions on weekdays. The different timing of emissions (NO_X in particular) between weekdays and weekends could retard the ozone decrease on weekends relative to weekdays.

- The **carryover near the ground hypothesis** is only marginally plausible, because it probably does not contribute significantly to the ozone weekend effect. Traffic activity data for freeways show that the volume of traffic on Friday and Saturday evenings is greater than it is on other days of the week. This activity occurs after surface temperatures begin cooling in the evening. Therefore, the extra emissions into this stable layer of air should remain near the ground and could participate in smog-forming processes following sunrise the next day.

  However, ground-level measurements of NO_X and VOCs (CO as a surrogate) at sunrise indicate that concentrations of ozone precursors at the surface are lower on weekends compared to weekdays. These observations indicate that the amounts of smog-forming emissions that carry over near the surface from Friday and Saturday nights is small relative to the amount of fresh emissions on weekend mornings. Therefore, carryover near the surface is not likely to be a significant cause of the ozone weekend effect.

- The **carryover aloft hypothesis** is plausible. During the Southern California Ozone Study in 1997, measurements aloft (200 to 5000 feet or more) found large amounts of ozone that carried over from one day to the next. A recent study of carryover aloft in the northeast states indicates that surface ozone concentrations can be strongly affected, even dominated, by materials that carry over aloft.

The lower amounts of ozone precursor emissions on weekends compared to weekdays (especially in the morning) may well interact differently with the ozone and radical precursors from aloft on weekends compared to weekdays. Conditions aloft and the subsequent interaction when atmospheric mixing increases during the morning are poorly characterized by surface-based measurements. The physical and chemical processes potentially at work here will overlap with other weekend effect hypotheses such as NO_X reduction, NO_X timing, and ozone quenching. For example, the large amounts of fresh NO emitted at the surface on weekdays may destroy ozone and radicals that mix down from aloft, thereby limiting their contribution to surface ozone concentrations. On weekends, however, NO concentrations can be significantly lower, so less ozone from aloft is destroyed, and ozone from aloft contributes to higher ozone measurements at the surface on Saturday and Sunday.

The main focus is that different surface conditions and the interactions with potentially different conditions aloft could cause the subsequent ozone concentrations at the surface to increase from weekdays to weekends. For example, ozone formation aloft could well be NO_X-limited and the large mass of ozone aloft could well be a large component of the eventual ozone burden in the surface layer. With midday emissions on weekends being comparable to weekdays, the weekend emissions would be into an environment with higher ozone concentrations (due to less scavenging and potentially more ozone aloft) and potentially a more efficient ozone production regime (VOC/NO_X ratio nearer 9 ppmC/ppm). The differing conditions at the surface and aloft from weekdays to weekends and the different chemical environment of their interaction could cause a greater influence of the air aloft on surface conditions and also weekend ozone concentrations to be higher than ozone on weekdays. An important but unknown facet of this hypothesis is whether ozone aloft (via carryover and new formation) is proportional to the peak surface ozone concentrations on the previous day. If it is, then the Sunday to Monday transition with surface ozone concentrations dropping from typically the highest of the week to the lowest of the week would suggest that ozone carryover aloft is not the primary cause of the weekend effect. However, if ozone aloft is proportional to the emission of ozone precursors on the previous day, then Monday might be expected (and as observed) to have the lowest ozone concentrations of the week. Thus, although the measurements to test the various nuances of this hypothesis are limited, the hypothesis is conceptually plausible.

- The **increased weekend emissions hypothesis** is <u>not plausible</u> as a <u>significant</u> contributor to the ozone weekend effect. The proposition that emissions of VOCs and NO_X increase on weekends is not consistent with most of the available data. Nevertheless, emissions in some areas may increase on weekends.

For example, Lynwood, in South Central Los Angeles, has some of the highest carbon monoxide concentrations in the U.S. At Lynwood, CO levels during the mid-day hours are higher on Saturday than any other day of the week. Ozone, however, tends to be highest on Sunday at all sites, including Lynwood, when CO at Lynwood is below the weekday levels. Better understanding of emissions in South Central L.A. and other regions is an important objective of activity studies. Data from such studies may reveal that emissions on weekends increase in selected locations and contribute to local variations in the ozone weekend effect.

- The **aerosol and UV radiation hypothesis** is plausible, but accurate data on light absorption and light scattering are scarce. Both laboratory experiments and ambient measurements are needed. Daily simultaneous measurements of emissions and ambient levels of PM2.5 (elemental carbon in particular) and ultraviolet sunlight are needed to clarify the contribution of this hypothesis to the ozone weekend effect.

