# Emissions Inventory Validation and Improvement: A Central California Case Study

Stephen B. Reid, Lyle R. Chinkin, Bryan M. Penfold, Erin K. Gilliland
Sonoma Technology, Inc., 1360 Redwood Way, Suite C, Petaluma, CA 94954
sreid@sonomatech.com

## ABSTRACT

The methodologies and data used to develop emission inventories are continually being refined and improved. New emission factors, activity data sets, and mobile source emission models have resulted in revised emission estimates that need to be evaluated for accuracy and usefulness for photochemical grid modeling and other applications. Sonoma Technology, Inc. (STI) used a variety of techniques to perform an emission inventory validation on an updated base-year inventory recently developed by the California Air Resources Board (CARB).

STI's review was performed on a gridded, temporalized version of the CARB inventory that was prepared for an ozone modeling application in Central California. STI compared the CARB emission inventory with ambient measurements collected in Central California during summer 2000. Measurements of speciated volatile organic compounds (VOCs), nitrogen oxides ($NO_x$), and carbon monoxide (CO) from over a dozen monitoring sites were compared with emissions data by calculating pollutant ratios and weight fractions. Comparisons were also made by day of week and by wind quadrant.

The results of these analyses showed that the latest CARB emission inventory, in general, shows better agreement with ambient data than previous emission inventories in California. However, this study also identified specific areas where further improvements are needed to the magnitude, temporal allocation, and/or spatial allocation of CARB emission estimates. This paper will demonstrate how emission validation techniques can be used to assess the accuracy of emission estimates for areas outside California.

## INTRODUCTION

Emission inventories are the foundations of air quality modeling and regulatory control strategy development. Therefore, the methodologies and data used to develop emission inventories are continually refined and improved. New emission factors, activity data sets, and mobile source emission models have resulted in revised emission estimates that need to be evaluated for accuracy and usefulness for photochemical grid modeling and other applications. Several techniques are used to evaluate emissions data: "common sense" review of the data; bottom-up evaluations that start with emissions activity data to estimate corresponding emissions; and top-down evaluations that compare emission estimates with ambient air quality data or that use ambient data to estimate emissions profiles. STI used a variety of top-down techniques to perform an emission inventory validation on an updated base-year inventory recently developed by CARB.

The updated inventory was developed as part of the Central California Ozone Study (CCOS), a multi-year program of meteorological and air quality monitoring, emission inventory development, data analysis, and air quality simulation modeling. The latest improvements made to the CCOS emission inventories by CARB include

- changes to CARB's on-road mobile source model, EMFAC, such as the redistribution of heavy-duty diesel vehicle miles traveled (VMT) and an adjustment to heavy-duty diesel emission factors;
- changes to CARB's off-road mobile source model, OFFROAD, such as the incorporation of new activity estimates for lawn and garden equipment and updated population estimates for pleasure craft; and
- refinements to the magnitude and spatial resolution of estimates of emissions from ocean-going vessels.

These improvements have impacted both the magnitude and spatial distribution of emissions. Updated emission estimates are utilized in photochemical modeling studies, and STI compared emission inventory and ambient air quality data to evaluate the latest CCOS emission representations for modeling. The results of this investigation are being used to make recommendations for meaningful improvements to emission inventories that will improve subsequent new photochemical ozone modeling results.

## TECHNICAL APPROACH

Using ambient measurements made during the CCOS field measurement program conducted in summer 2000, STI spatially and temporally compared emission estimates with ambient air quality data by calculating emission inventory- and ambient-derived pollutant ratios (including total nonmethane organic carbon [TNMOC]/$NO_x$, CO/$NO_x$, and individual hydrocarbon species such as benzene/toluene), and performing "fingerprint analyses" on the relative amounts of individual hydrocarbon species in the ambient data and emission inventory. In addition, STI assessed sources of uncertainty or bias associated with each analysis technique and integrated the results of previous research. The scope of work for the project was divided into the following elements:

1. Site selection and ambient data processing
2. Emission inventory acquisition and processing
3. Comparison of ambient and emission inventory data

The technical approach for each of these work elements is described in the sections that follow.

### Site Selection and Ambient Data Processing

STI investigated the available monitoring sites in the CCOS modeling domain to identify sites collecting ambient data of sufficient quality and quantity for comparison with emission inventory data (Chinkin, 2005). The following criteria were considered when evaluating air quality sites in the CCOS domain:

- Availability of $NO_x$, speciated VOCs, and wind direction measurements
- Availability of CO or TNMOC measurements
- Sufficient density of total organic gas (TOG) and $NO_x$ emissions around the site
- Number of distinct counts of VOCs, $NO_x$, and CO above the monitor detection limit and background thresholds (for this analysis, we used VOCs > 50 ppbC, $NO_x$ > 10 ppb, and CO > 0.150 ppm)

Examination of the site measurements relative to the criteria resulted in grouping the sites into five distinct "tiers". All sites that collected speciated VOC data and $NO_x$ measurements were classified as Tier 1, 2, or 3. Date from these sites were the most suitable for comparisons with emission inventory data. Only five sites met all the criteria listed above and were denoted Tier 1. Two additional sites failed one of these criteria and were denoted Tier 2. Seven additional sites failed two of the criteria and were denoted Tier 3. Tiers 2 and 3 sites are typically less suitable for comparison because of low emissions near the site or insufficient measurements. Sites with no speciated VOC data that had some CO or TNMOC measurements were also considered less suitable. Sites that collected more than 10 CO or TNMOC measurements, $NO_x$ measurements, meteorology measurements, and urban-like emissions of TOG and $NO_x$ were denoted Tier 4. Those sites that failed one of these criteria were considered Tier 5 (unsuitable for analysis).

