

7 Recommendations

California's routine databases on emissions and ambient air quality are uncommon in their extent and their quality. In addition, many special studies that address air quality issues have been conducted in California. Data from these sources have already answered many questions concerning the ozone weekend effect. However, the objectives of routine programs and special studies have not specifically included understanding day-of-week differences in ozone and other pollutants. It is not surprising, therefore, that a satisfactory explanation of the ozone weekend effect may require additional information to augment existing databases.

This chapter includes recommendations on the level of effort that will be required to definitively quantify the impacts of the plausible factors contributing to the ozone weekend effect. The multi-faceted research necessary to isolate the contributing factors to the ozone weekend effect must involve thorough planning, coordinated research, and a significant investment of time and resources, resources which are not currently available. Thus, section 7.1 is a recommended level of effort to fully address the ozone weekend effect and not a recommendation to perform all of the research as soon as possible. In fact, the research would benefit from coordinated, targeted studies designed to prioritize and refine the investigations

7.1 Recommendations for further research

This section presents a multi-disciplinary research program needed to resolve the cause(s) and implications of the ozone weekend effect. Without this effort, the cause(s) and implications may remain ambiguous. The cost and complexity of some recommendations (e.g., large scale field study) are great and it is imperative that existing data sets are thoroughly analyzed to further focus and design the studies needed to improve our understanding of the causes of the ozone weekend effect.

The recommendations in this section identify information needed to resolve the causes of the ozone weekend effect. Several hypotheses in this regard are discussed in Chapter 3 of the Staff Report. However, the data available for the analyses included in this report were not sufficient to separate or quantify the contributions of the various causes. Without the research outlined here, the relative importance of these hypothetical causes will be difficult to resolve.

This section integrates and extends many, but not all, of the recommendations given in earlier chapters and presents unified recommendations to guide future work.

7.1.1 Summary of research recommendations

The cause(s) of the ozone weekend effect are not yet clear. For example, the available data do not yet show whether ozone measured on weekends is higher because more ozone is created or because less ozone is destroyed. It is important

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to know the respective contributions of these and other atmospheric processes if we want to understand the overall weekend effect and its implications,

The recommendations that follow address basic research that will help to ensure that the atmospheric processes that produce the ozone weekend effect are understood and quantified well enough to permit informed decisions. In general, the recommended research would probably be accomplished most effectively in the South Coast Air Basin.

Significant gaps may exist in our understanding of certain atmospheric processes. If such gaps exist, they would also limit the realism of the currently available modeling tools used to project the impacts of emission changes. Therefore, the recommended research should be prioritized toward better characterization of key atmospheric processes and the adequacy of models toward reproducing the observed air quality results. Modeling limitations identified in this way should then be addressed.

High priority questions to be addressed are the following: 1) How important are heterogeneous chemical reactions to the ozone photochemical system? 2) Are the rates of formation and removal of critical components (e.g., HNO_3) properly represented? 3) How well do the current forms of air quality models replicate historical trends? 4) What are the critical limitations in model performance (e.g., chemical and physical processes, emission inventories) that need addressing first?

- **Improve data on ambient air quality**

Existing databases for ambient air quality must be augmented in several respects before the cause(s) of the ozone weekend effect can be determined. An expansion of routine sampling methods alone will not suffice. Instead, targeted and integrated field studies are recommended to gather the necessary ambient air quality data specifically focusing on transitions from weekdays to weekends and back again. Critically important is the accurate measurement of VOCs and NO_x for assessing VOC/ NO_x ratios. It is equally important to measure the amounts of pollutants aloft and their contributions to pollutant concentrations measured at the surface.

- **Improve emission inventories**

Emission inventories for each day of the week are needed to help determine the causes of the ozone weekend effect. In particular, day-of-week emission inventories are needed to support air quality models that simulate the ozone weekend effect. Separate inventories for Saturday and Sunday are essential. Although desirable, separate inventories for each of the five weekdays may not be necessary. A Friday inventory should be considered the highest priority of the five weekdays because of the greater evening activity. Much of the available activity data indicates that a Tuesday through Thursday composite is reasonable for characterizing mid-week emissions because of their similarity. On the other hand, some ambient air quality

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data suggest that Wednesdays are slightly different from other weekdays and therefore an individual weekday inventory may be most appropriate.