  Because motor vehicles, especially diesel-powered, are a major source of particles, it is plausible that aerosols in general and soot particles in particular are less abundant on weekends compared to weekdays. If so, ultraviolet sunlight should be more available near ground level on weekends to drive ozone-forming processes. Therefore, ozone-forming reactions may be more vigorous on weekends and contribute to higher ozone on Saturday and Sunday. Aerosols can have other complicating effects (e.g., light scattering, heterogeneous chemical reactions, ozone destruction) that complicate the isolation of effects. This hypothesis was proposed but not thoroughly investigated due to limited data. The limited amount of data and investigations performed to date suggest that this process might not be a major contributor to the ozone weekend effect.

- The **ozone quenching hypothesis** is plausible and significant but not determinant in the weekend effect. Ozone in the surface layer is destroyed by fresh NO emissions; this is especially evident especially during the hours when ozone is not being photochemically produced. The much greater NO emissions on weekday mornings compared to weekend mornings causes ozone concentrations on weekday mornings to be greatly suppressed and the photochemical formation of ozone to be retarded (delayed) by about an hour compared to weekends. Thus, the initial suppression and the later start (shorter formation period) cause ozone concentrations to be lower on weekdays than on weekends. Although ozone quenching can explain a large portion of the weekend increase in ozone concentrations, increased urbanization or vehicular activity is also necessary to account for the increasing spread of the ozone weekend effect. Furthermore, additional factors need to be invoked to explain the transition from Saturday to Sunday as the peak ozone day in recent years.

In summary, analyses of existing databases suggest that several possible causes of the ozone weekend effect are plausible. However, currently available data are not sufficient to separate and quantify the contributions of the various potential causes. Table 1 provides a summary of the consistency of the hypotheses with various observations.

What are the next steps?

The ARB and other interested parties are continuing to investigate the ozone weekend effect. The Technical Support Document for this report lists several projects sponsored by government and/or private institutions. These efforts acknowledge that understanding the causes of the ozone weekend effect and quantifying their respective contributions will require information that is not available today.

A research program involving field studies, laboratory experiments, and modeling exercises is recommended to fill this need. An outline of research options is provided in Chapter 5 of this report as a starting point for discussion and planning. Major elements of this research, with reference to the South Coast Air Basin, are the following:

- **Field studies**

Ambient measurements of VOCs and nitrogen-containing compounds are needed with high resolution in space and time, both at the surface and aloft.

Because the alternative hypotheses concerning the causes of the ozone weekend effect involve time-dependent changes in emissions and atmospheric conditions, hourly measurements are highly desirable. Because the ozone weekend effect is not uniform throughout a region, data for many locations are also highly desirable. Measurements "aloft" (three-dimensional space) are potentially vital for understanding the ozone weekend effect.

Measurements of VOCs are needed that account for all reactive species that are present in significant amounts in polluted ambient air. Improvements in monitoring methods are being pursued to make such measurements feasible on an hourly basis at many locations.

Routine NO_X measurements today are not specific for the sum of NO and NO_2. Instead, they include contributions from other compounds, such as N_2O_5, HNO_3, and PAN. These routine measurements also lack the precision needed to characterize VOC/NO_X ratios with satisfactory accuracy during the mid-day hours when ozone is high. New monitoring methods, however, may allow highly precise and specific, artifact free measurements of NO_2, nitrate radical (NO_3), and HNO_3. Such data could help resolve the causes of the ozone weekend effect.

Measurements of PAN, nitro-PAHs, particulate nitrates, and other compounds containing nitrogen are desirable for understanding the ozone weekend effect and for understanding the impact of NO_X emission reductions on multiple air pollutants.

To address these needs satisfactorily will require a significant investment in time and resources to carry out the appropriate field studies.

- **Laboratory experiments**

Previous laboratory experiments concerning the timing of NO_X emissions may need to be corroborated and expanded. Present generation smog chambers reduce experimental artifacts compared to earlier chambers, and this may alter the earlier results significantly.

Other laboratory investigations are needed to resolve the causes of the ozone weekend effect. Specifically, there is a need for studies on the sources and fates of free radicals because the radical budget is critical for determining the response of ozone to changes in VOC and NO_X at low VOC/NO_X ratios. Also, heterogeneous chemical reactions need additional investigation to better identify and quantify ozone destruction by particles and semi-volatile organics and the potential re-noxification when HNO_3

deposits to a surface. Historically, the smog chamber experiments sought to minimize wall effects. We need to investigate whether doing so has caused our chemical modeling representations to “lose touch” with the real world processes.

