

## APPENDIX C

### **Response of CARB Staff to Major Comments Received on Its Initial Draft Report "The Ozone Weekend Effect in California"**

In October 2000, the California Air Resources Board released a draft copy of a report summarizing various investigative data analyses conducted in-house to gain additional insights into the cause(s) of the Ozone Weekend Effect. This draft report, entitled "The Ozone Weekend Effect in California", consisted of two volumes - a Staff Report (SR) and an accompanying Technical Support Document (TSD). The SR was written for policy makers and general scientists. The TSD was written to communicate the more technical details of the staff analyses.

CARB staff received comments on the draft report from Air Improvement Resource, Inc. (AIR) on behalf of General Motors Corporation and from Envair on behalf of the Western States Petroleum Association (WSPA). The full texts of these comments are presented in Appendix A and Appendix B, respectively. CARB staff considered the internal and external comments on the initial draft SR and TSD and created draft final versions of the SR and TSD for peer review by experts in the University of California. The staff is grateful to the people who contributed their time and expertise to comment on the initial draft of the reports. Their efforts resulted in an improved draft final report that went out for peer review. Additional revisions will be made in response to the comments and suggestions of the peer reviewers before the final report is released.

The common themes contained in the comments were: 1) the existing data demonstrate that the NO<sub>x</sub> Reduction hypothesis best describes the Ozone Weekend Effect, 2) additional data collection efforts are not needed (and if collected, are not likely to change conclusions about the dominant cause of the Weekend Effect), and 3) photochemical modeling will answer the remaining questions. In general, it is staff's opinion that most of the existing data (experiments) were not collected (conducted) in a manner to specifically address various hypotheses of the Weekend (WE) Effect. The existing data do provide substantial support for the NO<sub>x</sub> Reduction hypothesis but, just because the amount of currently available data needed to test the NO<sub>x</sub> Timing or Carryover Aloft hypotheses is very limited, that does not mean those hypotheses are not valid or significant. The current air pollution databases were largely developed to support documentation of long-term trends or short term episodes for modeling. For example, meteorological variations exert the most dominant influence on ambient concentrations from day to day. Thus, short, episodic field studies do not have the robustness to filter the meteorological variations from the WE Effect. From the particulate matter (PM) perspective, the standard one-in-six day sampling schedule and variable lag times in laboratory analysis for the typical filter-based sampling create background noise from which it is difficult to extract a robust WE Effect signal for PM. Lastly, staff has reservations about the direct applicability of photochemical modeling results for specifically addressing WE Effect issues. The current state-of-art PM models have not been thoroughly validated under a variety of conditions. In general, photochemical modeling applications must appropriately address carryover aloft, temporal and spatial variations in emissions, photochemistry under low NO<sub>x</sub> conditions, and model performance in creating initial conditions to definitively characterize the

relative influence of the various factors potentially contributing to the Ozone WE Effect. With refinements to better address the hypotheses, models will serve as a valuable tool for addressing the causes (and relative contributions) of the WE Effect.

The purpose of this Appendix is to explicitly respond to the major external comments and to provide an indication why, or why not, the staff chose to reflect them in the draft final report. To facilitate a comparison of the specific comments and the staff's position, the comments and suggestions are presented in order within each comment letter.

**Major Comments from Air Improvement Resource, Inc.** (see Appendix A for full text)

- 1) 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.

1a) *The CARB staff was cautious in coming to their conclusions for a couple of reasons. First, the physical and chemical processes associated with ozone and particle pollution are very complex and our understanding of the processes and the data available to evaluate them are still incomplete. Although the available data are consistent with the NO<sub>x</sub> reduction hypothesis, the currently available data are generally insufficient to determine how well the other hypotheses explain what we observe. Although staff suspects that NO<sub>x</sub> reduction may be a factor in the Ozone Weekend Effect in some areas, the relative influence of the other potential factors cannot be established yet because the pertinent data for testing are unavailable. Because the available evidence is consistent with multiple hypotheses, staff is reluctant to conclude, based on circumstantial evidence, that NO<sub>x</sub> reduction is the primary cause of the WE Effect when other processes may have significant roles. Second, modeling is a tool used to help decision-makers; it is not a full and complete replication of what is actually occurring in the atmosphere. In fact, many of the modeling limitations tend to be in a direction that underestimates the influence of NO<sub>x</sub> emissions. Staff does not subscribe to the theory that the atmosphere operates in a specific manner because the model says so. Models are our best current representation of atmospheric processes and are continually being updated as new information and more efficient computing techniques become available. The modeling results however must always be interpreted within the context of the limitations of the model for representing specific processes. A new chapter (Ch. 6) has been added to the TSD to raise modeling issues associated with accurately addressing potential factors in the Ozone WE Effect. Staff is awaits the results of modeling applications that are well-designed (i.e., based on accurate representations of emission patterns, meteorology, and chemistry and are applied to isolate causes and effects as uniquely as possible) to test various hypotheses of the cause(s) of the Weekend Effect. These results, even with their limitations, will help guide future refined efforts to isolate the cause(s) of the Weekend Effect.*

*However, the staff is not convinced that the ozone weekend effect reflects the impacts of long-term emission controls. The short-term temporal, spatial, and compositional variations that occur from weekdays to weekends are not the same as the emission reductions associated with a control program. Thus, even if NO<sub>x</sub>-reduction were found to be a significant factor in the weekend effect, the suggestion for putting a "hold" on NO<sub>x</sub> controls for an ozone control strategy does not necessarily follow. Furthermore, the variety of conditions spatially and temporally (e.g., VOC-limited, neutral, or NO<sub>x</sub>-limited) constrains that the emissions of both ozone precursors be controlled from the ubiquitous motor vehicle sources so that*

*progress can be made in all regions of the state. The relative emphasis placed on one precursor over the other may be better left to regional planners addressing the specifics of their local situation. When ozone design days occur on weekends, control programs will be geared towards ameliorating the air quality problem. Of critical need now, is the development of a weekend emission inventory that accurately reflects the complex spatial, temporal, and compositional variations that do occur. Furthermore, the weekend baseline modeling must reasonably simulate a variety of atmospheric processes before the scenario results can confidently be used for guiding control strategies.*

*As indicated by Figures 1 through 4 in the comments, the percentage of locations with a positive weekend effect appears to be greater for the potential 8-hour standard than for the current 1-hour standard. If an 8-hour standard in the vicinity of 8 pphm were established, then appropriate modeling of weekend days would become even more important. In contrast to the figures however, results in Chock et al. (1999) indicate that the NO<sub>x</sub> disbenefit would be much weaker for the 8-hour standard than it is for the 1-hour standard. Furthermore, Sillman (1999) also cites modeling results showing that lower precursor concentrations and lower peak ozone values tend to be associated with a weaker VOC limitation, even given the same VOC/NO<sub>x</sub> ratio. As time permits, staff would like to take a closer look at related data to better isolate seasonal and NO<sub>x</sub> scavenging effects from the NO<sub>x</sub> reduction effect.*

- 2) 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.
- 2a) *There may be an element of caution in the Executive Summary but it is also evident from the TSD that many of the observations do not paint a consistent picture of the Weekend Effect at all times and in all places. Some of the data available for evaluating the hypotheses are limited in scope and robustness, and definitive conclusions on some of the hypotheses are not appropriate at this time. Staff has reviewed and revised the material to ensure a more complete connection between the staff report and the technical support document. As additional data and sound technical analyses become available to address the current unknowns and uncertainties, staff will be in a better position to quantify and rank the impacts of the various hypothetical processes.*

### **Comments on ARB strategy**

- 3) 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. ...Figure 1 shows that ozone decreases occurred prior to the start of NO<sub>x</sub> controls. ...The common element is, thus, VOC control. ...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. ...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.”

3a) *The ARB is primarily interested in the long-term effect of ozone control strategies and less so in the ozone weekend effect itself. Ozone, whether by maximum concentrations or by number of Stage I Episodes, has declined in a steady manner before and after automotive NO<sub>x</sub> controls began in 1975. If NO<sub>x</sub> controls were detrimental, or have become detrimental, to ozone as some conclude from the ozone weekend effect, the rate of improvement would have slowed throughout the 1980s and 90s. Furthermore, if more typical (less extreme) trend statistics are used (e.g., number of NAAQS violations), ozone has in fact declined at a faster rate during the period of greater NO<sub>x</sub> control (see table and figure below). During this same period, the ozone weekend effect became more prominent. Thus, there is no apparent relationship in the South Coast Air Basin between the impact of periodic NO<sub>x</sub> reductions associated with the weekend effect and the impact of long-term NO<sub>x</sub> reductions associated with an ozone control strategy -- weekend ozone concentrations increased relative to weekday concentrations at more sites while the overall (basin) long-term ozone trend decreased significantly. NO<sub>x</sub> controls are not only needed for ozone reductions in some areas but also to ameliorate other air quality problems such as nitrogen dioxide, nitric acid, peroxyacetylnitrates, and particulate matter. The most recent emission inventory numbers indicate that ROG controls have equaled or outpaced the NO<sub>x</sub> controls. Staff agrees that the limited amount of ambient NMOC data and uncertainties about the accuracy of O<sub>3</sub>, NMOC, and NO<sub>x</sub> monitoring methods (especially prior to 1980) make it difficult to assess previous trends. Furthermore, the ozone trends are not consistent among the various air basins and so additional factors may be involved. The dual nature of the ozone impacts resulting from NO<sub>x</sub> emissions is well known but the quote of Dr. Pitts is somewhat misleading. Dr. Pitts has always advocated NO<sub>x</sub> controls in addition to ROG controls because NO<sub>2</sub> photolysis is the only known source of atomic oxygen necessary for the formation of ozone in the troposphere (Pitts et al., 1983; Finlayson-Pitts and Pitts, 1993; Finlayson-Pitts, 2000).*

**Changes in Ozone<sup>1</sup> Relative to Variations in ROG and NO<sub>x</sub> Emissions<sup>2</sup>  
in the South Coast Air Basin**

