

June 30, 2003

**Appendix A**

**Comments from Air Improvement Resource, Inc.**

June 30, 2003

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**Air Improvement Resource, Inc. Comments on  
Air Resources Board October 2000 Draft Staff Report  
and October 2000 Draft Technical Support Document  
“The Ozone Weekend Effect in California”  
December 15, 2000**

Air Improvement Resource, Inc. (AIR), at the request of General Motors Corporation, has reviewed the October, 2000 Draft Staff Report (SR) and Draft Technical Support Document (TSD) concerning the ozone weekend effect in California. At the outset, some comments on the ARB process of investigating the scientific evidence relating to the ozone weekend effect and developing the draft report are appropriate. AIR scientists have been following the issue for several years, attending and participating in the Work Group meetings. The ARB staff is to be commended for conducting the investigation in an open process, encouraging cooperation among scientists studying the weekend phenomenon, and sharing draft analyses for comment by the entire scientific community. AIR appreciates the opportunity to comment on the October 2000 draft material. As noted in the Executive Summary of the SR, the issue of the cause or causes of the ozone weekend effect has become an important regulatory and scientific issue.

While the draft material lays out several hypotheses that have been offered to explain the ozone weekend effect, it does not go far enough in evaluating the various hypotheses with existing data. As documented below, there is additional evidence and logical analyses that can be used to evaluate the various hypotheses. The SR concludes that there are several plausible hypotheses and not enough data to discriminate among them. The staff lays out a multi-year research program that will, hopefully, be able to test the various hypotheses more rigorously. In particular, the staff recommends a major effort to (1) develop more comprehensive day-of-the-week emission inventories and air quality data, (2) use the data to develop base cases that model current day-of-the-week behavior, and (3) design and execute modeling studies to address the alternative hypotheses. In this scheme, the evaluation of the various potential causes is put off for at least several years, perhaps more. In the meantime staff concludes:

“Until the causes of the ozone weekend effect are determined satisfactorily, NO<sub>x</sub> reductions remain a rational and valid element of ozone control strategies in California.”

Based on the analyses discussed below, AIR believes that the case for Hypothesis #1 (NO<sub>x</sub> reductions) as the primary cause of the weekend ozone increase is much stronger than the case for any of the other hypotheses. In addition, the proximate modeling currently planned by the Coordinating Research Council will be able to evaluate many of the key issues related to the various hypotheses in the near future. Thus, staff and the ARB will be able to evaluate the implications of the weekend ozone phenomenon for NO<sub>x</sub> reductions in California’s ozone control strategy in the reasonably near future rather than waiting for several years.

There are several reasons why this path is preferable. First, if NO<sub>x</sub> reductions that are either currently planned or being considered are a net disbenefit for the environment, the sooner the ARB knows that the better. If the proximate modeling shows that it is a distinct possibility, the ARB should (1) set up an expedited process to complete the research plan laid out in the SR and TSD, and (2) put a hold on more NO<sub>x</sub> control until the issue is resolved. As more and more sources get controlled, the costs of emission control are rising and the number of remaining options is dwindling. If the ARB has chosen a less-than- optimum path to clean air, it will be very difficult to attain the federal and state air quality standards.

Second, because the highest ozone now occurs on weekends, the SIP updates required under California law must model weekend as well as weekday episodes. Therefore, an understanding of the implications of the weekend effect is needed as soon as possible so that SIP revisions focus on effective controls not counterproductive ones.

Third, as shown below, the weekend effect is more pronounced for 8-hour ozone concentrations than for 1-hour ozone concentrations. Therefore, if there is either a federal or California 8-hour ozone standard in the future, the likelihood of weekend episodes controlling overall emission reduction requirements will be increased.

The bulk of AIR's comments concern the SR. Unfortunately, several key pieces of information in the TSD or in the original ARB or ARB-sponsored studies are left out of the Staff Report. Thus, the draft conveys more uncertainty than is necessary based on a fuller account of the available data.

### **Comments on draft Staff Report**

#### **Comments on ARB strategy**

The Executive Summary (ES), referring to Figure 1, indicates that the ARB strategy of concurrent reductions of the primary ozone precursors, VOCs and NO<sub>x</sub>, has "been very successful at reducing ozone concentrations in California." While ozone has been reduced substantially in California, there are several problems with the SR characterization of the "success" of concurrent VOC and NO<sub>x</sub> reductions. First, Figure 1 shows that ozone decreases occurred prior to the start of NO<sub>x</sub> controls. The TSD indicates:

"The peak ozone concentrations in the SoCAB have declined over the years, irrespective of precursor control strategy." TSD at page 2.2-2.

In other words, ozone declined in the earlier period when VOC was being controlled and atmospheric NO<sub>x</sub> concentrations actually increased as well as in the more recent period when both VOC and NO<sub>x</sub> have been controlled. The common element is, thus, VOC control. Second, it is not clear to what extent VOC and NO<sub>x</sub> have actually been

reduced in the atmosphere due to the controls applied. Unfortunately, the lack of accurate atmospheric measurements of VOCs over the years limits our ability to determine the degree of precursor control that has actually been achieved during the long-period of ozone decline. Third, without this information, it is difficult to determine whether the strategy of “concurrent” VOC and NO<sub>x</sub> control has actually resulted in “concurrent” VOC and NO<sub>x</sub> reductions or some other combination of VOC and NO<sub>x</sub> reductions. Fourth, since the chemistry of ozone formation is clearly dependent on the relative amounts of VOC and NO<sub>x</sub>, a knowledge of the balance between recent VOC and NO<sub>x</sub> reductions is critical to understanding whether California’s NO<sub>x</sub> controls, once initiated, have helped or hindered the ozone reductions in various air basins.

The SR indicates that the relationship between ozone, NO<sub>x</sub> and VOCs is complex and that:

“...NO<sub>x</sub> promotes ozone formation when VOCs are relatively abundant but restricts ozone formation when VOCs are relatively scarce.” SR at page 1-2. This well-studied and accepted phenomenon results in the counter-intuitive result that when the ratio of VOC to NO<sub>x</sub> is low, ozone formation is VOC-limited and NO<sub>x</sub> reductions will increase ozone formation. Although the chemistry that causes this phenomenon is well-accepted, it has been difficult to deal with in the public policy arena. Many years ago, Dr. Jim Pitts wrote that this phenomenon is “the curse of control officials.”

The main issue in California is whether this phenomenon is the primary cause of the weekend ozone effect or not. The SR indicates several other hypotheses that might explain the weekend ozone effect. These are discussed in detail below. In addition, the SR posits that there may be a difference between periodic NO<sub>x</sub> reductions that occur each weekend and strategic NO<sub>x</sub> reductions that would produce steady NO<sub>x</sub> reductions on both weekdays and weekends. This appears to be a distinction without a difference. As indicated by Blier and Winer,