The required inventories must reveal in sufficient detail the quantity, the timing, and the location of VOC and NO_x emissions by day of week. Day-specific hourly emissions are needed for stationary and area sources as well as for mobile sources.

- **Improve modeling**

Dynamic photochemical simulation models, such as the Urban Airshed Model (UAM), are important tools for comparing alternative strategies for reducing emissions. Modeling exercises should be conducted to confirm the ability of today's models to replicate the historical air quality trends for weekdays and weekends. Modeling exercises should use new day-specific inventories to investigate how the mix of primary and secondary pollutants affects ozone formation on weekdays and on weekends.

Performance evaluations for modeling exercises investigating the ozone weekend effect must also consider the issues discussed in Chapter 6 of this Technical Support Document (e.g., adequate representation of photochemistry and mixing processes).

- **Improve information from laboratory experiments**

Experiments conducted some years ago may need to be updated to reflect present-day concentrations. New experiments should be designed to address important alternative causes of the ozone weekend effect.

Past experiments have already revealed important aspects of ozone-producing systems. However, these experiments were often designed from a generic perspective, and may not be directly applicable to the ozone weekend effect. For example, "dilution" experiments sometimes simulate the effect of a rising mixing height during the day. However, the dilution typically uses clean air, rather than "air aloft." This and other experiments where fresh emissions are introduced into an aging air mass should be repeated to reflect conditions found during recent and future air quality studies.

Also, laboratory experiments indicating the sensitivity of ozone to heterogeneous chemistry and chlorides need to be extended to real world settings.

7.1.1.1 Conduct a field study to augment the existing ambient air quality databases in the South Coast Air Basin

Existing databases for ambient air quality are inadequate to resolve the cause(s) of the ozone weekend effect. Despite extensive analyses by the ARB staff and others, the relative importance of the several causes outlined in Chapter 3 of the Staff Report have not yet been determined.

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To adequately quantify the contributions of different causes of the ozone weekend effect, the available air quality data must be more precise, more specific, and more extensive in time and space (particularly in the vertical dimension).

Air quality data must be more precise because small changes in pollutant concentrations may be important but below the limits of resolution for routine sampling equipment.

Air quality data must be more specific in two ways. First, artifacts that can inflate the measured concentrations of essential pollutants, such as NO_x, must be avoided. Second, methods that under-report essential pollutants, such as VOCs, must also be avoided.

Air quality data for significant species must be measured hourly because the timing of emissions and the time of transition between sensitivity to VOCs or NO_x are important issues.

Air quality data in three dimensions is vital for assessing the differing contributions of carryover aloft on weekdays versus weekends.

In addition, detailed observations are needed for multiple weekday-weekend transitions comprising Friday to Saturday to Sunday to Monday. Although one or two historical "episodes" that include weekend days are helpful, a broader view of differences between weekdays and weekends is needed.

Therefore, integrated field studies are recommended to gather the ambient air quality data needed to bridge the significant gaps in the data. An outline for the recommended study is presented here as a starting point for further discussion and planning.

7.1.1.1.1 Requirements for routine and for intensive sampling periods

To obtain a comprehensive database, 18 months of continuous sampling at surface sites would be needed. Beginning in May of one year and ending in October of the following year, the study would cover two ozone seasons and one winter. Such a study would encompass most of the range of typical meteorological variations. While less important for the O₃ Weekend Effect, sampling during the winter is needed to support research on weekday/weekend differences in fine particulate matter (PM_{2.5}) and other pollutants that have important health concerns during the winter months.