	1975	%) <sup>3</sup>	1980	%)	1985	%)	1990	%)	1995	%)	2000
<b>ROG (tpd)</b>	2882	-15	2452	-2	2407	-23	1850	-25	1374	-21	1092
<b>NO<sub>x</sub> (tpd)</b>	1850	-4	1780	+8	1923	-7	1780	-17	1473	-18	1208
<b>ROG/NO<sub>x</sub><sup>4</sup></b>	4.5	-11	4.0	-10	3.6	-17	3.0	-10	2.7	-4	2.6
<b>O<sub>3</sub> (days)</b>	218	-17	180	-8	166	-16	139	-28	100	-61	40

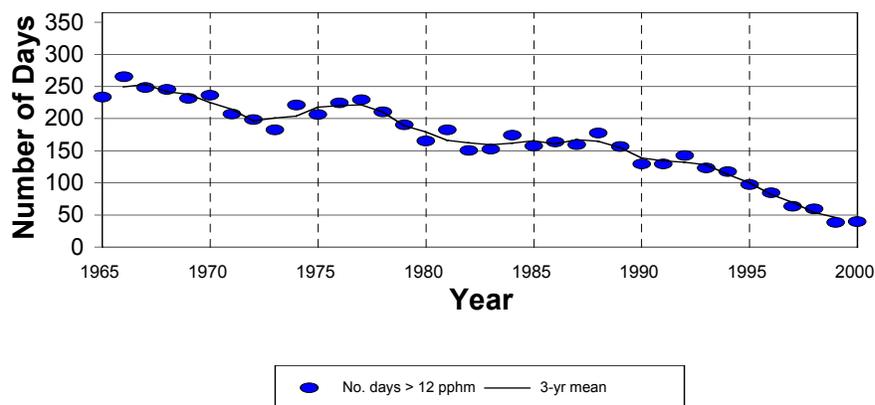
1 - number of days when the national ambient air quality standard (>12 pphm, 1-hr avg.) was violated somewhere within the air basin

2 - tons per day of reactive organic gases or oxides of nitrogen based on EMFAC2000 model (source: The 2001 California Almanac of Emissions & Air Quality)

3 - percent change during 5-year period

4 - molar ratio (CH<sub>4</sub>/NO<sub>2</sub>); mass ratio adjusted by molecular weights (46/16).

## NUMBER OF OZONE EXCEEDANCES South Coast Air Basin, 1965-2000



- 4) ...the SR posits that there may be a difference between periodic  $\text{NO}_x$  reductions that occur each weekend and strategic  $\text{NO}_x$  reductions that would produce steady  $\text{NO}_x$  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  $\text{NO}_x$  associated with weekend activity do not mimic longer-term  $\text{NO}_x$  reduction strategies, the report should document those reasons so they may be evaluated and tested.

- 4a) *Staff concurs that carryover primarily involves ozone and hydrocarbons because  $\text{NO}_x$  tends to react out faster than ozone or hydrocarbons. That is not to say that there is no carryover of nitrogenous compounds or that they cannot re-enter the photochemical system. Recent work by Mochida and Finlayson-Pitts (2000) and Saliba et al. (2000) indicates the potential for nitric acid to revert back to  $\text{NO}_2$  and active involvement in ozone photochemistry. Furthermore, some ozone data collected by lidar at El Monte Airport during SCOS97 indicate that ozone formation can begin above the surface mixing layer as soon as sunlight is present and before atmospheric mixing processes can carry fresh emissions up to that ozone layer. Obviously for this to occur, there needs to be a source (carryover) aloft of  $\text{NO}_2$ .*

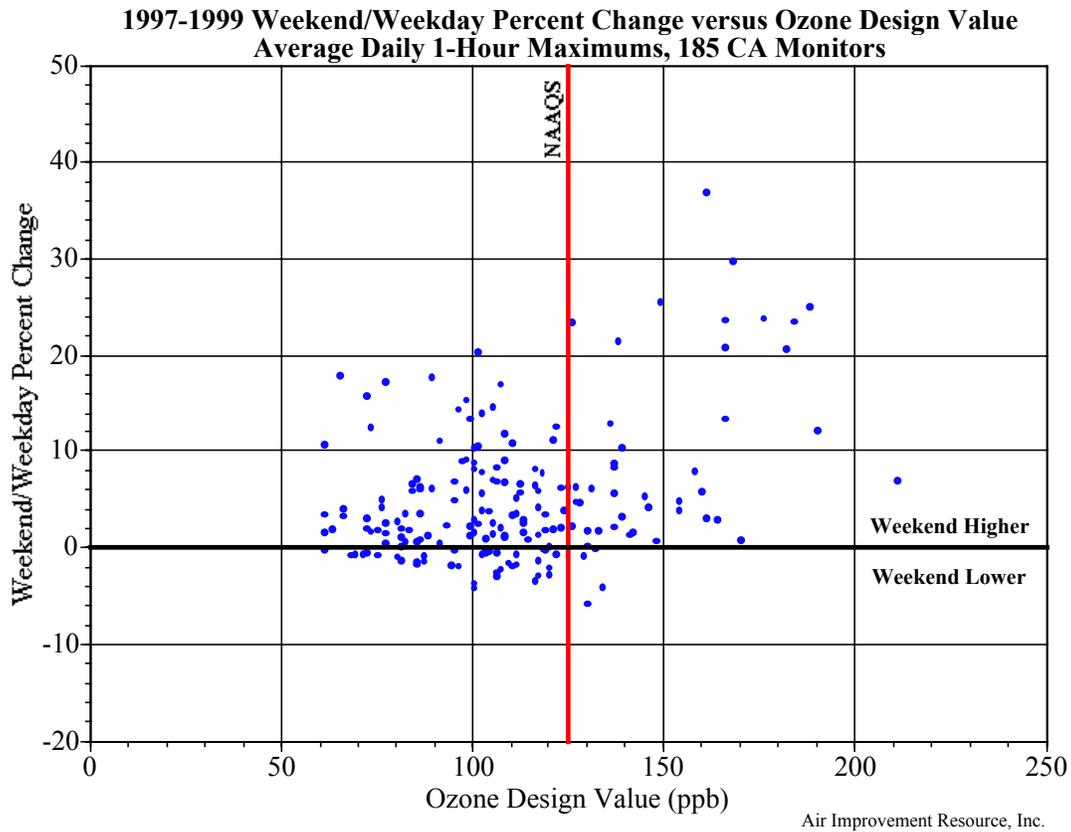
*Staff believes there is a distinct difference in the impacts from a decline in  $\text{NO}_x$  emissions on a weekend and from a consistent reduction at all times of the day by a  $\text{NO}_x$  control strategy. The weekend transition includes changes in the compositional, temporal, and spatial patterns that do not occur under a control program. These variations likely result in interactions that are different from a control strategy where emissions are proportionally reduced all hours of the day.*

*The comment focuses on the limited carryover of NO<sub>x</sub> over a 2-day period (i.e., weekend) because of its reactivity. The staff does not strongly disagree (conventional wisdom says NO<sub>x</sub> carryover is very limited although, as described in a preceding paragraph, new measurements are implying this is an area to keep an open mind). The focus of staff's position is not on the NO<sub>x</sub> carried over (or not carried over) after two days of declining emissions but on the interaction between the carryover of ozone (and NMOC) and the fresh NO<sub>x</sub> emissions. The amount of fresh NO<sub>x</sub> emissions (primarily in the form of NO) plays a crucial role in whether the day's photochemical processes begin with an initial baseline of ozone or not. The earlier start in the photochemistry on weekends when NO emissions are reduced relative to weekdays and ROG emissions allows more time for ozone formation before the process becomes precursor- or light-limited.*

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

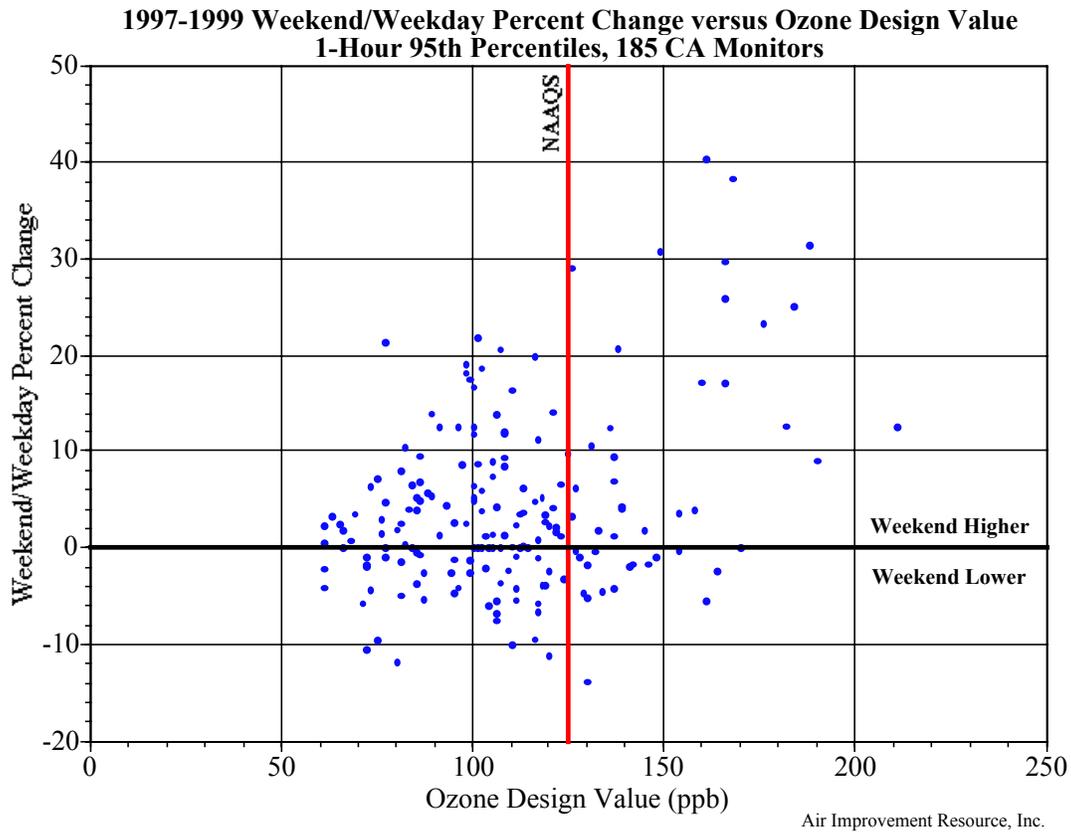
- 5) The ES correctly indicates that the weekend effect is real and that ozone increases of 25 to 32 % occur in key areas in spite of the fact that NO<sub>x</sub> emissions are decreased about 25 % on Saturday and 40 % on Sunday compared to midweek levels. The magnitude of the weekend effect throughout 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**