- **Emission inventory development**

More accurate and detailed emission inventories for each day of the week are needed to help determine both the causes of the ozone weekend effect and the appropriate regulatory responses. Day-of-week emission inventories are particularly needed by computer models that might be used to simulate the ozone weekend effect. Various projects leading toward day-of-week inventories are planned or already in progress.

- **Modeling exercises**

Computer models that simulate photochemical smog become more sophisticated with each passing year. Nevertheless, using these models to investigate the ozone weekend effect presents several unique challenges. Examples include the following:

1. Hourly emissions inventories for weekend days are not generally available.
2. Appropriate initial conditions and boundary conditions may not be known satisfactorily.
3. Some chemical mechanisms might not perform adequately under low-NO_X conditions (associated with ozone formation aloft) or under the wide spatial and diurnal range of ambient VOC/NO_X ratios.
4. Some recent research on surface chemistry indicates that HNO_3 is not a stable sink with respect to NO_X photochemistry as assumed in current photochemical mechanisms.
5. Vertical mixing processes used in some models may not represent realistic mixing of pollutants that carry over aloft.

Once these and other pertinent issues are addressed to help assure that models are incorporating the important processes and performing properly (i.e., correct answer for the right reasons), generic “what-if” modeling exercises could then be used to identify potentially significant factors governing the ozone weekend effect. Such exercises could effectively address the multiple hypotheses concerning the causes of the ozone weekend effect.

Is it realistic to expect the causes of the ozone weekend effect to be resolved?

Yes. With a realistic commitment of time and resources, the science, the data, and the analytical tools should converge to provide reasonably definitive answers concerning the ozone weekend effect. Furthermore, these same answers should clarify the relationship between periodic NO_X reductions on weekends and strategic NO_X reductions on all days. If so, the results would help us understand how CARB’s overall clean air strategy for addressing ozone, PM, and air toxics will address the rate of progress in achieving the ozone standards on both weekends and weekdays.

Should the Board modify its current policy of reducing both VOCs and NO_X?

No. After investigating the ozone weekend effect, reviewing the historical trends of air quality and emissions, and considering the health and environmental impacts, staff believes that no change is currently warranted in the CARB's strategy of reducing both ozone precursors in an expeditious manner. Major reasons for continuing the dual precursor control approach include:

1) Ozone concentrations and exceedances of health-based standards and indicators in the South Coast Air Basin declined dramatically during the 1990s when major reductions in NO_X and VOC were occurring,
2) Ozone concentrations continue to decline on weekends, although at a slower rate than on weekdays,
3) Significant uncertainties remain as to the causes of the ozone weekend effect and to the relevence of those causes to a long-term control strategy,
4) NO_X reductions are needed because ozone non-attainment regions are not always VOC-limited, and
5) NO_X emissions have a variety of negative environmental impacts.

What is the essence of the report? What should I remember?

The ozone weekend effect is a tendency for ozone concentrations in some areas to be higher on weekends than on weekdays. These results seem counterintuitive in that emissions of ozone precursors from primary sources are lower on weekends than on weekdays. Furthermore, of the two major precursors of ozone, nitrogen oxides (NO_X) appear to decline more than volatile organic compounds (VOCs). Over the last few decades, the geographic areas exhibiting the ozone weekend effect has increased - now including most air quality monitoring sites in the South Coast Air Basin, many sites in the San Francisco Bay Area Air Basin, and, most recently, some urban sites in the Central Valley. Based on these weekend effect phenomena, some observers conclude that attainment of ambient air quality standards for ozone will occur more efficiently without additional regulatory reduction of NO_X emissions.

This report outlines several possible factors contributing to the ozone weekend effect, and evaluates the consistency of the available data with each one. Seven possible factors were evaluated, and five were considered plausible as significant contributors to the ozone weekend effect. The plausible causes were NO_X reductions, different timing of emissions including NO_X, different amounts and impacts of pollutants that persist overnight aloft, different amounts of light-absorbing particulate matter in the air, ozone quenching by nitric oxide emissions, or some combination of these five hypotheses.