Air quality sampling in support of research on the ozone weekend effect will require intensive sampling on more days than most other field studies. Studies such as SCAQS and SCOS97 included intensive sampling operations on less than 20 days each, which was sufficient to acquire episodes for modeling representative "peak days" but was not sufficient to address the ozone weekend effect.

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The ozone weekend effect is embedded in the differences in ozone and its precursors for each day of the week. All seven days are important, with weekday-weekend transitions being most important. Furthermore, most days in an ozone season, rather than just a few episode days, will contain relevant information. A transition from 70 ppb ozone on Friday to 90 ppb on Saturday can be just as revealing as a transition from 140 ppb to 160 ppb.

It is particularly important to sample days in sequence so that Fridays can be compared to adjacent Saturdays, etc. In the combined data from 34 intensive sampling days during SCAQS and SCOS97, there are just four transitions from Friday to Saturday, one transition from Saturday to Sunday, and one transition from Sunday to Monday. Only one of the episodes includes Friday through Monday continuously.

Intensive sampling involves measurements of pollutants aloft (see paragraph 7.1.1.1.4 below) in addition to the continuous surface measurements. These data are difficult and expensive to acquire but are needed to characterize the size, composition, strength (concentrations), duration, and frequency of reservoirs of polluted air aloft. To do this well (i.e., have a sound statistical basis), a minimum of 15 intensive periods of 4 days each are needed, making a total of 60 intensive sampling days. Each four-day sequence must include Friday, Saturday, Sunday, and Monday.

7.1.1.1.2 Data quality

Highly accurate and reliable data are needed to identify and quantify the alternative causes of the ozone weekend effect. Therefore, measurements would be made using state-of-the-art, artifact-free methods that can be deployed in the field.

Thorough QA/QC procedures should be applied to assure the validity of all data. The QA/QC procedures should include representative co-located monitoring at two or more locations for each type of data.

7.1.1.1.3 Requirements for air quality sampling at the surface

◆ Resolution in time

For air quality measurements at the surface, hourly resolution is feasible and should be sufficient for all compounds of interest. Measurements at longer time intervals are significantly less useful and should not be pursued.

◆ Resolution in space

In each air basin to be considered, data are needed at sites representing source regions, sites representing receptor regions, and sites that help discriminate between alternative causes of the ozone weekend effect. The sites representing these categories may shift under differing meteorological conditions.

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In the South Coast Air Basin (SoCAB), seven to twelve locations are recommended to provide sufficient spatial coverage. One to three upwind, coastal sites would be drawn from Costa Mesa, Hawthorne, N. Long Beach, and West LA. Two or three central source sites would be drawn from Anaheim, Burbank, LA – N. Main, Lynwood, Pasadena, and Pico Rivera. Two or three downwind receptor sites would be drawn from Lake Elsinore, Lake Gregory, Riverside, San Bernardino, and Santa Clarita. Finally, two or three transitional (between the primary source and receptor regions) sites would be drawn from Azusa, Reseda, and Upland. For other air basins, a similar mix of sites would be selected.

A set of nine sites with intermediate spatial resolution is the following:

Coastal: N. Long Beach and West LA

Central: LA – N. Main, and Lynwood

Downwind receptors: Lake Gregory, Riverside, and Santa Clarita

Transitional: Reseda and Upland.

◆ **Required pollutants**

Measurements of the following pollutants are needed:

- *Aggregate hydrocarbons*

Hourly measurements for the duration of the field study are needed for total non-methane organic compounds (TNMOC). Understanding the ratio of TNMOC (or VOC) to NO_x is crucial for discriminating between alternative causes of the ozone weekend effect.

Accurate measurement of TNMOC is difficult. Summing of VOC species is not an appropriate substitute for TNMOC because the products of photochemical reactions involving VOCs are typically compounds that contain oxygen, and most of these compounds are not included in the list of VOCs analyzed. In addition, oxygenated compounds tend to escape detection by the methods commonly used to measure VOCs.