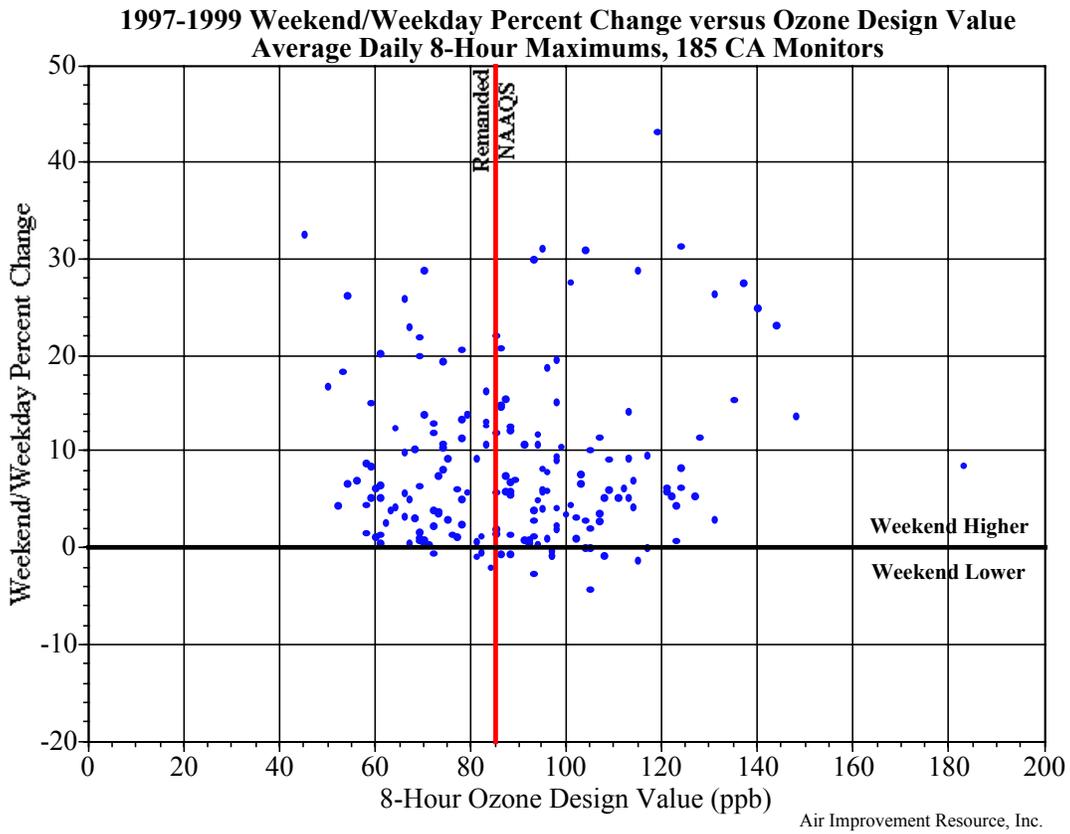
In Figure 2, the weekend-weekday behavior plotted is the 95<sup>th</sup> percentile of the daily 1-hour maxima. The 95<sup>th</sup> percentile was chosen to evaluate the weekend-weekday behavior for high ozone days. When compared with Figure 1, the results in Figure 2 are similar except that there is 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.



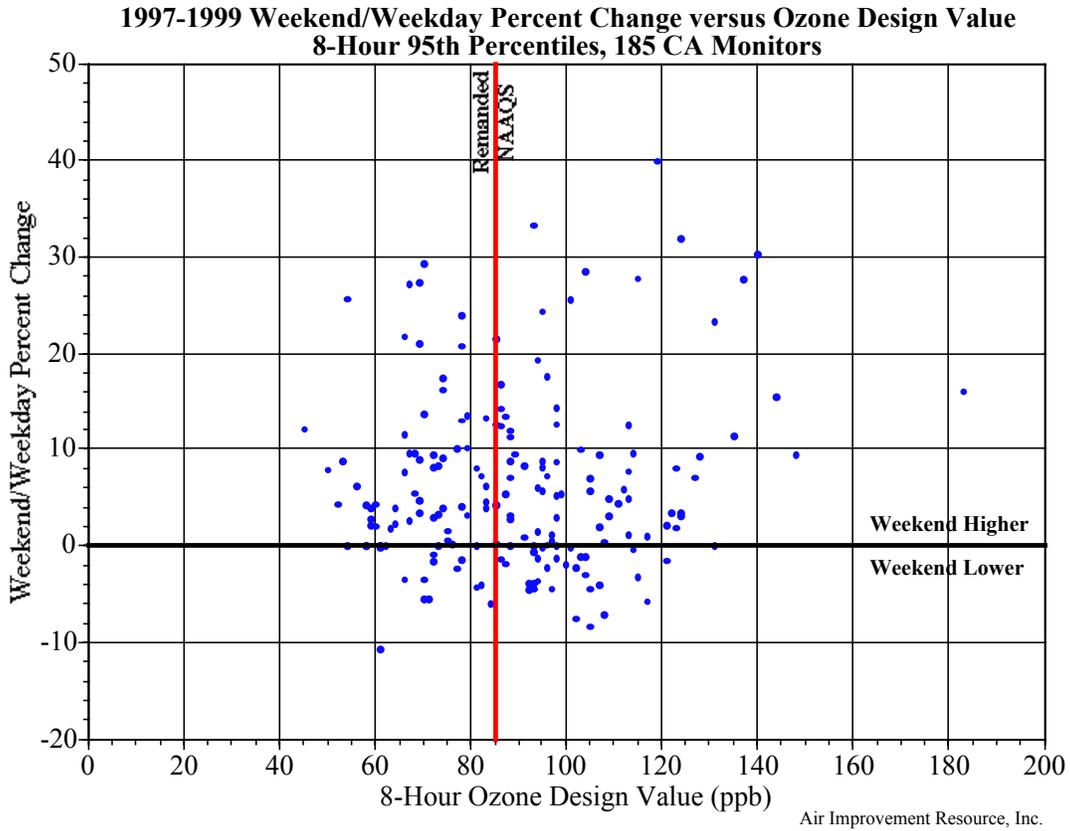
**Figure 2**

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.

*5a) The plots of the ozone weekend effect versus the design value illustrates that the weekend effect occurs at the majority of the monitoring sites in California, somewhat independently of the severity of the ozone problem. The fact that monitoring sites that exceed the ambient air quality standards may or may not experience the weekend effect illustrates the complexity of addressing the ozone problem. Because the sites with the highest design values often have the strongest weekend effect, the possibility is very real that design values can be determined by concentrations on the weekend and are more likely to be so in the future. A future staff analysis, time permitting, will include additional screening of these data to better quantify the effect on days when the concentrations exceed the California standard and to identify any spatial patterns.*

*The remanded 8-hour ozone standard is exceeded on more days than the national 1-hour standard. Many people have anticipated that the 8-hour O<sub>3</sub> concentrations would be more difficult to reduce than peak 1-hour concentrations if NO<sub>x</sub> controls were involved because the fresh NO emissions would have tended to help reduce one or both shoulders of the 8-hour O<sub>3</sub> peak. This tendency would be counteracted however by greater removal of OH radicals via reaction with higher NO<sub>2</sub> concentrations. The effects tend to balance as an in-house analysis (Larsen) indicated that, although more areas would violate the proposed 8-hour standard, it is only slightly more stringent than the current national 1-hour standard (114 ppb vs. 124 ppb). Nevertheless, the control efforts to attain the 8-hour standard would be greater because the concentration of the remanded 8-hour standard is much closer to the regional background concentrations of ozone (30-40 ppb and increasing in some areas) than the concentration of the 1-hour standard. The 8-hour and 1-hour O<sub>3</sub> concentrations are highly correlated and it is anticipated that peak concentrations of both averaging periods would decline together. This would be especially true in cases involving transport downwind of urban areas. As reductions of ozone precursors and ozone occur in the urban areas, the ozone concentrations in downwind areas associated with transport would decline commensurately. Furthermore, Chock et al. (1999) indicated that the disbenefit is less for 8-hour ozone than 1-hour ozone.*

*Staff agrees that the testing of hypotheses of the causes of the weekend effect must test how well the hypothesis can explain the variations observed among different locations. Complicating the analysis is the number of theoretical factors potentially involved and the likely variable contributions they make spatially and temporally.*

### Comments on causes of the weekend effect

6) ...periodic NO<sub>x</sub> reductions on weekends should mimic the steady NO<sub>x</sub> reductions from strategic regulations.

6a) *This third point of this section in the comment letter actually quotes the position of some people but does not represent the position of staff. For the staff position on this point, see response 4a).*

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

7) The short version [of the NO<sub>x</sub> reduction hypothesis] 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.” 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 prominent 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.

7a) *The SR will be revised to more clearly demonstrate the scientific basis and wide acceptance of the dual nature of NO<sub>x</sub> emissions on O<sub>3</sub> concentrations. However, staff will still note the limitations of smog chamber experiments and photochemical models in representing real-world processes. The models are sensitive to a variety of factors and outputs do vary depending on the specifics of any given application. In particular, ambient conditions are now quite low and the earlier smog chamber data might not adequately address photochemistry under these conditions. Staff is looking forward to new information that will be available from the next generation of smog chambers. This information will result in improved chemical mechanisms representative of lower NO<sub>x</sub> conditions for the photochemical models. However, it also needs to be noted that updated smog chamber work will not necessarily greatly improve the models’ abilities to represent the real world. For example, as mentioned earlier, recent work suggests that heterogeneous chemistry may have a significant influence on ambient conditions, particularly in the boundary layer where most air quality measurements are made. The unknown impacts of heterogeneous chemistry cannot be solved by the next generation of smog chambers because they are designed to minimize heterogenous chemistry on their walls.*

*The improved time-of-day and day-of-week gridded emission inventories being developed will better represent real world activities than the current inventories do. And although emission inventories are continuously being improved, there is no reason to believe that the emissions, meteorological, and chemical modeling will provide definitive answers. Modeling is a tool to help in the decision-making process and its refinements feed into adaptive management processes. Some concern has been expressed that the photochemical models used to develop the State Implementation Plan for ozone are the same models that will be used to investigate the ozone weekend effect but that staff are holding the weekend investigation modeling protocol to a higher standard than the SIP protocol. The model limitations in fact do apply to both applications but the difference is that the SIP modeling is constrained by a firm deadline while the scientific investigation is constrained by the best possible inputs and performance. Any work done with a scientific focus would undoubtedly also benefit future SIP applications.*

- 8) 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 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.

