ANALYSIS OF PAMS DATA IN CALIFORNIA VOLUME II: THE USE OF PAMS DATA TO EVALUATE REGIONAL EMISSION INVENTORIES IN CALIFORNIA

FINAL REPORT
STI-998392-1884-FR

By:
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Prepared for:
California Air Resources Board
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PREFACE

In accordance with the 1990 Clean Air Act Amendments, the U.S. Environmental Protection Agency (EPA) initiated the Photochemical Assessment Monitoring Stations (PAMS) program for serious, severe, and extreme ozone nonattainment areas. The PAMS networks monitor for volatile organic compounds (VOCs), ozone, oxides of nitrogen (NO_x), and meteorological parameters. The PAMS networks were designed to provide data for the assessment of population exposure, ozone formation, and evaluation of ozone control strategies. The EPA Office of Air Quality Planning and Standards has sought to provide the EPA regional offices and the states with the necessary analytical tools, training, and guidance to collect and use the PAMS data. To this end, the EPA, California Air Resources Board (ARB), Sacramento Metropolitan Air Quality Management District, San Joaquin Valley Unified Air Pollution Control District, and Ventura County Air Pollution Control District sponsored research into the analysis of PAMS air quality and meteorological data collected at the Districts' PAMS sites in Sacramento, Fresno, and Ventura counties and the ARB's long-term trend sites located in Los Angeles and San Diego. Requested tasks encompass upper-air meteorological data processing and analyses, emission inventory evaluation, and trends analyses. Results of the data analyses for these three topic areas are presented in three volumes:

Analysis of PAMS Data in California Volume I: The use of PAMS radar profiler and RASS data to understand the meteorological processes that influence air quality in selected regions of California. MacDonald C.P., Chinkin L.R., Dye T.S., Anderson C.B. (1999) Report prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC by Sonoma Technology, Inc., Petaluma, CA, STI-998391-1888-FR, May.

Analysis of PAMS Data in California Volume II: The use of PAMS data to evaluate regional emission inventories in California. Haste-Funk T.L., Chinkin L.R. (1999) Report prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC by Sonoma Technology, Inc., Petaluma, CA, STI-998392-1884-FR, May.

Analysis of PAMS Data in California Volume III: Trends analyses of California PAMS and long-term trend air quality data (1987-1997). Wittig A.E., Main H.H., Roberts P.T., Hurwitt S.H. (1999) Report prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC by Sonoma Technology, Inc., Petaluma, CA, STI-998393-1885-FR, May.

ACKNOWLEDGMENTS

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1. INTRODUCTION

1.1 BACKGROUND

Emission inventory development is a complex process that involves estimating and compiling emissions activity data from hundreds of point, area, and mobile sources in a given region. Because of the complexities involved in developing emission inventories, and the implications of errors in the inventory on air quality model performance and control strategy assessment, it is important to evaluate the accuracy and representativeness of any inventory that is intended for use in pollution control strategy assessment. One way to assess a regional emission inventory is to perform a top-down inventory evaluation by comparing ozone precursor emission estimates to ambient air quality data using ratio comparisons of hydrocarbon/NO_x and CO/NO_x (Haste et al, 1998a, b; Korc et al, 1993, 1995; Fujita et al., 1992, 1994). Comparison of ambient data and emission inventory estimates are useful for examining the relative mass and composition of the ambient air and emissions estimates.

The objective of this work effort is to assess the consistency of the most recently estimated regional emission inventory for three counties in California (e.g., Fresno, Sacramento, and Ventura counties) with ambient data. Ambient hydrocarbon, CO, and NO_x measurements collected during the summer of 1996 at six Photochemical Assessment Monitoring Stations (PAMS) located in Fresno, Sacramento, and Ventura counties were compared to 1996 county-wide emission estimates of hydrocarbon, CO, and NO_x. The 1996 ambient data were selected for this analysis to correspond to the most recent and readily available inventory for these counties. **Figure 1-1** depicts the State of California as well as the location of the PAMS monitoring sites in each of the three counties studied.

Comparisons of ambient data and emission estimates for hydrocarbon, CO, and NO_x are based on the premise that ambient concentrations are primarily influenced by fresh emissions emitted in the vicinity of the monitor. However, precursor transport, carryover effects, and chemical reactions can also influence ambient concentrations. The influence of these confounding effects on the comparison can be minimized (but not eliminated) by selecting monitoring sites located in areas with high emission rates, and by examining data collected when emission rates are high and reaction rates are low. Early morning sampling periods are the most appropriate to use when making emission comparisons because typically emissions are high, while wind speed, atmospheric mixing height, temperature, and chemical reactivity are low. Data from early morning sampling periods are most likely to contain minimal effects from upwind transport and photochemistry.

Comparisons of ambient data and emission estimates for hydrocarbon and NO_x are also based on the assumption that emission inventory NO_x estimates are more accurate than hydrocarbon estimates. Since NO_x emissions are directly associated with combustion sources (primarily point and mobile sources) and hydrocarbons are emitted by a much broader range of sources (both man-made and biogenic, as well as combustion and non-combustion processes), it is assumed that NO_x is more accurately estimated in emission inventories. Past studies suggest that NO_x emission estimates are fairly accurate, while hydrocarbon emission estimates are more uncertain (ARB, 1997; Gertler and Pierson, 1996).

1.2 OVERVIEW OF THE REPORT

This report consists of six sections. Section 2 provides a discussion of the technical approach and the uncertainty issues associated with top-down emission inventory evaluations. Section 3 describes the characteristics of the ambient air quality, meteorological, and emission inventory data used in the evaluation. Section 4 provides an analysis of the emission inventory including hydrocarbon/NO_x and CO/NO_x ratio analyses and detailed hydrocarbon composition. Section 5 includes a summary of results, conclusions, and recommendations on possible improvements to the inventory. Section 6 contains the report references. A list of hydrocarbon species measured at each monitoring site used in this study is provided in Appendix A.

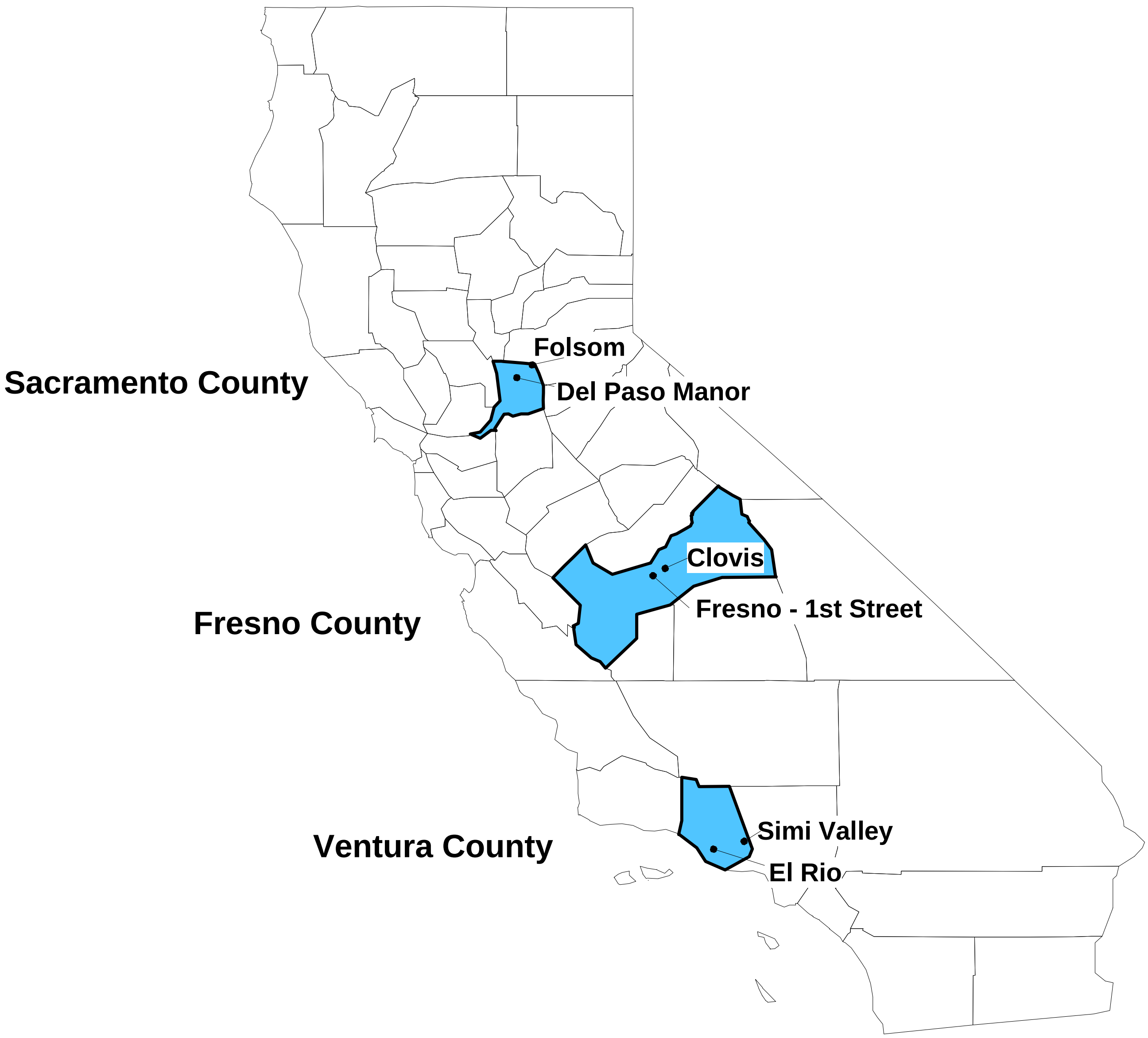


Figure 1-1. Map of California and the PAMS ambient monitoring site locations in Sacramento, Fresno, and Ventura counties.

2. TECHNICAL APPROACH USED AND UNCERTAINTY ISSUES FOR EMISSION INVENTORY EVALUATIONS

2.1 TECHNICAL APPROACH

Top-down emission inventory evaluations can be divided into two parts: 1) comparison of ambient- and emission inventory-derived hydrocarbon/NO_x and CO/NO_x ratios, and 2) comparison of chemical species groups and/or individual chemical species. Comparison of ambient- and emission inventory-derived hydrocarbon/NO_x and CO/NO_x ratios provides a method to compare the relative mass of pollutants in the ambient air and in the inventory. Because certain species are characteristic of emissions from specific source categories, comparisons of the species in the ambient air and in the emission inventory can serve as an indicator of the representativeness of the inventory.

In this study, comparisons between weekday ambient-derived ratios and emission inventory-derived hydrocarbon/NO_x and CO/NO_x ratios were calculated for each of the four wind quadrants surrounding the ambient monitor at each site and were compared to the county total emissions ratios. **Figure 2-1** depicts the spatial designation of the four wind quadrants surrounding an ambient monitor. Typically, analyses are performed by spatially matching a gridded, speciated, temporally resolved (hourly) emission inventory to the geographical position of the ambient monitoring site and the four wind quadrants surrounding the site. Detailed spatial analyses could not be made in this study, however, because the emission inventory data were resolved only to the county level. Instead, wind pattern analyses were conducted to determine the transport distances air parcels traveled during the morning ambient sampling period. Because of the various meteorological factors that could affect ambient pollutant ratios, ambient-derived ratios are presented for all four quadrants.

Data collected during the 0500-0800 PST sampling period were used for the analysis to capture a time period when fresh emissions are generally high, while temperature and chemical reactivity are low. It should be recognized that CO and NO_x emissions from point sources with elevated stacks may be injected above the morning inversion and, hence, may not contribute to surface-level concentrations. In order to examine the effects of elevated point source emissions, comparisons were made both including and excluding emissions from point sources.

Speciation profiles provide a detailed breakdown of the individual chemical species emitted by a specific source category. When an emission inventory is "speciated" each source category is assigned a speciation profile which is then used to disaggregate total hydrocarbon emissions into individual chemical compounds. Comparisons of the individual hydrocarbon species in the ambient air and in the inventory can provide insight into how well the speciation profiles used to disaggregate the emission inventory represent the chemical composition of the ambient air. Comparisons of the relative amounts of individual organic hydrocarbon species and species groups in the ambient data and in the inventory were made to evaluate the accuracy of the inventory speciation. Comparisons of the emissions from point, area, and on-road mobile sources were performed to evaluate how well the emissions from each source category compare with the ambient data.

2.2 UNCERTAINTY ISSUES

The uncertainties associated with comparisons of emission inventory-derived and ambient-derived hydrocarbon/NO_x and CO/NO_x ratios can be divided into three categories: (1) accuracy of the emission inventory, (2) accuracy of the measurements of ambient concentrations, and (3) suitability of comparisons. Issues that must be accounted for are listed below.

- Emission inventory-related issues such as spatial and temporal allocation, speciation profiles, and assignment of the correct profiles to source categories.
- Measurement-related issues such as data quality and validation including the influence of instrument detection limits and precision; the identification, misidentification, or lack of identification of species; potential sampling or handling losses of total mass or individual species; and the overall uncertainties of the ambient measurements.
- Comparison-related issues such as the matching of hydrocarbon species in the emission inventory and ambient hydrocarbon species; the temporal matching of the emissions and ambient data; and meteorological factors such as inversion height, wind speed, and wind direction which influence which emissions are sampled in the ambient air.
- Effect of background concentrations; fresh emissions are not the only influence on monitoring data.
- Meteorological effects; emissions injected above the morning inversion layer may not be detected at a ground level monitor.

Uncertainties associated with the emission inventory are inherent in the methodology used to develop the inventory. Emissions estimates are only as accurate as the underlying activity data and emission factors used to calculate the estimates. Emission inventory evaluations are typically performed on emissions data that are intended for use in air quality modeling, and therefore should be of the highest possible quality. Measurement-related uncertainties in the ambient data are minimized by using ambient data that have undergone exhaustive quality assurance/quality control (QA/QC) protocols and screening criteria. Comparison-related issues are addressed by matching individual chemical species in the ambient data and the inventory prior to analysis. Emissions and ambient data are compared for the same early-morning time period and are typically matched spatially by wind speed and direction.

In this study, the spatial matching of emissions and ambient data introduces a degree of uncertainty. Because the emissions data are resolved only at the county level, the county-total emissions were compared to the average of the ambient data samples, rather than to the individual quadrants' concentration ratios. In regions where ambient concentrations are fairly uniform, the county-total emissions comparison is more robust. However, in regions exhibiting high ambient concentration gradients, it is likely that a county-total emission inventory is not adequately resolved to make sound comparisons between the ambient data and the inventory.

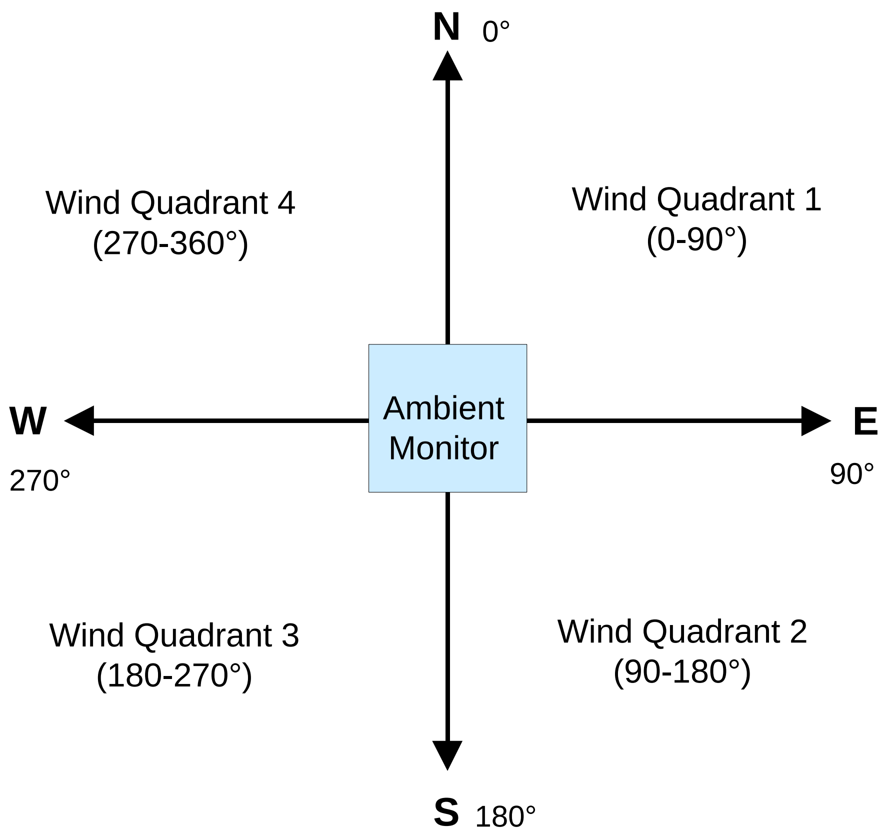


Figure 2-1. Wind quadrant definitions surrounding an ambient monitor. The quadrants represent the direction from which the wind is blowing.

3. AMBIENT AND EMISSION INVENTORY DATA

3.1 AMBIENT DATA

The ambient data used to evaluate the emission inventory for Sacramento, Fresno, and Ventura counties consisted of early morning weekday and Saturday surface meteorological data and surface concentrations of hydrocarbon, CO, and NO_x collected at six PAMS monitoring sites during the summer of 1996. Ambient air quality data from two sites in each county were acquired: Del Paso and Folsom in Sacramento; Clovis and Fresno in Fresno County; and El Rio and Simi in Ventura County. Monitoring sites were selected based on geographic location and diversity of emission source influences as well as the availability and quality of ambient data. Three-hour average hydrocarbon samples were collected at each site during the 0500-0800 PST period every six days from July through September 1996. Hourly CO and NO_x data were collected for the same time period at each site except at the Folsom site where CO was not measured.

3.1.1 Ambient Meteorological Data

Wind analyses were performed to determine air parcel travel distances for the 0500-0800 PST time period, corresponding to the air quality data collected from July through September 1996. To determine the 0500-0800 PST transport of surface emissions, vector average winds were calculated at each site. Frequency distributions of 0500-0800 PST average wind directions by quadrant for each site are shown in **Figure 3-1**.

From 0500-0800 PST, surface winds are predominately from the southeast in Fresno County (Clovis and Fresno) and Sacramento County (Del Paso and Folsom). In Ventura County at El Rio, early-morning winds are predominately from the northeast while early-morning winds at Simi Valley are typically from the south. Average transport distances for the 0500-0800 PST time period were calculated for each site. Three-hour transport distances in Fresno and Sacramento counties were approximately 13 km. The average transport distance in Ventura County is slightly higher, ranging from 15 to 20 km.

The wind summary presented above is useful for investigating the directional influence on the ambient monitor as well as how far emissions may have traveled to the monitor during the early morning. The wind summaries can also be used for comparing pollutant ratios in the ambient data to the emission inventory ratios for the spatial configurations corresponding to the four wind quadrants if a gridded emission inventory is available. However, because the inventory data used in this evaluation are resolved at the county level, a comparison between them and the ambient data by wind quadrant should not be made.

3.1.2 Ambient Air Quality Data

During the summer of 1996, hourly CO and NO_x data were collected at Clovis, Fresno, Del Paso, El Rio, and Simi Valley. No CO data were collected at Folsom in 1996. Three-hour average hydrocarbon samples were collected at each of the sites during the 0500-0800 PST period every six days from July through September 1996. At all six sites, 3-hr average hydrocarbon samples collected on weekdays at begin hour 0500 PST were used for the evaluation. Hourly weekday CO and NO_x data collected at begin hours 0500, 0600, and 0700 PST were averaged and matched to the 3-hr hydrocarbon samples for the ratio analyses.

Thorough quality assurance and screening analyses were performed on all of the ambient air quality and hydrocarbon data collected at each of the six sites. Minimum concentrations of ambient hydrocarbon and NO_x data were established to identify samples that are representative of fresh emissions and to eliminate samples at or near instrument detection limits. In this study, a hydrocarbon threshold of 100 ppbC and a NO_x threshold of 10 ppb were used to screen the data. Ambient samples not meeting these screening criteria were eliminated from further use in the analyses.

Table 3-1 shows the 0500-0800 PST weekday average total non-methane organic compounds (TNMOC), identified non-methane organic compounds (ID NMOC), NO_x, and CO concentrations at each site. The TNMOC concentrations include both identified and unidentified species while the ID NMOC is the sum of only the identified species. Note that no CO data were collected during the summer of 1996 at Folsom and only limited hydrocarbon and NO_x data (only three valid samples meeting screening criteria) were available at Folsom.

Typically PAMS sites designated as Type 2 (sites representative of fresh ozone precursor emissions) are used for the emission inventory evaluation. However, the Folsom site is designated as a Type 3 site, representative of maximum ozone impact. Because it is of interest to examine data collected at two different sites in each county, Folsom was included in the analyses and discussion presented in this report even though it is not a Type 2 site. However, as indicated in Table 3-1 there are not enough data for the Folsom site to perform robust analyses. Furthermore, the hydrocarbon concentrations at Folsom are significantly lower than concentrations at any of the other sites. Although the results of analyses performed for Folsom are presented in this report, they should not be over-interpreted.

Another way to compare sites and obtain an overall understanding of the data is to inspect various stratifications of selected pollutants. The data may be stratified in many different ways: by site, year, month, day of week, weekday/weekend, and time of day. One useful plot is a box-whisker plot (an example is shown in **Figure 3-2**). The box shows the 25^{th}, 50^{th} (median), and 75^{th} percentiles. The whiskers always end on a data point, so when the plots show no data beyond the end of a whisker, the whisker shows the value of the highest or lowest data point. The whiskers have a maximum length equal to 1.5 times the length of the box (the interquartile range). If there are data outside this range, the points are shown on the plot and the whisker ends on the highest or lowest data point within the range of the whisker. The "outliers" are also further identified with asterisks representing the points that fall within three times the interquartile range from the end of the box and circles representing points beyond this. Box-whisker plots of the ambient TNMOC, NO_x, and CO concentrations for each site are shown in **Figure 3-3**.

3.1.3 Spatial Variability and Characteristics of Ambient Data

The spatial variability of average ambient concentrations within an urban area is indicative of the spatial variability of emission strengths. Large differences in ambient concentrations among nearby sites may be due to large gradients in emissions. Small ambient concentration differences among sites in relatively close proximity are generally suggestive of fairly uniform spatial distributions of emissions within a region. Comparisons between ratios of species in spatially averaged emissions (e.g., county-wide emissions) and ambient air are likely to be more accurate in situations with low spatial variability in ambient concentrations.

Two ambient sites were selected for the inventory evaluation in each county. In Fresno County, the Clovis and Fresno sites are located within 6 km of one another. The average hydrocarbon, CO, and NO_x concentrations from 0500-0800 PST at Clovis and Fresno show a maximum concentration variation of about 30 percent, indicating that emissions in the Clovis-Fresno region are fairly uniform. In Ventura County, the El Rio and Simi Valley sites are located much farther apart (approximately 40 km) and, while hydrocarbon concentrations are consistent between the two sites, NO_x and CO concentrations vary by more than 50 percent, indicating rather large gradients in emissions within the county. Because of limited data available for Folsom, this comparison was not made for the two sites in Sacramento County. Based on the ambient data for the two sites in Fresno County, it is evident that emissions in the region of the ambient monitors are fairly uniform, so using a county-wide inventory is less of a concern when making ratio comparisons. However, in Ventura County where there is significant variability in ambient pollutant concentrations between sites, using a county-wide inventory for making ratio comparisons is of greater concern.

3.2 EMISSION INVENTORY DATA

County-wide total emissions for Fresno, Sacramento, and Ventura counties were provided by the California Air Resources Board (ARB). The inventories for each county contain speciated emissions estimates for an average summer 1996 weekday. Files were also provided for an average summer Saturday. The inventory contains total organic gasses (TOG), CO, and NO_x daily emission totals as well as speciated hydrocarbon emissions by source category for emission estimates from area, point, and mobile sources. The inventory was temporally disaggregated from a daily total to an hourly basis using temporal profile code assignments provided by the ARB. The inventory was also separated into point, area, and on-road mobile source emissions using a file containing source category codes defined by the ARB.