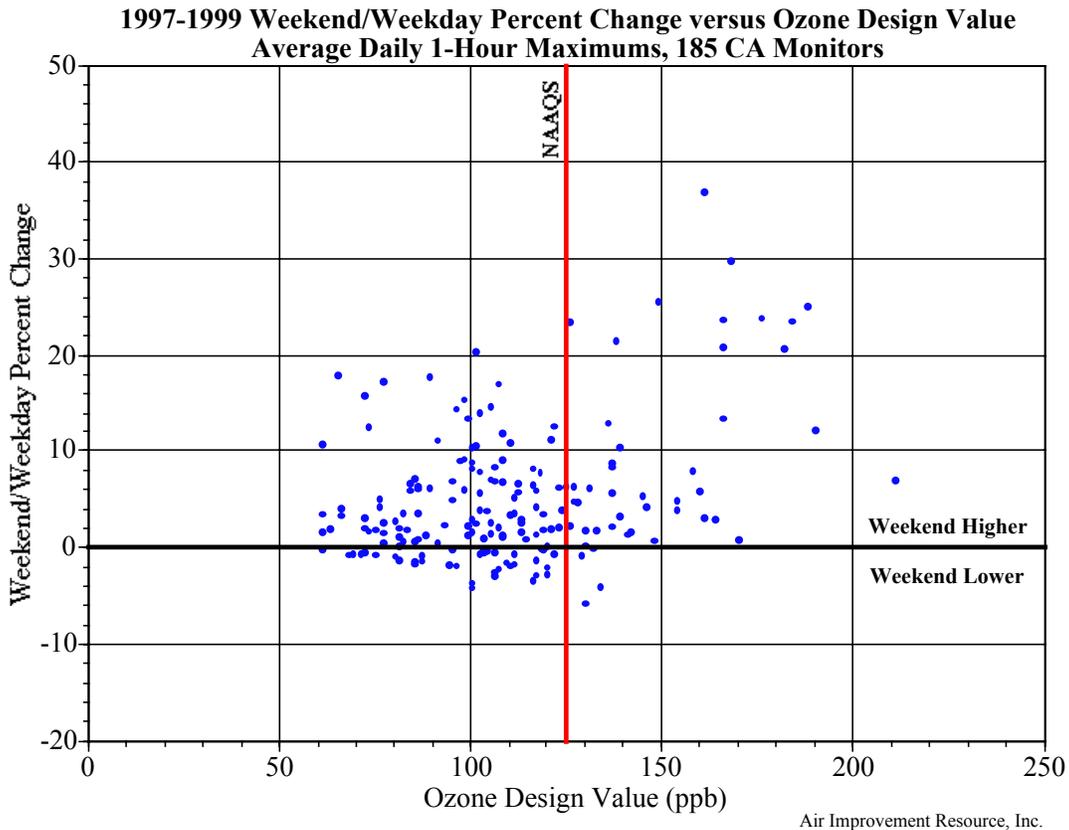
“Nitrogen oxides have shorter lifetimes than hydrocarbons and ozone & carryover over time periods longer than 8 hours involves mostly ozone and hydrocarbons.” Blier and Winer, report to ARB, 1999 at page 1-2.

If ARB staff has specific reasons (other than the hypotheses listed) to believe that the two day reductions in NO<sub>x</sub> associated with weekend activity do not mimic longer-term NO<sub>x</sub> reduction strategies, the report should document those reasons so they may be evaluated and tested.

### **Magnitude of the weekend effect**

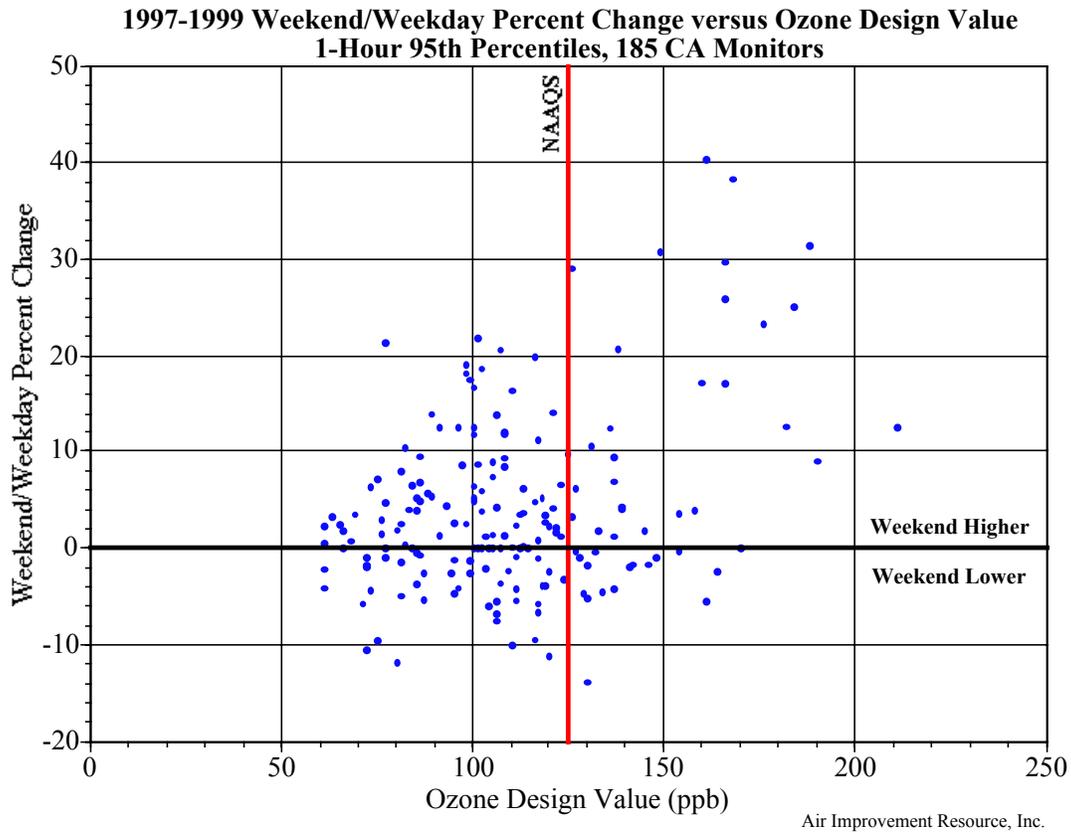
The ES correctly indicates that the weekend effect is real and that ozone increases of 25 to 32 % occur in key areas in spite of the fact that NO<sub>x</sub> emissions are decreased about 25 % on Saturday and 40 % on Sunday compared to midweek levels. The magnitude of the weekend effect throughout California is displayed in the following figures developed by AIR from the California ozone data in EPA’s AIRS database.

Figure 1 is a plot of 1997-1999 weekend-weekday ozone behavior versus the Design Value for 185 California sites. The weekend-weekday behavior that is plotted is the percent change in average weekend daily maximum 1-hour ozone concentrations compared to average weekday daily maximum 1-hour ozone concentrations. Note that there are a significant number of sites where the average weekend 1-hour ozone is between 10 and 30 % above the average weekday 1-hour ozone. Note also that there are no sites where the average weekend 1-hour ozone is below the average weekday by more than 10 %. Finally, note that there are a significant number of sites with demonstrably higher weekend ozone that also have design values for the federal 1-hour standard that exceed the standard.



**Figure 1**

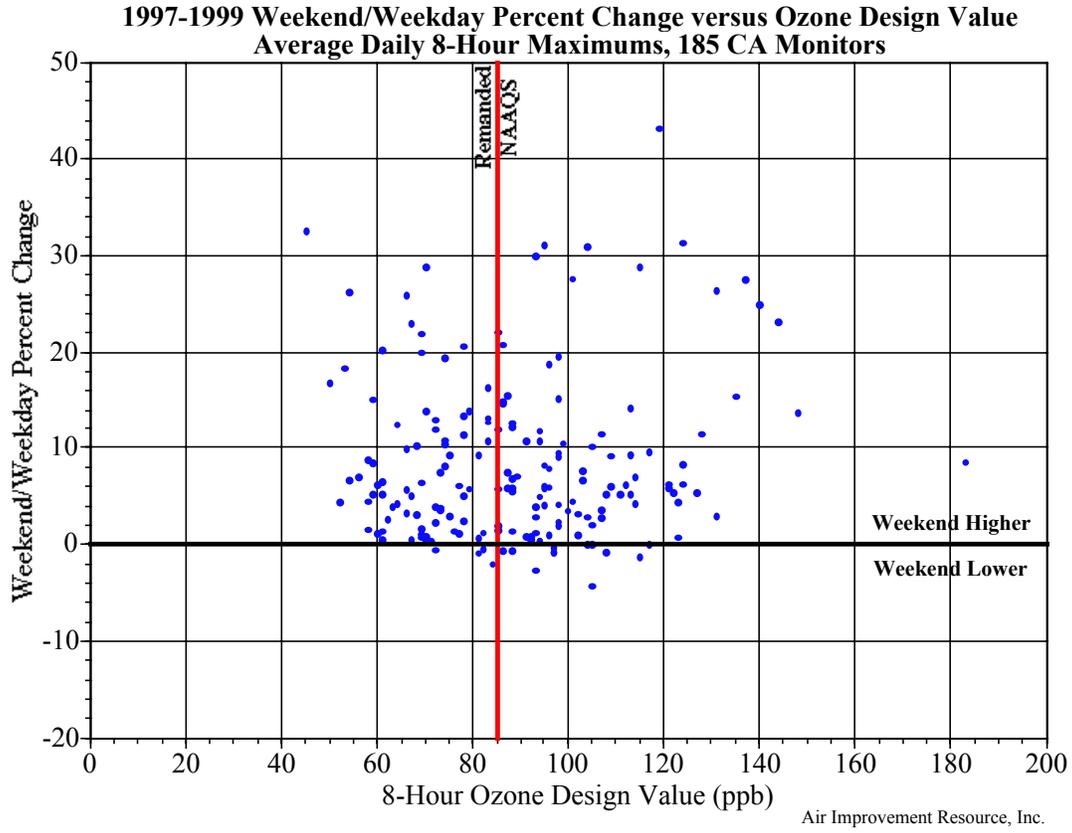
In Figure 2, the weekend-weekday behavior plotted is the 95<sup>th</sup> percentile of the daily 1-hour maxima. The 95<sup>th</sup> percentile was chosen to evaluate the weekend-weekday behavior for high ozone days. When compared with Figure 1, the results in Figure 2 are similar except that there is more vertical spread in the data. While there are more sites with lower 95<sup>th</sup> percentile ozone on weekends, some as much as 10 % lower, the number of sites with greater than 10 % higher 95<sup>th</sup> percentile ozone on weekends is unchanged and the maximum impact is now between 30 and 40 % increase. Note that the sites where peak ozone is substantially greater on weekends tend to have design values above the federal NAAQS.