Table 1 shows the 18 sites selected during that investigation and identifies the analysis technique(s) supported by the available data at each site. Figure 1 shows the geographic distribution of sites by tier designation. STI processed the ambient air quality and meteorological data collected at the 18 sites into formats needed for comparison with the emission inventory. Statistical analyses performed on the ambient air quality data include calculations of minima, maxima, means, medians, and confidence intervals. STI analyzed validated surface meteorological data to understand and account for the potential influences of meteorology—in particular, wind speed and direction—on the ratio comparisons.

## Emission Inventory Acquisition and Processing

Staff at the CARB provided STI with the latest gridded emission inventories prepared for the July/August 2000 modeling episode. Emissions were gridded to the 190- x 190-cell CCOS modeling domain at a resolution of 4 km. Specific emission inventory files provided by CARB included

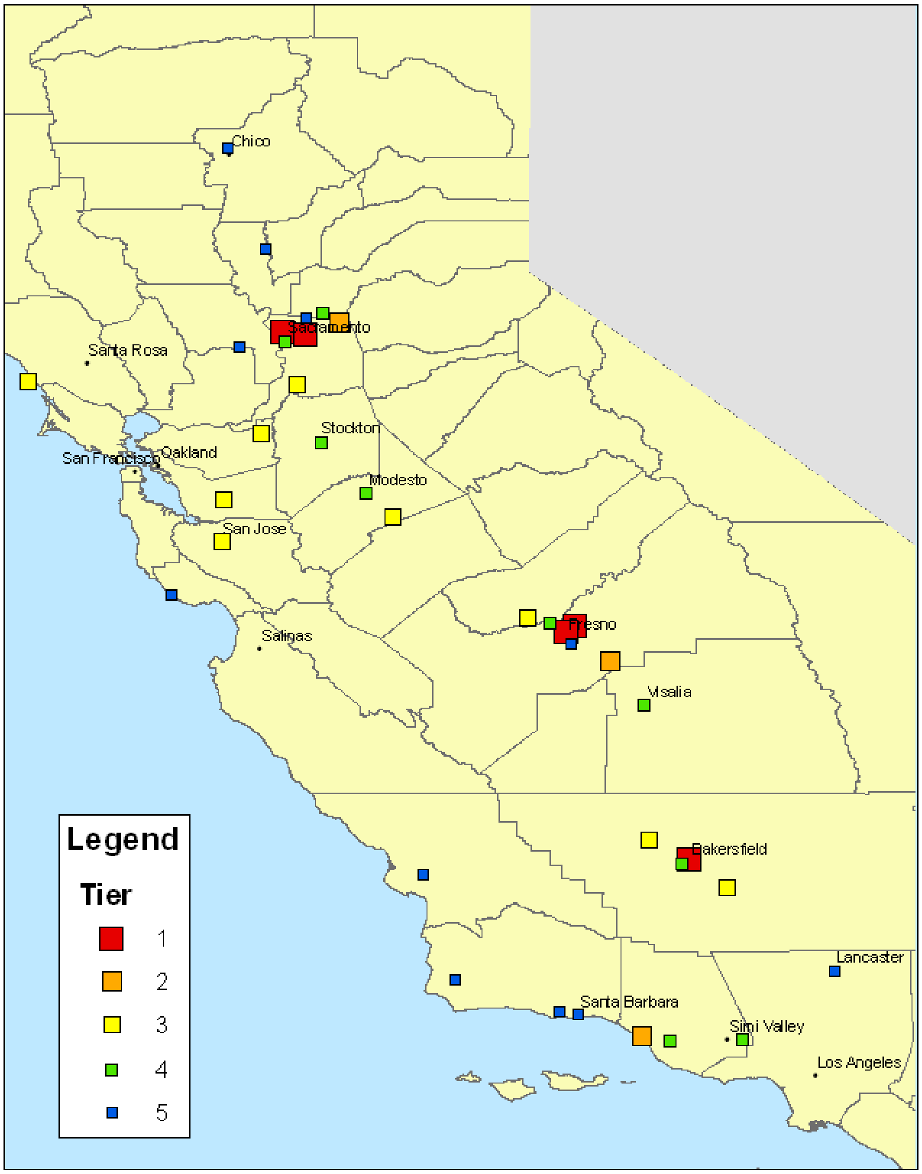
- gridded area and off-road mobile source emissions for an August 2000 weekday and weekend day;
- gridded surface and elevated point source emissions for an August 2000 weekday and weekend day;
- gridded, hourly on-road mobile source emission files for individual dates from July 27, 2000, through August 2, 2000;
- gridded, hourly biogenic emission files for individual dates from July 27, 2000, through August 2, 2000;
- organic gas speciation profiles and a cross-reference file to match profiles to inventory source categories; and
- temporal profiles used by CARB to distribute daily emission estimates across the hours of the day.