Individual source category emissions were examined to determine point, area, and on-road mobile source contributions to reactive organic gas (ROG) [defined as TOG minus methane], CO, and NO_x in the emission inventory during the 0500-0800 PST time period. **Figure 3-4** shows source category contributions to county total weekday point, area, and mobile source emissions from 0500-0800 PST as reported by the ARB for a) Fresno, b) Sacramento, and c) Ventura counties. This comparison does not distinguish measurable from non-measurable TOG. From Figure 3-4 we can see that:

- In Fresno County, point, area, and mobile sources all contribute significantly to ROG emissions. NO_x emissions primarily come from mobile and point sources, while CO emissions are mostly due to area and mobile sources.
- In Sacramento County, mobile sources are the major contributor to ROG, NO_x, and CO. Mobile sources contribute about 50 percent to ROG, 80 percent to NO_x, and 85 percent to CO emissions. Area sources are responsible for 15 to 30 percent of ROG, NO_x, and CO emissions in Sacramento County.
- Emissions in Ventura County are similar to those in Fresno County in that point, area, and mobile sources all contribute significantly to ROG. In Ventura County, NO_x and CO emissions are dominated by area and mobile sources.
- In all three counties, point sources contribute approximately 20 percent to ROG. In Fresno County, point sources also contribute significantly to total NO_x emissions, however, point source NO_x contributions are negligible in Sacramento and Ventura counties.

In summary, point, area and mobile sources contribute significantly to ROG emissions in all three counties. Area and mobile sources are the major contributors to NO_x emissions in Sacramento and Ventura, while point, area, and mobile sources all contribute significantly to NO_x emissions in Fresno.

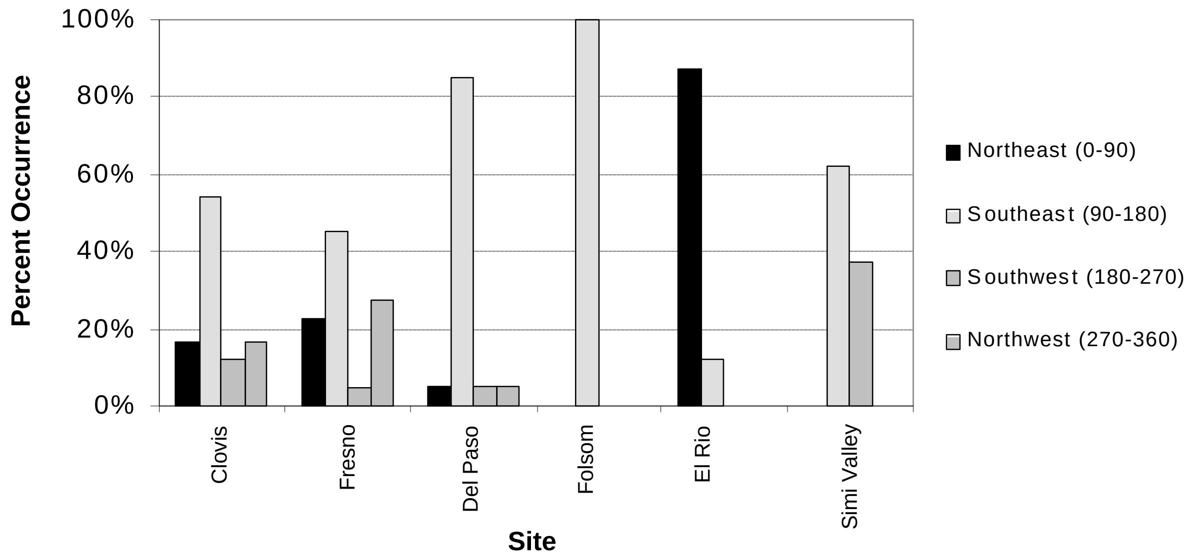


Figure 3-1. Frequency distribution of wind direction by quadrant for weekday data collected from 0500-0800 PST during the summer of 1996 in Fresno (Clovis and Fresno), Sacramento (Del Paso and Folsom), and Ventura (El Rio and Simi Valley) counties. Note that the quadrants define the direction from which the wind is coming and correspond to the quadrants shown in Figure 2-1.

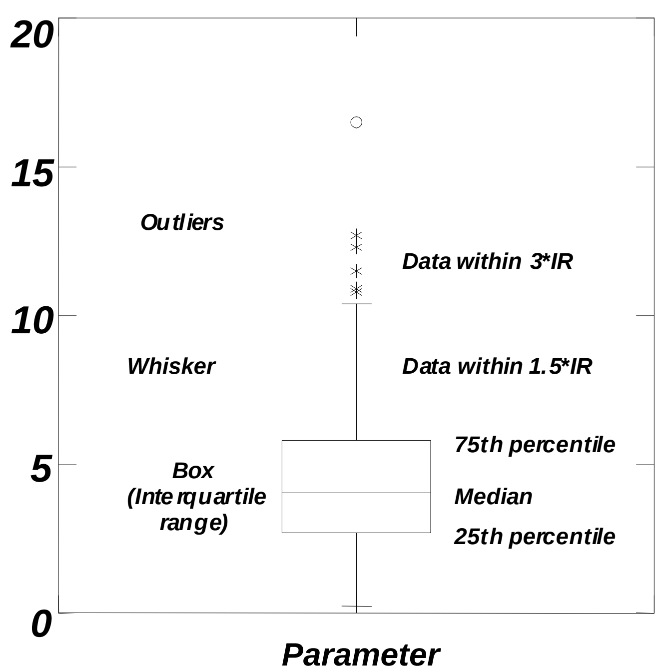


Figure 3-2. Annotated box-whisker plot.

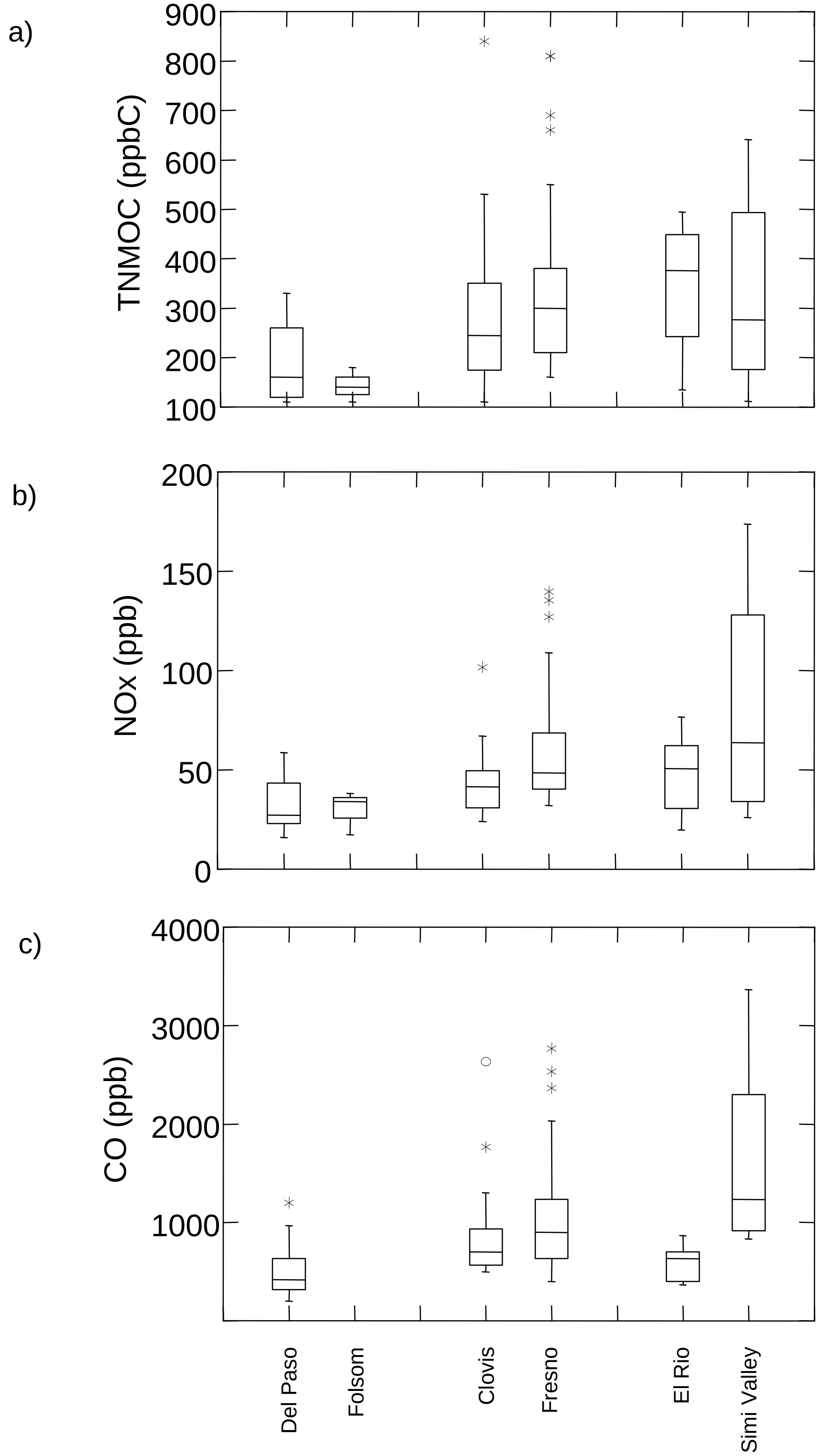


Figure 3-3. Box-whisker statistical plots of ambient a) TNMOC, b) NO_x, and c) CO concentrations at each site for all valid weekday samples collected at 0500-0800 PST during the summer of 1996.

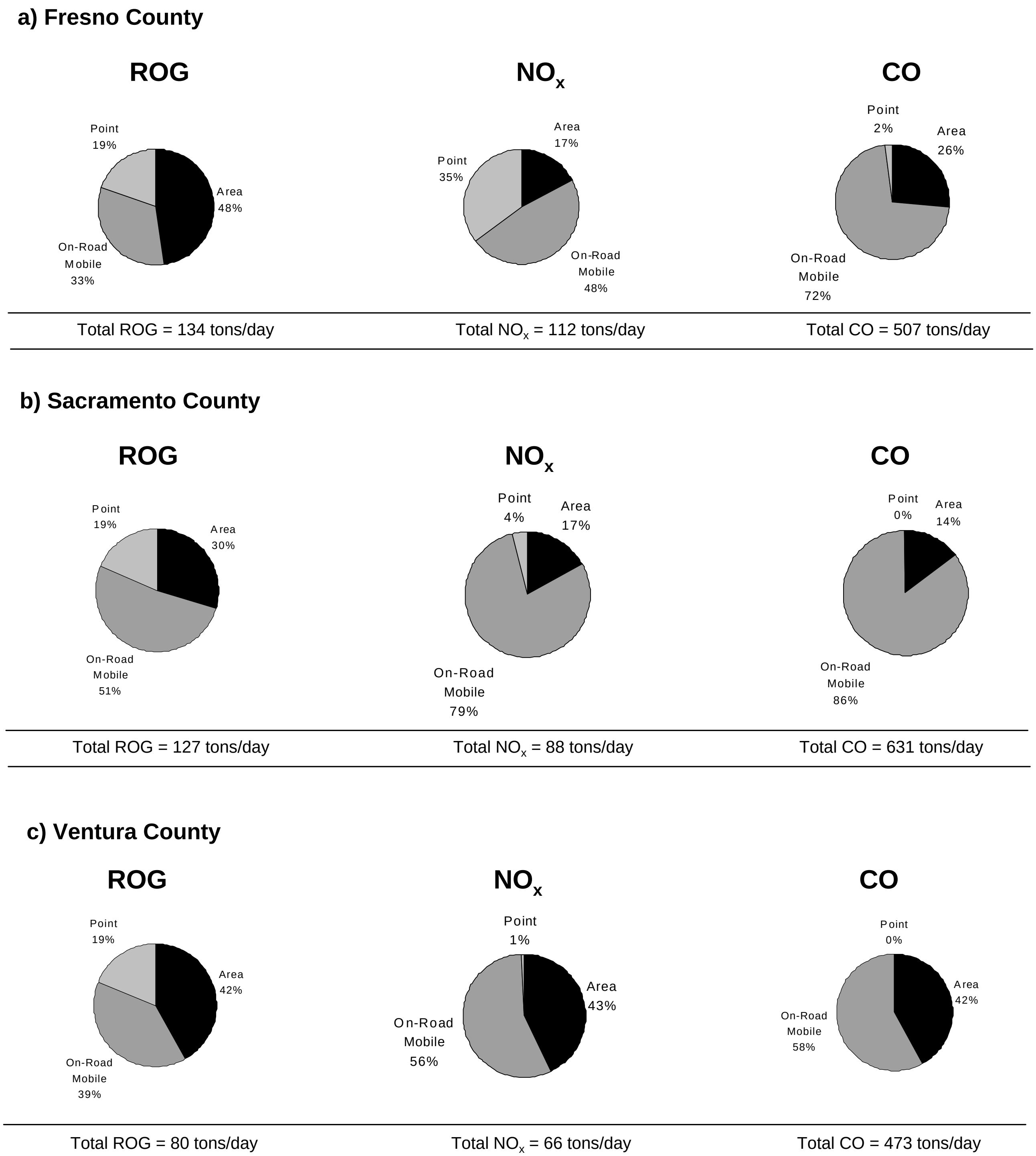


Figure 3-4. Source category contributions to ROG, NO_x, and CO for a) Fresno, b) Sacramento, and c) Ventura counties as reported in the weekday county-wide emission inventory provided by the ARB.

Table 3-1. Summary of the weekday ambient average TNMOC, identified NMOC, NO_x, and CO data meeting all validity and screening criteria at Fresno, Clovis, Del Paso, Folsom, El Rio, and Simi Valley.

Site ID	Site Name, County	# Valid Samples[a]	Average TNMOC ppbC[b]	Average ID NMOC ppbC[c]	Average NO_x ppb[d]	Average CO ppb
060190008	Fresno 1st Street, Fresno	22	355	291	63	1147
060195001	Clovis, Fresno	24	288	233	44	863
060670006	Del Paso Manor, Sacramento	20	186	132	33	510
060670012	Folsom, Sacramento	3	143	87	30	N/A
061113001	El Rio, Ventura	8	346	297	48	588
061112002	Simi Valley, Ventura	8	331	283	81	1638

[a] Only valid samples collected on weekdays from July through September 1996 (begin hours 0500, 0600, and 0700 PST) meeting all screening criteria were used to calculate the averages in the table.
[b] TNMOC = Total Non-Methane Organic Compounds includes both identified and unidentified compounds. Averages were calculated for all valid samples with TNMOC > 100 ppbC.
[c] ID NMOC = Identified Non-Methane Organic Compounds includes only those chemical compounds identified in the ambient air for samples corresponding to TNMOC > 100 ppbC.
[d] NO_x averages calculated for all valid samples with NO_x > 10 ppb to eliminate NO_x values at or near instrument detection limits.

4. EMISSION INVENTORY EVALUATION

4.1 HYDROCARBON/NO_X AND CO/NO_X RATIO ANALYSES

The relative amounts of hydrocarbon, CO, and NO_x in the emission inventory and in ambient air were examined by comparing hydrocarbon/NO_x and CO/NO_x ratios. These comparisons are based on weekday ROG emissions for each county and ambient weekday NMOC concentrations. For discussion purposes, ROG in the emission inventory and NMOC in the ambient data are used interchangeably and are referred to as hydrocarbons in the remainder of the report. The emission inventory includes hourly emissions for hundreds of organic species, CO, and NO_x. To accurately compare the emission inventory data and the ambient data, the speciated emission inventory files were processed to identify and select only the chemical species that were measured in the ambient air at each monitoring site. Ambient data were reported in units of parts per billion carbon (ppbC) and the emission inventory data were reported in kilograms (kg) per hour. In order to make the ratio comparisons, the emission inventory data were converted from a mass to a molar basis (from kg to molesC).

4.1.1 Weekday Hydrocarbon/NO_x Ratio Analyses

Comparisons between the 0500-0800 PST average weekday ambient-derived and average weekday emission inventory-derived hydrocarbon/NO_x ratios for Fresno, Sacramento, and Ventura counties are listed in **Table 4-1.** Table 4-1 lists the spatially averaged ambient ratios and the county-wide emissions ratios for each site. The results of the hydrocarbon/NO_x ratio comparison indicate that the ambient hydrocarbon/NO_x ratio at all four sites is higher than the emission inventory ratio. During the 0500-0800 PST time period, it is likely that NO_x (and CO) emitted from point source stacks may be suspended above the inversion layer and would consequently not be detected by the ambient monitor. To examine how sensitive the hydrocarbon/NO_x ratios are to point source NO_x, emission inventory-derived ratios were computed excluding these sources. **Figure 4-1** provides a graphic comparison of the county-wide emission-derived ratios, the county-wide emission-derived ratios without point source NO_x, and the spatially-averaged ambient-derived ratios for each site in each county, as well as the ambient-derived ratios by wind quadrant.

Examination of Figure 4-1 shows that the ambient–derived ratios vary somewhat by quadrant and do not compare well with the emission-derived ratios. In Sacramento and Ventura counties, point sources are not a major contributor to emissions during the 0500-0800 PST time period (as demonstrated in Figure 3-2). Consequently, excluding point source NO_x emissions from the ratio calculations does not significantly affect the ratio for these counties. However, in Fresno County point source NO_x emissions are significant (approximately 35 percent of total NO_x emissions) during the morning time period as shown in Figure 3-2a, and excluding these emissions from the ratio calculation increases the emission inventory hydrocarbon/NO_x ratio significantly. Note that the ambient ratios in Table 4-1 were calculated using all valid data meeting all screening criteria. Typically, the ambient to emission inventory ratio comparisons are made for the spatially averaged data as well as for each wind quadrant.

However, the ratio analysis by wind quadrant could not be performed on the emissions data because it is only resolved to the county level.

The ratio of the ambient- and emission inventory-derived hydrocarbon/NO_x ratios are shown in **Table 4-2**. The values in Table 4-2 were calculated by dividing the spatially averaged ambient hydrocarbon/NO_x ratios by the county total emission inventory hydrocarbon/NO_x ratio for each site. The emission inventory ratio used in the ambient to inventory ratio calculations for Sacramento and Ventura counties includes all sources for all sites. In Fresno County, the emission inventory ratio excluding point source NO_x was also compared to the ambient ratios. The comparisons of ratios show that in Fresno, ambient to emission inventory ratios including emissions from all source categories differ by about a factor of 3. When point source NO_x emissions are excluded from the emission inventory ratio, the ambient and inventory ratios only differ by 40 to 50 percent. Ratio comparisons in Sacramento County differ by about a factor of 2. In Ventura County, the ambient ratios at both monitoring sites are higher than the county total emissions ratios. The ambient ratio at El Rio is about 3 times higher than the inventory ratio while the ambient ratio at Simi Valley is 2 times higher than the inventory ratio.

4.1.2 Weekday CO/NO_x Ratio Analyses

Comparisons between the 0500-0800 PST average weekday ambient-derived and average weekday emission inventory-derived CO/NO_x ratios for Fresno, Sacramento, and Ventura counties are listed in **Table 4-3.** Table 4-3 lists the spatially averaged ambient ratios and the county-wide emissions ratios for each site. The results of the CO/NO_x ratio comparison indicate that at all but one site the ambient CO/NO_x ratio is higher than the emission inventory ratio. During the 0500-0800 PST time period, it is likely that NO_x (and CO) emitted from point source stacks may be suspended above the inversion layer and would consequently not be detected by the ambient monitor.

To examine how sensitive the CO/NO_x ratios are to point source CO and NO_x, emission inventory-derived ratios were computed excluding these sources. **Figure 4-2** provides a graphic comparison of the county-wide emission-derived ratios, the county-wide emission inventory-derived ratios without point source NO_x and CO, and the spatially-averaged ambient-derived ratios for each site in each county, as well as the ambient-derived ratios by wind quadrant.

Table 4-4 lists the ratio of the ambient- and emission inventory-derived CO/NO_x ratios. To examine the effects of removing point source emissions that may not have mixed to the surface during the morning time period (and consequently would not be detected by the ambient monitor), both point source NO_x and CO were omitted for the CO/NO_x ratio calculations.

In Fresno County, the CO/NOx ratio comparison between the ambient-derived ratio and the emission inventory-derived ratio including all emissions sources differs by factors of 2.7 and 2.6 at the Clovis and Fresno sites, respectively. Because point sources are a significant contributor to emissions during the 0500-0800 PST time period in Fresno, the effect of removing point source CO and NO_x emissions from the ratio calculations significantly improves the ambient to inventory comparisons. At the Clovis and Fresno sites, the effect of removing point source CO and NO_x emissions changes the ambient to emission comparison from 2.7 to 1.7 and from 2.6 to 1.6, respectively.

In Sacramento and Ventura counties, the CO/NO_x ratio comparisons indicate that the ambient CO/NO_x ratio at both sites is higher than the emission inventory ratio with the exception of El Rio where the ambient ratio is consistent with the inventory ratio. Ambient to emissions CO/NO_x ratios at the Del Paso site differ by a factor of 1.4. Ambient to emissions CO/NO_x ratios at the Simi Valley site in Ventura County differs by a factor of 1.8. The El Rio site and the Ventura County emission inventory CO/NO_x ratios are in agreement. Because point sources are not a major contributor to emissions in Sacramento and Ventura counties during the 0500-0800 PST time period, excluding point source NO_x and CO emissions from the ratio calculations does not significantly affect the emission inventory-derived ratio for these counties.

4.1.3 Potential Effects of Ambient Background Pollutant Concentrations

Selecting ambient monitoring locations which are dominated by fresh emissions is an important assumption in the use of ambient data to evaluate emission inventories. However, not all of the measured concentrations at even an emissions dominated location can be attributed to local emission sources. Some fraction of the observed data may be due to long-range transport, carry-over, or global background concentrations. As noted earlier, we selected the early morning hours to minimize these impacts. For example, because the morning period has low wind speeds and low mixing heights, the impacts from transport and mixing down of aloft carryover is minimized. Nevertheless, morning concentrations may be influenced in part by global background concentrations. To test the potential impact background concentrations could have on the ratios presented above, we have re-calculated the weekday ratios subtracting out global background levels (e.g., 30 ppbC for non-methane hydrocarbon, 200 ppb for CO, and 1 ppb for NO_x).

Tables 4-5a and b show the previously calculated ambient and emission inventory hydrocarbon/NO_x and CO/NO_x ratios as well as the ratios re-calculated accounting for background levels. As seen in the tables, for nearly all locations, the adjustments to account for background concentrations in the observed data result in improved comparisons between ambient-derived ratios and emission inventory-derived ratios. As before, the best comparisons result from the subtraction of point source CO and NO_x emissions from the ratios. Making adjustments for background and point sources results in differences between ambient-derived and emission inventory-derived hydrocarbon/NO_x ratios of about 30 percent in Fresno County, 70 percent in Sacramento County, and between 50 and more than 100 percent in Ventura County. The difference in Ventura County may be due to offshore hydrocarbon emissions not in the inventory but which are detected by the El Rio monitor. Making similar adjustments for background and point sources results in differences between ambient-derived and emission inventory-derived CO/NO_x ratios of about 30 to 40 percent in Fresno, Sacramento, and Ventura counties.

4.1.4 Weekday Versus Weekend Hydrocarbon/NO_x and CO/NO_x Ratio Comparison

Differences between weekday and weekend emissions activity such as driving behaviors and commercial businesses operations are likely to impact hydrocarbon/NO_x and CO/NO_x ratios. County-wide emissions estimates for Saturday were provided by the ARB for Fresno, Sacramento, and Ventura counties. The Saturday emissions data were processed in the same manner as the weekday emissions. Ambient hydrocarbon samples collected on Saturdays were limited, however. There were only four hydrocarbon samples collected at Fresno, Clovis, and Del Paso meeting our minimum threshold criteria for which to make the Saturday ratio comparisons. Since no data meeting our criteria were available for Ventura County, weekend comparisons are shown only for Fresno and Sacramento counties. **Table 4-6** lists the Saturday average ambient TNMOC, NO_x, and CO data meeting all validity and screening criteria at the sites in Fresno, Clovis, and Del Paso Manor.

Figure 4-3 shows the differences between the weekday and Saturday hydrocarbon/NO_x ambient ratios at Clovis and Fresno, and the weekend and weekday emissions ratios for Fresno County both including and excluding point source NO_x. **Figure 4-4** shows the weekday and Saturday ambient hydrocarbon/NO_x ratios at the Del Paso site and the weekday and Saturday emissions ratios for Sacramento County.