*8a) Staff will expand the discussion.*

- 9) 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.

*9a) Staff is in basic agreement with this comment. Photochemical modeling is the best available tool for addressing the complexities of the Weekend Effect. However, the limitations of modeling must not be ignored, particularly as they might directly influence conclusions (e.g., replication of polluted layers aloft, realistic time-of-day and day-of-week variations in emission inventories).*

- 10) 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.

10a) *VOC/NO<sub>x</sub> ratios provide insight into the site-specific relationships between ozone precursors and the subsequent peak ozone concentration. Early morning ratios are an important indicator of the afternoon's peak ozone concentration. However, atmospheric processes are complex and staff believes the changing meteorological and environmental conditions between 9 a.m. and the time of peak ozone (some 3-6 hours later) also exert some influence. We know that the atmospheric chemistry during this time drives NO emissions toward NO<sub>2</sub> and HNO<sub>3</sub> and that the oxidizing processes cause VOC/NO<sub>x</sub> ratios to increase as NO<sub>x</sub> compounds are removed from the photochemical system faster than the VOCs. The unknown factor is how influential the late conditions are compared to the initial conditions. Recent applications of the California Institute of Technology photochemical model (not published yet) indicate that the timing of NO<sub>x</sub> emissions do influence the resultant peak O<sub>3</sub> concentrations. The work of Hess, Johnson, et al. referenced in the report indicates that factors subsequent to 6-9 a.m. do have an influence on peak ozone. In fact, Johnson's Smog Production or Extent of Reaction work is the basis for Blanchard's application to data in California. Blanchard's extent of reaction results at the time of peak ozone concentration are very consistent with the spatial pattern of the Weekend Effect and implies that ozone formation in most of the SoCAB is VOC-limited.*

11) ...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 on 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.

11a) *In and of themselves, the other hypotheses probably cannot explain all of the WEE characteristics. For example, the NO<sub>x</sub> Timing hypothesis might explain why O<sub>3</sub> concentrations might be higher on Saturdays than weekdays and higher on Sundays than Saturdays. However, it probably does not explain why O<sub>3</sub> concentrations historically peaked late in the workweek, transitioned to Saturdays, and more recently transitioned to Sundays. Similarly, the Carryover Aloft, and the Aerosol & UV radiation hypotheses probably have difficulty explaining the long-term progression of the Weekend Effect. With cleaner fuels, etc., the anticipation is that the particulate matter and soot from mobile sources has declined somewhat and so would the effect of these hypotheses. However, the Weekend Effect has grown in time. O<sub>3</sub> quenching by NO, which occurs whenever and wherever O<sub>3</sub> and NO are*

*present, is likely to be a contributing factor, though not the sole factor. Assuming ozone formation in the surface layer has become VOC-limited as the uncertain VOC/NO<sub>x</sub> ratios indicate, the NO<sub>x</sub> Reduction hypothesis is also a likely factor contributing to the WD/WE differences.*

12) Another key question that must be answered by this hypothesis [NO<sub>x</sub> Reduction] 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.

*12a) Staff agrees with the general premise that VOC/NO<sub>x</sub> ratios have declined over the years in the SoCAB. As indicated by the emission estimates in the response to comment #3, ROG (VOC) have been reduced at a greater rate than NO<sub>x</sub> emissions. With the greater NO<sub>x</sub> than VOC reduction on weekends, the DRI analysis (and NO<sub>x</sub> Reduction hypothesis) can explain the Weekend Effect because, in a VOC-limited environment, the NO<sub>x</sub> reductions would tend to moderate the ozone decrease anticipated from the ROG reductions by themselves. However, the magnitude of emissions, and not just the ratio of emissions, helps determine the resultant ozone concentrations. As indicated in the table and figure associated with the response to comment #3, ozone decreased the most during the most recent 5-year period when the VOC/NO<sub>x</sub> ratio declined the least but NO<sub>x</sub> emissions declined the most (both O<sub>3</sub> precursors declined about 20%) since 1975. Most of the specialized studies have limited duration or infrequent sampling schedules that limit the number and significance of the analyses that can be performed.*

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

13) 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 on page 2-7 to illustrate the effect of timing on  $\text{NO}_x$  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/ $\text{NO}_x$  ratio of 51. In another experiment with an initial VOC/ $\text{NO}_x$  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/ $\text{NO}_x$  ratios from 15 to 50. In the SoCAB, measured VOC/ $\text{NO}_x$  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  $\text{NO}_x$ -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 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  $\text{NO}_x$  to different chambers, the effects of emission reductions as well as varying the VOC/ $\text{NO}_x$  ratio can be determined. When Kelly conducted such experiments in rural and remote areas, the photochemistry was  $\text{NO}_x$ -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  $\text{NO}_x$ -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  $\text{NO}_x$ -timing hypothesis.

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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, 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.

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.

*13a) Staff believes the Hess work on the impact on O<sub>3</sub> of additional NO<sub>x</sub> emissions is pertinent. It is true that the VOC/NO<sub>x</sub> ratio in the example was 51 and not representative of typical ambient conditions. The point of the illustration is that as ozone formation becomes more NO<sub>x</sub>-limited in the afternoon, fresh emissions of NO<sub>x</sub> can enhance O<sub>3</sub> formation. The author of the comment implied that at more typical VOC/NO<sub>x</sub> ratios (16.8) that the O<sub>3</sub> formation was decreased with the addition of NO<sub>x</sub>; this is not true. The rate of O<sub>3</sub> formation slowed slightly but the amount of O<sub>3</sub> continued to increase. Thus, is not unlike what we observe in the atmosphere on weekends. The O<sub>3</sub> formation begins earlier and might be expected to become NO<sub>x</sub>-limited sooner. However, the addition of more NO<sub>x</sub> (and VOC) when O<sub>3</sub> formation is becoming precursor limited allows O<sub>3</sub> to continue forming at essentially the same rate. Thus, the ozone formation rate does not change during the morning but, in effect, continues longer than would have been the case had not additional O<sub>3</sub> precursors been added. In the captive air irradiation experiments referenced in the comment, the initial precursors were added later in the morning so it's no surprise they produced less ozone.*

*The proximate modeling results from Environ's work will be helpful but may be limited unless the inputs are realistic and base conditions are replicated well. Environ is currently waiting for resolution of some questions about emission outputs from the EMFAC2000 model.*

*The suggestion about also separating the HDD and LDVs in the modeling analyses is a good idea (to address independent as well as synergistic effects).*

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

14) 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 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.

*14a) The amount of ozone aloft will vary depending on the variation by day-of-the-week and, probably more importantly, by meteorological conditions. Nevertheless, the point that carryover is not the dominant factor in determining afternoon ozone levels is acknowledged. However, staff is not as confident as the comment's author that existing photochemical models can determine the sensitivity of ground-level concentrations to conditions aloft unless, as noted in Chapter 6, that the model layers reasonably represent the air quality (ozone) layers aloft. The second comment addresses the spatial variations and suggests that chemistry is more of a factor than carryover. However, the background air quality and meteorology can*

*have significant influence. With the coastal marine layer in the western SoCAB and the variable frequency and timing of fumigation of air aloft, the influence of ozone carryover aloft will generally have little or no effect in coastal areas, more effect in the peak ozone regions of the basin, and less influence at the more rural downwind sites. The last paragraph of this section (the third (last) comment) suggests that the regulatory implications of the carryover aloft process are the same as for NO<sub>x</sub> reduction process – i.e., NO<sub>x</sub> controls, at least when exceeding ROG controls, can and will increase ozone concentrations. The significantly reduced NO<sub>x</sub> emissions on weekends interact with relatively abundant ozone (carryover plus global background concentrations). Because the carryover is relatively rich in VOCs (and perhaps ozone) and the surface layer is relatively poor in NO<sub>x</sub>, ozone formation in the mixed layer of air is very likely NO<sub>x</sub> limited. With proportionately less ozone scavenged by fresh NO emissions and the surface and aloft air being neutral or NO<sub>x</sub> limited, fresh NO<sub>x</sub> emissions associated with the mid-day peak in activity will cause ozone to form. On weekday mornings however, the surface layer of air will be neutral or VOC limited and the relatively large amount of fresh NO<sub>x</sub> emissions will scavenge more of the ozone from aloft. Thus, the NO<sub>x</sub> emissions not only reduce the ozone baseline of photochemical activity but they are emitted into a less NO<sub>x</sub> sensitive environment and ozone concentrations and production will remain less relative to the weekend formation.*

*On the other hand, ozone concentrations, many years ago, tended to be the minimum of the week on Monday and the maximum on Thursday, thus implying some influence of carryover because emissions are presumably down on weekends and fairly constant on workdays. Now, ozone concentrations on Monday and Thursday are similar to other weekdays. As emission controls reduce precursors and ozone, the amount of carryover would be expected to also decline although the relative impact might not. Ozone formation in much of the SoCAB may have moved to a VOC-limited environment that could accentuate the impact of carryover (relatively rich in VOC). The VOC-rich air from aloft could help increase ozone formation in the VOC-limited surface layer. This possibility is supported by several observations: 1) VOC emissions have always been reduced more than NO<sub>x</sub> emissions, 2) peak day ozone has shifted from Thursday to Saturday to Sunday despite progressively lower NO<sub>x</sub> emissions on these days of the week, and 3) Monday is no longer the minimum ozone day of the week as might be anticipated with the effects of reduced ozone precursor carryover and the relative increase in ozone scavenging by fresh NO emissions on Monday morning.*

*Thus, irrespective of which ozone precursor is reduced in the surface layer (at least when VOC-limited), the effect of carryover aloft is to increase weekend ozone concentrations relative to weekdays.*

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

- 15) 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.