**Table 1.** Monitoring sites selected for emissions reconciliation analyses.

| Site | Tier | Air District | Site Name | TNMOC/$NO_x$ Ratios | CO/$NO_x$ Ratios | Species Ratios | VOC Fingerprints |
|---|---|---|---|---|---|---|---|
| BGS | 1 | San Joaquin Valley | Bakersfield Stn. (Golden State) | X | X | X | X |
| CLO | 1 | San Joaquin Valley | Clovis Stn. | X | X | X | X |
| FSF | 1 | San Joaquin Valley | Fresno Stn. (First St.) | X | X | | |
| NAT | 1 | Sacramento | Sacramento/ Natomas Stn. | X | X | X | X |
| SDP | 1 | Sacramento | Sacramento Stn. (Del Paso Manor) | X | | X | X |
| FLN | 2 | Sacramento | Folsom Stn. | X | | X | X |
| PLR | 2 | San Joaquin Valley | Parlier Stn. | X | | X | X |
| SUN | 3 | Bay Area | Sunol Stn. | | | X | |
| ARV | 3 | San Joaquin Valley | Arvin Stn. | X | X | X | X |
| ELK | 3 | Sacramento | Elk Grove Stn. | X | | | X |
| M29 | 3 | San Joaquin Valley | Madera Stn. | X | | X | X |
| SHA | 3 | San Joaquin Valley | Shafter Stn. | X | | X | X |
| SJ4 | 3 | Bay Area | San Jose Stn. (4th St.) | | X | | |
| TSM | 3 | San Joaquin Valley | Turlock Stn. | | X | | |
| BAC | 4 | San Joaquin Valley | Bakersfield Stn. (California Ave.) | | X | | |
| GNBY | 4 | Sacramento | Granite Bay Stn. | | | X | |

STI applied CARB's temporal profiles to the area, off-road mobile, and point source emissions to generate hourly estimates for those source types. Temporal profile assignments were based on a CARB cross-reference file that matches diurnal profiles with individual source categories. For on-road mobile and biogenic sources, average weekday and weekend day emission estimates were produced from the day-specific files provided by CARB. STI then applied CARB's speciation profiles to all emission inventory files to disaggregate TOG emissions into individual chemical species. The resulting speciated inventories contained hundreds of chemical species; however, the ambient data collection and analysis methods are only capable of quantifying hydrocarbons containing between 2 and 12 carbon atoms (approximately). Therefore, to ensure that the same chemical compounds are being compared in the ratio comparisons, the individual chemical species reported in the emission inventory were matched to those measured in the ambient data. The emission inventory compounds that were not measured in the ambient samples were excluded from the analysis. Finally, prior to making comparisons between the emission inventory and ambient data, the emission inventory data were converted from mass to molar units.

**Figure 1.** Geographic distribution of monitoring sites used in the study.

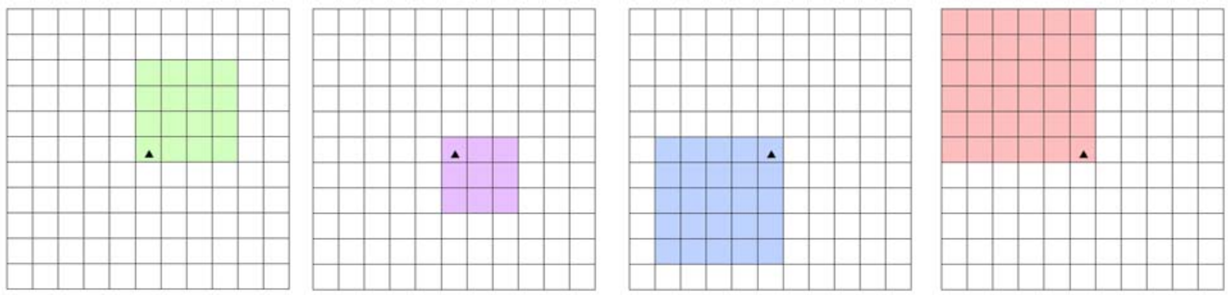



## Comparison of Ambient and Emission Inventory Data

For the selected sites, TNMOC/$NO_x$, CO/$NO_x$, and ratios of individual species (acetylene/benzene, acetylene/propylene, benzene/m- and p-xylene, benzene/o-xylene, benzene/toluene, toluene/m- and p-xylene, and toluene/o-xylene) were computed from the ambient and emission inventory data. To make consistent comparisons of TNMOC between the ambient and emission inventory data, only the species measured at the monitoring sites were used in the emission inventory calculations. In addition, ambient-derived ratios were compared with emission inventory-derived ratios by spatially matching ambient data by wind quadrant to corresponding grid quadrants (groups of grid cells) surrounding the ambient monitoring site. Grid analysis zones were selected for each site based on predominant wind speeds during the early morning hours (0500-1000 PDT). Average wind speeds were used to identify which grid cells to include in the ratio analyses based on approximate air parcel travel distance during the time period selected for analysis.