Table 4-7 lists the spatially averaged ambient Saturday hydrocarbon/NO_x ratio values and the county total Saturday emissions ratios for each site (shown in Figures 4-3 and 4-4). **Table 4-8** lists the ratio of the ambient- and emission inventory-derived hydrocarbon/NO_x ratios. The figures and tables reveal that ambient hydrocarbon/NO_x ratios at the Clovis site in Fresno County and Del Paso Manor in Sacramento County for Saturdays are quite different than the ambient weekday ratios, with Saturdays having much higher hydrocarbon/NO_x ratios. However, the weekday and Saturday ratios at the Fresno site are fairly consistent. Despite the large differences in weekday and weekend ambient-derived ratios, the weekday and Saturday emission inventory ratios are very similar in both counties analyzed. In general, the Saturday ambient-derived ratios compare more poorly with the Saturday emission inventory ratios, than do the weekday ratios. Ratio comparisons including emissions from all source categories in Sacramento County differ by about a factor of 3.5 and in Fresno County differ by a factor of 3 to 5. Excluding point source NO_x emissions has little impact in Sacramento County but improves the weekend comparison in Fresno County to a difference of a factor of 1.3 to 2.

Comparisons between the 0500-0800 PST Saturday average ambient and average emission inventory Saturday CO/NO_x ratios for Clovis and Fresno are shown in **Figure 4-5**. **Figure 4-6** shows the weekday and Saturday ambient CO/NO_x ratios at the Del Paso site and the weekday and weekend emissions ratios for Sacramento County.

Table 4-9 lists the spatially averaged ambient ratio values and the county total emissions ratios for each site (as shown in Figures 4-5 and 4-6). **Table 4-10** lists the ratios of the ambient- and emission inventory-derived CO/NO_x ratios. The results of the Saturday CO/NO_x ratio comparisons indicate that the Saturday ambient CO/NO_x ratio at all sites is higher than both the weekday ratio and the emission inventory ratio. In Fresno, the CO/NO_x ratio comparison between the ambient ratio and the emission inventory ratio including all emissions sources differs by a factor of 3.5 and 2.9 at the Clovis and Fresno sites, respectively. The effect of removing point source CO and NO_x emissions from the ratio calculations improves the ambient to emission inventory comparisons from 3.5 to 2.0 and from 2.9 to 1.7, respectively. In Sacramento County, the CO/NO_x ratio comparisons indicate that the ambient CO/NO_x ratio at Del Paso is higher than the emission inventory ratio by a factor of 1.8.

Comparison of the ratio of hydrocarbon/NO_x and CO/NO_x in the ambient air and in the emission inventory for weekdays and Saturdays indicates that there are differences in pollutant mass between what is observed in the ambient air on weekdays and what is observed on Saturdays. At Clovis and Del Paso, on average, Saturday hydrocarbon concentrations are higher while NO_x concentrations are lower during the morning time period. One would expect to observe differences in ambient concentrations between weekdays and weekends simply due to differences in emissions source activity (i.e., driving behavior, commercial business activity, power plant activity).

Ambient pollutant concentrations differ between weekdays and Saturdays; however, weekday and Saturday hydrocarbon/NO_x and CO/NO_x ratios in the emission inventory do not vary significantly. The emission inventory was investigated further and it was discovered that although the mass of hydrocarbon, NO_x, and CO emissions varies between the weekday and Saturday inventories, the source category temporal profile assignments in both inventories appear to be the same for weekdays and Saturdays. Because of differences in driving behavior and traffic patterns and other socio-economic factors during the week and on the weekend, we believe the emissions distributions should be different.

4.2 DETAILED HYDROCARBON COMPOSITION ANALYSES

Comparisons between the ambient composition and emission inventory composition of the major organic compound groups and individual hydrocarbon species were made. These comparisons are based on the county total emissions and the ambient data collected during the 0500-0800 PST time period. For comparison purposes, the speciated emission inventory data were further processed to include only the chemical species that were measured in the ambient air at each monitoring site.

4.2.1 Major Groups of Organic Compounds

The three major organic compound groups assessed in this study are paraffins, olefins, and aromatic compounds. Paraffins are hydrocarbon compounds whose molecules do not have multiple bonds between carbon atoms. Hydrocarbons whose molecules have carbon-carbon double bonds are called olefins, and those that contain a specific ring structure are called aromatic hydrocarbons. The relative amounts of the three major groups of organic hydrocarbons were examined in both the ambient air and in the emission inventory. Note that because it is the only compound of its group and also because of its low reactivity (Carter, 1994), acetylene is included in the paraffin group.

The species group comparisons are made by grouping the individual chemical compounds in the inventory and ambient air into their corresponding species groups. For example, the mass of the single bond hydrocarbons is summed in the paraffin group, the double bonded hydrocarbons are summed in the olefin group, etc. Generally, on a reactivity basis, olefin and aromatic compounds are more reactive than paraffin compounds. Although paraffin compounds make up most of the inventory, they are the least reactive. Since olefins and aromatics are much more reactive than paraffins, even small differences could potentially be important for ozone formation.

Figure 4-7 shows comparisons of the summer 1996 morning weekday (0500-0800 PST) ambient average and emission inventory average composition of paraffins, olefins, and aromatic compounds in Fresno, Sacramento, and Ventura counties, respectively. The figure shows that:

- The **paraffin** content of the emission inventory is about 40-60 percent in all three counties. The ambient paraffin content is also 40-60 percent at all sites except El Rio in Ventura County, which is about 80 percent. The emission inventory paraffin content is within 10 percent agreement with the ambient paraffin content at all sites except El Rio.
- The **olefin** content of the emission inventory at each site is about 15-25 percent. The ambient olefin content is consistently lower than the emission inventory content at each site. The olefin content is about 10 and 20 percent at all of the ambient sites.
- The **aromatic** content of the emission inventory is about 20-30 percent for all three counties and is consistent with the ambient aromatic content at five of the six ambient sites with the exception being El Rio, where the ambient aromatic component is only about 15 percent.

This comparison shows that while the emission and ambient compositions in Fresno and Sacramento counties are in generally good agreement, there is a consistent underestimation of the less reactive compounds and an overestimation of the more reactive compounds. In Ventura County, ambient data from Simi Valley follow a similar pattern to that in Fresno and Sacramento counties (e.g., slight underestimation of paraffins and overestimation of olefins and aromatics). However, at the El Rio site in Ventura County, ambient paraffins are much higher than in the emission inventory and ambient olefins and aromatics are much lower than in the emission inventory. The contributions of paraffins to the total hydrocarbons at El Rio are also much higher than at any of the other sites and likewise the contributions of olefins and aromatics are much lower than at any of the other sites. We can speculate that the increased paraffins may be associated with natural geogenic oil and gas seeps offshore of Ventura County.

4.2.2 Detailed Hydrocarbon Composition – All Source Categories

There were 55 to 65 individual hydrocarbon species measured from the 3-hr average canister samples at each site. The chemical compounds capable of being detected by the

PAMS automated gas chromatography systems are limited to C2-C10 alkanes, alkenes, alkynes, aromatic hydrocarbons, and undecane (C11). Formaldehyde, acetaldehyde, and acetone carbonyl data were also collected at all sites except Folsom. Therefore, the emissions of alcohols, ethers, acetates, glycols, esters, formates, organic amines, organic oxides, phenols, terpenes, organic acids, C11+ hydrocarbon compounds, and halogenated species were excluded from the inventory data in order to make the comparisons with the available ambient data. The ambient data include a category called "unidentified hydrocarbons" which is the sum of all species that were measured, but not individually identified. Appendix A contains a list of hydrocarbon species measured at each of the monitoring sites during the summer of 1996.

Figures 4-8 through 4-10 show comparisons of average weight percent composition of ambient hydrocarbon data collected on weekdays during the summer of 1996 from 0500-0800 PST and the weekday emission inventory weight percent composition of individual species for all source categories combined in Fresno, Sacramento, and Ventura counties. The vertical axis (y-axis) of the plots indicates the weight percent of each species as a fraction of the total weight percent of all identified species. The horizontal axis (x-axis) lists the individual chemical species identified by a number which corresponds to the key to the right of each plot. It is important to note that the number of identified species differs slightly among sites based on the compounds that were measured at each site. The relative weight percents of individual hydrocarbon compounds were calculated only for the subset of identified species without considering the unidentified species as part of the total identified hydrocarbon mass (i.e., [individual species concentrations / sum of identified species concentrations]*100).

The species compositions comparisons shown in Figures 4-8 through 4-10 show all chemical compounds that were measured in the ambient data and the corresponding species composition in the emission inventory. For discussion purposes, the species composition comparison is made based on two parameters: (1) the weight percent contribution of each species to the total weight percent in the ambient air and in the inventory, and (2) the relative percent difference between each chemical compound in the ambient air and in the emission inventory. Thus, small percent differences in relatively abundant compounds receive greater attention than relatively minor compounds with larger percent differences in compositions between the ambient air and the inventory.

Figures 4-8 through 4-10 show several discrepancies between the chemical species in the ambient air and in the inventory. Only the species (in both the ambient air and in the inventory) constituting more than 2 percent by weight are discussed here. The following observations summarize the comparison of the emission inventory hydrocarbon data and the ambient hydrocarbon chemical species data for each county:

Fresno County

- Individual chemical species compositions between the two ambient sites in Fresno County (Clovis and Fresno 1st Street) are fairly consistent. However, comparisons between ambient data and the Fresno County emission inventory show several differences in species composition. Most notable are ethane, ethylene, benzene, propylene, isobutylene, n-butane, n-hexane, acetone, and n-pentane which are all at least 25 percent higher in the emission inventory than in the ambient air. There are also several species that are higher in the ambient air than in the emission inventory including: isopentane, xylenes, propane, and formaldehyde. There were several chemical species that were measured in the ambient air but were either (1) not included in the emission inventory or are grouped into isomeric groups in the inventory, or (2) were reported as having 0 mass in the inventory.

- Ethane, ethylene, n-butane, n-pentane, and benzene concentrations are higher in the emission inventory than in the ambient data. Ethane and ethylene are both emitted during various combustion processes. N-butane and n-pentane are emitted via gasoline evaporation, and benzene is a major component of gasoline exhaust.
- Ambient compositions of propane, isopentane, xylenes, and formaldehyde are higher than the emission inventory compositions. Propane is emitted during combustion processes and has a tendency to accumulate in the atmosphere. Isopentane and xylenes are emitted in mobile source exhaust, and formaldehyde is a by-product of mobile source exhaust.

Sacramento County

- Individual chemical species compositions between the two ambient sites in Sacramento County (Del Paso and Folsom) are fairly consistent for the lighter compounds (acetylene-butane) but show differences in the C6 to C9 compounds. Because the ambient composition data collected at Folsom are limited, the remainder of this discussion will focus on data collected at Del Paso. Comparisons between ambient data collected at Del Paso and the Sacramento County emission inventory show differences in species composition similar to those observed for Fresno County. In addition to the emission inventory species overestimated in Fresno County (as noted above), the Sacramento County inventory also has higher concentrations of acetylene, ethylbenzene, toluene, methylcyclopentane, and 3-methylpentane than does the ambient data. The species that have higher concentration in the ambient air than in the emission inventory for Sacramento County are the same as those listed for Fresno County.
- Emissions estimates of acetylene, ethylbenzene, toluene, and 3-methylpentane are higher than the ambient data in Sacramento. Acetylene is a combustion product that has a tendency to accumulate in the atmosphere. Ethylbenzene, toluene, and 3-methylpentane are all components of gasoline production and exhaust. Toluene is also a component of many solvents.
- Ambient compositions of propane, isopentane, xylenes, and formaldehyde are higher than the emission inventory compositions as was the case in Fresno County.

Ventura County

- Individual chemical species compositions between the two ambient sites in Ventura County (El Rio and Simi Valley) are dissimilar for most species. Comparisons between ambient data collected at the two ambient sites and the Ventura County emission inventory show differences in species composition similar to those observed for Fresno and Sacramento counties. The species that have higher concentration in the ambient air than in the emission inventory for Ventura County are the same as those for Fresno and Sacramento counties.
- Acetylene, ethylene, propylene, benzene, toluene, m-xylene, and isobutylene concentrations are significantly higher in the emission inventory than in the ambient air at both El Rio and Simi Valley. Ambient data collected at the El Rio site have significantly higher concentrations of the following compounds: ethane, propane, isobutane, and n-butane than do both the emission inventory and the Simi Valley ambient site. Ethane, propane, and n-butane are known fugitive emissions from petroleum sources, while isobutane is a component of fuel. Ambient data collected at the Simi Valley site have significantly higher concentrations of propane, 1-butene, and isopentane than does the emission inventory.

4.2.3 Detailed Hydrocarbon Composition – Area, Mobile, and Point Sources

Significant differences exist between the ambient hydrocarbon species compositions and the overall county-wide inventory species compositions. To gain some insight into possible discrepancies by source category, the detailed hydrocarbon composition of the area, mobile, and point source inventory components were each compared with the ambient data. **Figures 4-11 through 4-13** show comparisons of average weight percent composition of weekday ambient hydrocarbon data collected during the summer of 1996 from 0500-0800 PST and weekday emission inventory weight percent composition of individual species for area, mobile, and point source emissions, respectively, in Fresno County from 0500-0800 PST. **Figures 4-14 through 4-16** show comparisons of average weight percent composition of ambient hydrocarbon data collected during the summer of 1996 from 0500-0800 PST and emission inventory weight percent composition of individual species for area, mobile, and point source emissions, respectively, in Sacramento County from 0500-0800 PST. **Figures 4-17 through 4-19** show comparisons of average weight percent composition of ambient hydrocarbon data collected during the summer of 1996 from 0500-0800 PST and emission inventory weight percent composition of individual species for area, mobile, and point source emissions, respectively, in Ventura County from 0500-0800 PST.

When examining the species plots for the individual source categories and for all source categories combined, it is important to note that the ambient data for each site is the same for all plots (e.g., only the emissions speciation changes). As a result, there are many differences in species compositions between the ambient data and the inventory, because some chemical compounds may be over-represented in one source category and under-represented in another (or vice-versa), relative to their contribution to the total mass of the emission inventory. In spite of this over- and under-weighting effect, some insights can be obtained from the comparisons. In this study, the inventory species that do not compare well with ambient data in the combined source category plots are also those with the largest differences in the individual comparisons as well. These are the species that the remainder of the discussion focuses on.

Fresno County Source Composition

Figure 4-11 shows the area source species composition in the emission inventory compared to the ambient species composition. The area source emissions composition shows that ethane, ethylene, benzene, and acetone are all significantly higher than in the ambient composition. Ethane and ethylene are combustion products while benzene and acetone are used in industrial processes and solvents. Because weight fraction of these species is higher in the inventory than in the ambient data, it is possible that these compounds are over-represented in the speciation profiles for area source fuel combustion and industrial processes in Fresno County or that the monitoring site is not being impacted by these source categories. Preliminary investigation of the emission inventory shows that the largest single source of ethane emissions is from farming operations (livestock waste). Recall that the ambient data collected at a single location is being compared to the county-wide emission inventory. It is evident that the livestock emissions reported in the inventory are not being detected by the ambient monitors and that in the case of ethane, the spatial matching discrepancies between the ambient data and the inventory are apparent.

Isopentane, xylenes, propane, and formaldehyde are all lower in the area source emissions compositions than the ambient data in Fresno County. Isopentane is either not reported in the emission inventory, or included in an isomer group and can not be disaggregated. Since isopentane is abundant in the ambient air, if it truly is an emitted species, it should be identified in the inventory as an individual species. Xylenes are used in industrial processes and as solvents while propane and formaldehyde are combustion products. Since these compounds are lower in the emission inventory than the ambient air, it is possible that: (a) the speciation profiles for industrial and combustion sources in the area component are under-representing these species; (b) the profiles are not representative of solvent and fuel use in Fresno County; and/or (c) the source types emitting these compounds are more directly impacting the monitoring site than on average in the county-wide emissions.

Figure 4-12 shows mobile source species composition in the emission inventory compared to the ambient species composition for Fresno County. The mobile source emission-derived species composition shows that ethylene, benzene, propylene, isobutylene, and n-pentane weight fractions are all significantly higher than the ambient data. It is possible that the speciation profiles for the mobile source evaporative and exhaust components of the emission inventory are over-representing these compounds. Propane and formaldehyde weight fractions are significantly lower in the mobile source emissions compositions than in the ambient data suggesting that these compounds may be under-represented in the mobile source evaporative and exhaust speciation profiles.

Figure 4-13 shows point source species composition in the emission inventory compared to the ambient species composition for Fresno. The point source emission-derived species composition shows that ethane, propane, isobutane, n-butane, n-pentane, and cyclopentane weight fractions are all significantly higher than in the ambient data. These species are all associated with petroleum use or processing suggesting that the speciation profiles for these activities may be over-representing these species in the emission inventory for Fresno County, or that the sources are not impacting the monitoring sites in proportion to the county-wide emission inventory.

Sacramento County Source Composition

Differences in chemical species compositions in Sacramento County demonstrate the same pattern as those in Fresno County. The same compositions that are overestimated in the Fresno County emission inventory are also overestimated in Sacramento County. In addition, acetylene, ethylbenzene, toluene, 3-methylpentane, methylcyclopentane, o-xylene, and isobutylene are overestimated in the Sacramento inventory.

Figure 4-14 shows area source species composition in the emission inventory compared to the ambient species composition in Sacramento County. Ethane, isobutane, n-butane, n-hexane, and cyclohexane weight fractions are significantly higher in the emissions-derived area source composition than in the ambient data. Since the composition of these species is higher in the inventory than in the ambient data, it is possible that these compounds are over-represented in the speciation profiles for area source fuel use or refueling processes in Sacramento County. Preliminary investigation of the emission inventory shows that the largest single source of ethane emissions in Sacramento County is from livestock feedlots. Since the ambient data collected at a single location is being compared to the county-wide emission inventory, it is evident that the livestock feedlot emissions reported in the inventory are not being detected by the ambient monitors in Sacramento County and that in the case of ethane, the spatial matching discrepancies between the ambient data and the inventory are apparent.

The ambient compositions of propane, isopentane, xylenes, and formaldehyde are higher than the emission inventory compositions in Sacramento County as is the case in Fresno County. Since these compounds have a lower weight fraction in the emission inventory than in the ambient air, it is possible that the speciation profiles for industrial and combustion sources in the area component are under-representing these species, the profiles are not representative of solvent and fuel use in Sacramento County, or the source types emitting these compounds are more directly impacting the monitoring site than on average in the county-wide emissions.

Figure 4-15 shows mobile source species composition in the emission inventory compared to the ambient species composition for Sacramento County. The mobile source emission-derived species composition shows that acetylene, ethylene, propylene, n-pentane, methylcyclopentane, benzene, toluene, and isobutylene weight fractions are all significantly higher than in the ambient data. It is possible that the speciation profiles for the mobile source evaporative and exhaust components of the emission inventory over-represent these compounds, and/or that the mobile source speciation profiles are not representative of gasoline in the region. Propane and formaldehyde weight fractions are significantly lower in the mobile source emissions compositions than the ambient data suggesting that these compounds may be under-represented in the mobile source evaporative and exhaust speciation profiles.

Figure 4-16 shows point source species composition in the emission inventory compared to the ambient species composition for Sacramento County. The point source emission inventory-derived species composition shows that ethane, propane, isobutane, n-butane, n-pentane, and toluene weight fractions are all significantly higher than in the ambient compositions. These species are all associated with petroleum use or processing suggesting that the speciation profiles for these activities may be over-representing these species in the emission inventory, or that the source types with these emissions are not impacting the monitoring site.

Ventura County Source Composition

As noted in previous sections, there are substantial differences in the ambient data collected at the two Ventura County sites. Species compositions between the two ambient sites in Ventura County are also quite different, indicating that the chemical composition of the ambient air in Ventura County varies significantly throughout the county. Consequently, there are large differences among both ambient sites and the county-wide emission inventory. Because the composition of the chemical species in the ambient air is different in different parts of the county, it follows that the county-wide emission inventory is not adequately resolved (spatially) to carry out the speciated comparison accurately. We have provided the comparisons, none-the-less, but caution against over-interpretation of the results.

Generally, differences in species compositions in Ventura County are similar to those in Sacramento and Fresno counties. The species composition comparison between the ambient data and the emission inventory for the El Rio and Simi Valley sites show that the emissions-derived compositions of acetylene, ethylene, propylene, benzene, toluene, xylenes, and isobutylene are significantly higher than the ambient compositions. At El Rio, ambient compositions of ethane, propane, and n-butane are all significantly higher than the Simi Valley and emission inventory compositions.

Figure 4-17 shows area source species composition in the emission inventory compared to the ambient species composition in Ventura County. Acetylene, ethylene, and propylene weight fractions are significantly higher in the emissions-derived area source composition while ethane, propane, and n-butane weight fractions are all lower. At El Rio, ambient compositions of ethane, propane, and n-butane are much higher than emissions compositions. Preliminary investigation of the emission inventory shows that the largest single source of ethane emissions in Ventura County is from wildfires. However, we suspect the largest source of ethane may be geogenic oil and gas seeps offshore of Ventura County.

Figure 4-18 shows mobile source species composition in the emission inventory compared to the ambient species composition for Ventura County. The mobile source emission-derived species composition shows that acetylene, ethylene, propylene, n-pentane, isomers of heptane (compounds containing seven carbon atoms), benzene, toluene, xylenes, and isobutylene weight fractions are all higher than in the ambient data. The mobile source emissions compositions are in better agreement with the ambient data at Simi Valley, suggesting that the mobile source component of the county-wide emission inventory is more representative of actual emission source contribution strengths in Simi Valley than in El Rio.

Figure 4-19 shows point source species composition in the emission inventory compared to the ambient species composition for Ventura County. The point source emission-derived species composition shows that ethane, propane, isobutane, n-butane, and n-pentane weight fractions are all significantly higher than in the Simi Valley ambient compositions, but are more consistent with El Rio (except for n-pentane which does not agree well with either ambient site). These compounds are indicative of petroleum-related processes. The point source composition comparison suggests that the point source component of the county-wide emission inventory is more representative of El Rio than Simi Valley.

4.2.4 Hydrocarbon Maximum Incremental Reactivity

Many different hydrocarbon compounds are emitted into the atmosphere, each with different chemical properties and reaction rates and each differing in its effect on ozone formation. One estimate of each compound's potential to form ozone is referred to as its "reactivity". The most relevant measure of each hydrocarbons' effect on ozone is the actual change in ozone formation in an airshed, as a result of changing the hydrocarbon composition in that airshed; this can be estimated using computer and theoretical models. The fact that reactivities depend on environmental conditions means that no single scale can predict reactivites under all conditions, nevertheless, the maximum incremental reactivity scale has proven to be useful for assessing the differences in ozone formation potential depending on what hydrocarbon compounds are present in the atmosphere. Maximum incremental reactivity is defined as the change in ozone caused by adding a small amount of test hydrocarbon to the emissions in an episode, divided by the amount of test species added (Carter, 1994).

Because the reactivities among hydrocarbon species vary significantly it is of interest to examine which species are important (or less important) to consider in terms of ozone formation. For example, abundant hydrcarbon species with relatively low reactivities are less important when considering ozone formation, while less abundant, but highly reactive species are more important. **Figures 4-20 through 4-22** illustrate comparisons of the summer 1996 weekday 0500-0800 PST ambient-derived and emission inventory average reactivity-weighted hydrocarbon species contribution to total reactivity (all source categories combined) in Fresno, Sacramento, and Ventura counties.

In general, reactivity-weighted contributions of ethylene, propylene, and isobutylene in the emission inventory are significantly higher than the ambient data for all three counties. Ambient-derived reactivity-weighted contributions for xylenes and formaldehyde are significantly higher than emissions data for all three counties. Other observations include:

- In Fresno County, ambient-derived reactivity-weighted contributions of isopentane and acetaldehyde are significantly higher than in the emission inventory.
- In Sacramento County, the emissions-derived reactivity of toluene is higher than the ambient data while the ambient-derived reactivity-weighted contributions of isopentane, 1,2,3- and 1,2,4-trimethylbenzene, 1,3-diethylbenzene, and acetaldehyde are higher than the emission inventory reactivity-weighted contributions.
- In Ventura County, ambient-derived reactivity-weighted contributions of 1-butene, isopentane, and 1,2,3-trimethylbenzene are higher than the emissions reactivity-weighted contributions.

The reactivity analysis highlights discrepancies in individual chemical species that favor ozone formation. This analysis combined with the chemical species weight percent analysis presented earlier, can help identify: (1) discrepancies in individual hydrocarbon species between the inventory and the ambient air and (2) which compound discrepancies are important when considering the ozone formation potential of the emissions mix. In some cases such as acetaldehyde, the weight percent differences between the ambient air and the emission inventory do not appear to be significant. However, on a reactivity basis, acetaldehyde is an important species because it has a high potential to form ozone. Both actual weight percent and reactivity should be considered when assessing the composition of the emission inventory and prioritizing of emission inventory improvement efforts.