15a) *Staff agrees that the initial studies in this area do not indicate an appreciable influence. However, the databases to support such studies are not extensive nor necessarily of high quality. With cleaner fuels and other controls, it is reasonable to think that particulate matter emissions from motor vehicles may have declined slightly over the years and thus lessening, not increasing, the Weekend Effect if this hypothesis were a major factor. Furthermore, future particulate matter controls on motor vehicles would make this contribution to the Weekend Effect even smaller. On the other hand, some people speculate that while control efforts may have reduced the total mass of particulate emissions, they have increased the number of particles. Some preliminary, unpublished photochemical modeling with the California Institute of Technology model indicates that changes in actinic flux on the order of 10-20 percent could help explain a significant portion of the Weekend Effect. It seems prudent to staff to embark on some more definitive data collection and analysis efforts as resources permit.*

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

16) Conclusion # 3 of the SR... ..discussion of conclusion # 4... 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 [PM10-nitrates] ... 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 NO<sub>x</sub> may not necessarily reduce nitrate concentrations if it also increases ozone formation.

16a) *Staff has included additional discussion on secondary pollutant formation processes in the report. Staff is not convinced that the current nitrate data do not indicate a weekday/weekend variation. As noted in Finding #14, 1997-1999 nitrate data collected in the SoCAB indicate that PM10-nitrate was lower on the weekends than on weekdays by an average of 13 percent and occurred at 14 of the 15 locations. The current measurements are based on a one-in-six-day sampling schedule of filter-based measurements. There are inherent deficiencies in this measurement technique and sampling frequency. More robust data collection and analysis are necessary to better address this uncertainty.*

### **Summary**

17) ...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 [on] 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.



17a) *The following observations are from the findings/observations noted in the ARB Staff Report and Technical Support Document. The consistency of each observation with the various hypotheses of the Weekend Effect is noted.*

<b>Observation</b>	<b>H #1</b>	<b>H #2</b>	<b>H #3</b>	<b>H #4</b>	<b>H #5</b>	<b>H #6</b>
Ground-level VOC/NO <sub>x</sub> ratios are in the VOC-limited regime for O <sub>3</sub> formation	Y					
Ground-level VOC/NO <sub>x</sub> ratios increase during daylight hours		Y				
Ground-level VOC/NO <sub>x</sub> ratios are higher on WEs than on WDs	Y	Y	Y	Y	Y	
Ground-level NO <sub>2</sub> /NO ratios are higher on WEs than on WDs	Y	Y				
NO <sub>x</sub> concentrations on WEs increase later but faster than on WDs		Y				
Traffic and precursor concentrations are greater on Fr & Sa nites			Y			
Precursor concentrations at sunrise are similar on WEs and WDs			N			
[O <sub>3</sub> ]s aloft (typically only measured during episodes) tend to be higher than background levels				Y		
VOC/NO <sub>x</sub> ratios are higher aloft that at ground-level				Y		
Precursor concentrations are lower on WEs than WDs at almost all sites					N	
WIM 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
The WE Effect is primarily evident in major urban areas	Y	Y	Y			
The 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 <sub>x</sub> emission reductions	N	Y				

H #1 – NO<sub>x</sub> Reduction hypothesis

H #2 – NO<sub>x</sub> Timing hypothesis

H #3 – Carryover at ground-level hypothesis

H #4 – Carryover Aloft hypothesis

H #5 – Increased Emissions hypothesis

H #6 – Soot and Sunlight hypothesis

**Comments on technical issues associated with photochemical modeling (Ch. 6)**

18) 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... 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.” ...Photochemical models are, however, uniquely situated to separate the effects of possible causal factors. 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.

*18a) The authors did not intend to create the impression that ARB staff is setting a higher standard for the performance of Weekend Effect modeling efforts than for regulatory modeling. Staff only intended to note that complexities associated with properly addressing the impacts of potential causes of the weekend effect. As noted in the comments, many of the issues apply both to the research into the Weekend Effect and to regulatory planning. The difference though is that the weekend application is using the model to address detailed physical and chemical processes while the regulatory application provides guidance on the relative impacts of air quality control programs. Any refinements made to the model as a result of efforts to more accurately simulate atmospheric processes will benefit regulatory modeling efforts in the future. In both applications, it is a matter of doing the best possible science within the constraints imposed by limited resources.*

19) **Weekend emission inventory.** ...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. 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.

*19a) Emission inventories are constantly being refined and improved to address deficiencies and modeling needs. As these improvements occur, they are incorporated into modeling applications. For regulatory modeling, staff uses the best information available at the time. For scientific investigative modeling, the staff has more time and flexibility to better ensure that the physical and chemical processes and activities are well characterized and the results are consistent with what is occurring in the atmosphere. As noted, the uncertainties in some emissions and activities can be bounded. Because the recent and long-term trends of ozone*

*concentrations on the South Coast Air Basin has been significantly downward with the current dual control strategy, staff does not feel the urgency to get an immediate answer to the causes of the weekend effect. A "quick and dirty" effort to get some answers now can lead to erroneous results, conclusions, and possibly regulations that could undo the recent progress and thereby erode public support of the air quality program.*

20) **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  $\text{NO}_x$  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? ...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  $\text{NO}_x$  disbenefits under some conditions and  $\text{NO}_x$  benefits under other conditions. The rates of the individual chemical reactions underlying the duality of  $\text{NO}_x$  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.

20a) *The SAPRC mechanism was only mentioned as an example. The main point is that the control program has reduced ambient  $\text{NO}_x$  concentrations to low levels, particularly during mid-day, and that the chemical mechanism used in modeling efforts must have been validated for low- $\text{NO}_x$  conditions. Without proper characterization of atmospheric chemistry under the current range of ambient conditions, confidence in the modeling results is greatly reduced. Furthermore, even "state-of-the-art" models do not include heterogeneous chemistry that may turn out to be very important for characterizing real-world reactions.*

21) **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.

21a) *Photochemical models have improved over the years in how they simulate changing conditions in the vertical dimension. It is true that characterization of the vertical dynamics is important for all modeling applications but it is even more important for assessing the contribution carryover aloft might play in the weekend effect. An estimate of the significance of this process cannot be made if the process is not characterized in a realistic manner.*

22) **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.

22a) *To properly assess the potential contribution of carryover in the surface layer, it is important the model accurately reproduce the ambient conditions which can and do differ significantly from weekday evenings to weekend evenings. A model cannot accurately quantify an impact of a change in activity if it cannot faithfully reproduce the change in the causative activity.*

23) **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. ... 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. ... 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.

23a) *The staff does not believe the weekend modeling is more important than the SIP modeling and therefore requires a higher performance standard. However, if modeling is to be used to conduct scientific inquiry into the causes of air quality impacts, care must be taken to ensure the operative atmospheric processes are characterized accurately. Otherwise, the modeling results could say as much or more about the model's formulation than they would about the impact of the actual processes occurring in the atmosphere. Staff desires that the weekend effect modeling faithfully characterize the conditions for the actual reasons. Even if more rigorous modeling applications indicate that NO<sub>x</sub> reduction indeed is a major contributor to the weekend effect, the regulatory policy implications would need further scrutiny. Although the weekend effect has been evident in the western portion of the SoCAB for decades, there does not appear to be a strong association with it and ozone trends in the western basin or the peak ozone regions of the basin. Although the ozone weekend effect is stronger than ever in the SoCAB, the ozone air quality has never been better in the basin. To change a long-standing, successful strategy in response to a partially understood temporary day-of-week effect could be imprudent. Until the causes of the weekend effect and the regulatory*

*implications of those causes are understood, any changes in the current successful policy of dual precursor control are unwarranted.*

### **Comments on Chapter 8**

24) 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, 20001 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.

*24a) The primary purpose of the report was to summarize various data analyses conducted by ARB staff as they investigated potential causes of the weekend effect. The staff deemed it appropriate to include a compendium of prior work and to note concurrent efforts that were underway or planned to elucidate the weekend effect. Because some of the concurrent efforts were completed before this report was finalized, it might be appropriate to include a short summary of the results. However, it will be awkward to be constantly summarizing external material as it becomes available, particularly after the version being peer reviewed. It definitely would be inappropriate for staff to include summaries for work that is still preliminary and not released as a final report. In addition, it is generally best to cite peer-reviewed literature.*

**Major Comments from Envair** (see Appendix B for full text)**Executive Summary**

1) A key commonality of the three plausible hypotheses with supporting data is that all involve the effects of NO<sub>x</sub> on ozone; the hypotheses are in fact tightly linked. They differ in the degree of emphasis placed on the effects of mid-day emissions of NO<sub>x</sub>, and the relative contributions of carryover ozone to peak ozone concentrations.

*1a) NO<sub>x</sub> figures prominently in the hypotheses because of its dual nature in promoting and inhibiting ozone formation. The hypotheses must account for the morning pulse of emissions available for photochemical production being smaller and later on weekends than on weekdays. To have increased ozone on weekends then the relatively greater reduction in NO<sub>x</sub> emissions compared to VOC must increase ozone formation or factors changing the chemical environment must be different. Although most hypotheses include a NO<sub>x</sub> component, the implications for NO<sub>x</sub> control can be different.*

2) Ongoing field studies are already in place to provide further data for understanding the weekend effect (Fujita et al., 2000). The need for an additional comprehensive and extended field program to further distinguish among the plausible explanations of the weekend effect is not apparent. A more productive use of resources would be to focus on evaluating geographically-targeted ozone control strategies, rather than on testing hypotheses of the weekend effect. Further analysis of data from the 1997 Southern California Ozone Study (SCOS97) and the ongoing Central California Ozone Study (CCOS) projects, along with modeling studies, should be pursued. An additional topic meriting further investigation is the effect of VOC and NO<sub>x</sub> reductions on aerosol nitrate formation. Existing studies indicate that aerosol ammonium-nitrate formation in California is typically not limited by the availability of ammonia. However, existing work from the San Joaquin Valley Integrated Monitoring Study of 1995 (IMS95) also suggests that VOC reductions may reduce the rate of aerosol nitrate formation more effectively than NO<sub>x</sub> reductions in areas where ozone formation is VOC limited. This topic should be investigated through analyses of data from the Central California Regional Particulate Air Quality Study (CRPAQS), along with modeling studies.