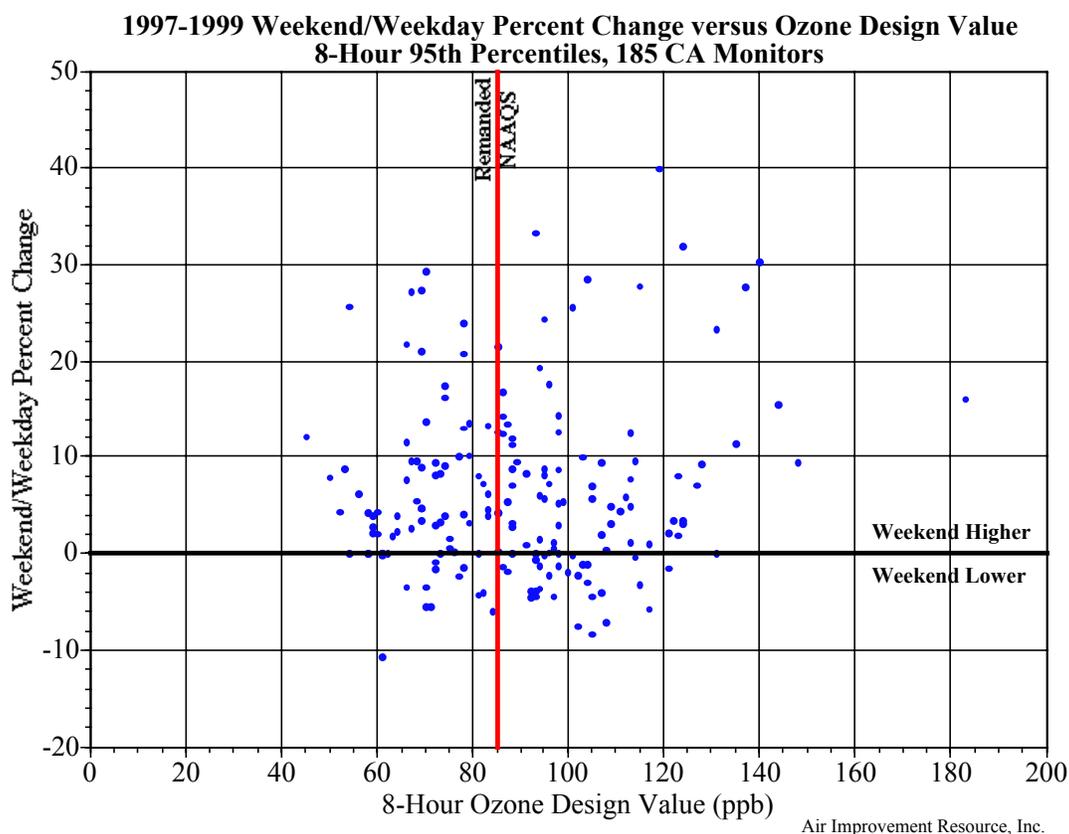
**Figure 2**

California has a state ozone standard of 0.09 ppm (or 90 ppb) for 1-hour. While the definition of the California ozone standard is slightly different from the definition of the federal 1-hour ozone standard, for the purposes of this display, the small difference can be ignored. Therefore, the sites to the right of a vertical line at about 90 ppb in Figures 1 and 2 are sites that exceed the California ozone standard. It is clear that higher weekend ozone is also a problem when sites that exceed the California standard are considered.

Figure 3 is a plot of weekend-weekday ozone behavior for the average daily maximum 8-hour ozone metric. Figure 4 is a companion plot for the 95<sup>th</sup> percentile 8-hour ozone concentration. The vertical lines in Figures 3 and 4 represent the now-remanded federal 8-hour ozone standard. If that standard survives the current judicial review, or if California sets an 8-hour ozone standard in the future, it is clear that higher weekend ozone will be an even greater concern for achieving any 8-hour ozone standard than it is for a 1-hour standard.



**Figure 3**



**Figure 4**

Several of the Findings in Chapter 3 of the SR are pertinent to our discussion of the causes of the weekend effect. In particular, Finding # 3 (that the ozone weekend effect is not static but changes with time so that ozone is now highest on Sunday throughout the Basin) is an important finding that may be useful in discriminating among potential causes. In addition, Finding # 4 (the effect tends to diminish at downwind locations) can also be an important discriminator. The combination of these findings indicates that the spatial extent of the weekend effect has grown substantially so that it now occurs at even far downwind sites as noted on page 3-3 of the SR.

#### **Comments on causes of the weekend effect**

In the section of the Executive Summary entitled “Why do some believe the ozone weekend effect implies that major reductions in NO<sub>x</sub> emissions will be counter-productive for reducing ozone,” the staff summarizes three points. First, that laboratory smog chamber experiments have demonstrated the NO<sub>x</sub> benefit-disbenefit behavior that varies as a function of VOC/NO<sub>x</sub> ratio. Second, that surface VOC/NO<sub>x</sub> ratios in the SoCAB are in the range expected to show a NO<sub>x</sub> disbenefit. The text then goes on to indicate that “if this complex air basin acts like a simple smog chamber, then reducing NO<sub>x</sub> emissions should (hypothetically) promote ozone formation.” Third, as discussed above, that periodic NO<sub>x</sub> reductions on weekends should mimic the steady NO<sub>x</sub> reductions from strategic regulations.

Next, the staff introduces other possible causes of the ozone weekend effect. These include the NO<sub>x</sub>-timing hypothesis, the carryover near the ground hypothesis, the carryover aloft hypothesis, the increased weekend emissions hypothesis, and the soot and sunlight hypothesis. After discussing each, the SR concludes that the increased weekend emissions hypothesis is not plausible and the carryover near the surface hypothesis is not likely to be an important factor. We agree; we will not discuss those any further.

For the remaining hypotheses that the SR indicates are plausible, we will provide additional comments. In each case, there are additional pieces of information that bear on the plausibility of the hypothesis and, therefore, need to be included in the SR and TSD.

### **Comments on NO<sub>x</sub> reduction hypothesis**

The presentation of the scientific basis for the NO<sub>x</sub> reduction hypothesis in the body of the SR does a reasonable job of explaining the hypothesis. However, the short version in the Executive Summary that is noted above leaves the impression that the basis is only “smog chamber” experiments and specifically states that “if this complex air basin acts like a simple smog chamber, then reducing NO<sub>x</sub> emissions should (hypothetically) promote ozone formation.” The synopsis of Hypothesis #1 on page 2-4, however, indicates that laboratory experiments and air quality models indicate that reducing NO<sub>x</sub>, under certain conditions, may lead to increased ozone. In fact, the basics of ozone formation that are represented in the ozone isopleths of an EKMA diagram are undergirded by more than 30 years of detailed laboratory studies of individual chemical reactions, smog chamber studies of both artificial and real atmospheric mixtures, the careful construction and testing of detailed chemical mechanisms, and numerous applications of atmospheric models that include representations of chemistry, meteorology, and transport. The air quality models that show this phenomenon include the models that are used in California’s SIP development. The basic chemistry is well-understood and accepted by the scientific community as evidenced by its pre-eminent place in the discussions of ozone formation in the 1991 National Academy of Sciences Ozone Report and the more recent NARSTO Ozone Assessment. Therefore, the SR and particularly the ES should be revised to acknowledge these facts.