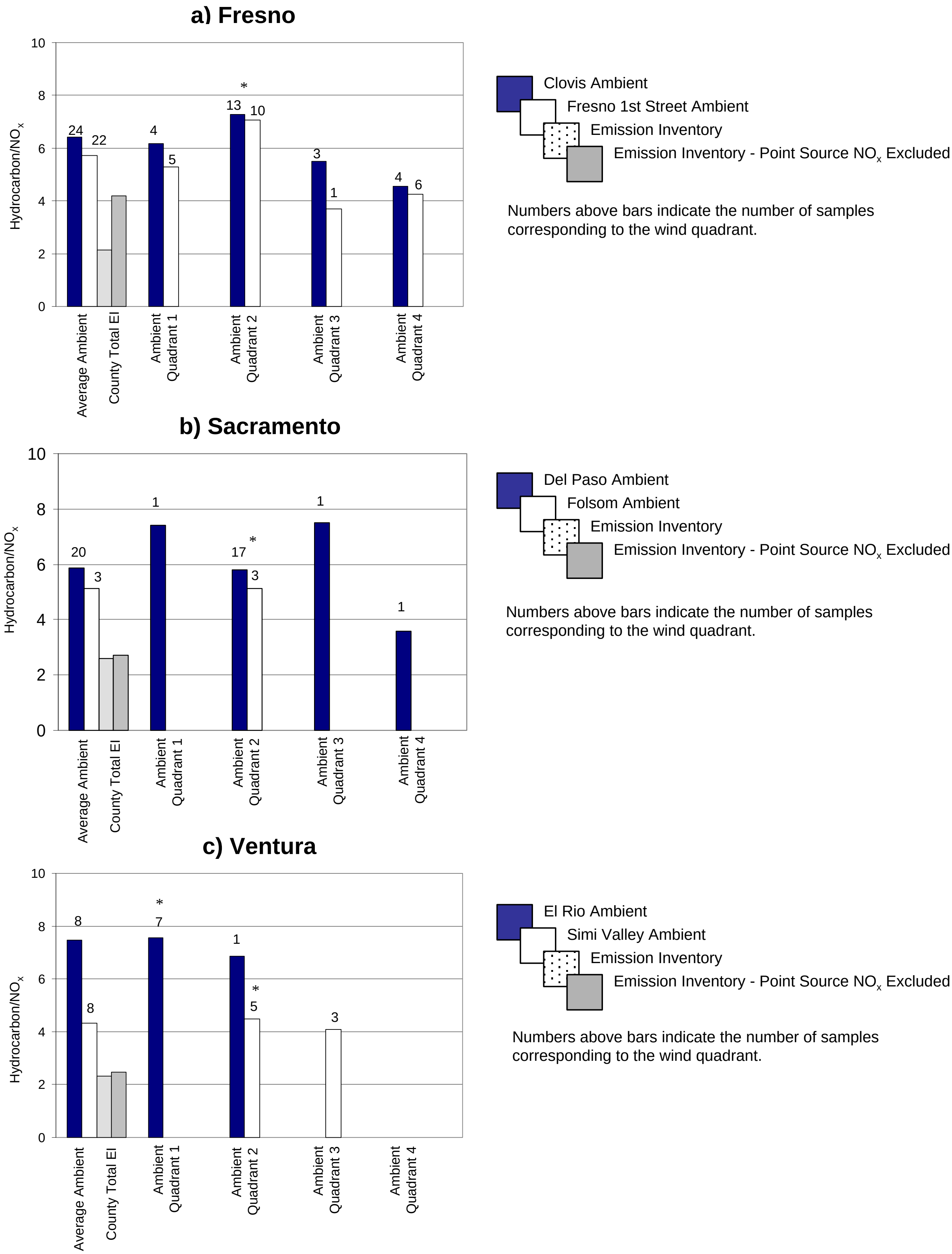


Figure 4-1. Weekday average ambient and average county total emission inventory (EI) hydrocarbon/NO_x ratios in a) Fresno, b) Sacramento, and c) Ventura counties from 0500-0800 PST. Asterisks above bars identify predominant wind direction.

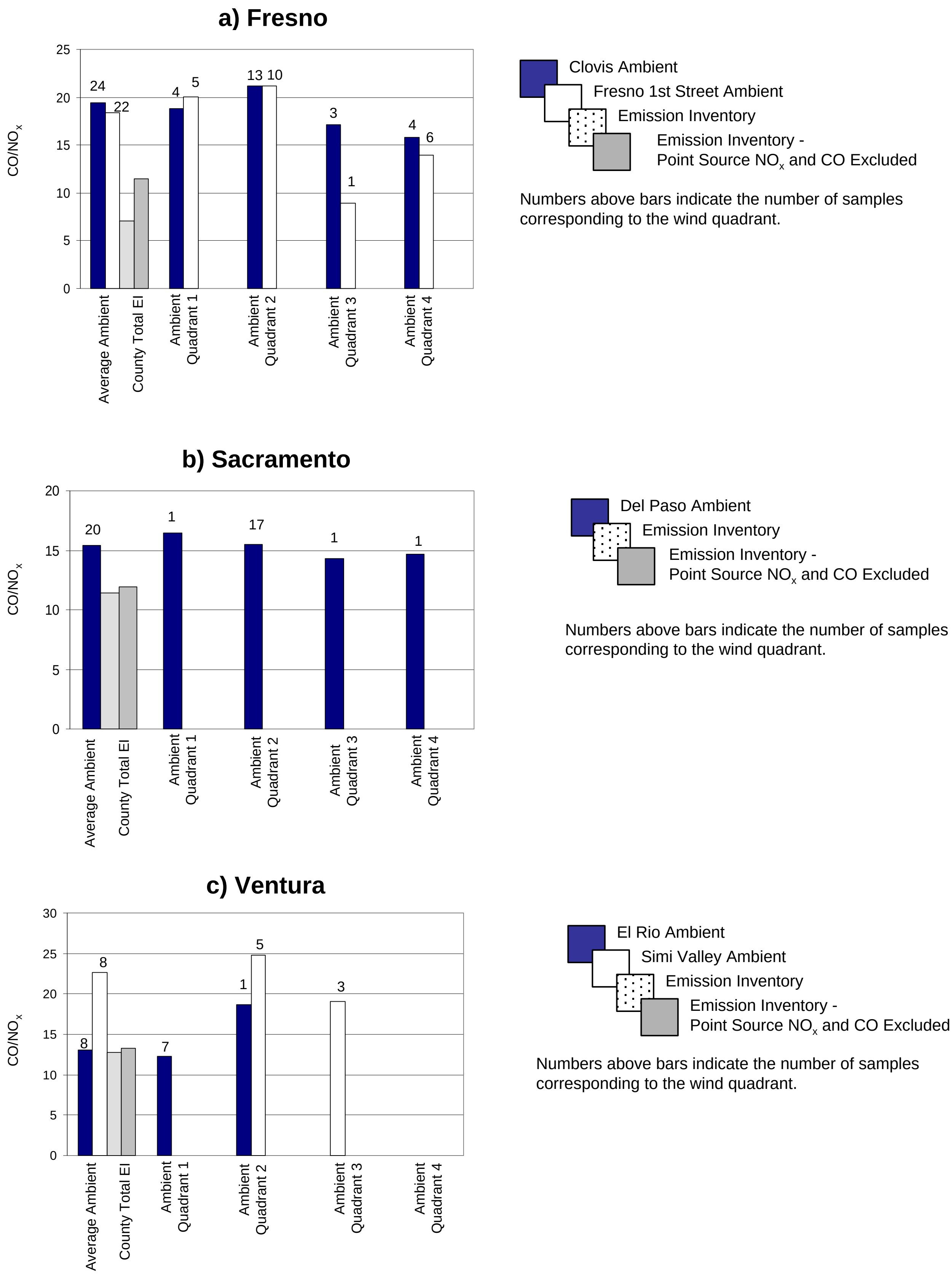


Figure 4-2. Weekday average ambient and average county total emission inventory (EI) hydrocarbon CO/NO_x ratios in a) Fresno, b) Sacramento, and c) Ventura counties from 0500-0800 PST.

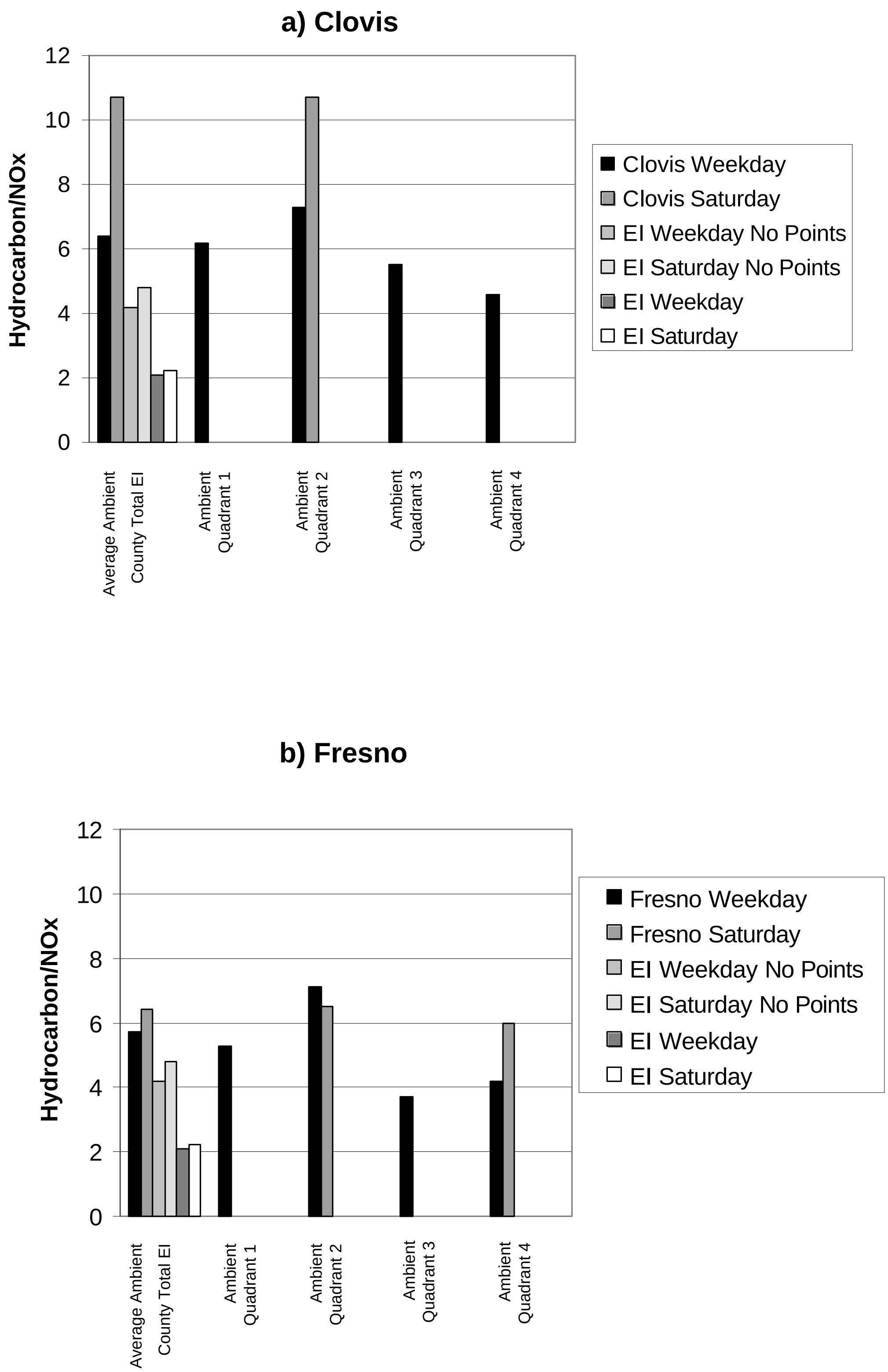


Figure 4-3. Average ambient and average county total emission inventory (EI) weekday and Saturday hydrocarbon/NO_x ratios at a) Clovis and b) Fresno from 0500-0800 PST.

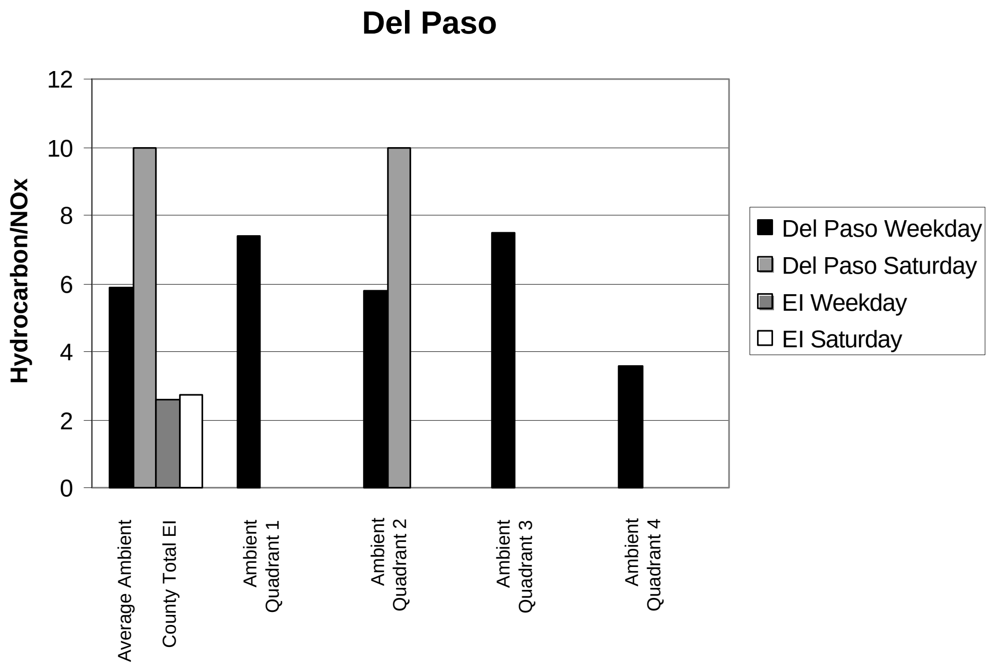


Figure 4-4. Average ambient and Sacramento County total emission inventory (EI) weekday and Saturday hydrocarbon/NO_x ratios at Del Paso from 0500-0800 PST.

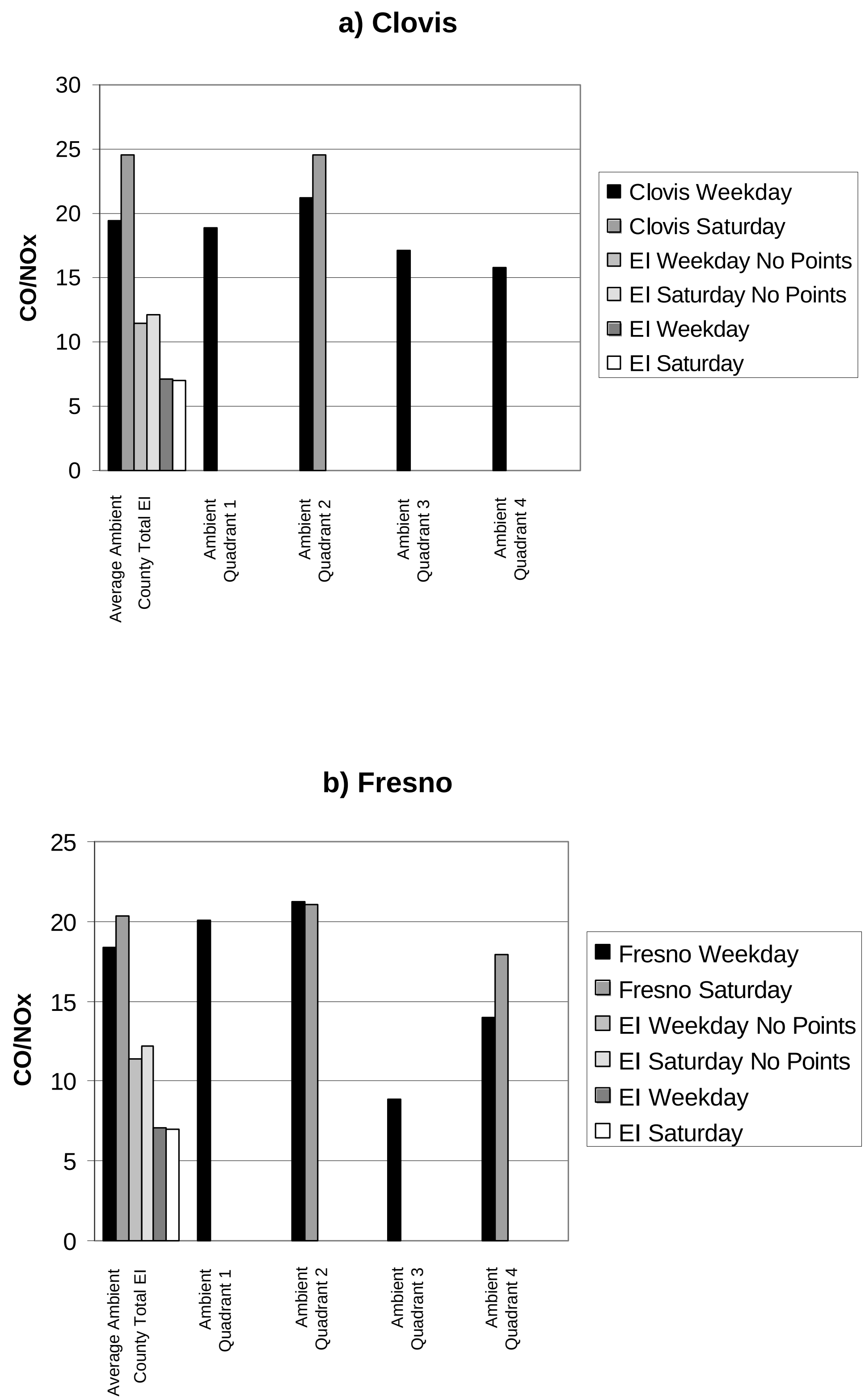


Figure 4-5. Average ambient and average county total emission inventory (EI) weekday and Saturday CO/NO_x ratios at a) Clovis and b) Fresno from 0500-0800 PST.

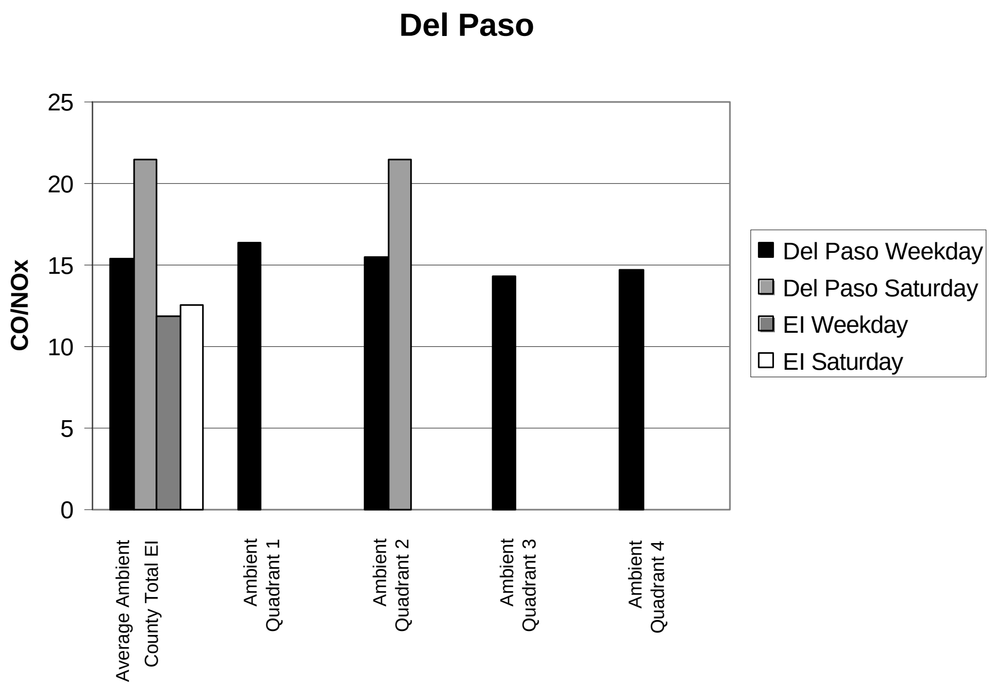


Figure 4-6. Average ambient and Sacramento County total emission inventory (EI) weekday and Saturday CO/NO_x ratios at Del Paso from 0500-0800 PST.

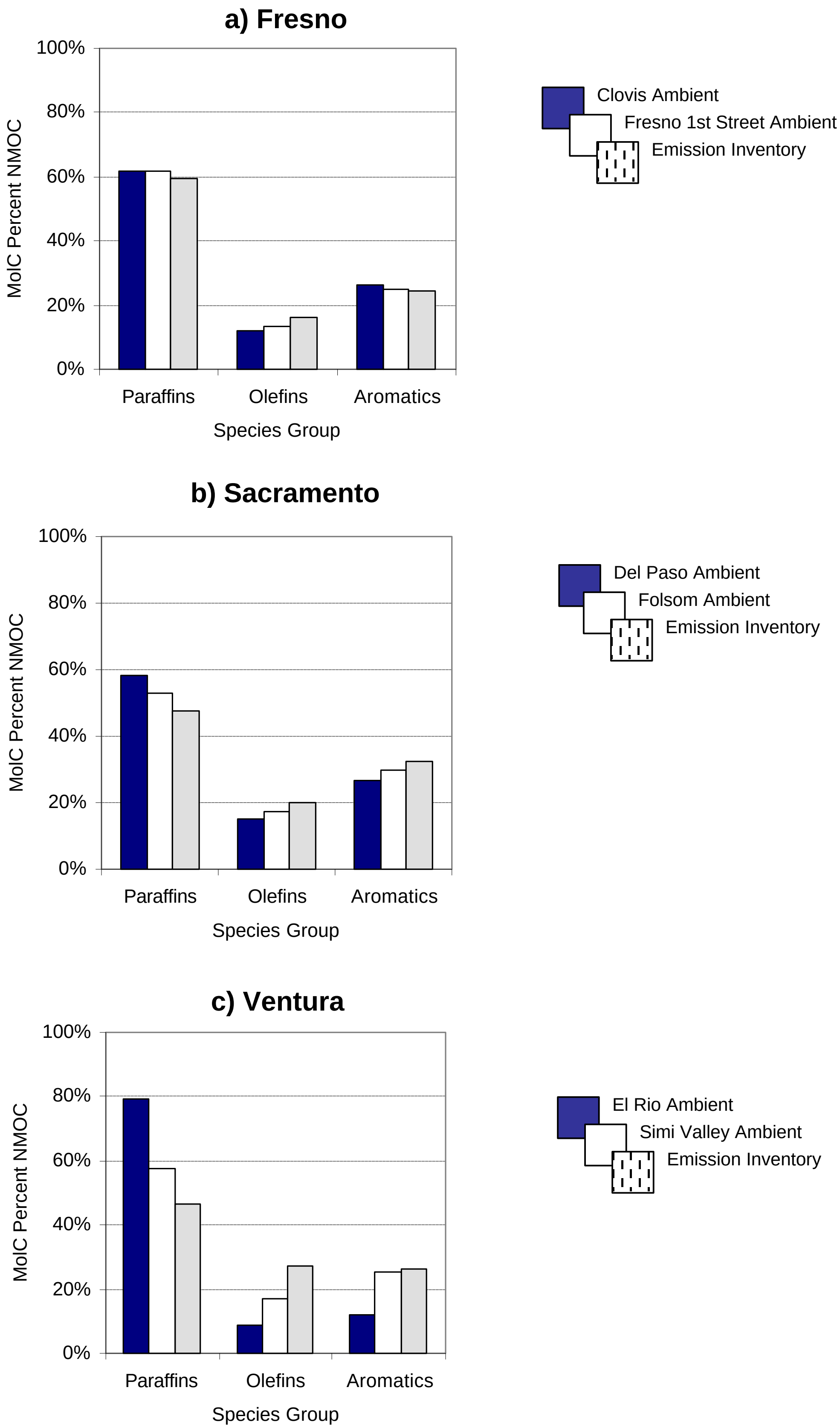
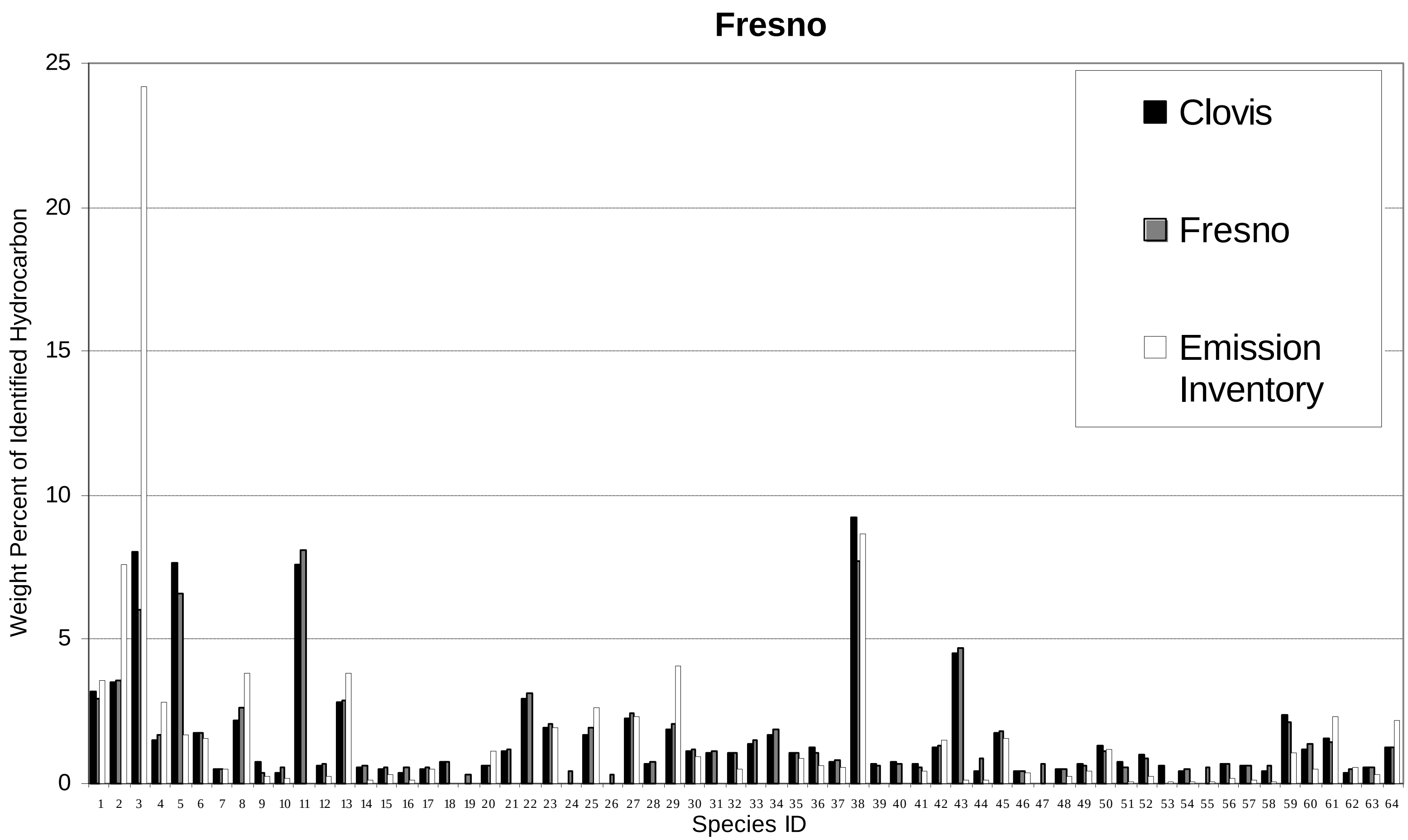