This report concludes that the available data are not sufficient to determine the actual causes responsible for the ozone weekend effect. The available data provide support for NO_X reduction as a factor but much of the data are also consistent with the other plausible factors. Because the currently available data are not well-suited for testing the plausibility of several causes or for attributing the overlapping factors among the causes, it is speculative to conclude that NO_X reduction is the cause of the ozone weekend effect. Recommendations for further research are offered to elucidate the relative influence of all factors that contribute to the varied observations of the ozone weekend effect. Full evaluation of these potential factors will involve research in a variety of disciplines including field measurements, laboratory studies, and modeling exercises. For example, current photochemical air quality models are based on chemical mechanisms that have minimized the effects of heterogeneous chemical reactions while the air near ground level has plenty of surfaces (e.g., aerosols, vegetation, buildings) upon which additional reactions can occur. Recent work suggests that some heterogeneous reactions may enable NO_X products to remain in reactive forms rather than being removed from the photochemical system as termination products (e.g., nitric acid). Because of the complex variety of features associated with the presence or non-presence of the ozone weekend effect and its evolving nature, the weekend effect presents an opportunity for thoroughly evaluating the reliability of air quality models when weekend modeling results are compared with observations.

Table 1. The following observations are from the findings/observations noted in the Staff Report and Technical Support Document. The consistency of each observation with the various hypotheses of the ozone weekend effect is noted.

Observation \ Hypothesis:	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**
Ground-level VOC/NO_X ratios are in the VOC-limited regime for O_3 formation	Y						
Ground-level VOC/NO_X ratios increase during daylight hours	Y	Y					
Ground-level VOC/NO_X ratios are higher on WEs than on WDs	Y	Y	Y	Y	Y		Y
Ground-level NO_2/NO ratios are higher on WEs than on WDs	Y	Y					Y
NO_X concentrations on WEs increase later but faster than on WDs		Y					Y
Traffic and precursor concentrations are greater on Fr & Sa nights			Y				
Precursor concentrations at sunrise are similar on WEs and WDs			N				
$[O_3]$s aloft (typically only measured during episodes) tend to be higher than background levels				Y			
VOC/NO_X ratios are higher aloft that at ground				Y			
Precursor concentrations are lower on WEs than WDs at almost all sites					N		Y
Weight-in-Motion data indicate lower traffic on WEs than WDs at all but peripheral locations					N		
HD truck traffic is down dramatically on WEs compared to WDs						Y	
UV radiation decreases only slightly from WDs to WEs						N	
WE Effect is primarily evident in major urban areas	Y	Y	Y				Y
WE Effect has expanded eastward over the SoCAB over the years	Y	Y	Y				
Ozone trends down on both WDs & WEs but slower on WEs	Y	N					
Ozone trends down fastest during period of greatest NO_X emission reductions	N	Y					N

#1 – NO_X Reduction hypothesis
#2 – NO_X Timing hypothesis
#3 – Carryover at ground-level hypothesis
#4 – Carryover Aloft hypothesis
#5 – Increased Emissions hypothesis
#6 – Aerosol and UV radiation hypothesis
#7 – Ozone Quenching hypothesis

Y = yes, supports hypothesis
N = no, contradicts hypothesis
blank = neither strongly supports or contradicts hypothesis

After investigating the ozone weekend effect, reviewing the historical trends of air quality and emissions, and considering the health and environmental impacts, staff believes that no change is currently warranted in the CARB's strategy of reducing both ozone precursors in an expeditious manner. The available data do not indicate that the changes in ozone precursors and ozone itself on weekends are representative of the changes that might be anticipated with regulatory reductions in NO_X. Major reasons for continuing the dual precursor control approach include:

1) Ozone concentrations and exceedances of health-based standards and indicators in the South Coast Air Basin declined dramatically during the 1990s when major reductions in NO_X and VOC were occurring,
2) Ozone concentrations continue to decline on weekends, although at a slower rate than on weekdays,
3) Significant uncertainties remain as to the causes of the ozone weekend effect and to the pertinence of those causes to a long-term control strategy,
4) NO_X reductions are needed because ozone non-attainment regions are not always VOC-limited, and
5) NO_X emissions have a variety of environmental impacts.

The California Air Resources Board (CARB) will continue to examine the atmospheric chemistry of NO_X as it is a key precursor of not only ozone but also particulate matter (PM) and other compounds with health and environmental concerns. These include nitrogen dioxide (NO_2), nitric acid (HNO_3), nitrous acid (HONO), peroxyacetylnitrate (PAN), nitro-polycyclic aromatic hydrocarbons (nitro-PAHs), regional haze, and nitrate deposition with subsequent fertilization and eutrophication of soils and surface waters.

Even should future research determine that the ozone weekend effect is: 1) due to relatively greater NO_X reductions than VOC reductions on weekends and 2) representative of the effects of regulatory NO_X controls, regulators must consider the comprehensive impacts of NO_X emissions. Many studies indicate that PM, in particular, but also NO_2, HNO_3, and other nitrogen containing pollutants have adverse health impacts, sometimes even greater than ozone does.