To fully explain the chemistry of ozone formation, the explanation of NO<sub>x</sub>-ozone chemistry on page 2-5 should be expanded to include two additional key NO<sub>x</sub> reaction paths and the concept of the photo-stationary-state. The titration reaction of NO with ozone to form NO<sub>2</sub> as well as the class of chain-carrying reactions of NO with radicals to form NO<sub>2</sub> should be included. The two reactions already noted on page 2-5 show how NO<sub>2</sub> can both promote and inhibit ozone formation. The two major NO reactions noted above show how NO can both promote and inhibit ozone formation. Finally, the classic concept of the photo-stationary-state should be introduced. As explained in the 1991 National Academy Ozone Report, ozone at steady-state depends on the rate of NO<sub>2</sub> photolysis and the ratio of NO<sub>2</sub> to NO. In the absence of other processes that convert NO to NO<sub>2</sub>, the photolysis of NO<sub>2</sub> is balanced by the reaction of NO with ozone to re-

form NO<sub>2</sub> and ozone does not build up. When hydrocarbons are present, however, they participate in the chain-carrying reactions that convert NO to NO<sub>2</sub> without using up an ozone molecule. Thus, the amount and kind of hydrocarbons present determine the ratio of NO<sub>2</sub> to NO which, in turn, along with the light intensity determines the ozone concentration during daylight hours. In this complex chemistry the VOC/NO<sub>x</sub> ratio plays an important role and determines whether a given change in NO<sub>x</sub> will increase or decrease ozone.

The fundamental issue is not whether the NO<sub>x</sub>-disbenefit phenomenon occurs, but to what extent it occurs in various locations in California and to what extent other hypotheses may play a role in the ozone weekend effect. As documented in the SR and TSD, the NO<sub>x</sub> reduction hypothesis is plausible and is supported by a wide range of analyses that are consistent with it being the primary cause of the weekend effect. In fact, we are not aware of any of the analyses carried out to date that are not consistent with the hypothesis. We recognize, however, that some analyses and observations are consistent with multiple hypotheses. Because of the complexities of the chemistry and meteorology involved, air quality modeling is needed to distinguish the separate effects of the various shifts in activity and emissions from weekdays to weekends.

The SR indicates that measurements of VOC/NO<sub>x</sub> ratios are an indication of VOC-limited conditions, and notes that the weekday and weekend ratios in the SoCAB are consistent with this hypothesis. But questions are raised concerning the accuracy of the ratios and whether multi-hour average ratios determined by many air parcels affect daily maximum ozone. There are, however, independent analyses with observational indicators by Blanchard that show the extent of reaction at the time of peak ozone is consistent with the hypothesis in those areas with higher weekend ozone.

As noted in Figures 1 to 4 above, the magnitude and even direction of the weekend effect varies significantly across California. The SR indicates that “concentrations of ozone precursors seem to decrease on weekends almost everywhere.” (SR at page 1-3) A key issue that needs discussion in the SR is how the various hypotheses can explain these basic facts, including the changes in the weekend effect that have been observed. The atmospheric chemistry of ozone formation (the theory behind the NO<sub>x</sub> reduction hypothesis) can explain the presence of a large weekend effect in urban areas. It can explain why the effect is diminished downwind and reverses far downwind. It can also explain the growth in the spatial extent of the weekend effect. It is not clear to us how any of the other hypotheses can explain these differences.

Another key question that must be answered by this hypothesis is how ozone can be going down on both weekdays and weekends if NO<sub>x</sub> reductions can increase ozone. If the local chemical conditions are in the VOC-limited regime (above and to the left of the ridge line in Figure 2-1), equal reductions of VOC and NO<sub>x</sub> will continuously reduce ozone. However, NO<sub>x</sub> reductions, by themselves, increase ozone. The draft report of DRI/STI’s retrospective analysis of ambient data used an EKMA diagram in this way to show how the chemical state of the SoCAB had changed over the years. They indicated that the VOC and NO<sub>x</sub> program had put the basin more into the VOC-limited

regime (by reducing VOC somewhat more than NO<sub>x</sub>) so that the NO<sub>x</sub>-focused shift to weekends now increases ozone more broadly than before. As noted above, accurate long-term VOC data are not available. However, there are other data that corroborate this general view of what has occurred in the basin. Specialized studies that report VOC/NO<sub>x</sub> ratios and ambient trend data for individual air toxics (that are present in vehicle exhaust) indicate that VOC concentrations have been dramatically reduced over the past 35 years and VOC/NO<sub>x</sub> ratios are lower than in the past. ARB should fully evaluate these sources of data.

### **Comments on NO<sub>x</sub>-timing hypothesis**

While there are differences in the timing as well as the magnitude of emissions between weekdays and weekends, it is unlikely that the timing differences will be able to explain the weekend effect. The ES indicates:

“The timing difference is potentially important because laboratory experiments indicate that NO<sub>x</sub> emitted later in the day can produce ozone more efficiently.”

The example discussed in the SR at page 2-7 to illustrate the effect of timing on NO<sub>x</sub> efficiency comes from Fig. 4 of Hess et al. 1992. However, the experiment (267L) that was adapted to develop Figure 2-2 had an initial VOC/NO<sub>x</sub> ratio of 51. In another experiment with an initial VOC/NO<sub>x</sub> ratio of 16.8, the rate of ozone production was decreased when NO was injected. ARB was aware that the experiment at a ratio of 51 is not applicable to the SoCAB. The TSD indicates:

“When applied to the ozone weekend effect in the SoCAB, the experiments by Hess et al. have a potentially important drawback. The experiments used initial VOC/NO<sub>x</sub> ratios from 15 to 50. In the SoCAB, measured VOC/NO<sub>x</sub> ratios at the surface are generally between 5 and 10.” TSD at page 6.1-14.

This is not just a potentially important drawback, it is a major flaw in the interpretation and use of the Hess et al. experiments. The discussion of the NO<sub>x</sub>-timing hypothesis should be modified to incorporate this caveat and, therefore, highly qualify the degree of plausibility of the hypothesis

In addition, the results from a series of more pertinent experiments should be added to the discussion. Kelly has carried out numerous captive air irradiations in downtown Detroit, suburban Detroit, Houston and two locations in the SoCAB.<sup>1</sup> These are outdoor

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<sup>1</sup> N. A. Kelly, “Characterization of fluorocarbon-film bags as smog chambers,” *Environ. Sci. Technol.*, **16**, page 763, 1984; N. A. Kelly, “Ozone/precursor relationships in the Detroit Metropolitan Area derived from captive-air irradiations and an empirical photochemical model,” *J. Air Pollut. Control Assoc.*, **35**, page 27, 1985; N. A. Kelly, “An analysis of ozone generation in irradiated Houston air,” *J. Air Pollut. Control Assoc.*, **31**, page 565, 1981; N. A. Kelly, “Captive air irradiations in Houston, Texas,” Paper No. 80-50.6, presented at the 73<sup>rd</sup> Air Pollution Control Association Annual Meeting, Montreal,

smog chamber experiments that use natural sunlight and ambient temperatures and in which ambient air is the primary source of reactants. By operating several chambers simultaneously and by diluting the ambient mixture with clean air or by adding either VOC or NO<sub>x</sub> to different chambers, the effects of emission reductions as well as varying the VOC/NO<sub>x</sub> ratio can be determined. When Kelly conducted such experiments in rural and remote areas, the photochemistry was NO<sub>x</sub>-limited as expected. However, in the urban areas, the photochemistry was VOC-limited and NO additions reduced ozone formation. At several locations, Kelly also filled the chambers at several different times to determine the impact of timing on the ozone formation potential of the mixtures. In suburban Detroit as well as in Houston, the earliest captured mixture produced by far the most ozone. These experiments are important because they were conducted in metropolitan areas that have higher ozone on weekends throughout the area (Detroit) as well as just in portions of the area (Houston). While they do not exactly mimic the NO<sub>x</sub>-timing changes in the atmosphere, they do suggest that the photochemical potential of precursors emitted later in the day is reduced rather than increased as posited by the NO<sub>x</sub>-timing hypothesis.