*2a) Additional data (field studies) are needed to definitively and thoroughly address unknowns and uncertainties associated with the Weekend Effect. Probably the most critical need is for activity data for the generation of day-specific emission inventories. Ultimately, gridded day-of-week emission inventories with hourly resolution will be needed for definitive testing of hypotheses of the Weekend Effect. Other data needs include better information on VOC and NO<sub>x</sub> speciation, atmospheric processes aloft, and accurate modeling of these parameters. The difficulty with special studies is that the large meteorological variations often obscure other processes and limit the statistical significance.*

*In regard to using information from previous aerosol studies in the San Joaquin Valley for modeling studies, it is the staff's belief that secondary aerosol formation processes are significantly different in the San Joaquin Valley and South Coast. In*

*addition, the analyses supporting VOC controls to reduce nitrates (i.e., NO<sub>3</sub>) are limited and need additional confirmation. Furthermore, aerosol models, although dramatically improved, are still in need of refinement and results must be interpreted in terms of the assumptions and model limitations.*

### **Why Does the Weekend Effect Occur?**

- 3) Recommendations in the CARB report include steps for acquiring data that would permit further evaluation of the "soot and sunlight" hypothesis. However, the need for such an evaluation should not be overrated. As discussed below, existing data already support three other hypotheses considered plausible by the CARB report - thus, measurements now indicate that the "soot and sunlight" hypothesis cannot be the only cause of the weekend effect.
- 3a) *The limited data and analysis to date suggest that the Soot & Sunlight (Aerosol & UV Radiation) hypothesis does not explain a large portion of the Weekend Effect. However, the limited amount of data, its uncertain quality, and the dramatic shift in heavy-duty diesel activity on weekends encourages some refinements in order to be definitive about its relative contribution. Some preliminary photochemical modeling by Dr. Donald Dabdub (UC-Irvine) indicates that increased ultraviolet radiation can have a significant influence on weekend ozone concentrations. However, the limited amount of current UV data indicate a very small increase on weekends - not enough to have a significant effect on ozone concentrations. On the other hand, theoretical work by Liao (1999) indicates a potentially stronger effect from soot particles, particularly when cloud layers are involved.*
- 4) The CARB report also notes that aerosol nitrate, derived from NO<sub>x</sub>, can constitute a substantial portion of fine particulate mass. However, during warmer months when ozone concentrations reach high values, aerosol nitrate concentrations are low at most locations; conversely, aerosol nitrate concentrations are highest during winter months, when ozone concentrations are lowest. The temperature dependence of aerosol nitrate is related to an equilibrium reaction between aerosol nitrate and its gas-phase precursors, nitric acid and ammonia, which favors the gas-phase species as temperatures increase. Thus, aerosol nitrate is generally not a significant component of the aerosol mass during the time periods of interest for understanding the ozone weekend effect. However, aerosol nitrate formation is affected by both VOC and NO<sub>x</sub> emission levels, as discussed later. Therefore, both ozone and aerosol formation need to be addressed in considering emission control strategies.
- 4a) *Mr. Blanchard's comments appear to be based primarily on data from the Central Valley of California. The formation of nitrate aerosols is dependent on several factors in addition to temperature (e.g., ammonia, humidity). Although both the Central Valley and the South Coast have ammonia sources and cool, moist meteorological conditions, the most conducive meteorology occurs at different times of the year. While winter is the dominant season in the Central Valley, the regular on-shore flow of the coastal marine layer can provide cool and moist conditions throughout the year. While high ozone and nitrate concentrations do not generally occur on the same day, they can occur during the same season. The bottom line*

*though, which Mr. Blanchard and staff agree on, is that both ozone and aerosol formation need to be addressed when considering emission control strategies.*

*Fresh NO<sub>x</sub> emissions, which primarily consist of nitric oxide (NO) undergo reactions with ozone and peroxy radicals to form nitrogen dioxide (NO<sub>2</sub>). The NO<sub>2</sub> can be directly converted to nitric acid via the homogenous gas-phase reaction with the hydroxyl radical. This is the principal formation mechanism for nitric acid in the daytime. During the nighttime, nitric acid is formed via the reaction of NO<sub>2</sub> and NO<sub>3</sub> to form dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>), which can then react with water (H<sub>2</sub>O) to form two molecules of HNO<sub>3</sub>. The principal chemical loss process for gas-phase nitric acid is its reaction with gaseous ammonia to form ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>). This reaction, which is reversible, is believed to be the primary source of fine (<2.5 μm diameter) nitrate aerosol in California's urban air.*

*The atmospheric chemistry leading to formation of particulate nitrate is fairly complicated. The rates of transformations depend on the concentrations of many intermediate species (including ammonia and radical species) involved in the photochemical system of reactive organic gases and NO<sub>x</sub>. Ambient concentrations of secondary particles are not necessarily proportional to the quantities of their precursor emissions since the rates at which they form and their gas/particle equilibria may be controlled by factors other than the concentration of the precursor gas. The rate of NO<sub>x</sub> oxidation and the branching ratio between inorganic and organic nitrates depend on the specific environmental conditions (e.g., temperature and relative humidity) in addition to reactant concentrations.*

*PM-nitrate concentrations vary seasonally according to the nature of the predominant emission and meteorological factors in the area. However, PM-nitrate concentrations exhibit less seasonal variation in the South Coast Air Basin than in other air basins (e.g., the Sacramento valley Air Basin and San Joaquin Valley Air Basin where concentrations are higher during winter than during summer). The limited seasonal variation in PM-nitrate concentrations in the SoCAB is rather unique compared to other areas of California. Apparently, secondary particulate formation during the summer months in the SoCAB is commensurate with the typical high production during the cooler months of the winter. Although nitrate production is greatest during the winter months, the nitrate fraction remains significant during the summer in the SoCAB.*

- 5) In these statements of the three hypotheses, a key commonality is that all three involve the effects of NO<sub>x</sub> on ozone: in each case, fresh NO emissions lower ozone concentrations by virtue of the reaction of NO with ozone, and they reduce rates of ozone formation by lowering radical concentrations. These hypotheses are therefore tightly linked, and are not mutually exclusive. They differ in the degree of emphasis placed on the effects of mid-day emissions of NO<sub>x</sub>, and the relative contributions of carryover ozone to peak ozone concentrations. The hypotheses were formulated as distinct explanations, because the CARB report argues that the NO<sub>x</sub>-reduction and NO<sub>x</sub> timing hypotheses "have substantially different policy implications with respect to NO<sub>x</sub> controls as an ozone control measure." Similarly, in situations where there may be substantial contributions of carryover ozone to peak values, control strategies may differ from those used where little carryover occurs.

5a) *NO<sub>x</sub> changes are a major focus because NO<sub>x</sub> reductions can temporarily increase or decrease ozone concentrations. Specific situations are shaped by a variety of processes and a single precursor control strategy will likely not work well in all situations.*

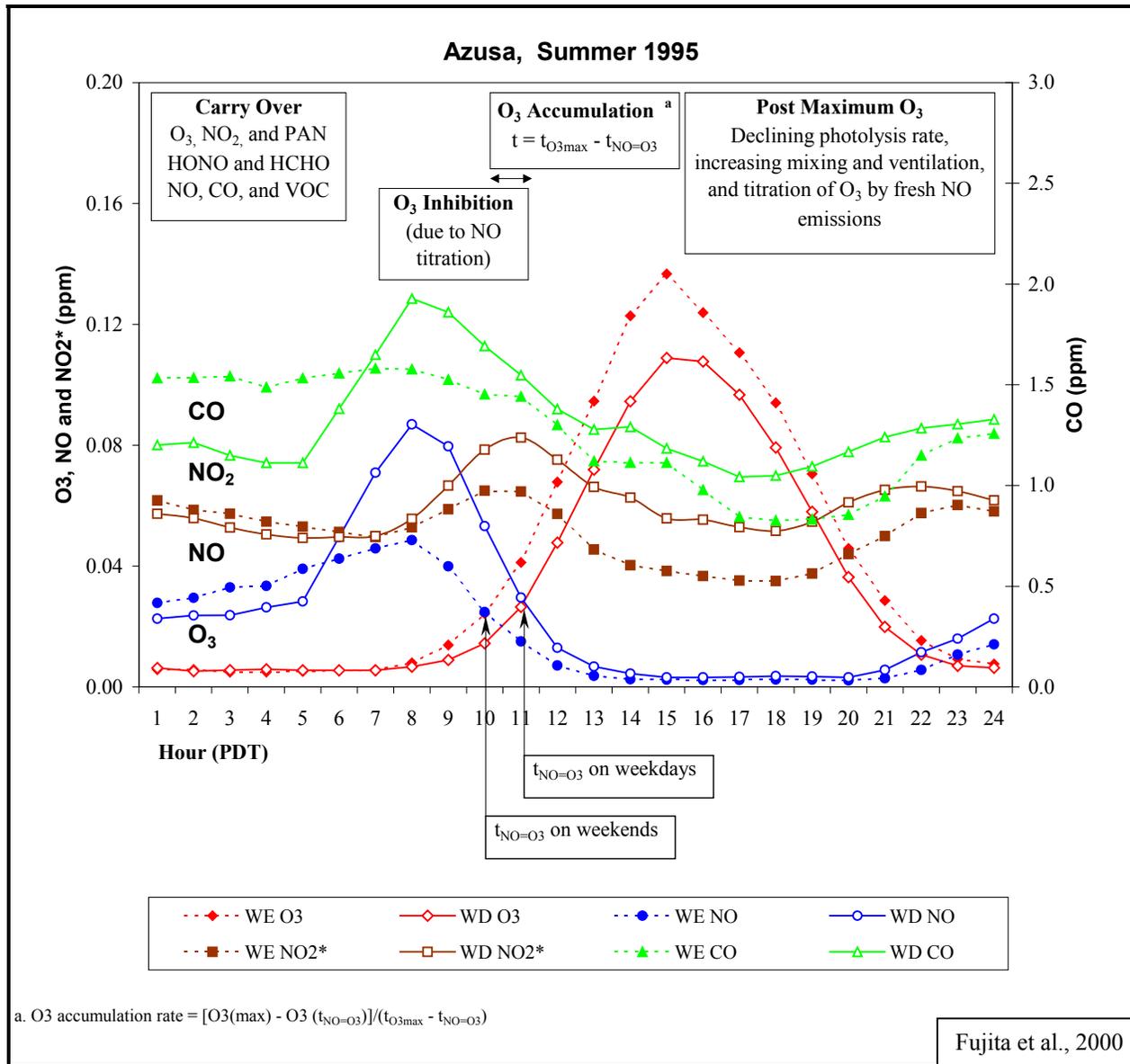
6) The same evidence supports the initial premise of the NO<sub>x</sub>-timing hypothesis, but evidence for its second premise is lacking:

"Because less NO<sub>x</sub> is present to depress the concentration of radicals, the photochemical system becomes more active earlier in the day. As activities and emissions increase toward mid-day, the fresh NO<sub>x</sub> enters this more active system, participates in ozone-generating reactions more efficiently, and leads to higher weekend ozone compared to weekdays."