Comparisons between ambient- and emission inventory-derived TNMOC/$NO_x$, CO/$NO_x$ and ratios of individual species were made for both individual wind quadrants and full extent analysis zones surrounding each site. Figure 2 illustrates an example of a full extent grid analysis zone centered on an ambient monitoring site, and the wind quadrant definitions, whose extents vary according to the observed wind speeds at each site. The wind quadrant grid extents are larger at sites where wind speeds are greater and smaller where wind speeds are light.

**Figure 2.** Example illustration of the spatial configuration of grid cells for which ambient- and emission inventory-derived ratios comparisons were calculated. The center point (▲) represents the ambient monitoring site, blank grid cells represent the entire analysis zone, and the colored grid cells represent the wind quadrant definitions and quadrant analysis zones.




For ambient data, both average and median pollutant ratios were calculated, and for the emission inventory data, ratios were calculated both including and excluding elevated point source emissions. Finally, comparisons between ambient- and emission inventory-derived pollutant ratios were also made for both weekdays and weekend days.

In addition to ratio comparisons, the chemical composition of hydrocarbons reported in the emission inventory was compared with the chemical composition of the ambient air at individual monitoring sites. These "fingerprint" analyses are used to determine how accurately the speciation of the emission inventory compares with the data measured at ambient monitoring sites. Hydrocarbon compositions were based on species groupings defined by CARB's modeling emissions data system (MEDS) (Allen, 2001). Table 2 shows the 35 group definitions used by CARB; the species measured at each monitoring site were assigned to one of these groups for purposes of comparison.

**Table 2.** CARB organic gas group definitions.

| | | | | | |
|---|---|---|---|---|---|
| 1 | Low reactives | 13 | Halogens | 25 | Propylene |
| 2 | Ethylene | 14 | Terpenes | 26 | 1,3-butadiene |
| 3 | Benzene | 15 | Glycols | 27 | Toluene |
| 4 | C6+ Alkanes | 16 | Styrenes | 28 | Acetaldehyde |
| 5 | C4+ Alkenes | 17 | Alkynes | 29 | MTBE |
| 6 | C8+ Aromatics | 18 | Amines | 30 | Ethanol |
| 7 | C3+ Aldehydes | 19 | Formaldehyde | 31 | Acetylene |
| 8 | Alcohols | 20 | Methane | 32 | Isoprene |
| 9 | Ketones | 21 | Ethane | 33 | C6-C11 Alkanes |
| 10 | Esters | 22 | Propane | 98 | Unclassified |
| 11 | Ethers | 23 | Butanes | 99 | Unidentified |
| 12 | Acids | 24 | Pentanes | | |

## RESULTS

### TNMOC/$NO_x$ Ratios

Ambient- and emission inventory-derived TNMOC/$NO_x$ ratios were calculated for 11 sites. Table 3 shows calculated ratios for the full grid extent around each monitoring site, and the data show that median ambient ratios are 1.4 to 6.3 times higher than emission ratios calculated with elevated sources excluded (for most sites, the emission ratios change little when elevated sources are included). The emission ratios reasonably approximated the ambient ratios for 6 sites, and these sites were primarily located in urban areas. For 2 other sites (SDP and PLR), the emission ratios reasonably approximated the ambient ratios for 3 of the 4 wind quadrants. For the remaining 3 sites where ambient ratios were consistently higher than emission ratios by a factor of two or more (BGS, M29, and SHA), 2 are "Tier 3" sites with relatively low emission densities in the area around the monitoring site.

**Table 3.** TNMOC/$NO_x$ ratios by site (emission ratios for full grid extent around each site).

| Station | Tier | Ambient Data | | Emission Inventory | | Median/EI - Low Level Only | Average/EI - Low Level Only |
|---|---|---|---|---|---|---|---|
| | | Median | Average | Low Level + Elevated | Low Level Only | | |
| Sacramento Area | | | | | | | |
| Elk Grove (ELK) | 3 | 5.0 | 5.5 | 3.6 | 3.6 | 1.4 | 1.5 |
| Folsom (FLN) | 2 | 6.7 | 7.3 | 4.3 | 4.4 | 1.5 | 1.7 |
| Sacramento - Natomas (NAT) | 1 | 3.9 | 3.8 | 3.1 | 3.1 | 1.2 | 1.2 |
| Sacramento - Del Paso Manor (SDP) | 1 | 7.4 | 7.8 | 3.6 | 3.6 | 2.1 | 2.2 |
| Fresno Area | | | | | | | |
| Clovis (CLO) | 1 | 7.5 | 7.9 | 3.9 | 3.9 | 1.9 | 2.0 |
| Fresno - First Street (FSF) | 1 | 5.1 | 5.4 | 3.9 | 3.9 | 1.3 | 1.4 |
| Madera (M29) | 3 | 9.4 | 10.8 | 1.2 | 1.5 | 6.3 | 7.2 |
| Parlier (PLR) | 2 | 6.9 | 7.3 | 2.2 | 3.2 | 2.2 | 2.3 |
| Bakersfield Area | | | | | | | |
| Arvin (ARV) | 3 | 4.8 | 5.9 | 3.4 | 3.3 | 1.5 | 1.8 |
| Bakersfield - Golden State (BGS) | 1 | 6.3 | 6.7 | 1.8 | 1.9 | 3.3 | 3.5 |
| Shafter (SHA) | 3 | 5.9 | 6.4 | 2.3 | 2.3 | 2.6 | 2.8 |