Because of the complexities of ozone formation, photochemical modeling is required to fully evaluate the NO<sub>x</sub> timing hypothesis. The ENVIRON proximate modeling can be used to evaluate traffic-induced NO<sub>x</sub> changes. The activity data in the TSD suggests that there are two parts to the NO<sub>x</sub>-timing changes. First, heavy-duty truck activity and NO<sub>x</sub> emissions are expected to be substantially reduced during all hours on weekend days. Second, car and light truck activity is shifted in time because of the greatly reduced morning commute on weekend days. Since these two categories have different activity patterns and have different regulatory requirements, the modeling should evaluate the activity shifts both separately and in combination.

### **Comments on carryover aloft hypothesis**

This hypothesis assumes that carryover aloft occurs on all days of the week, but that carryover exerts a greater influence on weekends. In both cases, the hypothesis suggests that morning concentrations of NO<sub>x</sub> titrate ozone and quench radicals. However, the higher weekday concentrations of NO<sub>x</sub> do more to reduce ozone and radicals so that they have little effect on surface concentrations. On weekends, according to this hypothesis, carryover ozone and radicals are not quenched as much and thereby cause higher surface ozone concentrations. The interactions between chemistry and meteorology that involve carryover aloft are complex. In addition, carryover in the SoCAB is more complex than in other locations because of the

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Quebec, Canada, June 1980; N. A. Kelly, "Photochemical ozone formation in outdoor smog chambers and its sensitivity to changes in precursors at a suburban Detroit site," in Wolff G. T., Hanish J. L. and Schere K. L.(editors), "The Scientific and Technical Issues Facing Post-1987 Ozone Control Strategies, Air Pollution Control Association, Pittsburgh, PA, pages 110-123, 1988; N. A. Kelly and R. F. Gunst, "Response of ozone to changes in hydrocarbon and nitrogen oxide concentrations in outdoor smog chambers filled with Los Angeles air," *Atmos. Environ.*, **24**, Part A, page 2991, 1990.

presence of land-sea breezes and mountains. Additional data on the composition of layers aloft would be helpful, but existing models can be applied now to determine the sensitivity of ground-level ozone to the relevant parameters.

We have three additional comments on this hypothesis-two that relate to its plausibility and one that relates to the implications of the hypothesis for regulatory NO<sub>x</sub> reductions. First, the premise for this hypothesis, that ozone carryover is the same from day-to-day but ground-level NO<sub>x</sub> emissions are different on weekdays and weekends is not correct. In reality in the SoCAB, peak ozone levels during mid-day when the atmosphere is well-mixed are now highest on Sunday. This means that the ozone available for carryover is not the same from day to day. Since ozone, on average, is lower on Mondays than on Sundays, the carryover of ozone from Sunday to Monday, on average, is substantially greater than the carryover of ozone from Monday to Tuesday. Since the morning NO<sub>x</sub> emissions on Monday and Tuesday are comparable, the impact of different levels of carryover can be compared by evaluating the levels of ground-level ozone on Monday and Tuesday afternoon. These levels are similar, which argues that carryover is not a dominant factor in determining mid-afternoon ozone levels.

Second, if the carryover hypothesis is correct, it should be able to explain the spatial extent of the weekend effect. The hypothesis would predict that ozone should be higher on weekends at all sites with significant weekday NO<sub>x</sub> emissions and the same on weekdays and weekends at sites with little or no NO<sub>x</sub> emissions. The data, however, indicate that there are urban sites in the southeast U. S. (with high biogenic emissions) and rural sites where ozone is lower on weekends. This suggests that VOC/NO<sub>x</sub> chemistry rather than carryover is the primary cause of the weekend effect.

Finally, if the carryover aloft hypothesis is true, the NO<sub>x</sub> reduction program over the past several decades has made NO<sub>x</sub> become more efficient at making ozone on weekdays as well as on weekends. And importantly, future NO<sub>x</sub> reductions will make NO<sub>x</sub> more efficient at making ozone on both weekdays and weekends. Thus, if this hypothesis is true, the impact of carryover has been to reduce the benefits from NO<sub>x</sub> emission controls. As such, the implication of this hypothesis for regulatory NO<sub>x</sub> reductions is the same as for the NO<sub>x</sub> reduction hypothesis. In either case, less NO<sub>x</sub> means more ozone. So if further study supports this hypothesis as a significant cause or the primary cause of higher weekend ozone, the policy implications are that NO<sub>x</sub> reductions should be either avoided or approached cautiously.

### **Comments on soot and sunlight hypothesis**

This hypothesis fits in the general category of anthropogenic changes that might affect ozone by influencing the meteorological variables that affect ozone formation. Changes in light scattering or absorption that affect solar radiation and, thereby, NO<sub>2</sub> photolysis or changes in temperature that influence other chemical reactions fall in this category. While the soot and sunlight hypothesis is plausible as a factor that would increase ozone on weekends, analyses carried out for ARB in an earlier study indicate that solar radiation is not significantly higher on weekends. In addition, the earlier analyses found

that there is a small temperature decrease on weekends that, by itself, could reduce ozone formation on weekends by from 5 to 10 ppb. These earlier analyses are discussed in more detail below. On balance, the measured changes in meteorological variables are too small to account for the weekend effect and, if anything, may cause lower ozone formation on weekends.

In addition, because soot levels have been decreasing in California, the difference between weekday and weekend soot levels is also becoming smaller. Thus, the magnitude of any soot and sunlight effect has been getting smaller over time. This is inconsistent with the increase in the strength and spatial extent of the ozone weekend effect. Finally, since soot levels are forecast to continue decreasing, the effect will continue to get smaller in the future. For these reasons, the soot and sunlight effect should be put in the category of plausible but not likely to be a significant factor.

One of the objectives of the UCLA study (Blier and Winer, 1999) discussed on page 1-7 was:

“To investigate, for the first time in the SoCAB, whether anthropogenic influences, for example, heat island effects and vehicle use patterns (and their resulting particulate emissions), cause differences between SoCAB micrometeorology on weekend days vs. weekdays.” Blier and Winer, 1999 at page 1-2.

Blier and Winer evaluated weekday/weekend temperature differences in 5 years of data from 11 sites for the 3-month interval June 15 to September 15. They evaluated temperatures at four times of day. They concluded:

“In 85 of the 88 cases examined, the weekday temperature was warmer than the weekend temperature. It thus appears there may have been a small difference in temperature between weekdays and weekend days that could be associated with anthropogenic influences.”

The temperatures on weekdays averaged 0.6 to 0.7 degree F higher than on weekends. These small differences were not statistically significant. In addition, Blier and Winer concluded that the small magnitudes of the temperature differences suggest that any feedback on SoCAB air pollution levels will be exceedingly small. However, they did not estimate that impact. Based on earlier work by Blier and Winer and others, however, the impact would not be exceedingly small.

In their 1996 report to ARB, Blier and Winer evaluated the surface meteorological conditions on high ozone days versus average ozone days. They found that the average maximum surface temperature at all (except one) of the monitoring stations with temperature data was 9 degree F or more higher on the high ozone days. They concluded that surface heating was a significant feature associated with daily peak ozone levels. The association of high ozone with high surface temperatures has been reported by others. The U. S. EPA's July 1996 Criteria Document for Ozone

summarizes a number of studies of the relationship between peak ozone and temperature. At several eastern U. S. urban sites, the rate of increase is 2 to 5 ppb per degree F. The CD also indicates that Kelly and Gunst<sup>1</sup> report a linear relationship between maximum ozone and temperature in outdoor captive air experiments conducted in the SoCAB. In Kelly and Gunst's experiments, the rate of increase was 10.5 ppb/degree F. This is in good agreement with the temperature effect Blier and Winer had in their comparison high and average ozone days. They report an average 11 or 12 degree F difference at various sites in the high ozone areas of the SoCAB between 28 days that averaged 150 ppb peak ozone and 28 days that had peak ozone between 250 and 330 ppb. Assuming a linear relation as found by Kelly and Gunst, the rate observed by Blier and Winer was 8 to 16 ppb/degree F. For the weekend decrease of 0.6 to 0.7 degree F reported by Blier and Winer 1999, the resulting ozone decrease would be 5 to 10 ppb. This is not an "exceedingly small" impact. And, importantly, it is opposite in direction to the ozone increases observed on weekends.