As found by all studies and noted above, the photochemical system does become active earlier on weekends. However, the rates of accumulation of ozone do not accelerate during the middle of the day at sites showing a weekend effect. Although Fujita et al. (2000) showed that 9 the 13 sites in the South Coast Air Basin showed a higher rate of ozone accumulation on Sundays during the period 1995 through 1998, no sites showed an acceleration of ozone formation just prior to the time of occurrence of the peak ozone concentration. Moreover, diurnal profiles show that the differences between weekend and weekday ozone concentrations begin early, with the earlier weekend "starting" time for ozone formation (when O<sub>3</sub> and NO concentrations become equal), and continue throughout the morning; the weekend effect does not occur as a sudden acceleration of ozone production at mid-day (see Figures 3 through 5 for examples). However, in some locations the data are not inconsistent with a small mid-day effect coinciding with the apparent input of fresh emissions, but this effect is modest in comparison with the differences between weekday and weekend ozone concentrations that can be traced through to earlier in the morning.

6a) *During mid-day, motor vehicle activity (and presumably emissions) is comparable on weekdays and weekends. If ozone formation on the weekend is not VOC-limited by mid-morning because the photochemistry became efficient sooner and the NO<sub>x</sub> concentrations were relatively lower than the VOC concentrations initially compared to weekdays, the mid-day emissions of both VOC and NO<sub>x</sub> can act as fuel for the formation of additional ozone. The precursors will continue producing more ozone until its formation becomes precursor- or light-limited. The ozone formation rate (efficiency) doesn't necessarily change dramatically but, without VOC as a limiting precursor initially, ozone production occurs a couple of hours longer on weekends than on weekdays and thus resulting in higher ozone concentrations. Looking at the weekday and weekend diurnal profiles of ozone (e.g., Chapter 2 of the TSD), one sees a tendency for the weekend ozone peak to occur slightly earlier in the western portion of the SoCAB and slightly later in the eastern portion of the SoCAB. Looking at the data figure below (courtesy of Fujita, 2000) from Azusa (central portion of the basin where the time of the weekday and weekend peaks in concentration is similar), it is apparent that the hourly differences in ozone concentrations (WE - WD) increase until the peak hour. Furthermore, the hour-by-hour formation rate on weekends is slightly faster than on weekdays at Azusa. Interestingly, the hourly difference between weekend and weekday concentrations is essentially the same magnitude but opposite sign as the hourly difference between weekend and*

*weekday NO<sub>2</sub> concentrations. In effect, the total oxidant (O<sub>3</sub> + NO<sub>2</sub>) levels are similar on weekdays and weekends but the equilibrium between the oxidants shifted.*



- 7) Diurnal concentration profiles also show that ambient CO and NO<sub>x</sub> concentrations after about 4 a.m. on weekends are reasonably parallel with weekday concentrations. Some differences do occur, perhaps suggesting more sustained weekend emissions levels between about 8 and 10 a.m., or somewhat greater increases (but not greater concentrations) of precursor concentrations between approximately 10 a.m. and 1 p.m. than on weekdays. On the whole, however, the weekend precursor concentration profiles resemble weekday profiles; they do not resemble the hypothetical weekend emission profile shown as Figure 2-4 of the CARB report.
- 7a) *Figure 2-4 is a conceptual profile of diurnal variations in emissions, not ambient concentrations. Ambient concentration profiles are not exactly similar to the emission profiles because concentrations are a function of emissions, meteorology, and chemistry. In particular, the meteorology enhances the effects of emissions around sunrise and sunset when the air is stable and minimizes the effects of emissions during the middle of the day when atmospheric dispersion is usually greatest. The Fujita et al. figure (shown above) of concentrations at Azusa does not show relatively parallel concentrations of CO and NO<sub>x</sub> for the WD/WE profiles. However, the NO<sub>2</sub> and O<sub>3</sub> profiles are the same general shape on WDs and WEs and the sum of NO<sub>2</sub> and O<sub>3</sub> is quite constant between WDs and WEs.*
- 8) As noted in the CARB report (Figure 2-2), chamber experiments support the idea that ozone production can be accelerated in a system that has reached a state of NO<sub>x</sub> limitation by injecting fresh NO<sub>x</sub>. However, the weekend effect occurs at VOC-limited sites, not NO<sub>x</sub>-limited locations. Therefore, the relevance of the cited chamber experiments as an explanation of the weekend effect is not apparent.
- 8a) *This is probably the root of many of the comments on the report and why staff is unwilling to "jump on the NO<sub>x</sub> reduction bandwagon" at this point. The limited number of monitoring sites with VOC and NO<sub>x</sub> data indicate that ozone formation is probably VOC-limited during the morning hours. The even more limited data on afternoon conditions indicates that VOC/NO<sub>x</sub> ratios increase from the initial morning conditions but ozone formation probably still is not NO<sub>x</sub>-limited. Staff has a few concerns about analysts deducing/assuming that ozone formation is therefore VOC-limited throughout the day at all locations. First, after several hours of photochemistry, many of the hydrocarbons in the atmosphere have become partially oxidized and are not detected by routine monitoring methods. A recent study (Paulson, 1999) indicated that standard VOC measurements can be on the order of 30% low. Even standard gas chromatography methods probably underestimate the true amount of VOCs in atmospheric samples (Lewis et al., 2000). Furthermore, current NO<sub>x</sub> monitoring techniques tend to overestimate the NO<sub>x</sub> concentrations (particularly during the day) because they include additional oxidized forms of NO<sub>x</sub> (e.g., HNO<sub>3</sub>, PAN). These monitoring biases indicate that NMOC/NO<sub>x</sub> ratios are higher than ambient data indicate. In addition, NO<sub>x</sub> concentrations, because of their high reactivity, have declined to typical detection limits. Most monitoring stations are in urban locations near heavily traveled roadways and thus might not be fully representative of a spatially-weighted VOC/NO<sub>x</sub> ratio due to the impact of fresh emissions. Furthermore, chemistry modules in photochemical models do not always*

*represent low-NO<sub>x</sub> chemical reactions well. In essence then, there is sufficient uncertainty about VOC/NO<sub>x</sub> ratios during the period of peak photochemistry that staff is reluctant to say that ozone formation is VOC-limited throughout the day. The essence of the NO<sub>x</sub> Timing hypothesis is that ozone formation is no longer VOC-limited (and may even be NO<sub>x</sub>-limited) by mid-day when weekend emissions are comparable to weekday emissions. If ozone formation has not already become radical-limited, these emissions will contribute to increased ozone formation; weekends more so than weekdays because the VOC/NO<sub>x</sub> ratios are higher.*

- 9) Those aspects of the "NO<sub>x</sub>-timing" hypothesis that have not been resolved by existing data appear to be amenable to reasonably straight-forward analyses using either photochemical box models or three-dimensional gridded models. The need for "Accurate, artifact free measurements of VOCs and NO<sub>x</sub> in three dimensions" (Austin et al., 2000) may not be sufficiently pressing to warrant the expense of special field sampling.
- 9a) *Staff concurs that special field sampling to collect the requisite types and amounts of data (especially aloft) would be very expensive. Staff however is not confident that currently available modeling applications would necessarily arrive at the correct conclusion for the correct reasons. Staff believes that additional improvements are needed in models before definitive progress can be made on this front (e.g., meteorological module on handling layers aloft, emission inventories reflective of the spatial, temporal, and chemical variations in emissions, chemistry modules appropriate for low NO<sub>x</sub> conditions).*
- 10) Ample evidence supports the existence of higher concentrations of ozone aloft. As noted in the CARB report, during morning hours of the SCOS97 when ozone concentrations at surface sites were depleted, concentrations were often in the range of 40 to 80 ppbv at ~400 m to 4000 m agl; occasionally, concentrations of 140 ppbv or more were observed. During the 1987 Southern California Air Quality Study (SCAQS), aloft ozone concentrations exceeding 200 ppbv were recorded (Roberts and Main, 1992). Aircraft measurements recorded average aloft ozone concentrations in the range of 60 to 120 ppbv in the San Joaquin Valley and Bay Area during the 1990 San Joaquin Valley Air Quality Study (SJVAQS) (Blumenthal et al., 1997).
- 10a) *Staff agrees and has no comment.*
- 11) As noted in the CARB report (Austin et al., 2000), it is likely that air masses aloft are typically more aged than those at the surface, implying that further formation of ozone aloft may often be limited by the availability of NO<sub>x</sub>. Analyses of surface and aloft measurements of NO<sub>x</sub> and hydrocarbons collected at various locations in the San Francisco Bay Area and the San Joaquin Valley during the 1990 SJVAQS have provided evidence that aloft air masses are more aged than surface samples during early morning hours, and are more aged than afternoon aloft samples (Blumenthal et al., 1997). These conclusions were supported by comparing ratios of VOC/NO<sub>x</sub>, xylenes/benzene, and toluene/benzene (xylenes and toluene react more rapidly than benzene, so departures of those ratios from the ratios characteristic of fresh emissions provides an indication of aging). Data from other locations (see Figure 6)

show that situations occur where early morning surface layers have low concentrations of ozone, depleted by reaction with fresh NO<sub>x</sub> emissions, whereas NO<sub>x</sub> levels in layers aloft are low and ozone concentrations have reached the maximum levels possible without further input of fresh emissions. In the examples shown, ozone formation remained VOC-limited throughout the following daytime hours at the urban locations.