Hourly measurements are needed to better characterize rapid changes in concentrations (e.g., morning mixing processes) and diurnal variations, particularly in relation to hourly changes in VOC/ NO_x ratios. The 3-hour interval in the PAMS program is too coarse for these purposes. In addition, it has been reported that the PAMS data may underestimate the total VOCs by 30 percent or more.

- *Speciated hydrocarbons*

Measurements of selected hydrocarbon species are needed in addition to the aggregate TNMOC data. The standard set of compounds measured in the PAMS program is minimally sufficient. Additional compounds should be included if they will help discriminate between alternative causes of the ozone weekend effect.

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Hourly measurements of speciated hydrocarbons are not needed for every day of the field study. Previous analyses of PAMS data have shown consistency in the relative concentrations of different VOC species. However, measurements are needed in sufficient quantity to note significant differences between hourly profiles by day-of-week. Hourly samples on as few as 2 to 4 days for each day of the week (14 to 28 days total) could be sufficient for this purpose.

- *Compounds containing nitrogen*

Routine measurements of NO_x includes several nitrogen-containing compounds in addition to NO and NO_2 . The compounds that are partially captured include PAN, gaseous nitric acid, nitrate particles, and N_2O_5 , among other reactive compounds containing nitrogen. Routine methods for NO_x measure a portion of these important compounds in aggregate rather than separately.

Routine NO_x data are available at many locations but these data lack the precision as well as the specificity needed to obtain accurate estimates of important ratios. For example, VOC/NO_x , O_3/NO_y , and NO_2/NO may help show which alternative causes of the ozone weekend effect are important. Progress in understanding the ozone weekend effect is unlikely without state-of-the-art measurements for nitrogenous compounds.

- NO_x

Nitrogen oxides, or NO_x , is a major focus of weekend effect research. According to the NO_x -reduction hypothesis, the ratio of VOCs to NO_x is the dominant factor determining the ozone weekend effect. The ratio of NO_2 to NO is also a factor in NO_x -timing hypothesis. The ratios of O_3 to NO_y aloft may indicate whether conditions there are mostly NO_x -limited or VOC-limited.

Conventionally, the term NO_x refers to the sum of NO and NO_2 . However, routine measurements for NO_x have two drawbacks, as noted above. First, the routine method lacks specificity since compounds such as gaseous nitric acid (HNO_3) and peroxyacetylnitrates (PAN) can interfere and appear as NO_2 to the instrument. Second, the routine method cannot quantify NO_x accurately at very low concentrations. Relatively recent advances in monitoring methods have essentially overcome both of these limitations.

Direct, accurate, and specific measurements of both NO and NO_2 are needed hourly throughout the duration of the study to help resolve the cause(s) of the ozone weekend effect.

- Total reactive nitrogen: NO_y

Total reactive nitrogen, or NO_y , is the sum of NO_x , gaseous nitric acid, PAN, and other reactive nitrogenous compounds such as HONO and N_2O_5 . NO_y is an important part of analyses that concern the ozone weekend effect.

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The ratio O_3/NO_Y can help indicate whether a photochemical system is in a VOC-limited or NO_X -limited condition. It has been suggested that low concentrations of NO_Y alone may indicate NO_X -limited conditions. The concentration of NO_Y may be a crucial factor when assessing the impact of carryover aloft on ozone formation.

Accurate and specific measurements of NO_Y are needed hourly throughout the duration of the study to help resolve the cause(s) of the ozone weekend effect.

- Total reacted nitrogen: NO_Z

The total reacted nitrogen, or NO_Z , is equal to $NO_Y - NO_X$. The slope of a line relating ozone (ppb) to NO_Z (ppb) has been called the "ozone production efficiency." This parameter may be helpful in assessing the role of the NO_X -timing hypothesis in the ozone weekend effect. According to this hypothesis, the timing of NO_X emissions on weekends causes the smaller amount of NO_X on weekends to be more efficient in producing ozone compared to the larger amount of NO_X on weekdays.

Because NO_Z is NO_Y minus NO_X , high quality NO_Z data depends on the collection of high quality NO_X and NO_Y data.