Figures 3 through 6 show TNMOC/$NO_x$ ratios by wind quadrant[1] and day of week[2] for sites in the Sacramento area. Overall, agreement between ambient- and emission inventory-derived ratios at these sites is significantly better on weekdays than weekend days. Sacramento area sites are heavily influenced by on-road mobile source emissions, which may indicate that hydrocarbon emissions from light-duty vehicles are underestimated on weekends, that $NO_x$ emissions from heavy-duty vehicles are overestimated on weekends, or both.

At the Elk Grove site (see Figure 3), ambient-derived TNMOC/$NO_x$ ratios are slightly (20-30%) higher than emission inventory-derived ratios in wind quadrants 1 and 3, while the emission inventory-

[1] On all bar charts, the ambient value represents the median, and error bars represent the 25$^{th}$ and 75$^{th}$ percentiles. Wind quadrants or days of week without error bars indicate that less than 5 data points were available.

[2] Day of week ratios were calculated for the full grid extent around each monitoring site, as there were insufficient data points to calculate ratios by wind quadrants for weekend days.

derived ratios are 10-40% higher in quadrants 2 and 4 (though these ambient ratios are based on less than 5 data points).

At the Folsom site (see Figure 4), ambient- and emission inventory-derived TNMOC/$NO_x$ ratios agree to within 60% at all wind quadrants. For wind quadrants with at least five ambient data points, agreement is closest in quadrant 4, which shows the highest overall emission density. At the Sacramento Natomas site (see Figure 5), ambient- and emission inventory-derived TNMOC/$NO_x$ ratios agree to within 60% at all wind quadrants except quadrant 3, which has a higher contribution of TNMOC and $NO_x$ emissions from area and non-road mobile sources than other quadrants.

Agreement between ambient- and emission inventory-derived TNMOC/$NO_x$ ratios is poorest at the Sacramento Del Paso Manor site (see Figure 6), though the ratios agree to within 80% at all wind quadrants except quadrant 3. Further investigation showed that two large shopping centers are located about 1 km southwest of the SDP site (see Figure 7), so the low TNMOC/$NO_x$ ratio in the emission inventory may be the result of a failure to capture hot-soak emissions from vehicles parked in this shopping area.