Figure 4-7. Average ambient weekday and average county total emission inventory (EI) paraffin, olefin, and aromatic species group composition for a) Fresno, b) Sacramento, and c) Ventura from 0500-0800 PST.



1 acetylene
2 ethylene
3 ethane
4 propylene
5 propane
6 isobutane
7 1-butene
8 n-butane
9 trans-2-butene
10 cis-2-butene
11 isopentane
12 1-pentene
13 n-pentane
14 isoprene
15 trans-2-pentene
16 cis-2-pentene
17 2-methyl-2-butene
18 2,2-dimethylbutane
19 cis-3-hexene
20 cyclopentane
21 2-methyl-2-butene
22 2-hexene
23 3-methylpentane
24 2-methyl-1-pentene
25 n-hexane
26 trans-2-hexene
27 methylcyclopentane
28 2,4-dimethylpentane
29 benzene
30 cyclohexane
31 2-methylhexane
32 2,2-dimethylbutane
33 3-methylhexane
34 2,2,4-trimethylpentane
35 n-heptane
36 methylcyclohexane
37 2,3,4-trimethylpentane
38 toluene
39 2-methylheptane
40 3-methylhexane
41 n-octane
42 ethylbenzene
43 m & p-xylene
44 styrene
45 o-xylene
46 n-nonane
47 isopropylbenzene
48 n-propylbenzene
49 1,3,5-trimethylbenzene
50 1,2,4-trimethylbenzene
51 o-ethyltoluene
52 m-ethyltoluene
53 p-ethyltoluene
54 1,3-diethylbenzene (meta)
55 1,4-diethylbenzene (para)
56 1,2,3-trimethylbenzene
57 n-decane
58 n-undecane
59 formaldehyde
60 acetaldehyde
61 acetone
62 1,3-butadiene
63 2,5-dimethylhexane
64 isobutylene

Figure 4-8. Comparison of the 0500-0800 PST weekday average ambient and average emission inventory chemical species composition for area, point, and mobile sources combined for the Clovis and Fresno PAMS sites and the Fresno County emission inventory.

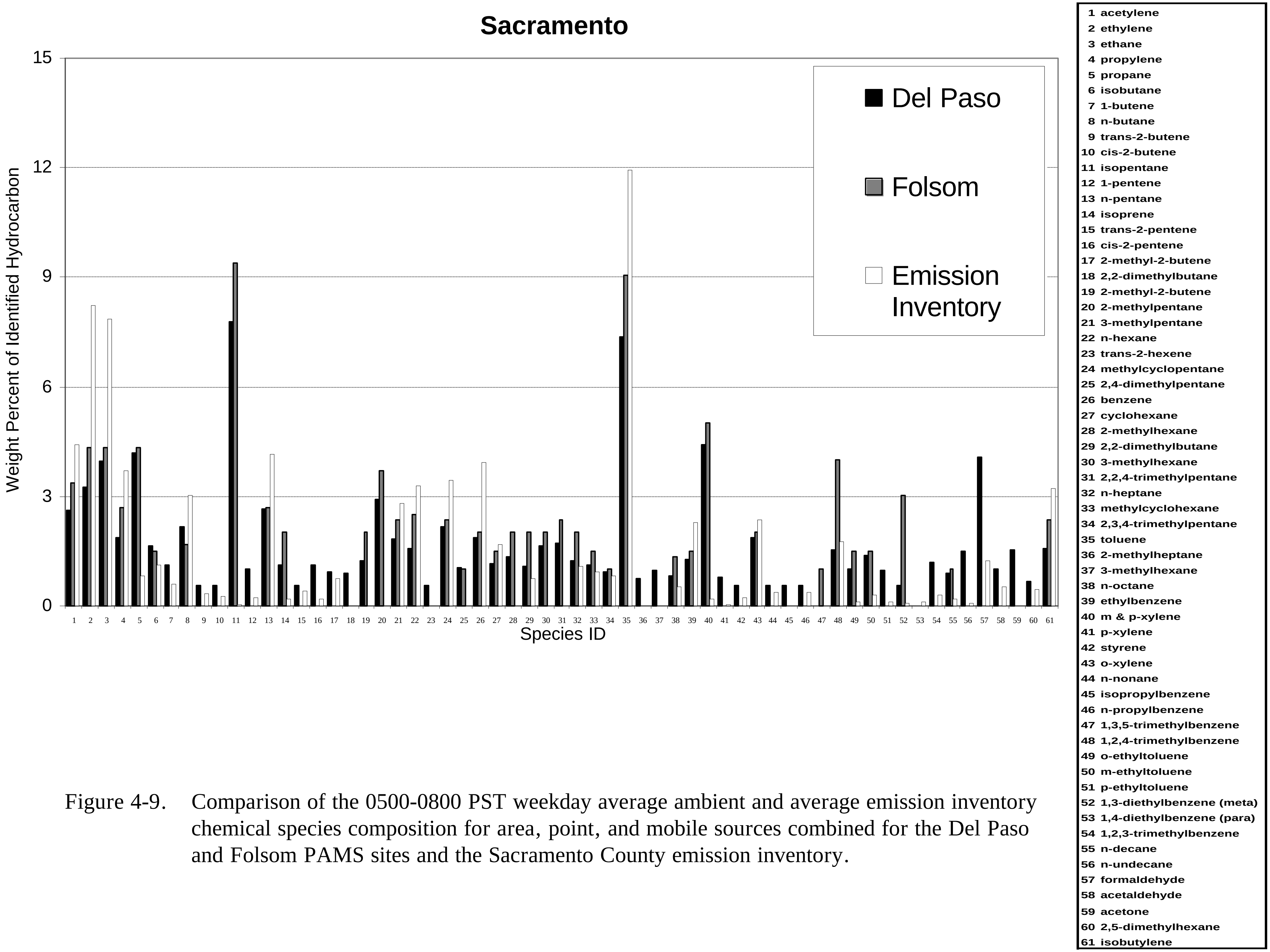


Figure 4-9. Comparison of the 0500-0800 PST weekday average ambient and average emission inventory chemical species composition for area, point, and mobile sources combined for the Del Paso and Folsom PAMS sites and the Sacramento County emission inventory.

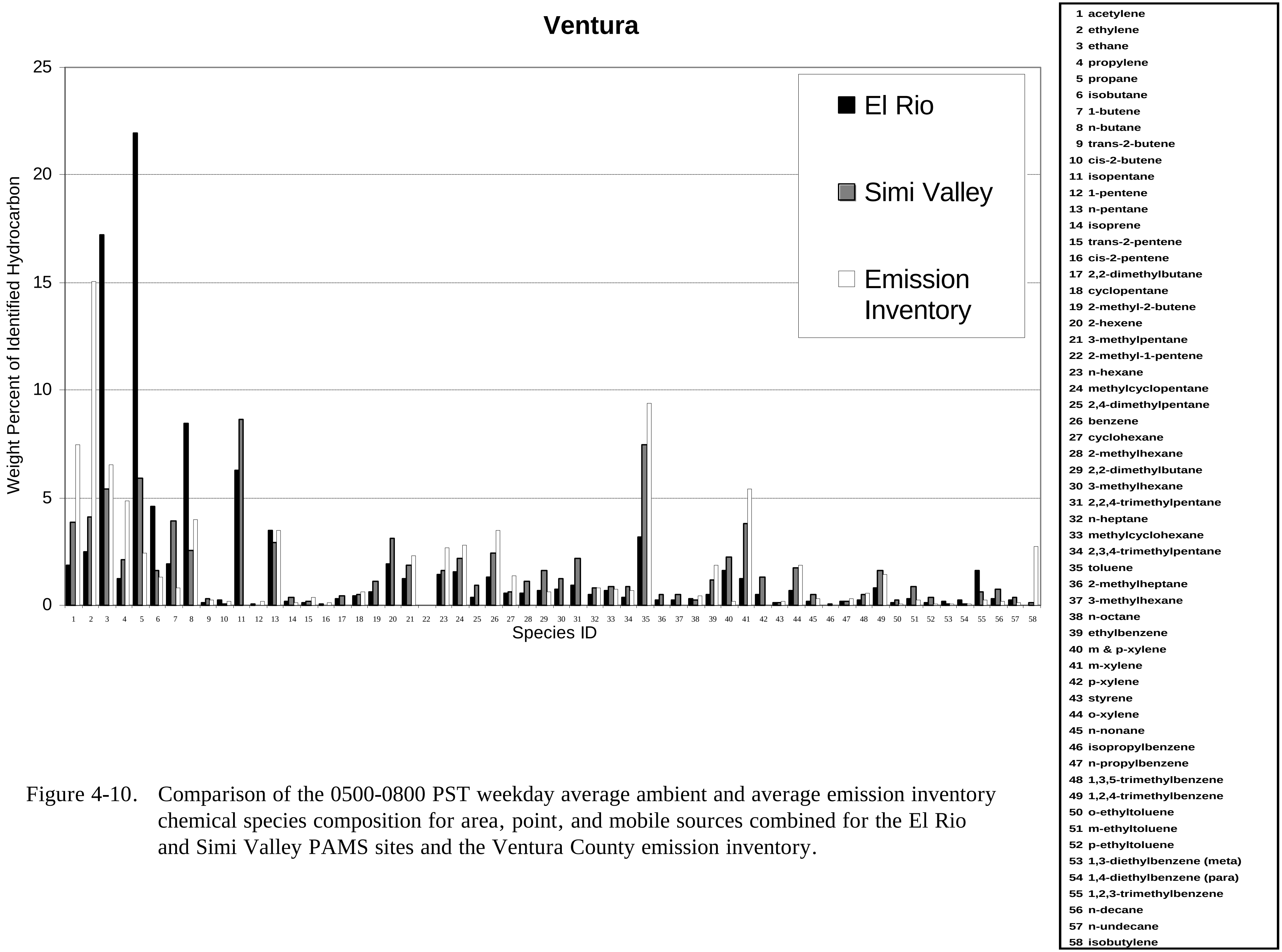
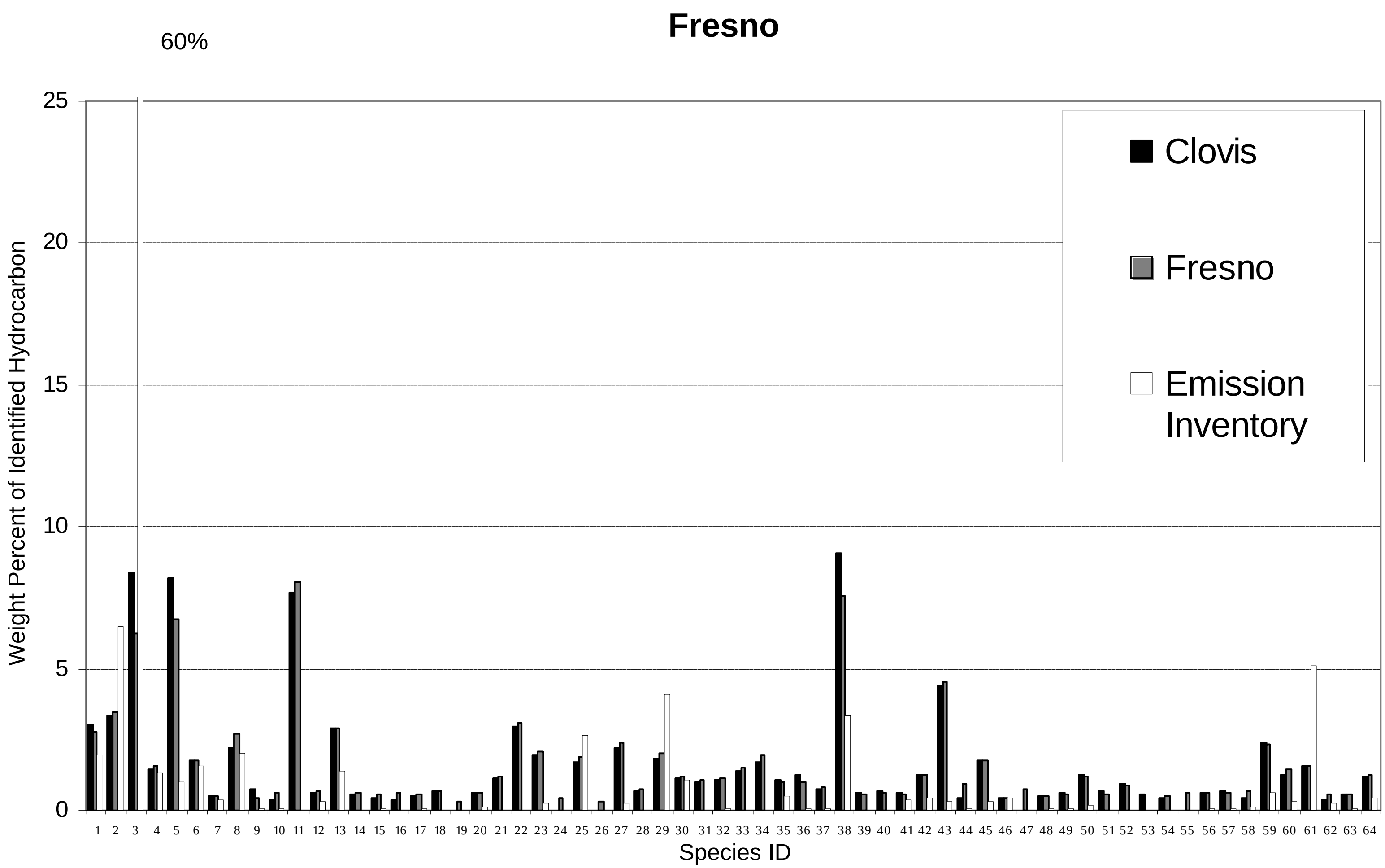


Figure 4-10. Comparison of the 0500-0800 PST weekday average ambient and average emission inventory chemical species composition for area, point, and mobile sources combined for the El Rio and Simi Valley PAMS sites and the Ventura County emission inventory.



1 acetylene
2 ethylene
3 ethane
4 propylene
5 propane
6 isobutane
7 1-butene
8 n-butane
9 trans-2-butene
10 cis-2-butene
11 isopentane
12 1-pentene
13 n-pentane
14 isoprene
15 trans-2-pentene
16 cis-2-pentene
17 2-methyl-2-butene
18 2,2-dimethylbutane
19 cis-3-hexene
20 cyclopentane
21 2-methyl-2-butene
22 2-hexene
23 3-methylpentane
24 2-methyl-1-pentene
25 n-hexane
26 trans-2-hexene
27 methylcyclopentane
28 2,4-dimethylpentane
29 benzene
30 cyclohexane
31 2-methylhexane
32 2,2-dimethylbutane
33 3-methylhexane
34 2,2,4-trimethylpentane
35 n-heptane
36 methylcyclohexane
37 2,3,4-trimethylpentane
38 toluene
39 2-methylheptane
40 3-methylhexane
41 n-octane
42 ethylbenzene
43 m & p-xylene
44 styrene
45 o-xylene
46 n-nonane
47 isopropylbenzene
48 n-propylbenzene
49 1,3,5-trimethylbenzene
50 1,2,4-trimethylbenzene
51 o-ethyltoluene
52 m-ethyltoluene
53 p-ethyltoluene
54 1,3-diethylbenzene (meta)
55 1,4-diethylbenzene (para)
56 1,2,3-trimethylbenzene
57 n-decane
58 n-undecane
59 formaldehyde
60 acetaldehyde
61 acetone
62 1,3-butadiene
63 2,5-dimethylhexane
64 isobutylene

Figure 4-11. Comparison of the 0500-0800 PST average ambient and average emission inventory chemical species composition for the Clovis and Fresno PAMS sites and the area source component of the Fresno County emission inventory.