- Nitric acid: HNO_3

Gaseous nitric acid, $HNO_3(g)$, has been used in relation to hydrogen peroxide to discriminate between VOC-limited and NO_X -limited photochemistry. In addition, the nitric acid concentration can indicate the rate at which nitrogen-containing compounds are removed from the ozone-producing system. The faster nitrogen is removed, the faster the atmosphere changes from a VOC-limited condition to a NO_X -limited condition. The timing of this transition on different days of the week may be an important factor in assessing the contributions of several hypotheses.

Accurate and specific measurements of $HNO_3(g)$ are needed in sufficient quantity to note significant differences between hourly profiles by day-of-week. Hourly samples on 10 days for each day of the week (70 days total) could be sufficient for this purpose.

- Peroxyacetylnitrates: PAN

Peroxyacetylnitrates, or PAN, is a family of compounds that are notoriously difficult to measure. These compounds contain two parts, an organic radical and NO_2 . PAN has been identified as a source of both NO_2 and reactive organic species in polluted air masses transported long distances. PAN may also be an important indicator of the impact of carryover, especially carryover aloft.

Accurate and specific measurements of PAN are needed in sufficient quantity to note significant differences between hourly profiles by day-of-week. Hourly samples on 10 days for each day of the week (70 days total) could be sufficient for this purpose.

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- *Other species*

If reliable and accurate methods are available to measure nitrous acid (HONO), hydrogen peroxide (H₂O₂), hydroxyl radicals (*OH), and nitrate radicals (*NO₃) these species should be included on enough days to provide useful contrasts between weekdays and weekends.

Data for elemental carbon (black particulate matter) and solar radiation should also be collected at each surface site. These data are necessary to assess the importance of the “aerosol and UV radiation” hypothesis concerning the impact of ultra-violet radiation on the ozone weekend effect. According to this hypothesis, vehicular activity is much lower on weekends resulting in large reductions in elemental carbon. With less black particulate matter, less UV radiation is absorbed and more UV radiation is available to initiate the photochemical reactions that lead to ozone.

7.1.1.1.4 Requirements for measurements aloft

Data from the 1997 Southern California Ozone Study (SCOS97) and other field studies indicate that layers of polluted air sequestered aloft can contain high concentrations of aerosols and ozone. Furthermore, such layers aloft may be routine rather than unusual.

An extensive measurement program is necessary to determine the frequency and persistence of polluted layers aloft, to quantify the pollutants contained in such layers, to evaluate diurnal patterns aloft, and to quantify how surface concentrations are affected. Measurements aloft are required for a minimum of 15 weekday-weekend transitions, that is, Friday to Saturday to Sunday to Monday. This means a minimum of 60 days for collecting samples aloft.

- ◆ **Resolution of measurements aloft in time and space**

It is not feasible to acquire some types of data aloft with the same high resolution that is feasible at the surface. For example, an ideal sampling plan might call for measurements every 50 meters between the surface and 1000 meters for each hour. At this resolution, the data collected aloft would be 20 times as much as the surface data for the same period. Although compromise may be necessary, the study design must remain sufficient to achieve the goals.

Measurements aloft should characterize a minimum of four locations in the SoCAB – a central location and three surrounding locations. The geographical orientation of the South Coast Air Basin suggests the need for five locations. These five locations are the following: (central) San Gabriel Valley, (northwest) San Fernando Valley, (west) coastal LA, (south) Orange County, and (east) Riverside or San Bernardino County. Specific locations might be Cal Poly-Pomona, CSU-Northridge, UCLA, UC-Irvine, and UC-Riverside.

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Measurements aloft should be collected with enough resolution to characterize the important layers in the lower atmosphere and their interactions with pollutants at the surface. One design that may be satisfactory would gather integrated samples, one between 100 and 200 meters, one between 200 and 500 meters, and another between 500 and 1000 meters. Alternatively, measurements might be taken at heights based on significant changes in temperature or humidity.