**Figure 3.** TNMOC/$NO_x$ ratios by wind quadrant and day of week for the Elk Grove site.

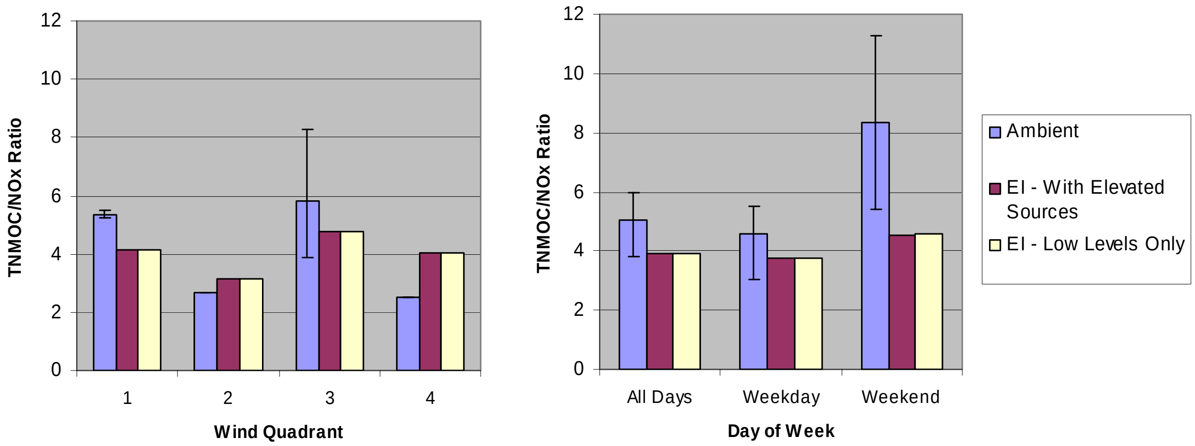



**Figure 4.** TNMOC/$NO_x$ ratios by wind quadrant and day of week for the Folsom site.

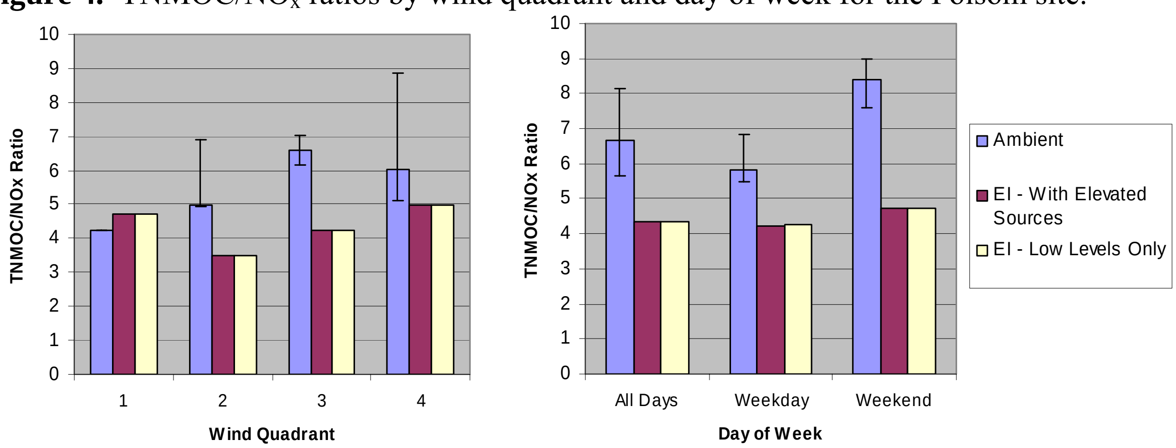


**Figure 5.** TNMOC/$NO_x$ ratios by wind quadrant and day of week for the Sacramento Natomas site.

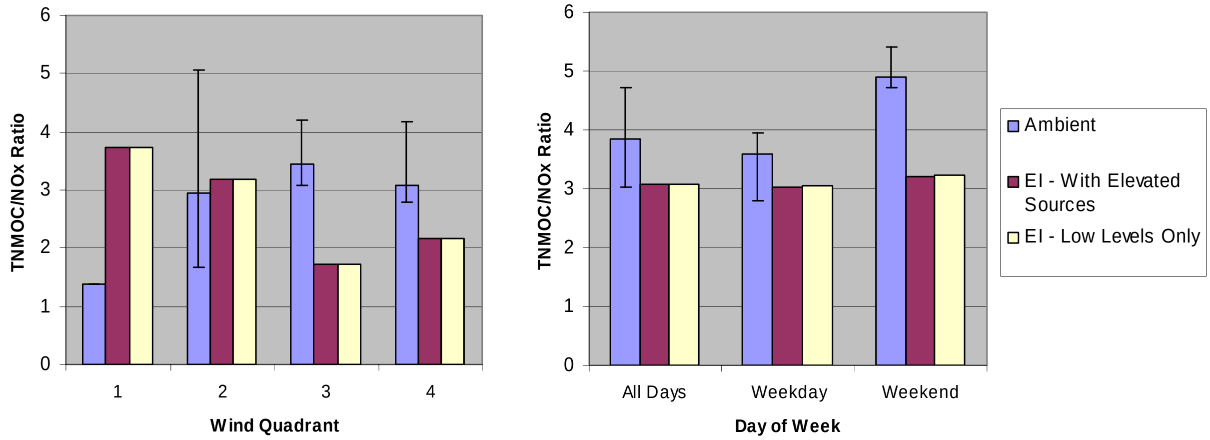
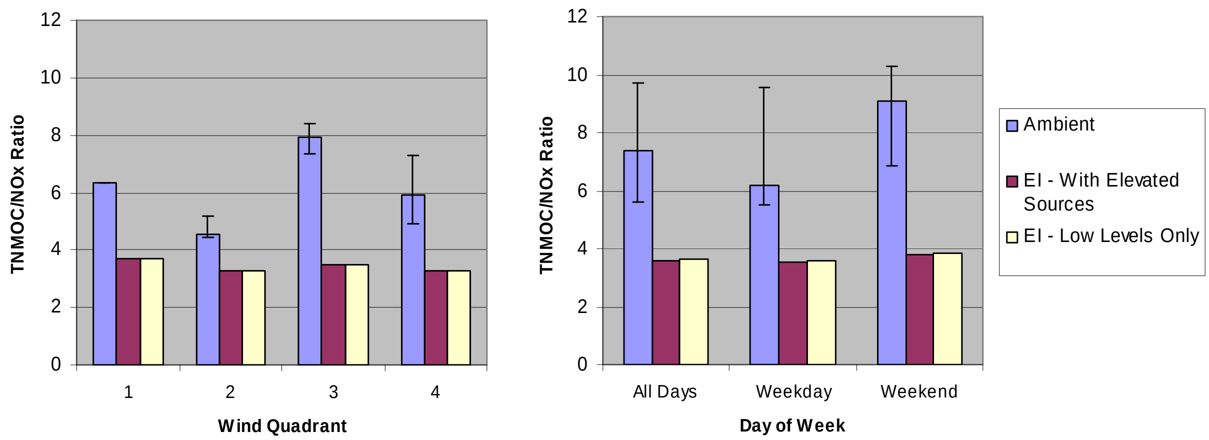



**Figure 6.** TNMOC/$NO_x$ ratios by wind quadrant and day of week for the Sacramento Del Paso Manor site.




Figures 8 through 11 show TNMOC/$NO_x$ ratios by wind quadrant for the Fresno area. Unlike the Sacramento area sites, agreement between ambient- and emission inventory-derived ratios at sites in the Fresno area does not vary significantly on weekdays versus weekend days. At the two urban sites in the region (Clovis and Fresno First Street), emission inventory-derived TNMOC/$NO_x$ ratios are within 50% of emission inventory-derived ratios in all wind quadrants except for quadrant 3 at the Clovis site, where the ambient-derived ratio is 2.1 times higher than the emission inventory-derived ratio (see Figures 10 and 11). This quadrant contains large residential areas that have developed between Clovis and Fresno, and the current spatial allocation of area source emissions may not capture new “fill in” growth in this region.