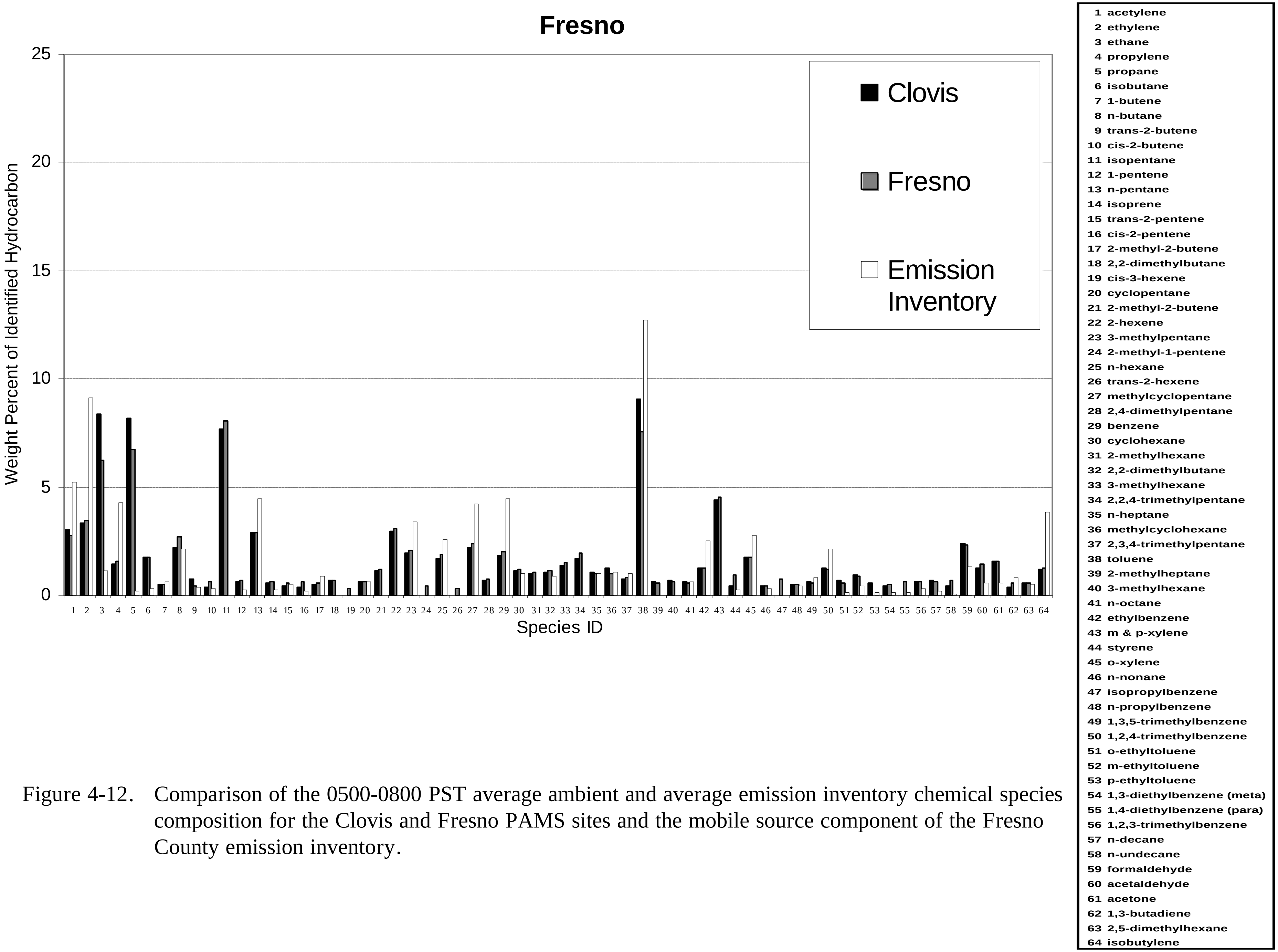
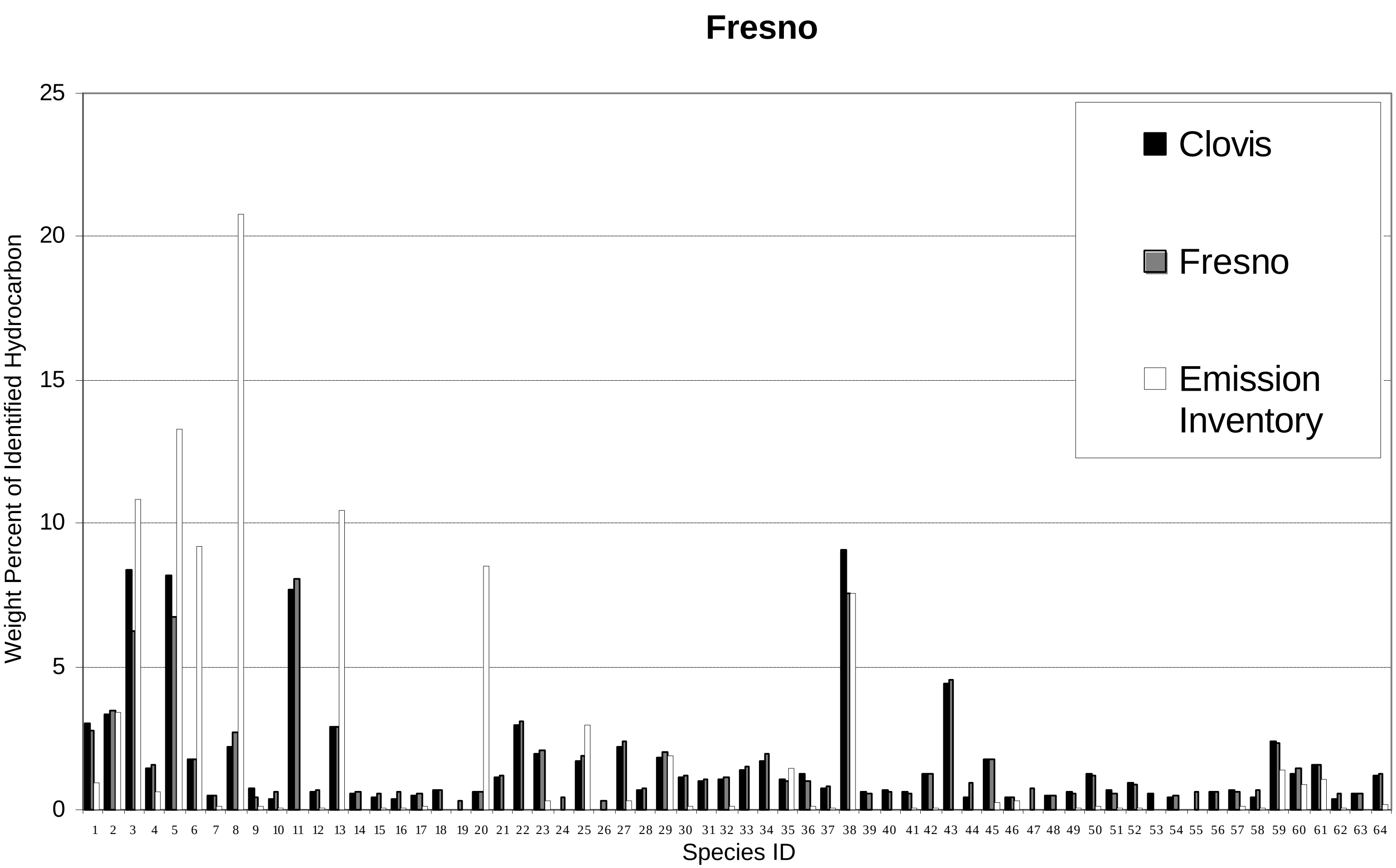
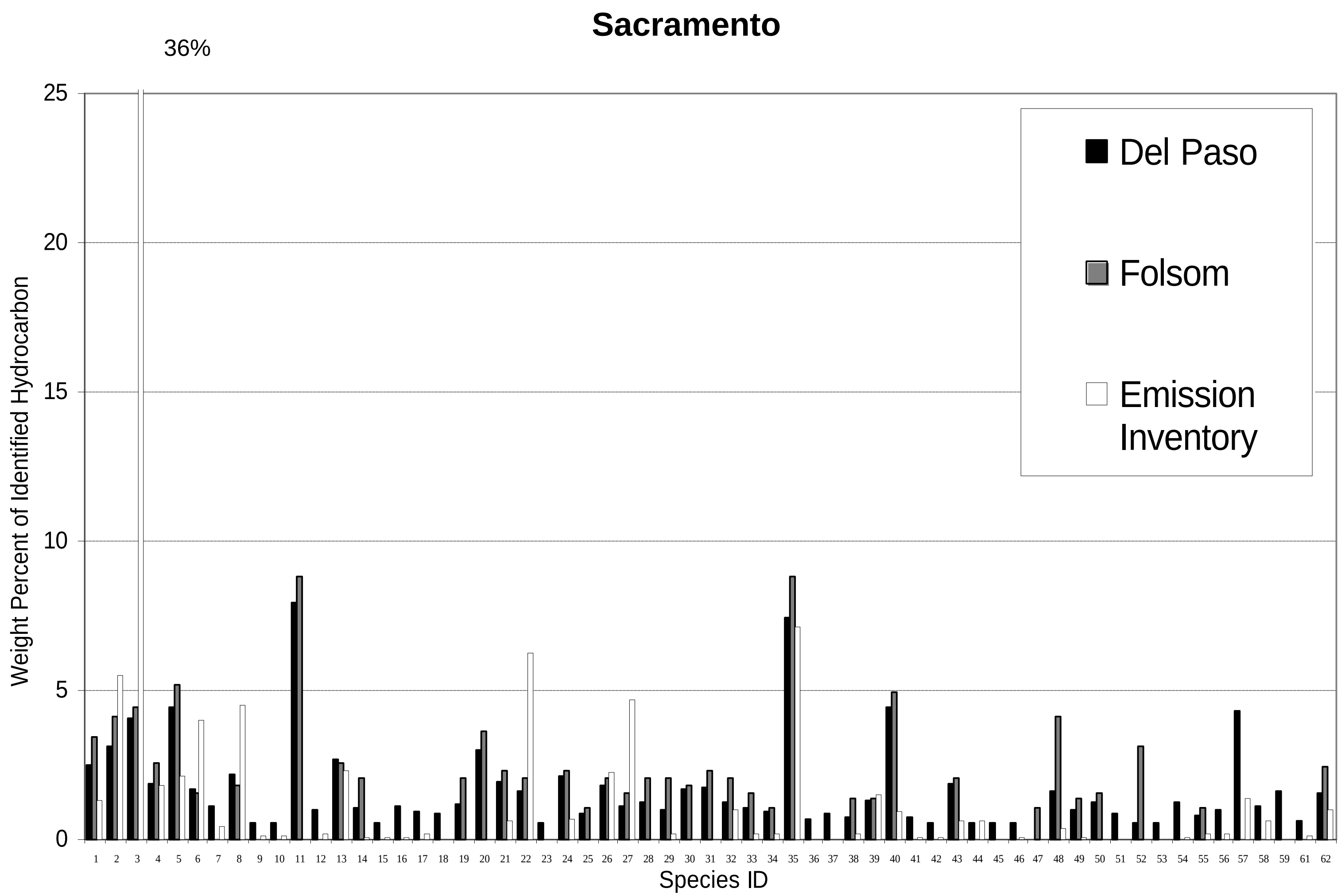


Figure 4-12. Comparison of the 0500-0800 PST average ambient and average emission inventory chemical species composition for the Clovis and Fresno PAMS sites and the mobile source component of the Fresno County emission inventory.



1 acetylene
2 ethylene
3 ethane
4 propylene
5 propane
6 isobutane
7 1-butene
8 n-butane
9 trans-2-butene
10 cis-2-butene
11 isopentane
12 1-pentene
13 n-pentane
14 isoprene
15 trans-2-pentene
16 cis-2-pentene
17 2-methyl-2-butene
18 2,2-dimethylbutane
19 cis-3-hexene
20 cyclopentane
21 2-methyl-2-butene
22 2-hexene
23 3-methylpentane
24 2-methyl-1-pentene
25 n-hexane
26 trans-2-hexene
27 methylcyclopentane
28 2,4-dimethylpentane
29 benzene
30 cyclohexane
31 2-methylhexane
32 2,2-dimethylbutane
33 3-methylhexane
34 2,2,4-trimethylpentane
35 n-heptane
36 methylcyclohexane
37 2,3,4-trimethylpentane
38 toluene
39 2-methylheptane
40 3-methylhexane
41 n-octane
42 ethylbenzene
43 m & p-xylene
44 styrene
45 o-xylene
46 n-nonane
47 isopropylbenzene
48 n-propylbenzene
49 1,3,5-trimethylbenzene
50 1,2,4-trimethylbenzene
51 o-ethyltoluene
52 m-ethyltoluene
53 p-ethyltoluene
54 1,3-diethylbenzene (meta)
55 1,4-diethylbenzene (para)
56 1,2,3-trimethylbenzene
57 n-decane
58 n-undecane
59 formaldehyde
60 acetaldehyde
61 acetone
62 1,3-butadiene
63 2,5-dimethylhexane
64 isobutylene

Figure 4-13. Comparison of the 0500-0800 PST average ambient and average emission inventory chemical species composition for the Clovis and Fresno PAMS sites and the point source component of the Fresno County emission inventory.



1 acetylene
2 ethylene
3 ethane
4 propylene
5 propane
6 isobutane
7 1-butene
8 n-butane
9 trans-2-butene
10 cis-2-butene
11 isopentane
12 1-pentene
13 n-pentane
14 isoprene
15 trans-2-pentene
16 cis-2-pentene
17 2-methyl-2-butene
18 2,2-dimethylbutane
19 cis-3-hexene
20 cyclopentane
21 2-methyl-2-butene
22 2-hexene
23 3-methylpentane
24 2-methyl-1-pentene
25 n-hexane
26 trans-2-hexene
27 methylcyclopentane
28 2,4-dimethylpentane
29 benzene
30 cyclohexane
31 2-methylhexane
32 2,2-dimethylbutane
33 3-methylhexane
34 2,2,4-trimethylpentane
35 n-heptane
36 methylcyclohexane
37 2,3,4-trimethylpentane
38 toluene
39 2-methylheptane
40 3-methylhexane
41 n-octane
42 ethylbenzene
43 m & p-xylene
44 styrene
45 o-xylene
46 n-nonane
47 isopropylbenzene
48 n-propylbenzene
49 1,3,5-trimethylbenzene
50 1,2,4-trimethylbenzene
51 o-ethyltoluene
52 m-ethyltoluene
53 p-ethyltoluene
54 1,3-diethylbenzene (meta)
55 1,4-diethylbenzene (para)
56 1,2,3-trimethylbenzene
57 n-decane
58 n-undecane
59 formaldehyde
60 acetaldehyde
61 acetone
62 1,3-butadiene
63 2,5-dimethylhexane
64 isobutylene

Figure 4-14. Comparison of the 0500-0800 PST average ambient and average emission inventory chemical species composition for the Del Paso and Folsom PAMS sites and the area source component of the Sacramento County emission inventory.

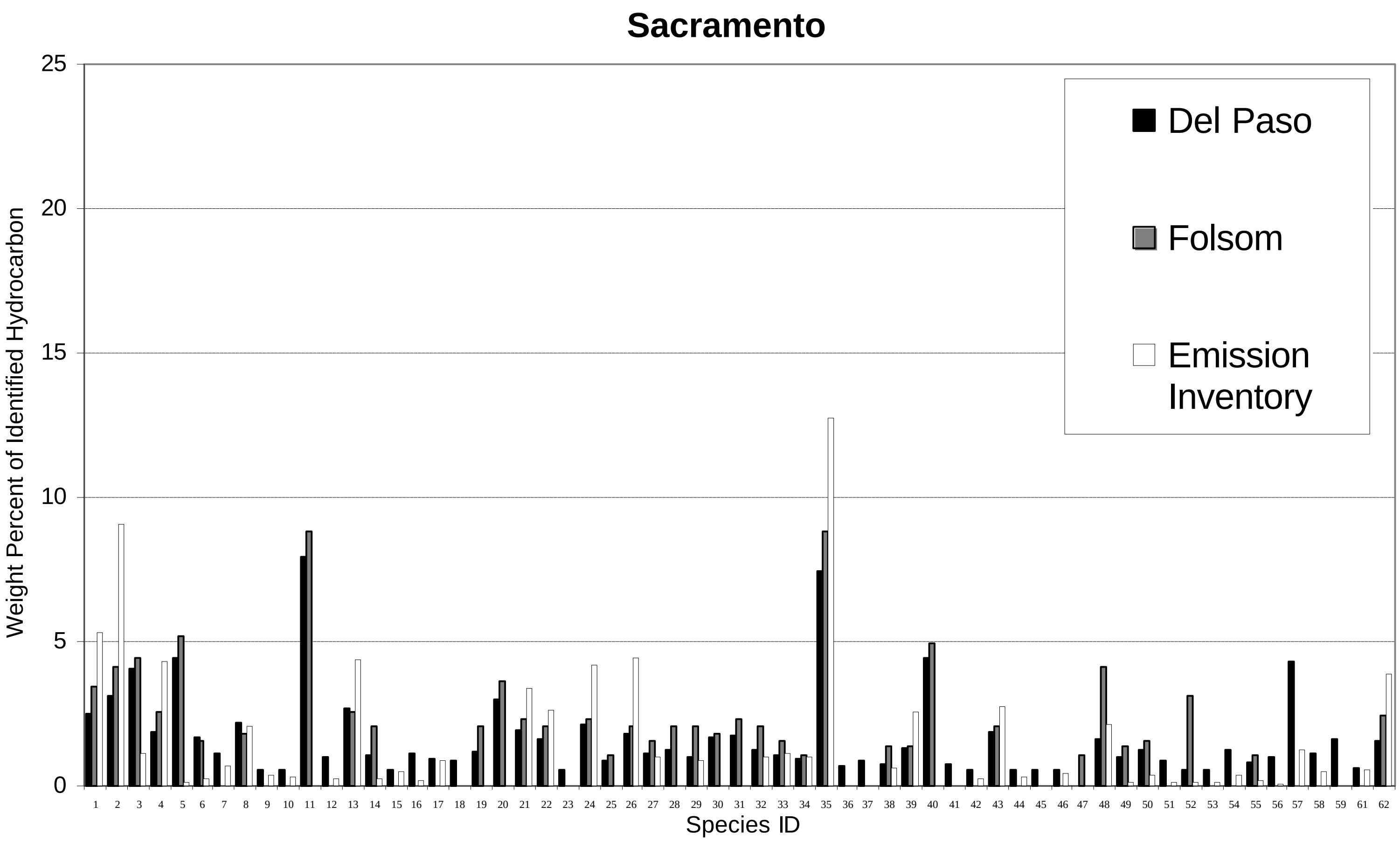


Figure 4-15. Comparison of the 0500-0800 PST average ambient and average emission inventory chemical species composition for the Del Paso and Folsom PAMS sites and the mobile source component of the Sacramento County emission inventory.

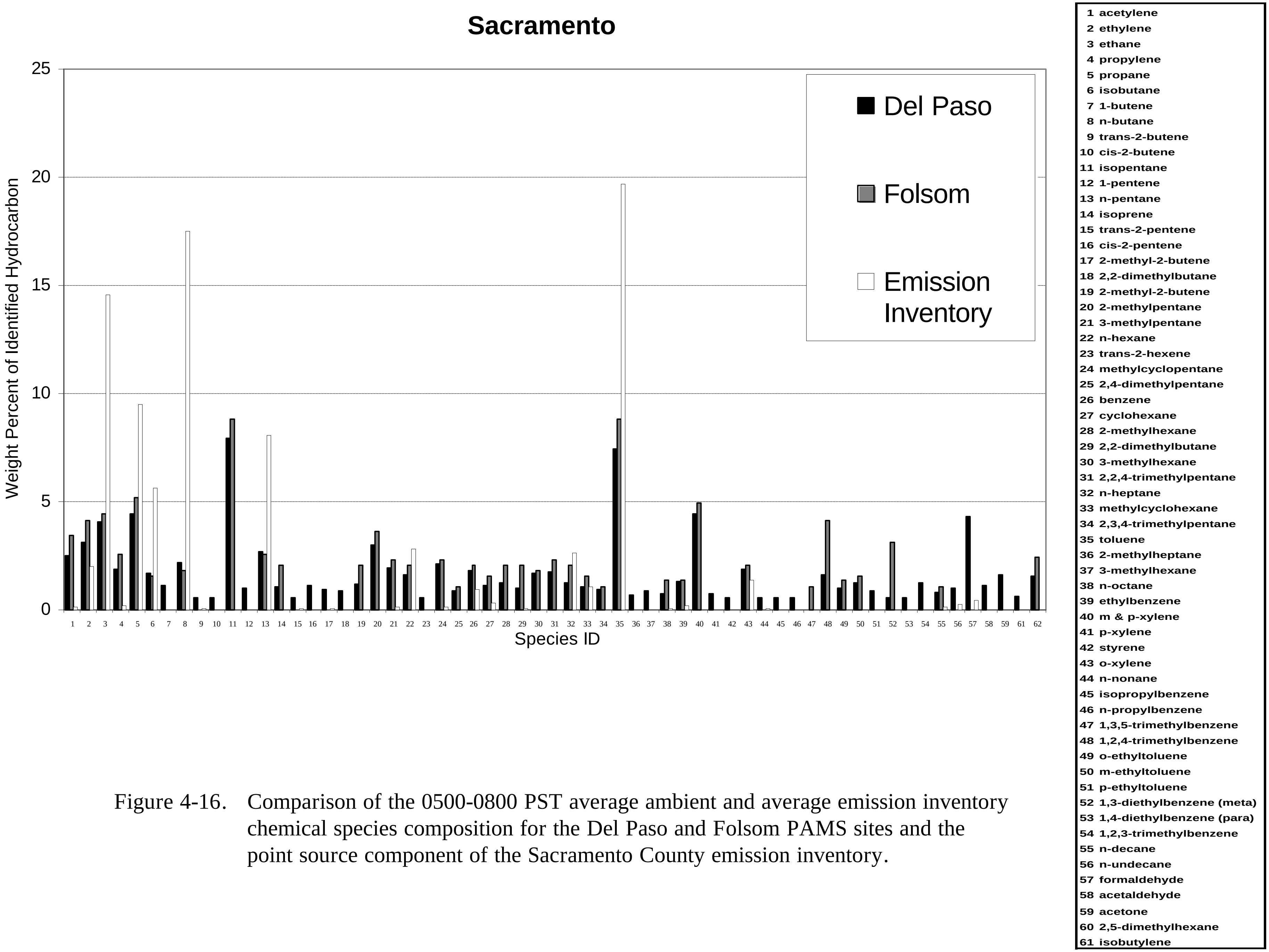


Figure 4-16. Comparison of the 0500-0800 PST average ambient and average emission inventory chemical species composition for the Del Paso and Folsom PAMS sites and the point source component of the Sacramento County emission inventory.

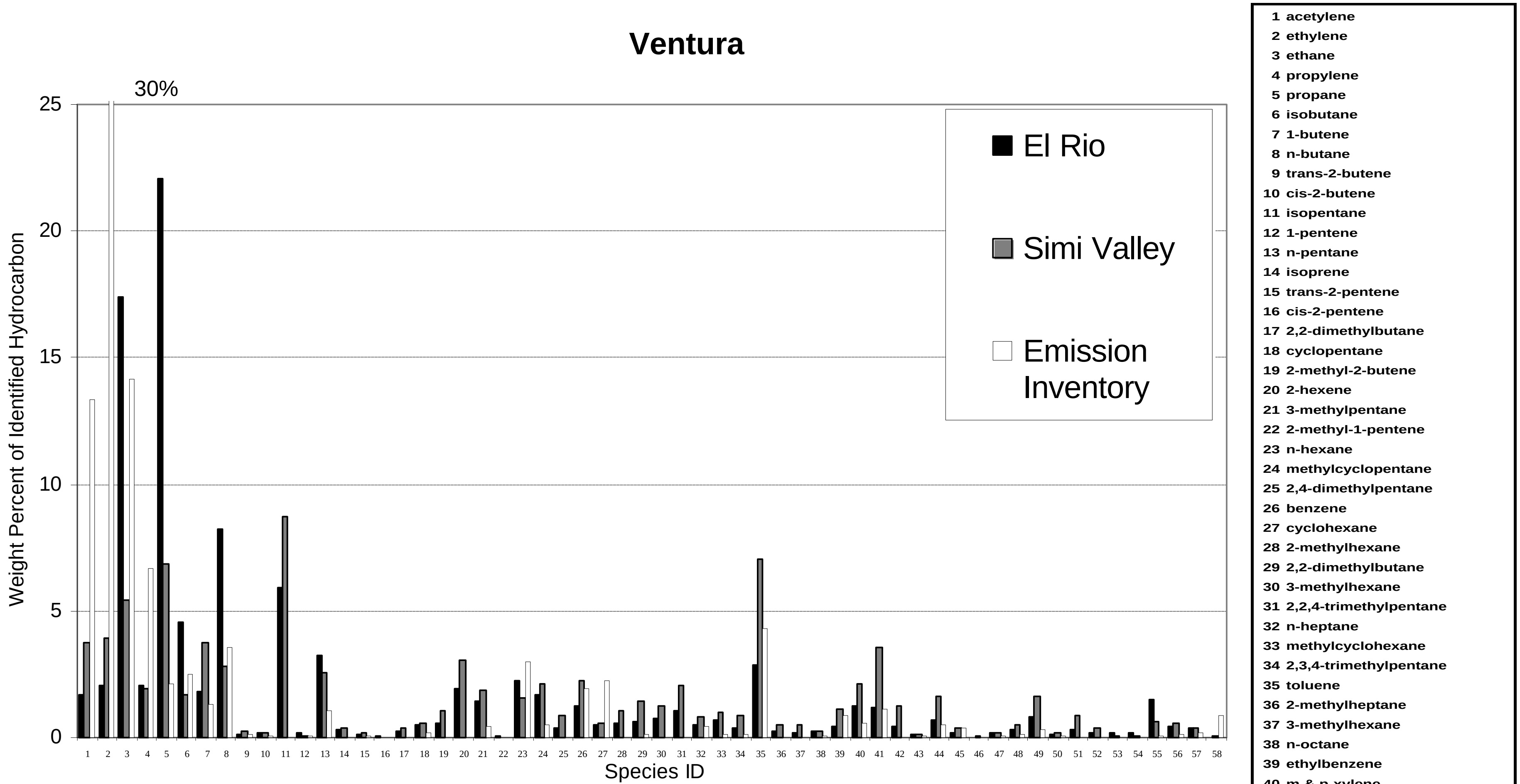


Figure 4-17. Comparison of the 0500-0800 PST average ambient and average emission inventory chemical species composition for the El Rio and Simi Valley PAMS sites and the area source component of the Ventura County emission inventory.