Hourly measurements aloft are highly desirable but may not be feasible for the 60 days (minimum) that are required (see section 7.1.1.1.1 above). Instead, it may be satisfactory to sample hourly during daylight hours, with less frequent sampling during the remaining hours. Some nighttime sampling is vital for determining the identity and quantity of pollutants that carry over aloft.

◆ **Methods**

Aircraft, balloons, towers, and other means may be used to gather the needed data aloft. Remote sensing instruments (e.g., LIDAR) would allow some measurements to be sampled with finer resolution in space and time.

Sampling methods used aloft should provide accuracy and precision similar to the sampling methods used for surface measurements.

◆ **Pollutants**

Measurements aloft should include the same spectrum of pollutants as measured at the surface whenever possible.

◆ **Tracers**

The proportional contributions of fresh emissions from the surface and aged emissions from aloft may be crucial to a proper understanding of the ozone weekend effect. Tracers might be used to increase our understanding of vertical mixing and the weekend effect. Tracers released aloft before sunrise and subsequently measured at ground level might help attribute the surface concentration of a pollutant to fresh emissions from the surface and to aged emissions from aloft in the proper proportions.

This information is needed to help evaluate the validity of the “carryover aloft” hypothesis. This information may also help validate the performance of photochemical simulation models used to explore the causes of the ozone weekend effect.

7.1.2 Analyses of the ozone weekend effect in other regions

For the most part, this report focuses on results of analyses concerning the South Coast Air Basin. One naturally asks, “What do similar analyses show in other regions of California?” Some of the technical chapters recommend such analyses. At this time, however, extensive investigation of other regions is not recommended

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because of limited data characterizing composition, historical trends, and spatial variations.

The SoCAB is relatively rich in the extent and variety of data collected. Nevertheless, the data were inadequate to resolve key issues. The dense monitoring network was encouraging, but very few locations collected crucial hydrocarbon data. The rich database for freeway traffic was interesting, but the data did not include surface streets and did not resolve light-duty and heavy-duty activity by hour. WIM classification data were helpful, but the number of sites is limited. More in-depth field studies have been carried out in the SoCAB than any other basin, but the available data on air quality aloft remain inadequate for the present task.

Despite the generous sources of data in the SoCAB, the analyses were inconclusive. Therefore, analyses in other regions should be carried out only if such studies are considered both vital and feasible. Otherwise, valuable resources are likely to purchase nothing but additional inconclusive results.

7.1.3 Develop day-specific emission inventories to support efforts to model weekday-weekend differences in ozone

Day-of-week hourly emission inventories are needed to support photochemical modeling simulations of the ozone weekend effect. To date, day-of-week emission inventories used in modeling exercises have been largely speculative. Day-specific hourly emissions are needed for mobile, stationary, and area sources.

The following recommendations address work already planned or in progress and work that may be needed in addition to present plans.

7.1.3.1 Acquire and analyze hourly data for on-road vehicle activity by vehicle class throughout the SoCAB.

The traffic data presented in Chapter 5 were lacking in at least four ways. First, the data did not include freeways in the Riverside and San Bernardino County portions of the SoCAB. Second, the hourly freeway data for Los Angeles and Orange Counties were not segregated by vehicle class. Third, no data for surface street activity were considered for any part of the SoCAB. Fourth, the WIM classification data were not provided in an hourly format. The recommendations that follow address these issues.

7.1.3.1.1 Acquire hourly data from WIM stations and use these data to disaggregate hourly freeway data by vehicle class

The California Department of Transportation (CALTRANS) maintains a limited network of Weigh-in-Motion (WIM) stations on state highways. These stations can provide important information on weekday-weekend differences in the volume and composition of traffic. Each station collects hourly data on the frequency of vehicles

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in 14 different vehicle classes. Hourly traffic data are important because they can be compared more effectively with hourly data on ambient air quality. Hourly WIM data are analyzed and compared to hourly air quality data in Chapter 5.3 of this report.

ARB and CALTRANS now cooperate each year to summarize the hourly traffic data from all WIM stations in California. At this time, comprehensive summaries for 2001 and 2002 are available.