Blier and Winer (1999) also looked for a day-of-the-week signal in relative humidity and visibility data. No day-of-the-week signal was evident for relative humidity. Although there was some evidence of a day-of-the-week signal in visibility, the results were not statistically significant. In their conclusions, they indicate:

"There was a slight tendency for lower visibility days to occur most often on Friday and Saturday at Azusa during the period 15 June to 15 September 1992-94." Blier and Winer, 1999 page 8-3

Finally, Blier and Winer evaluated day-of-the-week variation in solar radiation intensity. SCAQMD solar radiation data were available for 1994-1996 from Azusa, Pico Rivera, LA-North Main and Upland. As an initial analysis, they chose to investigate the observations from Pico Rivera. As in the temperature analysis, they evaluated the observations at four times of day. They concluded:

"At Pico Rivera, the mean radiation intensity was found to be slightly lower on weekdays (Tuesday/Wednesday) than on weekend days (Saturday/Sunday) for each of the four hours examined, however, the result was not statistically significant..." Blier and Winer, 1999 page 8-3

The results reported in Table 5-12 of Blier and Winer indicated weekend solar radiation intensity was 1.3 % higher at 1100 PST and 1.5 % higher at 1400 PST. Because the magnitude of the effect was so small and not statistically significant, the authors did not bother to evaluate radiation intensity at the other sites where data was available. On balance, Blier and Winer found small differences in a number of meteorological variables none of which were statistically significant and some of which would tend to offset one another.

While expanded measurements and analyses can never do any harm, it is extremely unlikely that the soot and sunlight hypothesis will be able to explain any significant

fraction of the weekend effect. In addition, any research program should evaluate temperature effects that would tend to offset the soot effects.

### **Comments on control of NO<sub>x</sub> for other purposes**

The ES properly notes that secondary products of NO<sub>x</sub> emissions contribute to ambient levels of several pollutants. Of these products, NO<sub>2</sub> and particulate nitrate are of concern because there are air quality standards that limit their presence in the atmosphere. In the case of NO<sub>2</sub>, both the federal and California air quality standards have now been attained in the SoCAB (as well as throughout California) so further reductions in NO<sub>x</sub> to reduce NO<sub>2</sub> would be counter-productive if they increase ozone. In the case of particulate nitrate, the standards are PM<sub>10</sub> standards. Although there is not a specific standard for nitrate, nitrate is a substantial contributor to overall PM levels. Conclusion # 3 of the SR includes the statement:

“NO<sub>x</sub> reductions are almost certainly beneficial in reducing concentrations of some other pollutants such as PM-nitrates, nitrogen dioxide and PAN.” SR at page 4-2

The discussion of conclusion # 4 includes the statement:

“Not surprisingly, nitrate concentrations tend to be lower on weekends compared to weekdays.” SR at page 4-4

These statements, however, are not supported by the material in the TSD or in the Findings section of the SR. One of the bullet points in Finding # 14 is:

“Some day-of-week comparisons of particulate matter concentrations are difficult to interpret. For example, measured PM<sub>10</sub>-nitrates in the SoCAB can be lowest on a mid-week day in some locations. No simple explanation in terms of source strengths, atmospheric chemistry, or meteorology is readily available.” SR at page 3-9

More to the point is the discussion of PM in the TSD. That discussion first indicates that nitrate shows a strong spatial variation with low concentrations at coastal locations and high concentrations at inland locations. However, the TSD goes on to indicate:

“Dichot-PM<sub>2.5</sub>, SSI-nitrate, and SSI-sulfate are virtually the “same” for all days of week.” TSD at page 3.1-8

The reason for similar nitrate levels on weekends when NO<sub>x</sub> concentrations are reduced is addressed in the conclusions of Section 3.1 of the TSD. That section notes that the formation of secondary particles (such as nitrate) from precursors:

“...is a complex non-linear process so we should not expect to see a one-to-one relationship between precursor emissions and ambient secondary PM concentrations.” TSD at page 3.1-8

The text goes on to point out:

“...there are several factors influencing the relationship between NOx emissions and particulate nitrate concentrations, which might act to reduce the impact of decreases in weekend NOx emissions on ambient 24-hour average nitrate concentrations. For example, photochemical conditions that lead to higher ozone on weekends may also increase the fraction of NOx that is converted to nitric acid and particulate nitrate.” TSD at page 3.1-8

Thus, the conclusions and summary sections of the SR fail to inform the reader that (1) nitrate is not substantially lower on weekends, and that (2) the likely reason is that the higher photochemical activity on weekends (as evidenced by ozone formation) is increasing the rate of nitrate formation. The important policy implication that should be provided to the reader is that reducing NOx may not necessarily reduce nitrate concentrations if it also increases ozone formation.

## Summary

The October 2000 Draft Staff Report and Technical Support Document do a good job of establishing the existence and magnitude of the ozone weekend effect. The ARB analyses also document the reduced vehicle activity and precursor concentrations that accompany increased ozone levels on weekends. The draft documents also do a good job of laying out several hypotheses for explaining the weekend effect. However, as documented above, additional information and analysis can reduce the number of plausible hypotheses so that they can be evaluated with photochemical modeling in the near future. Based the discussion in the body of these comments, several of the statements and conclusions in the Staff Report need to be revised.

For each hypothesis, several expectations are listed. It would be more appropriate to start with the findings (from ARB and other current analyses) and evaluate the hypotheses against all the findings. In this way, we believe the number of plausible hypotheses will be reduced.

**Comments by Air Improvement Resource, Inc. on new material  
(Chapter 6 and sub-chapters of Chapter 8)  
presented in the Air Resources Board  
November 2001 Draft Technical Support Document  
“The Ozone Weekend Effect in California”  
December 14, 2001**

**Comments on Chapter 6**

There are several misleading arguments made in this chapter. First, it is implied that using models to study the cause(s) of the weekend effect is more difficult than other applications of photochemical models when it is stated that the ozone weekend effect involves small changes in ozone and large, transient changes in emissions. However, the changes in ozone associated with the weekend effect are not small (on average, the peak ozone concentration in Pomona on Sundays in 1997-99 was 25 ppb higher than the average peak on weekdays; the SR at page 4-1 indicates that weekend ozone is 30% higher in the South Coast and 25 % higher in San Francisco Bay area). In particular, they are not small compared to how models are used in an AQMP attainment demonstration where ppb differences above or below the standard are important. In addition, simulations for attainment demonstrations have to deal with large transient changes in biogenic emissions because biogenic emissions respond strongly to changes in sunlight and temperature.

Second, it is argued that modeling the weekend effect “calls for a more detailed performance evaluation than is common, to diagnose potential problems in the inventory and to ensure that the model is properly simulating the relevant physical processes.” Further, the text indicates that “to resolve the contributions of several factors successfully, a model’s performance analysis should show the model is appropriately sensitive to changes in the plausible contributing factors,” and that “a complete performance evaluation for modeling the ozone weekend effect should include assessments of the model’s sensitivity to each of the hypothesized factors.” This chapter confuses application of the model to determine causes of the weekend effect with performance evaluation of the model. The performance analysis or evaluation cannot show “appropriate sensitivity” to changes in the plausible contributing factors because (1) we do not know, a priori, what the sensitivity should be, and (2) we are using the model to determine the sensitivity. As we use the model to determine the sensitivity to the individual factors, there are no atmospheric measurements with which to compare. A simulation of all the (emissions and possibly meteorological) changes associated with the weekend effect could, theoretically, be compared with specific weekend observations, but that, while useful, would not help resolve the contribution of the individual factors.

Photochemical models are, however, uniquely situated to separate the effects of possible causal factors. As the initial ENVIRON proximate modeling shows, the model can evaluate specific hypotheses (in this instance mass or timing changes) holding everything else constant. The ARB has already indicated that two of the six hypotheses

are not plausible, so that reduces the number of possibilities to four. As indicated above, there is evidence in the South Coast that there is a small reduction in UV and a small reduction in temperature on weekends. Changes of this magnitude can be simulated in the models. The fourth hypothesis, carryover aloft, is not a direct change of model inputs from weekdays to weekends, but it is a hypothesis that can be evaluated with the models.

The chapter argues that modeling the weekend effect calls for a more detailed performance evaluation than is common. We would argue that that is not the case. In applying the model in an attainment demonstration, the model is being used to make decisions on the reduction in VOC and NO<sub>x</sub> emissions in order to predict either absolute ozone concentrations within a ppb or so or relative reductions within a percent or so. The resulting control strategies and regulations cost literally tens or hundreds of millions of dollars or more. For understanding the weekend effect, the model must be able to discriminate hypotheses that can increase ozone formation from strategies that can't and then give a rough idea of the contributions of the various hypotheses that can increase ozone. So the model is being used to discriminate between the direction of effects and to give a rough, not a precise, idea of the magnitude of the effects. We would submit that this is a less rigorous application than an attainment demonstration.