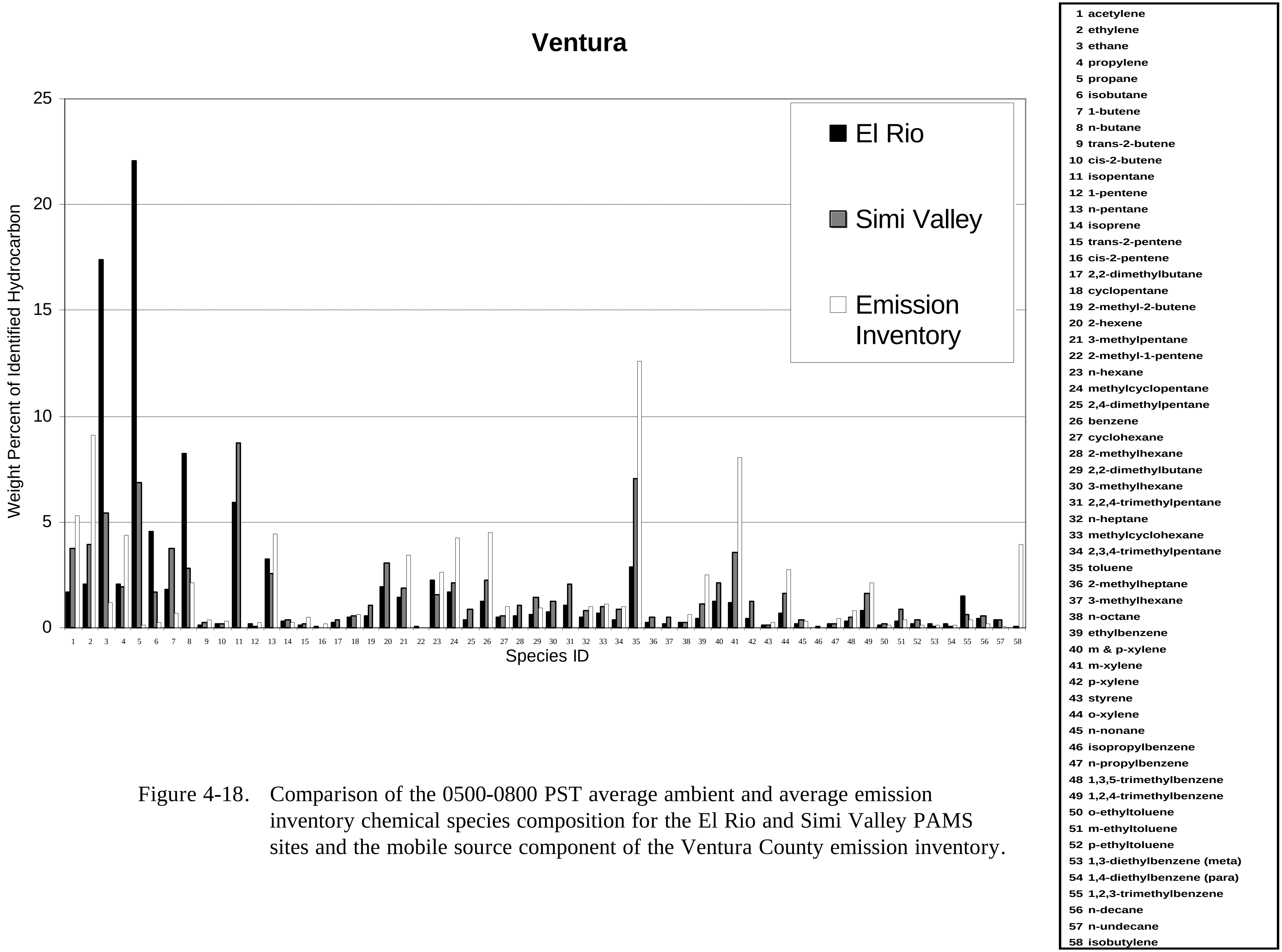
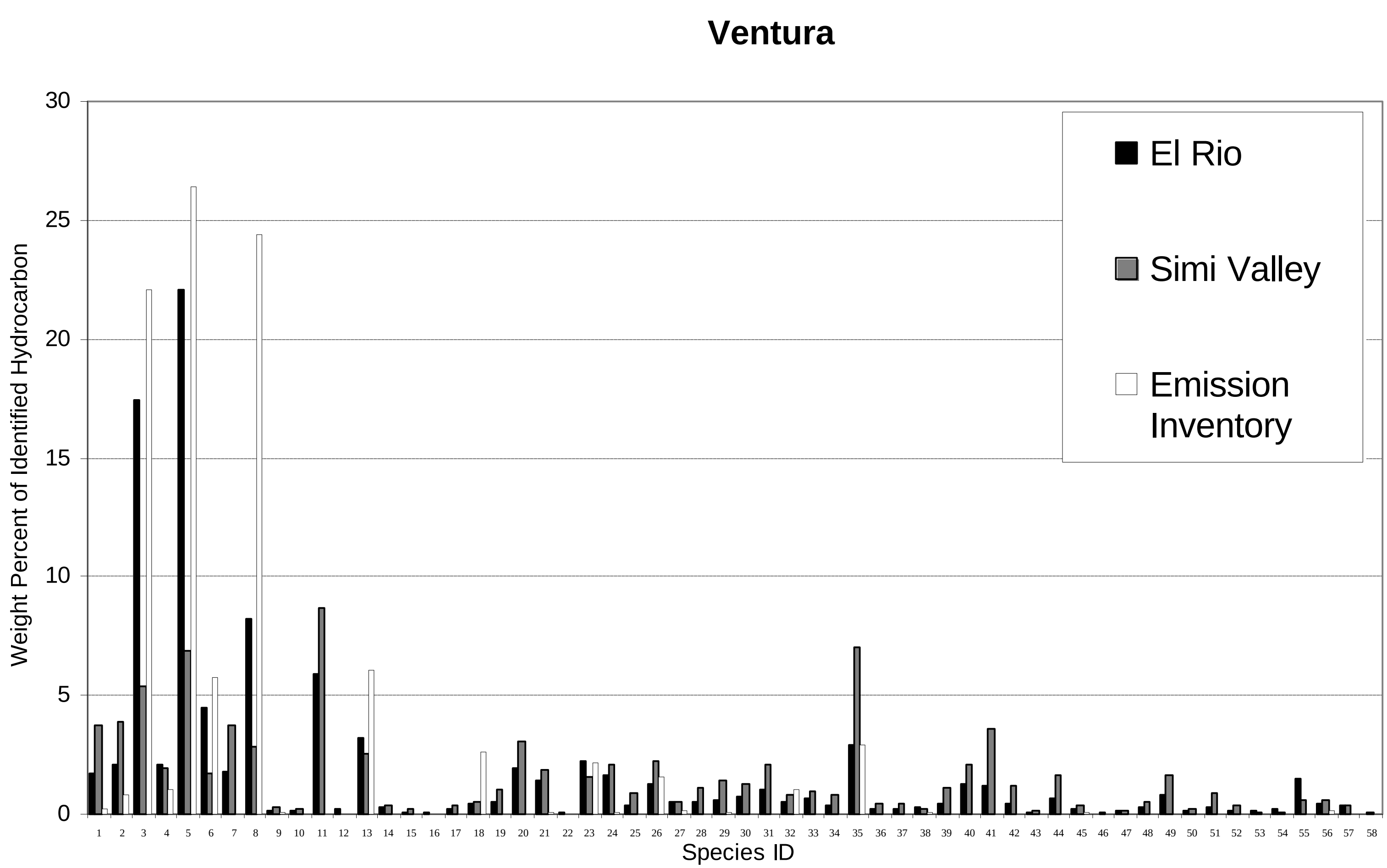


Figure 4-18. Comparison of the 0500-0800 PST average ambient and average emission inventory chemical species composition for the El Rio and Simi Valley PAMS sites and the mobile source component of the Ventura County emission inventory.



1 acetylene
2 ethylene
3 ethane
4 propylene
5 propane
6 isobutane
7 1-butene
8 n-butane
9 trans-2-butene
10 cis-2-butene
11 isopentane
12 1-pentene
13 n-pentane
14 isoprene
15 trans-2-pentene
16 cis-2-pentene
17 2,2-dimethylbutane
18 cyclopentane
19 2-methyl-2-butene
20 2-hexene
21 3-methylpentane
22 2-methyl-1-pentene
23 n-hexane
24 methylcyclopentane
25 2,4-dimethylpentane
26 benzene
27 cyclohexane
28 2-methylhexane
29 2,2-dimethylbutane
30 3-methylhexane
31 2,2,4-trimethylpentane
32 n-heptane
33 methylcyclohexane
34 2,3,4-trimethylpentane
35 toluene
36 2-methylheptane
37 3-methylhexane
38 n-octane
39 ethylbenzene
40 m & p-xylene
41 m-xylene
42 p-xylene
43 styrene
44 o-xylene
45 n-nonane
46 isopropylbenzene
47 n-propylbenzene
48 1,3,5-trimethylbenzene
49 1,2,4-trimethylbenzene
50 o-ethyltoluene
51 m-ethyltoluene
52 p-ethyltoluene
53 1,3-diethylbenzene (meta)
54 1,4-diethylbenzene (para)
55 1,2,3-trimethylbenzene
56 n-decane
57 n-undecane
58 isobutylene

Figure 4-19. Comparison of the 0500-0800 PST average ambient and average emission inventory chemical species composition for the El Rio and Simi Valley PAMS sites and the point source component of the Ventura County emission inventory.

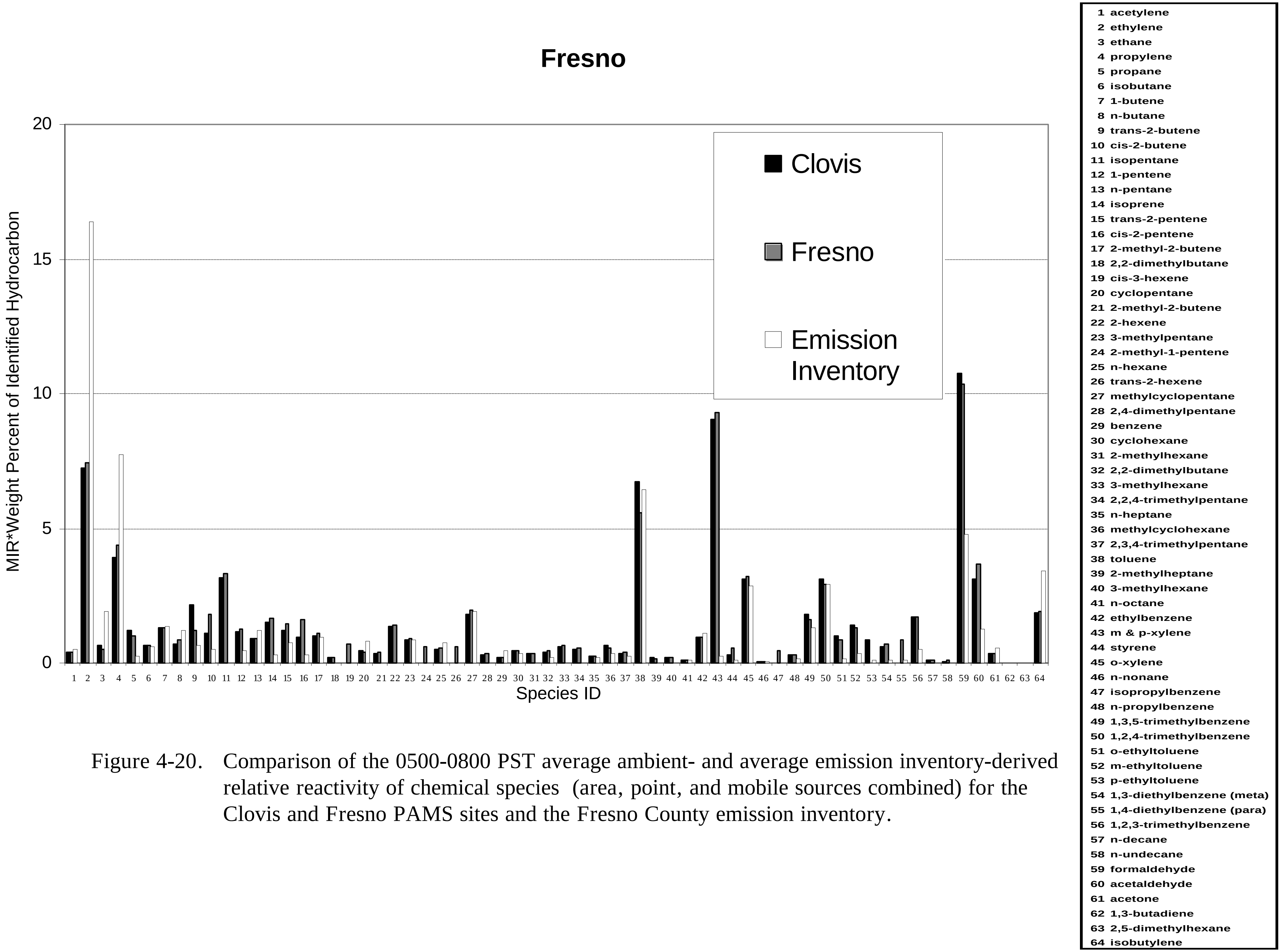
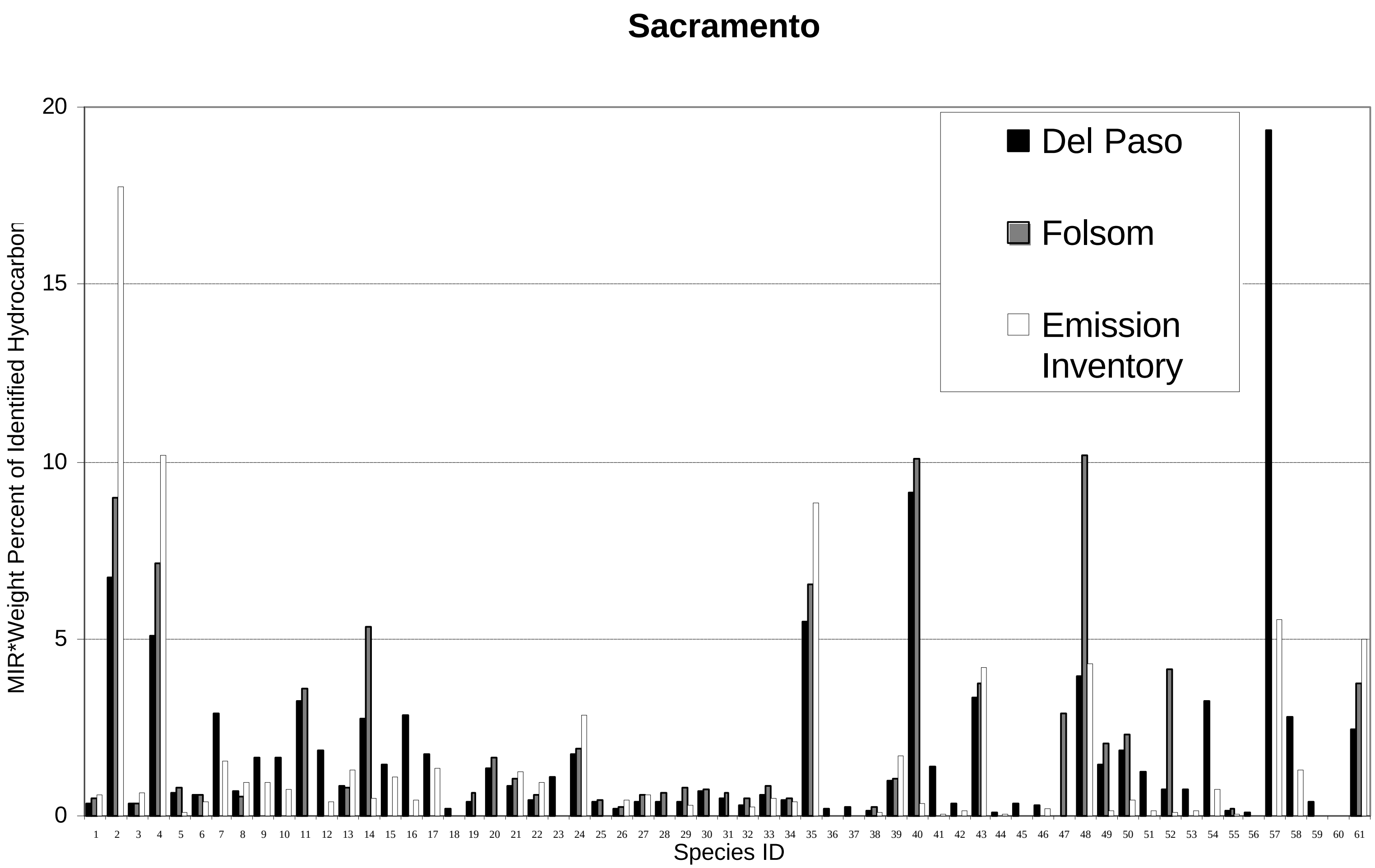


Figure 4-20. Comparison of the 0500-0800 PST average ambient- and average emission inventory-derived relative reactivity of chemical species (area, point, and mobile sources combined) for the Clovis and Fresno PAMS sites and the Fresno County emission inventory.



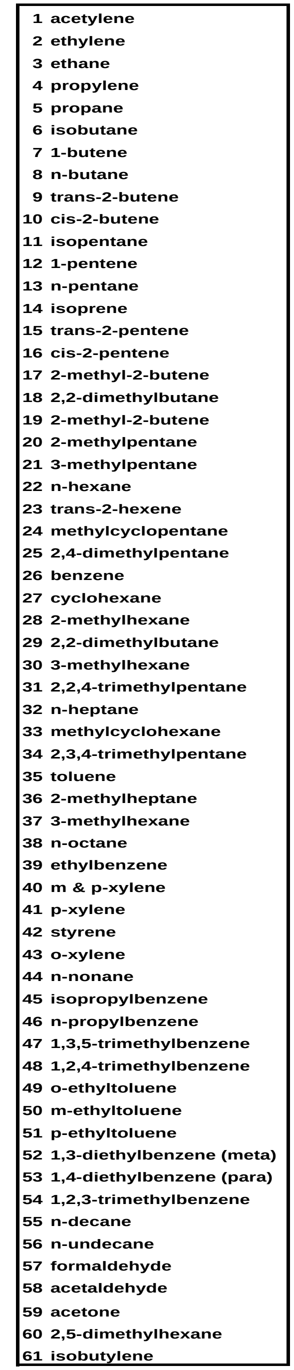


Figure 4-21. Comparison of the 0500-0800 PST average ambient- and average emission inventory-derived relative reactivity of chemical species (area, point, and mobile sources combined) for the Del Paso and Folsom PAMS sites and the Sacramento County emission inventory.

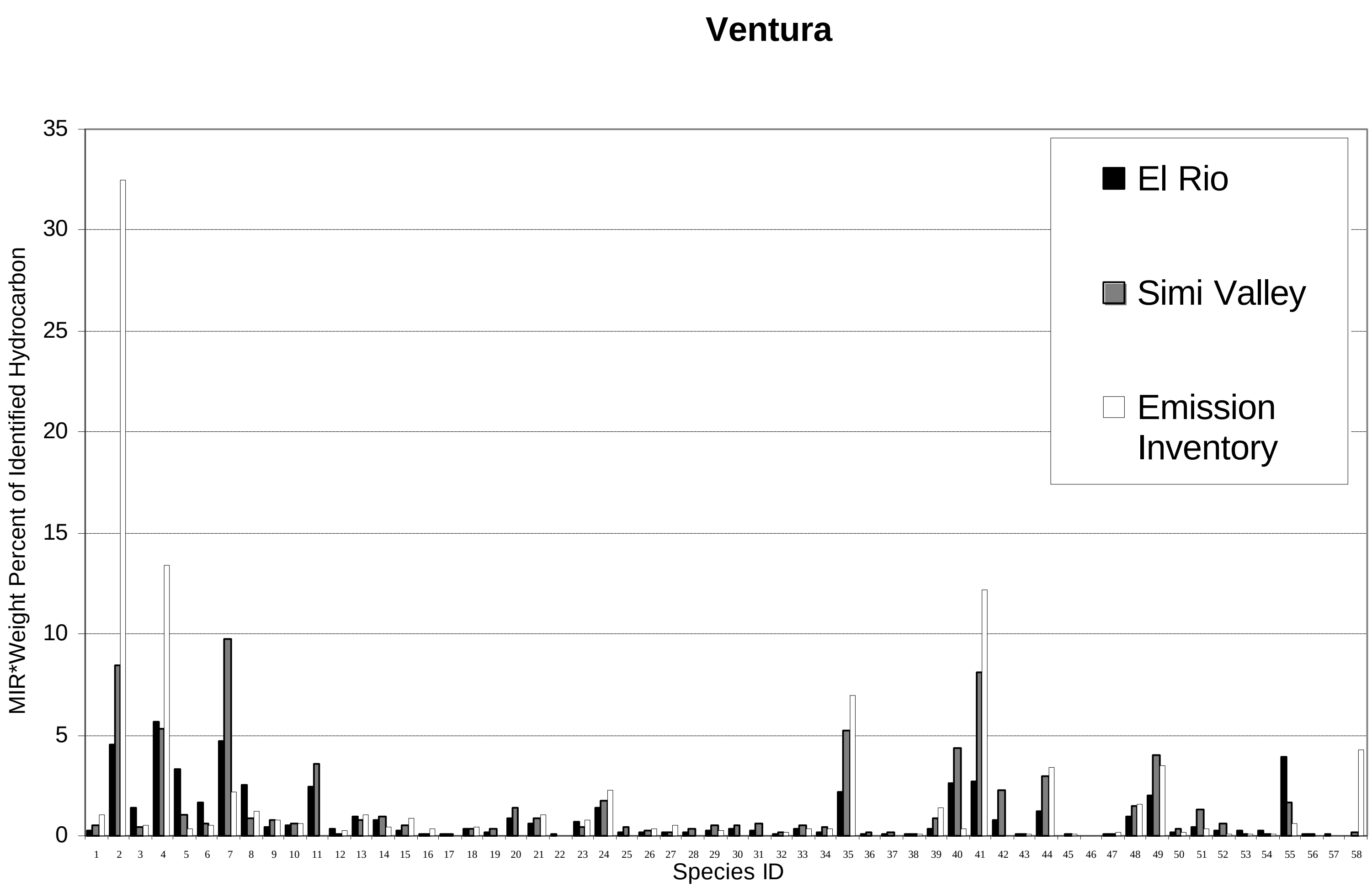


Figure 4-22. Comparison of the 0500-0800 PST average ambient- and average emission inventory-derived relative reactivity of chemical species (area, point, and mobile sources combined) for the El Rio and Simi Valley PAMS sites and the Ventura County emission inventory.

1 acetylene
2 ethylene
3 ethane
4 propylene
5 propane
6 isobutane
7 1-butene
8 n-butane
9 trans-2-butene
10 cis-2-butene
11 isopentane
12 1-pentene
13 n-pentane
14 isoprene
15 trans-2-pentene
16 cis-2-pentene
17 2,2-dimethylbutane
18 cyclopentane
19 2-methyl-2-butene
20 2-hexene
21 3-methylpentane
22 2-methyl-1-pentene
23 n-hexane
24 methylcyclopentane
25 2,4-dimethylpentane
26 benzene
27 cyclohexane
28 2-methylhexane
29 2,2-dimethylbutane
30 3-methylhexane
31 2,2,4-trimethylpentane
32 n-heptane
33 methylcyclohexane
34 2,3,4-trimethylpentane
35 toluene
36 2-methylheptane
37 3-methylhexane
38 n-octane
39 ethylbenzene
40 m & p-xylene
41 m-xylene
42 p-xylene
43 styrene
44 o-xylene
45 n-nonane
46 isopropylbenzene
47 n-propylbenzene
48 1,3,5-trimethylbenzene
49 1,2,4-trimethylbenzene
50 o-ethyltoluene
51 m-ethyltoluene
52 p-ethyltoluene
53 1,3-diethylbenzene (meta)
54 1,4-diethylbenzene (para)
55 1,2,3-trimethylbenzene
56 n-decane
57 n-undecane
58 isobutylene

Table 4-1. Average ambient- and emission inventory-derived hydrocarbon/NO_x ratios for the ambient weekday data collected from 0500-0800 PST during the summer of 1996 and 0500-0800 PST county total emission inventory data at Fresno, Sacramento, and Ventura counties. Note that these data are shown graphically in Figure 4-1.

County and Site	Spatially Averaged Ratio[a]
Fresno County	
Clovis Ambient	6.4
Fresno Ambient	5.7
Emission Inventory	2.1
Emission Inventory (Point Source NO_x Excluded)	4.2
Sacramento County	
Del Paso Ambient	5.9
Folsom Ambient	5.1
Emission Inventory	2.6
Emission Inventory (Point Source NO_x Excluded)	2.7
Ventura County	
El Rio Ambient	7.5
Simi Valley Ambient	4.3
Emission Inventory	2.3
Emission Inventory (Point Source NO_x Excluded)	2.5

[a] The ambient ratios shown in the spatially averaged column correspond to the average of all valid ambient data meeting the screening criteria at each site. The emission inventory ratios correspond to county total emissions.

Table 4-2. Ratios of the ambient- and emission inventory-derived weekday hydrocarbon/NO_x ratios in Fresno, Sacramento, and Ventura counties.

County and Site	Ambient/Emission Inventory Ratio
Fresno County	
Clovis	3.0
Clovis-Emission Inventory Excluding Point Source NO_x	1.5
Fresno	2.7
Fresno- Emission Inventory Excluding Point Source NO_x	1.4
Sacramento County	
Del Paso	2.3
Folsom	2.0
Ventura County	
El Rio	3.3
Simi Valley	1.9

Table 4-3. Average ambient- and emission inventory-derived weekday CO/NO_x ratios for the ambient data collected from 0500-0800 PST during the summer of 1996 and 0500-0800 PST county total emission inventory data at Fresno, Sacramento, and Ventura counties. Note that these data are shown graphically in Figure 4-2 and no CO data were available for Folsom in 1996.

County and Site	Spatially Averaged Ratio[a]
Fresno County	
Clovis Ambient	19.4
Fresno Ambient	18.4
Emission Inventory	7.1
Emission Inventory (Point Source CO and NO_x Excluded)	11.4
Sacramento County	
Del Paso Ambient	15.4
Emission Inventory	11.4
Emission Inventory Point Source CO and NO_x Excluded)	11.9
Ventura County	
El Rio Ambient	13.1
Simi Valley Ambient	22.6
Emission Inventory	12.8
Emission Inventory Point Source CO and NO_x Excluded)	13.3

[a] The ambient ratios shown in the spatially averaged column correspond to the average of all valid ambient data meeting the screening criteria at each site. The emission inventory ratios correspond to county total emissions.

Table 4-4. Ratios of the ambient- and emission inventory-derived weekday CO/NO_x ratios in Fresno, Sacramento, and Ventura counties.

County and Site	Ambient/ Emission Inventory Ratio
Fresno County	
Clovis	2.7
Clovis- Emission Inventory Excluding Point Source CO and NO_x	1.7
Fresno	2.6
Fresno- Emission Inventory Excluding Point Source CO and NO_x	1.6
Sacramento County	
Del Paso	1.4
Ventura County	
El Rio	1.0
Simi Valley	1.8

Table 4-5a. Average ambient- and emission inventory-derived hydrocarbon/NO_x ratios for the ambient weekday data collected from 0500-0800 PST during the summer of 1996 accounting for background concentrations and 0500-0800 PST county total emission inventory data at Fresno, Sacramento, and Ventura counties.