7.1.3.1.2 Acquire and analyze hourly summaries for vehicle activity by class on surface streets throughout the SoCAB.

Approximately half of the total vehicle miles traveled in the SoCAB occur on freeways; the remaining VMT occur on surface streets. Vehicle activity data for surface streets are less readily available compared to freeway data. Nonetheless, these data are needed to complete the picture of on-road motor vehicle activity by hour and day of week in the SoCAB.

Hourly traffic counts on surface streets by vehicle class are needed throughout the SoCAB. At least three vehicle classes – light-duty, medium-duty, and heavy-duty – should be supported.

Data should be gathered in each of the eleven sub-domains identified in Section 5.2 of this report. Additional sub-domains of Riverside and San Bernardino Counties should also be included. The existing air quality monitoring stations at Fontana, Lake Elsinore, Redlands, Riverside, San Bernardino, and Upland could be used as center-points for sub-domains of Riverside and San Bernardino Counties.

In each sub-domain, hourly data should be collected for a representative sample of surface street locations for a minimum of four complete weeks.

7.1.3.1.3 Update analyses that were based on 1997 traffic data to synchronize them with analyses of more recent data

The hourly traffic profiles available from 1997 may be satisfactory for some time to come. However, as significant doubts arise about their representativeness, the earlier analyses of 1997 traffic data should be updated using concurrent data.

7.1.3.2 Quantify WD/WE emission differences for important stationary-source and area-source categories

Emissions from some categories of stationary-sources and area-sources may be substantially different on weekends compared to weekdays. A two-stage effort is recommended. First, identify significant stationary-sources and area-sources that are likely to operate differently on weekends compared to weekdays. Some of these efforts have already begun. Second, gather sufficient information to characterize the activity levels of these sources by hour by day-of-week.

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This effort should focus on the SoCAB first and other air basins as resources and priorities allow.

◆ **Identify important emission categories with day-of-week variations**

The search for important categories of stationary-sources and area-sources begins with categories that emit a significant fraction of the total VOC or NO_x emissions. For comparison to mobile source categories, on a weekday in the SoCAB in 1995, trucks emit almost 20% of the total NO_x emissions from all sources, while fuel combustion at stationary sources accounts for approximately 10% of the total.

The search continues by selecting those categories that are likely to operate differently on weekends compared to weekdays. Important differences may include quantitative changes in activity and qualitative changes in activity, such as a change in location.

◆ **Collect information needed to characterize emissions by hour by day-of-week for the important emission categories**

The current structure for the emission inventory for stationary sources reserves space for codes that indicate the days of operation per week and the hours per day when operating. This information would provide a basis for constructing day-specific hourly emission inventories. However, many districts have not yet reported the detailed temporal information describing the activity patterns of each facility.

For the important source categories, the needed data to construct satisfactory day-specific hourly inventories should be collected.

◆ **Analyze existing data from continuous monitoring of major industrial sources of NO_x emissions**

During the last decade, many major industrial sources of NO_x emissions installed “in-stack” or continuous emissions monitoring (CEM) systems. Facilities in several source categories may qualify, including oil refineries, electric utilities, co-generation facilities, and others requiring high-temperature fuel combustion.

The plumes from these sources are buoyant due to their high temperature and tend to inject NO_x emissions into polluted layers aloft. In the morning, surface measurements are not likely to capture NO_x from buoyant plumes. Day-of-week comparisons of NO_x measurements aloft with activity profiles for sources with buoyant plumes may be an important factor in understanding the ozone weekend effect.

Day-of-week emission profiles for NO_x from facilities with CEM should be constructed. Some testing of facilities without CEM should be performed to confirm that the emission profiles for similar types of facilities with CEM could be applied to facilities without CEM.

7.1.4 Design and execute modeling studies of the ozone weekend effect

Dynamic simulation models such as the Urban Airshed Model (UAM) are important tools for comparing alternative strategies for reducing emissions. These models can simulate the effects of changes in emissions that have not yet been experienced in the real world.