In both types of applications, of course, we would want to conduct as rigorous a performance evaluation of the modeling system as possible. In the current AQMP update, various modeling systems, chemistry modules, episodes, and emission inventories are being evaluated to choose the best combination for the AQMP update. The evaluation of the base case performance for the various combinations will be used to choose the base case modeling platform for the AQMP update. Because of this effort, the ARB has a wide range of modeling tools and input data bases available with which to evaluate the hypotheses for the weekend effect. When the issue of diesel traps increasing the fraction of NO<sub>2</sub> in exhaust arose recently, ARB quickly used several models, chemistry modules, and episodes to evaluate increases in ozone and nitric acid that might be associated with a regulation that reduced diesel particulate matter. It would be straightforward for ARB staff to evaluate the NO<sub>x</sub> reduction and NO<sub>x</sub> timing hypotheses in several modeling systems to compare with the ENVIRON study. The sensitivity to various carryover aloft assumptions could also be evaluated; however, this is not as important, because, as noted earlier, the regulatory implications of the carryover aloft hypothesis are the same as those of the NO<sub>x</sub> reduction hypothesis.

The bulk of Chapter 6 is a discussion of four issues that staff indicates should be carefully considered during model application for the weekend effect. Each is discussed below. However, a common comment on each issue is the fact that it is an issue for all performance evaluations not just weekend effect studies.

**Weekend emission inventory.** Emission inventory issues, like poverty, will always be with us. However, weekend inventories are being developed for the South Coast AQMP update because there are weekend days in the episodes being considered and because the highest ozone now occurs on Sunday. It is possible, even likely, that the

weekend days will be the controlling days in the AQMP update. Therefore, the ARB and SCAQMD cannot wait for several years for a weekend inventory. In fact, when the weekend issue first surfaced in the 1994 AQMP, the South Coast District did a quick sensitivity test and showed that reduced emissions simulating a weekend could increase ozone levels. As noted above, the weekend inventory used for weekend effect studies need not be as accurate as the weekend inventory for the AQMP.

In fact, the traffic data reported by ARB and STI and the other activity data gathered by STI can be used to develop an initial base case weekend inventory. For the categories of emissions where there are still questions, sensitivity analyses can be used to bound the possibilities. As noted below, most of these categories are either quite small or are expected to have lower emissions on weekends.

**Performance of chemical mechanisms.** Questions of how to develop chemical mechanisms, how to validate mechanisms and which mechanism to use are also not specific to the weekend effect. Issues related to accurate performance at low NO<sub>x</sub> apply equally to the simulation of future weekdays as well as current or future weekends. The text implies that ozone modeling with a mechanism other than SAPRC-99 is suspect. Is that the staff position? Does the staff believe that the many modeling analyses in the literature of global and regional background ozone are, therefore, suspect because they did not use SAPRC-99 or because they are simulating such low NO<sub>x</sub> conditions that it is impossible to verify their predictions with laboratory experiments? How was SAPRC-99 thoroughly validated? What experiments from what laboratories were used to develop the mechanism? Then what other experiments from how many other laboratories were used to validate it? What are the uncertainties associated with these experiments and the mechanism? We ask these questions not to demean the development of SAPRC-99 in any way, because it may be the best available mechanism, but to point out that there are many ozone formation mechanisms in use throughout the world and that they all contain the inorganic nitrogen chemistry that leads to NO<sub>x</sub> disbenefits under some conditions and NO<sub>x</sub> benefits under other conditions. The rates of the individual chemical reactions underlying the duality of NO<sub>x</sub> effects have been established over the years in many laboratories around the world. Finally, modelers of the weekend effect can use several state-of-the-art mechanisms to evaluate the impact of chemical mechanism on the result.

**Model performance when simulating air quality aloft.** This is an issue for all performance evaluations and is no more important for the weekend effect than for AQMP attainment demonstrations.

**Model performance in establishing the initial context for each day.** This section ends with the claim that the modeling of weekends requires special attention to the fidelity of the concentration fields on Saturday and Sunday morning. However, it is not obvious that the early morning conditions should be more important than conditions later on the day on weekends.

**Conclusions and recommendations.** The text indicates that these four issues require special attention when modeling the weekend effect and that appropriate criteria could be significantly tighter compared to the criteria that are suitable for most other modeling studies. We disagree. As noted above, the study of the weekend effect is looking for directional changes resulting from emission changes and the relative magnitude of different emission, timing, and meteorological effects postulated to explain the weekend ozone changes. Therefore, modeling the weekend effect is a less stringent, less stressful application of a model than attempting to predict the absolute ozone concentrations corresponding to a specified set of emissions, which is what is done in attainment demonstrations.

If there is poor model performance so that an important factor is overlooked in modeling the weekend effect, there is very little downside risk since the modeling is not being used to make regulatory decisions. Decisions on regulatory controls are made in the AQMP process. On the other hand, if an important factor is overlooked due to poor model performance in an attainment demonstration, the plan may not have the intended effect and air quality may not improve as fast as possible or may worsen. Therefore, the performance criteria for attainment demonstration modeling should be tighter than for sensitivity analyses used to model possible causes of the weekend effect.

We are concerned that the chapter appears to have been written to provide reasons for ARB to raise the bar so that staff can ignore the results of the proximate modeling and delay ARB's own modeling of the weekend effect. The ramifications of this choice are not attractive. NO<sub>x</sub> controls that are, on balance, counterproductive may be adopted without ever being carefully evaluated. This could lead to higher ozone and nitrate exposures as well as higher costs for California citizens than otherwise necessary. . . Importantly, if, in several years, ARB's modeling of the weekend effect confirms the massive data that demonstrate the existence of NO<sub>x</sub> disbenefits, the ARB and industry may be locked into a less than optimum path to clean air. At that point it may be impossible to change the direction of the control strategy. On the other hand, if the staff acknowledges the importance of the NO<sub>x</sub> reduction hypothesis and the existence of NO<sub>x</sub> disbenefits in portions of California, no changes in actual emission controls will occur until they are carefully evaluated in attainment demonstrations.

To determine the policy implications of the weekend effect, we don't need complete understanding of the exact contributions of the various possible causes, as suggested in the SR. If it is established that NO<sub>x</sub> reduction is a significant contributor, then it is clear that future NO<sub>x</sub> reductions should be carefully evaluated in ozone and PM modeling of both weekdays and weekends to determine the extent of NO<sub>x</sub> disbenefits and the trade-offs associated with further NO<sub>x</sub> controls. We submit that it has been established that NO<sub>x</sub> reduction is a significant contributor and that, therefore, the ARB should change its policy so that the specific benefits and disbenefits of NO<sub>x</sub> control be evaluated in each AQMP update including the updates currently underway.

### **Comments on Chapter 8**

Although the mix of studies summarized in this chapter includes studies that have been completed, studies that have been completed in part, and studies that have not yet been begun, the presentation format is the same. For studies where there are results, the results should be summarized and, most importantly, the findings and their implications should be integrated into the appropriate sections of the SR. For the studies that were presented and discussed at the October 23, 2001 Work Group meeting, reports are being prepared. The findings in these studies must be integrated into the SR before the material is presented to the Board. As noted in earlier sections, the ENVIRON proximate modeling and the Envair analyses of weekday/weekend differences in various nitrogenous products have important findings and implications. In addition, the DRI and STI studies provide important confirming information that needs to be considered in drawing conclusions.

**ENVIRON Presentation** One particularly important aspect of the ENVIRON modeling is the fact that the simulations presented in October separated the effects of a reduction in NOx mass from a change in NOx timing. This is a direct test of the first two hypotheses in the SR in a modeling system and for an episode that shadows the Air Quality Management Plan update that is now in progress. The simulations changed only the highway vehicle inventories in ways that mimic the weekend changes, but with separate simulations for the NOx mass change and the NOx timing change as well as a simulation of the combined changes. The results clearly show that the mass change increases ozone over a wide portion of the South Coast while the timing change has a much smaller impact. ENVIRON is carrying out additional simulations to address other hypotheses and questions that have been raised in the Work Group and in the draft ARB material. The results of these simulations will be presented at the January 23, 2002 meeting of the Work Group; when available, they should be summarized in the TSD and their implications for understanding the causes of the weekend effect should be discussed in the SR.