County and Site	Spatially Averaged Ratio	Background Adjusted Ratio	Ambient/ Emission Inventory	Adjusted Ambient/ Emission Inventory	Ambient/ Emission Inventory (without point sources)	Adjusted Ambient/ Emission Inventory (without point sources)
Fresno County						
Clovis Ambient	6.4	5.8	3.0	2.8	1.5	1.4
Fresno Ambient	5.7	5.2	2.7	2.5	1.4	1.2
Emission Inventory	2.1					
Emission Inventory (Point Source NO_x Excluded)	4.2					
Sacramento County						
Del Paso Ambient	5.9	5.1	2.3	2.0	2.2	1.9
Folsom Ambient	5.1	4.1	2.0	1.6	1.9	1.5
Emission Inventory	2.6					
Emission Inventory Point Source NO_x Excluded)	2.7					
Ventura County						
El Rio Ambient	7.5	6.9	3.3	3.0	3.0	2.8
Simi Valley Ambient	4.3	3.8	1.9	1.7	1.7	1.5
Emission Inventory	2.3					
Emission Inventory Point Source NO_x Excluded)	2.5					

Table 4-5b. Average ambient- and emission inventory-derived CO/NO_x ratios for the ambient weekday data collected from 0500-0800 PST during the summer of 1996 accounting for background concentrations and 0500-0800 PST county total emission inventory data at Fresno, Sacramento, and Ventura counties.

County and Site	Spatially Averaged Ratio	Background Adjusted Ratio	Ambient/ Emission Inventory	Adjusted Ambient/ Emission Inventory	Ambient/ Emission Inventory (without point sources)	Adjusted Ambient/ Emission Inventory (without point sources)
Fresno County						
Clovis Ambient	19.4	14.6	2.7	2.1	1.7	1.4
Fresno Ambient	18.4	14.8	2.6	2.5	1.6	1.2
Emission Inventory	7.1					
Emission Inventory (Point Source NO_x and CO Excluded)	11.4					
Sacramento County						
Del Paso Ambient	15.4	8.1	1.4	0.7	1.3	0.7
Emission Inventory	11.4					
Emission Inventory Point Source NO_x and CO Excluded)	11.9					
Ventura County						
El Rio Ambient	13.1	8.2	1.0	0.7	1.0	0.6
Simi Valley Ambient	22.6	19.2	1.8	1.5	1.7	1.4
Emission Inventory	12.8					
Emission Inventory Point Source NO_x and CO Excluded)	13.3					

Table 4-6. Summary of the Saturday ambient average TNMOC, NO_x, and CO data meeting all validity and screening criteria at Fresno, Clovis, and Del Paso Manor.

Site ID	Site Name, County	# Valid Samples	Average TNMOC ppbC[b]	Average NO_x ppb[c]	Average CO ppb
060190008	Fresno 1st Street, Fresno	4	275	44	900
060195001	Clovis, Fresno	4	315	30	742
060670006	Del Paso Manor, Sacramento	4	228	29	507

[a] Only valid samples collected on Saturdays from July through September 1996 (begin hours 0500, 0600, and 0700 PST) meeting all screening criteria were used to calculate the averages in the table.
[b] TNMOC = Total Non-Methane Organic Compounds includes both identified and unidentified compounds. Averages were calculated for all valid samples with TNMOC > 100 ppbC.
[c] NO_x averages were calculated for all valid samples with NO_x > 10 ppb to eliminate NO_x values at or near instrument detection limits.

Table 4-7. Average ambient- and emission inventory-derived Saturday hydrocarbon/NO_x ratios for the ambient data collected from 0500-0800 PST during the summer of 1996 and 0500-0800 PST county total emission inventory data for Fresno and Sacramento counties. Note that these data are shown graphically in Figures 4-3 and 4-4.

County and Site	Spatially Averaged Ratio[a]
Fresno County	
Clovis Ambient	10.7
Fresno Ambient	6.4
Saturday Emission Inventory	2.2
Saturday Emission Inventory (Point Source NO_x Excluded)	4.8
Sacramento County	
Del Paso Ambient	10.0
Saturday Emission Inventory	2.7
Saturday Emission Inventory (Point Source NO_x Excluded)	2.9

[a] The ambient ratios shown in the spatially averaged column correspond to the average of all valid ambient data collected on Saturdays meeting the screening criteria at each site. The emission inventory ratios correspond to county total emissions.

Table 4-8. Ratios of the ambient- and emission inventory-derived Saturday hydrocarbon/NO_x ratios in Fresno and Sacramento counties.

County and Site	Ambient/ Emission Inventory
Fresno County	
Clovis	4.9
Clovis- Emission Inventory (Excluding Point Source CO and NO_x)	2.2
Fresno	2.9
Fresno- Emission Inventory (Excluding Point Source CO and NO_x)	1.3
Sacramento County	
Del Paso	3.7

Table 4-9. Average ambient- and emission inventory-derived Saturday CO/NO_x ratios for the ambient data collected from 0500-0800 PST during the summer of 1996 and 0500-0800 PST county total emission inventory data for Fresno and Sacramento counties. Note that these data are shown graphically in Figures 4-5 and 4-6.

County and Site	Spatially Averaged Ratio[a]
Fresno County	
Clovis Ambient	24.6
Fresno Ambient	20.3
Saturday Emission Inventory	7.0
Saturday Emission Inventory (Point Source NO_x Excluded)	12.2
Sacramento County	
Del Paso Ambient	21.5
Saturday Emission Inventory	11.9
Saturday Emission Inventory (Point Source NO_x Excluded)	12.5

[a] The ambient ratios shown in the spatially averaged column correspond to the average of all valid ambient data collected on Saturdays meeting the screening criteria at each site. The emission inventory ratios correspond to county total emissions.

Table 4-10. Ratios of the ambient- and emission inventory-derived Saturday CO/NO_x ratios in Fresno and Sacramento counties.

County and Site	Ambient/ Emission Inventory Ratios
Fresno County	
Clovis	3.5
Clovis- Emission Inventory (Excluding Point Source CO and NO_x)	2.0
Fresno	2.9
Fresno- Emission Inventory (Excluding Point Source CO and NO_x)	1.7
Sacramento County	
Del Paso	1.8

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5. CONCLUSIONS FROM THE EMISSION INVENTORY EVALUATION AND RECOMMENDATIONS

Comparisons between ambient data and emission estimates for hydrocarbon, CO, and NO_x are based on the premise that early morning ambient pollutant concentrations (when emissions are high, and wind speed, atmospheric mixing height, and chemical reactivity are low) are dominated by fresh emissions in the vicinity of the monitor. In this study, comparisons of the ambient- and emission inventory-derived hydrocarbon/NO_x and CO/NO_x ratios as well as comparisons of individual hydrocarbon species compositions were made for six PAMS monitoring sites located in Fresno, Sacramento, and Ventura counties (two sites in each county). The ambient data used in this comparison were collected from 0500-0800 PST during the summer of 1996.

To further maximize the influence of nearby emissions and minimize the influence of transported emissions, periods with generally high average ambient hydrocarbon concentrations were selected for analysis at each site. In order to obtain a useful number of samples with sufficiently high concentrations above instrument detection limits, minimum hydrocarbon and NO_x thresholds of 100 ppbC and 10 ppb, respectively, were established.

The daily speciated emission inventory was prepared by the ARB. Daily total emissions were speciated and temporally allocated to the 0500-0800 time period using profile code cross-reference files and source category code files provided by the ARB. The inventory was then converted from a mass to a molar basis and placed on a common basis with the ambient data to include only the chemical species capable of being detected by the PAMS monitoring systems.

The strength of a top-down emission inventory evaluation is that it can be used to identify areas of an emission inventory that appear to be suspect. This methodology cannot be used to quantify the absolute errors in an inventory, but can be used to compare the relative amounts of pollutants in the inventory and the ambient air. The chemical species analysis can be used to characterize the chemical composition of the inventory and the ambient air and help to identify which major source types of the inventory appear to need improvement.

5.1 CONCLUSIONS – HYDROCARBON/NO_X AND CO/NO_X RATIO ANALYSES

Significant differences between the 1996 ambient data and the 1996 ARB inventory for Fresno, Sacramento, and Ventura counties exist at the sites examined in this study. The following conclusions summarize the major findings of the hydrocarbon/NO_x and CO/NO_x ratio analyses:

- In general, weekday ambient hydrocarbon/NO_x ratios at the two sites in Fresno and Sacramento are fairly consistent within each county, while ambient ratios at the two sites in Ventura County are quite different. This indicates that ambient concentrations in Fresno and Sacramento counties are fairly uniform throughout the counties, while in Ventura

County, there are concentration gradients in the ambient air throughout the county. Consequently, the county-wide average emission inventory ratios do not compare well with either ambient site in Ventura County and the inventory is not spatially resolved enough to make robust recommendations based on the ratio comparisons. Conversely, we believe that the relatively even concentrations between site pairs in Sacramento and Fresno counties allow the reasonable use of county-wide emissions in the ratio comparisons.

- Ratio comparisons were made for cases both including and excluding point source emissions. In Sacramento and Ventura counties, point source NO_x emissions are not significant during the 0500-0800 PST time period and therefore do not affect the emissions ratios. However, in Fresno County, point sources contribute about 35 percent of total NO_x emissions during the morning time period. Consequently, excluding point source NO_x emissions from the ratio calculations significantly changed the ambient-ratio to emission inventory-ratio comparisons.
- In Fresno County, the weekday ambient hydrocarbon/NO_x ratio is approximately a factor of 3 higher than the inventory when all emissions sources are included in the ratio calculation and about a factor of 1.5 to 2.0 when point source NO_x is excluded from the calculation. Area and mobile sources are the main contributors to hydrocarbon emissions in Fresno County. Because these are the dominant emissions sources, it is likely that the hydrocarbon component of these categories is underestimated and/or the NO_x component is overestimated.
- In general, the results of the weekday hydrocarbon/NO_x ratio comparisons indicate that the hydrocarbon component of the emission inventory appears to be underestimated by a factor of 2.0 to 2.5 in Sacramento County and 2.0 to 4.0 in Ventura County. Area and mobile sources are the main contributors to emissions in Sacramento and Ventura counties. Because these are the dominant emissions sources, it is likely that the hydrocarbon component of these categories is underestimated, and/or the NO_x component is overestimated.
- The results of the weekday CO/NO_x ratio comparisons indicate that the ambient CO/NO_x ratios are approximately a factor of 2 higher than emissions ratios in Fresno and Ventura counties, and a factor of 1.5 higher in Sacramento County. This suggests that the CO component of the inventory is underestimated and/or the NO_x component is overestimated.
- The results of the Saturday hydrocarbon/NO_x and CO/NO_x ratio comparisons indicate that, on average, Saturday ambient hydrocarbon concentrations are higher than weekday concentrations while NO_x concentrations are lower. Consequently, the Saturday ambient ratios are significantly higher than the weekday ambient ratios. The hydrocarbon/NO_x and CO/NO_x ratios in the emission inventory do not vary significantly between the weekday and Saturday inventories. It appears as though the Saturday emission inventory is not representative of Saturday ambient conditions.
- While the mass of hydrocarbon, NO_x, and CO are slightly different between the weekday and Saturday emission inventories, it appears that no adjustment was made for weekend temporal profile assignments.

- In general, adjusting ambient concentrations to account for the influence of background concentrations led to a small improvement in the comparisons between ambient- and emission inventory-derived ratios.

5.2 CONCLUSIONS – HYDROCARBON SPECIES ANALYSES

The following conclusions summarize the major findings of the individual hydrocarbon species and species group analyses:

- This comparison shows that while the emission composition and the ambient compositions in Fresno and Sacramento counties are in generally good agreement, there is a consistent underestimation of the less reactive compounds and an overestimation of the more reactive compounds.
- In Ventura County, ambient data from Simi Valley follows a similar pattern to that in Fresno and Sacramento counties (e.g., slight underestimation of paraffins and overestimation of olefins and aromatics). However, at the El Rio site in Ventura County, the concentration of ambient paraffins is much higher than in the inventory, and the concentration of ambient olefins and aromatics is much lower than in the emission inventory. The contributions of paraffins to the total hydrocarbons at El Rio are also much higher than at any of the other sites and likewise the contributions of olefins and aromatics are much lower than at any of the other sites. We can speculate that the increased paraffins may be associated with natural geogenic oil and gas seeps offshore of Ventura County which may not be fully accounted for in the emissions industry.
- In general, the individual species composition comparisons indicate that there are several compounds in the emission inventory that are either (1) not individually identified or (2) reported below detection limits. One of these compounds is isopentane, an abundant compound in the ambient air that is quite reactive. Isopentane should be identified in the emission inventory.
- In Ventura County, species compositions between the two ambient sites are significantly different indicating that the chemical composition of the ambient air in Ventura County varies throughout the county. The county-wide average inventory does not correspond well with either ambient site, which show large differences as well between the two sites' ambient species compositions.
- There are uncertainties associated with the spatial matching of ambient data and the county-wide emission inventory data. Such uncertainties are apparent for all three counties in the case of ethane. The major sources of ethane in Fresno and Sacramento counties are from livestock. We speculate that ethane in Ventura County may be associated with natural geogenic oil and gas seeps offshore of Ventura County. While the absolute mass of ethane emissions from these categories may be correct in the inventory, it appears that ethane from these sources is not detected in the vicinity of the ambient monitors. Consequently, in the species comparison plots, there are large discrepancies in the ambient- and emission inventory-derived ethane compositions.

- Significant differences between ambient and area source emission inventory acetylene ethane, ethylene, propane, propylene, and formaldehyde compositions in Fresno and Sacramento counties may be indicative of the emission inventory containing too much area source combustion activity from 0500-0800 PST. Ethane is also characteristic of evaporative emissions from vehicle refueling which may be misrepresented during this time period. Vehicle refueling evaporative profiles may not reflect properties of the newly reformulated fuels in use in California.
- In Fresno County, differences between area source emissions compositions of benzene, xylenes, and acetone suggest that the area source speciation profiles for Fresno County may not accurately represent benzene and xylene solvent use in the area. The mobile source emissions compositions indicate that the mobile source exhaust speciation profiles may not accurately reflect benzene compositions in fuel.
- In Fresno and Sacramento counties, differences between ambient and emissions compositions of propane and formaldehyde indicate that the mobile source exhaust speciation profiles do not accurately represent these compounds.
- In Sacramento County, differences between ambient and emissions compositions of isobutane, n-butane, n-hexane, and cyclohexane suggest that evaporative emissions from vehicle refueling or the transporting of petroleum products is misrepresented in the inventory.
- In Ventura County, chemical species compositions of ethane, propane, and n-butane at El Rio suggest that this site is influenced by a natural gas combustion source, and/or petroleum production sources while species compositions at Simi Valley suggest that this site is primarily influenced by area and mobile source emissions.
- Although the Ventura County inventory does not compare well with either site, the point source component of the inventory appears to better match ambient chemical compositions at the El Rio site.
- Discrepancies in emissions and ambient chemical compositions of the following compounds are important when assessing the reactivity of the inventory and the ambient air: isopentane, toluene, trimethylbenzenes, diethylbenzenes, 1-butene.

5.3 RECOMMENDATIONS

The following recommendations on possible improvements to the emission inventory are based on the results and conclusions of the emission inventory reconciliation.

- Area and mobile sources combined constitute approximately 80 percent of the total hydrocarbon component of the emission inventory while point sources contribute the remaining 20 percent. Because area and mobile sources are the dominant categories in the inventory, future inventory improvement should focus on these source categories.
- Temporal profile assignments in the Saturday emission inventory should be reviewed and revised as necessary to reflect weekend emissions activity.

- The apparent under-estimation of absolute mass of hydrocarbon, NO_x, and CO emissions from area and mobile source categories should be investigated.
- The top area and mobile source emissions sub-categories should be identified and reviewed. The speciation profiles used to disaggregate the hydrocarbon emissions should be reviewed as well as the temporal code assignments.
- The following source categories are likely assigned unrepresentative speciation and/or temporal profiles: area source fuel combustion, gasoline refueling evaporative emissions, gasoline exhaust emissions, and petroleum product storage and transportation.
- A bottom-up evaluation of the inventory should be performed including review of emissions sources and activity data in each region.
- It is recommended that the emission inventory be gridded for future top-down evaluations.

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APPENDIX A

HYDROCARBON SPECIES MEASURED AT CLOVIS, FRESNO, DEL PASO, FOLSOM, EL RIO, AND SIMI VALLEY DURING THE SUMMER OF 1996

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Table A-1. Hydrocarbon species measured at the Clovis, Fresno 1st Street, Del Paso, Folsom, El Rio, and Simi Valley PAMS monitoring sites during the summer of 1996.

Clovis	**Fresno**	**Del Paso**	**Folsom**	**El Rio**	**Simi Valley**
acetylene	acetylene	acetylene	acetylene	acetylene	acetylene
ethylene	ethylene	ethylene	ethylene	ethylene	ethylene
ethane	ethane	ethane	ethane	ethane	ethane
propylene	propylene	propylene	propylene	propylene	propylene
propane	propane	propane	propane	propane	propane
isobutane	isobutane	isobutane	isobutane	isobutane	isobutane
1-butene	1-butene	1-butene	n-butane	1-butene	1-butene
n-butane	n-butane	n-butane	isopentane	n-butane	n-butane
trans-2-butene	trans-2-butene	trans-2-butene	1-pentene	trans-2-butene	trans-2-butene
cis-2-butene	cis-2-butene	cis-2-butene	n-pentane	cis-2-butene	cis-2-butene
trimethylbenzene	trimethylbenzene	isopentane	isoprene	isopentane	isopentane
isopentane	isopentane	1-pentene	trans-2-pentene	1-pentene	1-pentene
1-pentene	1-pentene	n-pentane	2-methyl-2-butene	n-pentane	n-pentane
n-pentane	n-pentane	isoprene	2,2-dimethylbutane	isoprene	isoprene
isoprene	isoprene	trans-2-pentene	cis-3-hexene	trans-2-pentene	trans-2-pentene
trans-2-pentene	trans-2-pentene	cis-2-pentene	cyclopentane	cis-2-pentene	cis-2-pentene
cis-2-pentene	cis-2-pentene	2-methyl-2-butene	2-methyl-2-butene	2,2-dimethylbutane	2,2-dimethylbutane
2-methyl-2-butene	2-methyl-2-butene	2,2-dimethylbutane	2-hexene	cyclopentane	cyclopentane
2,2-dimethylbutane	2,2-dimethylbutane	cis-3-hexene	3-methylpentane	2-methyl-2-butene	2-methyl-2-butene
cis-3-hexene	cis-3-hexene	2-methyl-2-butene	n-hexane	2-hexene	2-hexene
cyclopentane	4-methylpentene	2-hexene	cis-2-hexene	3-methylpentane	3-methylpentane
2-methyl-2-butene	cyclopentane	3-methylpentane	methylcyclopentane	2-methyl-1-pentene	2-methyl-1-pentene
2-hexene	2-methyl-2-butene	n-hexane	2,4-dimethylpentane	n-hexane	n-hexane
3-methylpentane	2-hexene	trans-2-hexene	benzene	methylcyclopentane	methylcyclopentane

Clovis	Fresno	Del Paso	Folsom	El Rio	Simi Valley
2-methyl-1-pentene	3-methylpentane	cis-2-hexene	cyclohexane	2,4-dimethylpentane	2,4-dimethylpentane
n-hexane	2-methyl-1-pentene	methylcyclopentane	2-methylhexane	benzene	benzene
trans-2-hexene	n-hexane	2,4-dimethylpentane	2,2-dimethylbutane	cyclohexane	cyclohexane
cis-2-hexene	trans-2-hexene	benzene	3-methylhexane	2-methylhexane	2-methylhexane
methylcyclopentane	cis-2-hexene	cyclohexane	2,2,4-trimethylpentane	2,2-dimethylbutane	2,2-dimethylbutane
2,4-dimethylpentane	methylcyclopentane	2-methylhexane	n-heptane	3-methylhexane	3-methylhexane
benzene	2,4-dimethylpentane	2,2-dimethylbutane	methylcyclohexane	2,2,4-trimethylpentane	2,2,4-trimethylpentane
cyclohexane	benzene	3-methylhexane	2,3,4-trimethylpentane	n-heptane	n-heptane
2-methylhexane	cyclohexane	2,2,4-trimethylpentane	toluene	methylcyclohexane	methylcyclohexane
2,2-dimethylbutane	2-methylhexane	n-heptane	2-methylheptane	2,3,4-trimethylpentane	2,3,4-trimethylpentane
3-methylhexane	2,2-dimethylbutane	methylcyclohexane	3-methylhexane	toluene	toluene
2,2,4-trimethylpentane	3-methylhexane	2,3,4-trimethylpentane	n-octane	2-methylheptane	2-methylheptane
n-heptane	2,2,4-trimethylpentane	toluene	ethylbenzene	3-methylhexane	3-methylhexane
methylcyclohexane	n-heptane	2-methylheptane	m & p-xylene	n-octane	n-octane
2,3,4-trimethylpentane	methylcyclohexane	3-methylhexane	o-xylene	ethylbenzene	ethylbenzene
toluene	2,3,4-trimethylpentane	n-octane	n-nonane	m & p-xylene	m & p-xylene
2-methylheptane	toluene	ethylbenzene	isopropylbenzene	m-xylene	m-xylene
3-methylhexane	2-methylheptane	m & p-xylene	n-propylbenzene	p-xylene	p-xylene
n-octane	3-methylhexane	p-xylene	1,3,5-trimethylbenzene	styrene	styrene
ethylbenzene	n-octane	styrene	1,2,4-trimethylbenzene	o-xylene	o-xylene
m & p-xylene	ethylbenzene	o-xylene	o-ethyltoluene	n-nonane	n-nonane
styrene	m & p-xylene	n-nonane	m-ethyltoluene	isopropylbenzene	isopropylbenzene
o-xylene	p-xylene	isopropylbenzene	p-ethyltoluene	n-propylbenzene	n-propylbenzene
n-nonane	styrene	n-propylbenzene	1,3-diethylbenzene (meta)	1,3,5-trimethylbenzene	1,3,5-trimethylbenzene
isopropylbenzene	o-xylene	a-pinene	1,4-diethylbenzene (para)	1,2,4-trimethylbenzene	1,2,4-trimethylbenzene
n-propylbenzene	n-nonane	1,2,4-trimethylbenzene	n-decane	o-ethyltoluene	o-ethyltoluene
a-pinene	isopropylbenzene	b-pinene	n-undecane	m-ethyltoluene	m-ethyltoluene
1,3,5-trimethylbenzene	n-propylbenzene	o-ethyltoluene	2,5-dimethylhexane	p-ethyltoluene	p-ethyltoluene

Clovis	Fresno	Del Paso	Folsom	El Rio	Simi Valley
1,2,4-trimethylbenzene	a-pinene	m-ethyltoluene	isobutylene	1,3-diethylbenzene (meta)	1,3-diethylbenzene (meta)
b-pinene	1,3,5-trimethylbenzene	p-ethyltoluene		1,4-diethylbenzene (para)	1,4-diethylbenzene (para)
o-ethyltoluene	1,2,4-trimethylbenzene	1,3-diethylbenzene (meta)		1,2,3-trimethylbenzene	1,2,3-trimethylbenzene
m-ethyltoluene	b-pinene	1,4-diethylbenzene (para)		n-decane	n-decane
p-ethyltoluene	o-ethyltoluene	1,2,3-trimethylbenzene		n-undecane	n-undecane
1,3-diethylbenzene (meta)	m-ethyltoluene	n-decane		isobutylene	isobutylene
1,4-diethylbenzene (para)	p-ethyltoluene	n-undecane			
1,2,3-trimethylbenzene	1,3-diethylbenzene (meta)	formaldehyde			
n-decane	1,4-diethylbenzene (para)	acetaldehyde			
n-undecane	1,2,3-trimethylbenzene	acetone			
formaldehyde	n-decane	1,3-butadiene			
acetaldehyde	n-undecane	1-hexene			
acetone	formaldehyde	2,5-dimethylhexane			
1,3-butadiene	acetaldehyde	isobutylene			
2,5-dimethylhexane	acetone				
isobutylene	1,3-butadiene				
	2-methyl-1-butene				
	1-hexene				
	2,2,4-trimethylpentane				
	2,5-dimethylhexane				
	2,4-dimethylhexane				
	2,3-dimethylhexane				
	2,2-dimethylpropane				
	isobutylene				