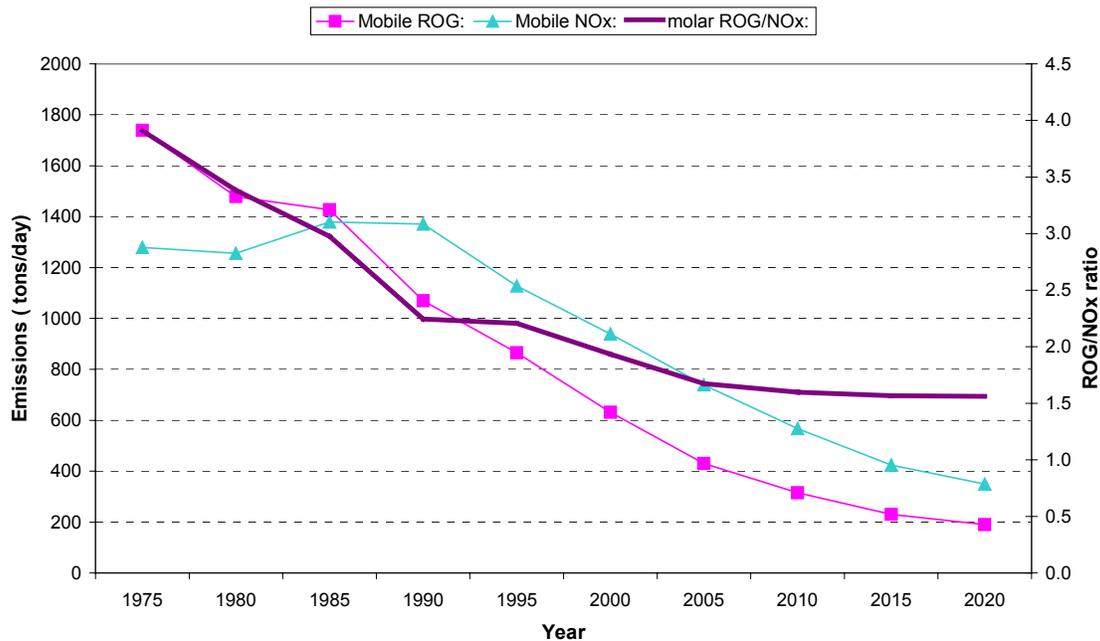
- 11a) *Staff is not convinced that ozone concentrations observed aloft in the morning have "reached the maximum levels possible without further input of fresh emissions." Ozone lidar data collected during SCOS97-NARSTO indicated the potential for ozone concentrations aloft to increase after sunrise but before the lower atmosphere became sufficiently unstable to carry fresh emissions aloft to the layer of increasing ozone. Additional work is needed to investigate whether the increase in ozone concentrations aloft (between 500 and 1500 feet) was due to photochemistry or to transport over the lidar site. For various reasons noted earlier, staff is not totally convinced that ozone formation remains VOC-limited throughout daylight hours at urban locations.*
- 12) Many locations showing aged air aloft nonetheless exhibit same-day surface concentrations of ozone and precursor species that are indicative of VOC limitation. Specific cases must be studied carefully using modeling and a variety of data analyses to establish the probable consequences of various levels and combinations of VOC or NO<sub>x</sub> emission reductions.
- 12a) *The presence of ozone aloft does not necessarily mean that surface concentrations (and processes) will be affected by it. Staff agrees that studies need to be carefully planned to address specific uncertainties and the consequences under a variety of conditions.*
- 13) The CARB report concludes that each of the three hypotheses discussed here is plausible, but none is proven and all may play some role. However, the CARB report and all other studies found considerable evidence to support the NO<sub>x</sub>-reduction hypothesis, and that hypothesis is consistent with expectations derived from theory and from modeling studies. Also, sufficient evidence exists to show that aloft ozone concentrations exceed surface concentrations at many times and places, and do contribute to ground-level ozone values as vertical mixing occurs during the day. In the next section, control implications are considered. Indeed, what is needed is not further testing of these hypotheses. Rather, the primary need is to delineate control strategies that are effective at all times and places, including areas that are VOC-limited, areas that are NO<sub>x</sub> limited, and areas dominated by transported ozone.
- 13a) *In essence, this has been the policy of the Board – adopting stringent VOC and NO<sub>x</sub> controls on ubiquitous mobile sources to reduce precursors of both ozone and PM. The tendency in most urban areas is to have relatively high precursor concentrations and low VOC/NO<sub>x</sub> ratios. In contrast, the tendency in most rural areas, particularly downwind of urban areas, is to have relatively low precursor concentrations and high VOC/NO<sub>x</sub> ratios. Thus, VOC controls will tend to have more benefit reducing peak ozone concentrations in urban source regions and NO<sub>x</sub>*

*controls will tend to have most ozone control benefit in downwind receptor regions. The dual precursor control approach (i.e., both VOC and NO<sub>x</sub>) addresses ozone formation in areas that are VOC-limited, NO<sub>x</sub>-limited, and transport impacted.*

### **What are the Implications for Ozone Control Strategies?**

- 14) Because of the range of conditions occurring throughout California, statewide emission-reduction strategies must include both VOC and NO<sub>x</sub>. Locally, however, ozone formation is either limited by VOC or by NO<sub>x</sub>, and the most effective local control strategies will target the limiting precursor in each area. As reported in Austin et al. (2000), ozone concentrations have trended strongly downward in the South Coast Air Basin since 1980, so the control strategies that have been employed have indeed been successful. However, the data cannot show that those strategies have been optimal, as no alternatives to the historical emission control program exist for comparison. ...Unlike the difference between weekdays and weekends, the NO<sub>x</sub> reductions occurring over the period 1980 through 1998 were accompanied by even stronger VOC reductions; thus, ozone concentrations declined throughout the South Coast Basin and the Bay Area, even at sites that exhibit a weekend effect.
- 14a) *It is true that we do not know definitively what strategy was or will be most effective. We can only note that the most rapid improvement in ozone air quality observed since control programs were implemented occurred in the last 5 - 10 years when VOC, and particularly NO<sub>x</sub>, reductions were large. The rate of NO<sub>x</sub> reductions for mobile sources has always been the same or less than the rate of VOC reductions (see figure below) and staff recommends continued adherence to this approach in light of the potential viability of NO<sub>x</sub>-reduction hypothesis as a factor in the ozone weekend effect and the potential relevance of the weekend effect to long-term regulatory controls. Because mobile source regulations typically apply statewide, staff agrees that local control strategies must be developed that efficiently address the unique characteristics of ozone formation in each area.*

### ROG & NO<sub>x</sub> Emission Trends for Mobile Sources Summer, South Coast Air Basin



15) These observations are testable using three-dimensional model studies with appropriate databases and model evaluation.

15a) *Staff reiterates the limitations of models without proper spatial and temporal characterization of emissions and proper replication of atmospheric processes aloft and photochemical processes.*

16) However, like ozone, the rate of formation of nitric acid may be limited either by radicals or by NO<sub>x</sub>. Therefore, in some situations, aerosol nitrate formation may be more effectively reduced through reductions of VOC than NO<sub>x</sub> emissions (Pun and Seigneur, 1999). More specifically, existing work suggests that VOC reductions may reduce the rate of aerosol nitrate formation especially in areas where ozone formation is VOC limited. Additional research efforts should be directed to this topic.

16a) *In some cases, VOC controls may be necessary to reduce particulate nitrate. Staff encourages further research in this area.*

#### What Research Efforts are Needed?

17) The CARB report concludes that "Accurate, artifact-free measurements of VOCs and NO<sub>x</sub> in three dimensions are needed to assess the contributions of the "NO<sub>x</sub>-reduction" hypothesis, the "NO<sub>x</sub>-timing" hypothesis, and the "Carryover aloft" hypothesis." Yet, regardless of the relative contributions of each process to the overall weekend effect, ample scientific evidence exists to indicate that the range of conditions in California requires geographically-focused reductions of VOC and NO<sub>x</sub> emissions, with emphasis on VOC reductions in areas known to be strongly VOC-

limited (e.g., most of the San Francisco Bay Area, South Coast Air Basin, and San Diego Air Basin) and NO<sub>x</sub> reductions where ozone is NO<sub>x</sub>-limited. Since the latter require statewide strategies in some cases (e.g., motor vehicles), careful consideration should be given to the balance of VOC and NO<sub>x</sub> controls imposed within the coastal metropolitan areas. Regardless of the exact contributions of each plausible cause to the overall weekend effect, the undisputed magnitudes of the increased weekend ozone concentrations within the San Francisco Bay Area, South Coast Air Basin, San Diego Air Basin, and some urban locations within the Central Valley indicate that control strategies in which NO<sub>x</sub> emission reductions exceed VOC emission reductions are likely to aggravate ozone concentrations in those areas. The weekend effect provides a clear test case.

*17a) As noted before, staff is not convinced that the Weekend Effect provides a clear test case of the impacts associated with future NO<sub>x</sub> controls. However, staff does not disagree with Mr. Blanchard's points.*

18) Ongoing field studies are already in place to provide further data for understanding the weekend effect (Fujita et al., 2000). Thus, a more productive use of resources would be to focus on evaluating geographically-targeted ozone control strategies, rather than on testing hypotheses of the weekend effect. Further analysis of data from the SCOS97 and CCOS projects, along with modeling studies, should be pursued. An additional topic meriting further investigation is the effect of VOC and NO<sub>x</sub> reductions on aerosol nitrate formation. This research need was previously identified by analyses conducted under the Central California Regional Particulate Air Quality Study (CRPAQS) and should be investigated further using data from the Central California Regional Particulate Air Quality Study, along with modeling studies.

*19a) Please see the above responses to 2a) and 17a).*

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