The 10/23/01 ENVIRON figures that compare the diurnal patterns of simulated precursors and ozone in Azusa from the combined changes with the observations in Azusa as documented by Fujita et al. have two important implications. First, the comparison indicates that the predictions from the modeling system compare favorably with observations in terms of the diurnal patterns of both precursors and ozone and in terms of the changes occurring from weekdays to weekends. Second, the comparison suggests that the changes in the on-highway motor vehicle inventory are the dominant factor in the weekend effect. This, in turn, suggests that considerations of the balance or ratio between emissions of VOC and NOx from the on-highway fleet are as important as considerations of the overall magnitude or level of emissions in reducing ozone exposures in the South Coast and other major urban areas in California.

There is another result from the ENVIRON work presented in October that is particularly relevant. The simulation of mass-only changes is a simulation of mass changes on a weekday in the South Coast. It is a direct sensitivity test of a NOx-focused mass change on weekdays in the South Coast. As such, it does not depend on the ability to

model weekends. The fact that a reduction of 67 tons per day of VOC and 300 tons per day of NO<sub>x</sub> on one day and 132 tons per day of VOC and 414 tons per day of NO<sub>x</sub> on a second day (with weekday activity levels and patterns) can increase ozone dramatically over a major portion of the South Coast on both days is a strong confirmation of the NO<sub>x</sub> reduction phenomenon. Although it is referred to in the document as a “hypothesis,” there is ample data in the literature, as acknowledged by the 1991 National Academy ozone study and the 2000 NARSTO ozone study and in the SR, to state that the phenomenon exists. It is important to note that the base weekday inventory in the simulation was developed by ARB, and that the base case performance<sup>1</sup> is as good or better than previous simulations of the South Coast.

One potential criticism of the ENVIRON study is that it evaluated a two-day change in emissions rather than a continuous change over the episode. However, there are many simulations of ozone in the South Coast and elsewhere that have evaluated continuous changes and reported increases in ozone from reductions in NO<sub>x</sub>. Recently for example, Chock et al.<sup>2</sup> report that NO<sub>x</sub> disbenefits are prominent in the ozone isopleths developed for a 1987 episode that has been used for the AQMP. They report that NO<sub>x</sub> disbenefits occur in isopleths for both 1-hour and 8-hour ozone responses.

Because of the well-known dual nature of NO<sub>x</sub> effects, many investigators have evaluated the sensitivity of VOC and NO<sub>x</sub> reductions and some have developed isopleth diagrams for the response of ozone concentrations to precursor changes. For example, in a 1983 paper, Roth et al.<sup>3</sup> evaluated the sensitivity to VOC and NO<sub>x</sub> reductions in the South Coast and concluded that VOC emission reduction was an effective means of reducing peak ozone and that NO<sub>x</sub> reductions imposed in addition to VOC reductions would be counterproductive in reducing peak ozone concentrations. In 1992, Wagner, Wheeler, and McNerny<sup>4</sup> of the ARB staff evaluated the effect of emission inventory uncertainty on the sensitivity of emission reductions for one of the SCAQS episodes in the South Coast. Wagner et al. thoroughly evaluated a factor of three increases in the VOC inventory and 25 % changes in the NO<sub>x</sub> inventory, developing many isopleth diagrams as part of their study. Although the sensitivity of ozone to precursor changes was affected by the uncertainty in the inventories, the authors concluded that the uncertainty did not affect the relative direction of the sensitivities and that “at current NO<sub>x</sub> emission rates, reductions in NO<sub>x</sub> emissions consistently cause peak ozone and exposure to increase and reductions in VOC emissions consistently cause peak ozone and exposure to decrease.” During the development of the 1994 AQMP for the South Coast, the City of Los Angeles initiated a study to evaluate alternative ozone attainment plans that could be more cost-effective and more feasible to achieve. O’Donnell, et al.<sup>5</sup> developed isopleth diagrams for peak hourly and 8-hour ozone concentrations as part of that work that showed NO<sub>x</sub> disbenefits. Thus, there are many ozone simulations of the South Coast that have reported NO<sub>x</sub> disbenefits from continuous emission reductions that are similar to the ENVIRON weekday simulations.

The question of whether one would expect a difference between the response to a two-day change in emissions and the response to a continuous change over an episode is amenable to study with atmospheric models. It is basically a question of the carryover

or memory of the system. As noted earlier, Blier and Winer in a 1999 report for ARB indicated that the lifetime of NO<sub>x</sub> is relatively short. Moreover, to negate the NO<sub>x</sub> disbenefit, any effect would have to be major and in some way change the direction of the model's response not just the magnitude of the response.

**Envair Presentation** In addition, to the results of the Envair analysis discussed earlier, Envair's analysis shows (using basic atmospheric photochemistry) how nitrate and PAN as well as ozone show similar response functions to precursor emission reductions -- with a regime of VOC-limited responses, a regime of NO<sub>x</sub>-limited responses, and a ridge of maximum photochemical activity and product formation between the other two regimes. While the shapes of the isopleths and orientation of the ridge line may vary between pollutants and vary with meteorology, this fundamental chemistry explains how ozone and PAN can be increased on weekends while nitric acid and nitrate are essentially unchanged in the face of reduced emissions of NO<sub>x</sub> in a VOC-limited region.

**DRI Presentation** The Fujita et al. measurement program shows how gasoline and diesel vehicles can be treated as separate NO<sub>x</sub> sources. When this is done with the ambient observations collected in their field study, the apportionment of NO<sub>x</sub> between the two categories and from weekdays to weekends is essentially in agreement with the emission inventory.

**STI Presentation** The STI activity study confirmed several findings from the ARB analyses of traffic using freeway traffic counters and weight in motion sensors. They also evaluated activity on surface streets to some extent and found similar patterns compared to the freeway data. While there are some differences and additional surface street data would be helpful, there is nothing in the data available to date that would lead one to change the overall understanding of the activity and emission differences between weekdays and weekends. That understanding, based on activity information and ambient precursor measurements, is that there are overall emission reductions on weekends (with NO<sub>x</sub> reductions greater than VOC reductions) accompanied by a major timing shift in highway vehicle emissions and modest changes in the spatial distribution of emissions. The STI study also provides new information on several emission categories beyond highway-vehicles. They found that NO<sub>x</sub> emissions from point sources are reduced on weekends by 10 % and that small business activities are down by 50 % or more on weekends. They carefully evaluated lawn and garden equipment activity and showed that this small category of emissions is not substantially increased on weekends. The remaining source categories for which there is not much weekday/weekend activity information are either small emission categories (like residential and recreational) that might have some weekend increases or somewhat larger categories such as construction or ROG point sources that would be expected to be lower on weekends.

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<sup>1</sup> G. Yarwood and R. Morris, “CAMx Model Performance for the August 3-7, 1997 SCOS Ozone Episode, ENVIRON memorandum to B. Bailey (CRC), D. McNerny (ARB), J. Casmassi (SCAQMD), and G. Gero (City of Los Angeles), July 11, 2001.

<sup>2</sup> D. P. Chock, T. Y. Chang, S. L. Winkler, and B. I. Nance, “The impact of an 8 hr ozone air quality standard on ROG and NOx controls in Southern California,” *Atmos. Environ.*, **33**, pages 2471-2485, 1999.

<sup>3</sup> P. M. Roth, S. D. Reynolds, T. W. Tesche, P. D. Gutfreund, and C. Seigneur, “An appraisal of emission control requirements in the California South Coast Air Basin,” *Environment International*, **9**, pages 549-571, 1983.

<sup>4</sup> K. Wagner, N. Wheeler, and D. McNerny, “The effect of emission inventory uncertainty on Urban Airshed Model sensitivity to emission reductions,” presented at the International Conference, Tropospheric Ozone: Nonattainment and Design Value Issues, Air and Waste Management Association, Boston, MA, October 28-30, 1992.

<sup>5</sup> C. O'Donnell, R. E. Morris, and D. F. Shearer, “Performance of an Alternative Ozone Attainment Demonstration of the Los Angeles Region for the 1994 State Implementation Plan,” Air and Waste Management Association paper A735, 1994.