Effective and reliable simulations require satisfactory agreement between model predictions and appropriate “base case” conditions. The modeling exercises recommended here should not be carried out until such a suitable base case for a weekend episode has been developed. When a satisfactory base case is available, a carefully designed series of modeling exercises should be run. These exercises should address all of the alternative hypotheses concerning the cause(s) of the ozone weekend effect.

The Coordinating Research Council and the National Renewable Energy Laboratory recently contracted with ENVIRON to carry out a series of modeling exercises related to the ozone weekend effect. Although, these exercises included a day-of-week emission inventory based on freeway activity data, the emission inventory is still in need of significant improvement (e.g., activity data for surface streets). In addition, other modeling issues raised in Chapter 6 of this document were not addressed. The framework for these exercises and the results should be fully considered before further modeling exercises are designed and executed.

The results of the photochemical modeling exercises should be compared to the ambient data and to the results of selected laboratory experiments, such as those described in the next section.

7.1.5 Update laboratory experiments and extend laboratory data concerning alternative causes of the ozone weekend effect

Scientists have carried out many useful experiments that reveal aspects of ozone-producing systems. These experiments are often designed from a generic perspective instead of a location-specific perspective. Some of these classic experiments should be repeated using conditions specific to those found during the air quality sampling discussed above. In addition, new experiments should be done to isolate important points that may discriminate between the alternative hypotheses described in Chapter 3 of the Staff Report.

7.1.5.1 Evaluation of model accuracy for a wide range of VOC/NO_x ratios when NO_x concentrations are low

Chemical mechanisms used in photochemical simulation models should be validated for conditions that presently prevail on weekdays and weekends. Because the VOC/NO_x ratio is a crucial factor affecting the role of NO_x in ozone formation, chemical mechanisms should be validated for a range of VOC/NO_x ratios between two and forty (e.g., 2, 4, 6, 8, 10, 15, 20, 30, 40). Because ozone formation rates appear to decrease under low NO_x conditions, chemical mechanisms should also be

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validated for NO_x concentrations (mixing ratios) between zero and 100 ppb [e.g., 0, 10, 20, 30, 40, 60, 80, 100]. This joint spectrum of VOC/NO_x ratios and NO_x concentrations corresponds roughly to present-day conditions in the SoCAB at the surface and aloft.

7.1.5.2 Evaluation of NO_x-timing effects

Experiments conducted by Hess, et al., considered some effects of NO_x timing (cf. references for Chapter 3 of the Staff Report). These experiments did not always use real-world conditions because their purpose was to emphasize differences between alternative chemical mechanisms used in photochemical models. Nevertheless, the experiments indicated that fresh NO injected around mid-day may cause a large increase in ozone.

When applied to the ozone weekend effect in the SoCAB, the experiments by Hess et al. have a potentially important drawback. The experiments used initial VOC/NO_x ratios from 15 to 50. Current data in the SoCAB indicate that VOC/NO_x ratios at the surface are generally between 5 and 15 depending on the day of week and the time of day. In addition, the experiments may have used mixtures of VOC species that differ substantially from those that prevail in the SoCAB today.

Selected laboratory experiments that alter the timing and the amount of NO_x emissions should be carried out. These experiments should use conditions that reflect the best available data for VOCs and NO_x in the SoCAB. The chief focus of these experiments is to assess the plausibility of the NO_x-timing hypothesis.

7.1.5.3 Laboratory evaluation of the effects of carryover aloft

The effect on surface ozone concentrations of materials that carryover aloft is an important question for further research. If possible, smog chamber experiments should be used to investigate the effects of "aged," ozone-rich air on the ozone production from fresh emissions.

Earlier experiments have considered dilution effects and some timing effects. Dilution, however, has been explored using clean air to dilute contaminated air such as that found near the surface. Dilution experiments should be carried out in which the air used to "dilute" contains materials that simulate the air that may carryover aloft.

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