At the Madera site, ambient-derived TNMOC/$NO_x$ ratios are 3 to 10 times higher than emission inventory-derived ratios. Because this is a rural site with very low emission densities, it is likely that the site is primarily impacted by transported pollutants rather than local sources. At the Parlier site, another rural site in the Fresno area, ambient-derived TNMOC/$NO_x$ ratios are 1.3 to 2.5 times higher than emission inventory-derived ratios. Quadrant 3 has the poorest agreement between ambient- and emission inventory-derived ratios, and this quadrant contains the town of Selma and a large winery (see Figure 12) that could not be identified in the point source inventory provided by CARB.

**Figure 7.** Wind quadrant 3 of the Sacramento Del Paso Manor site.

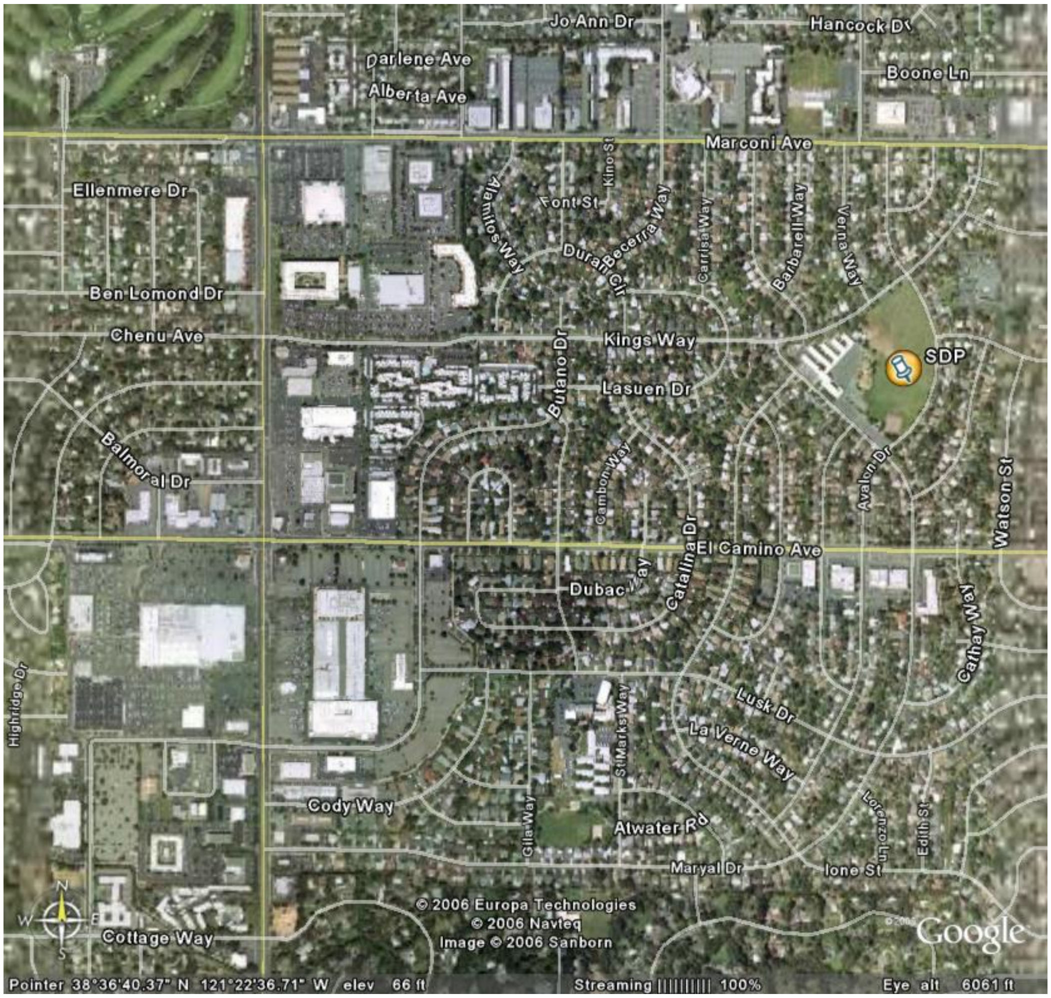



**Figure 8.** TNMOC/$NO_x$ ratios by wind quadrant and day of week for the Clovis site.

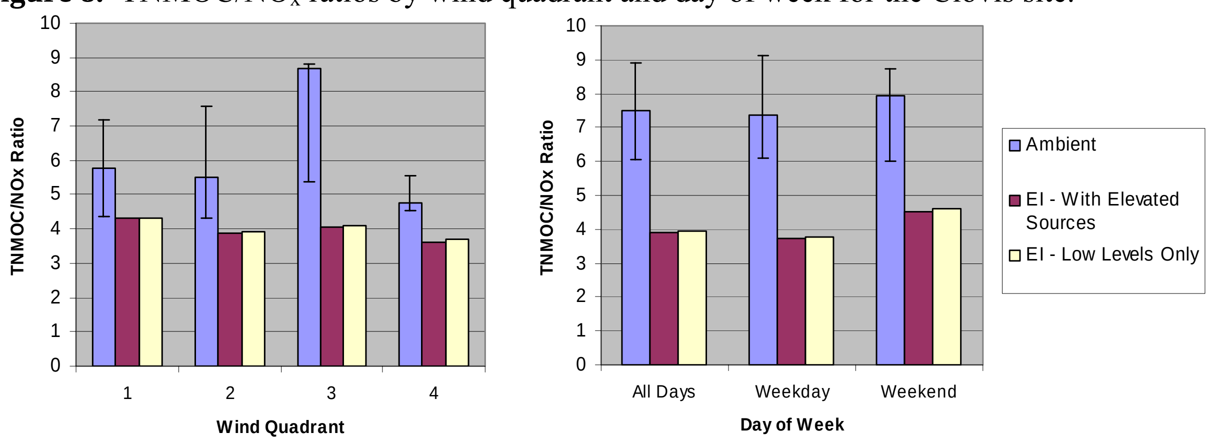


**Figure 9.** TNMOC/$NO_x$ ratios by wind quadrant and day of week for the Fresno First Street site.

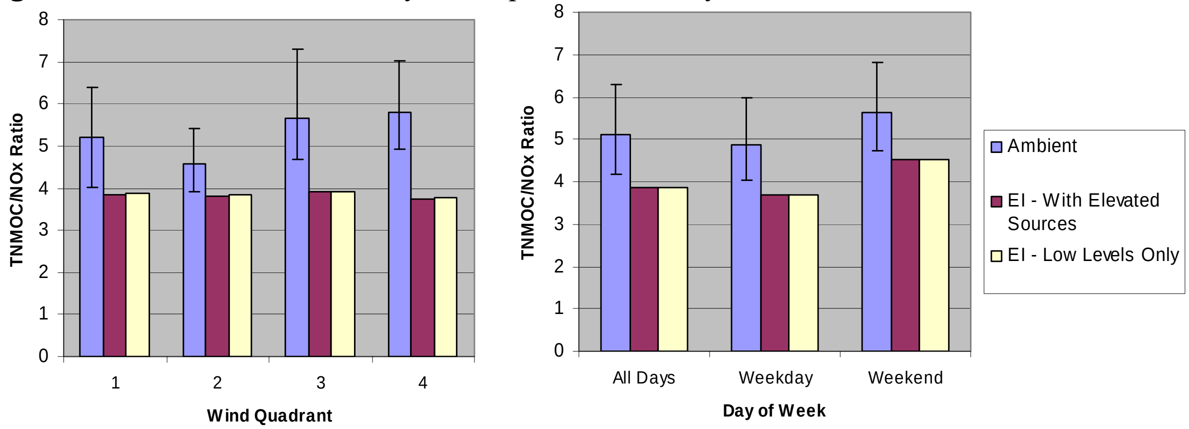



**Figure 10.** TNMOC/$NO_x$ ratios by wind quadrant and day of week for the Madera site.

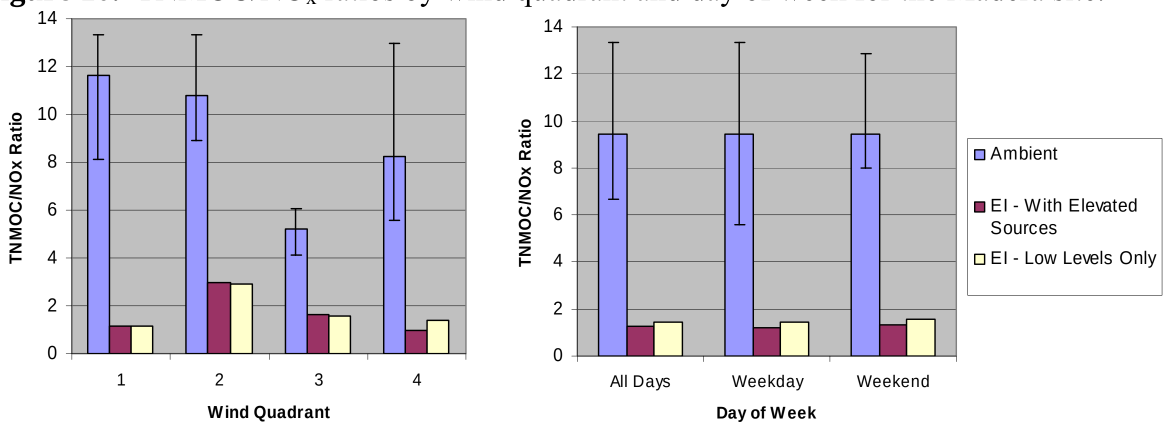



**Figure 11.** TNMOC/$NO_x$ ratios by wind quadrant and day of week for the Parlier site.

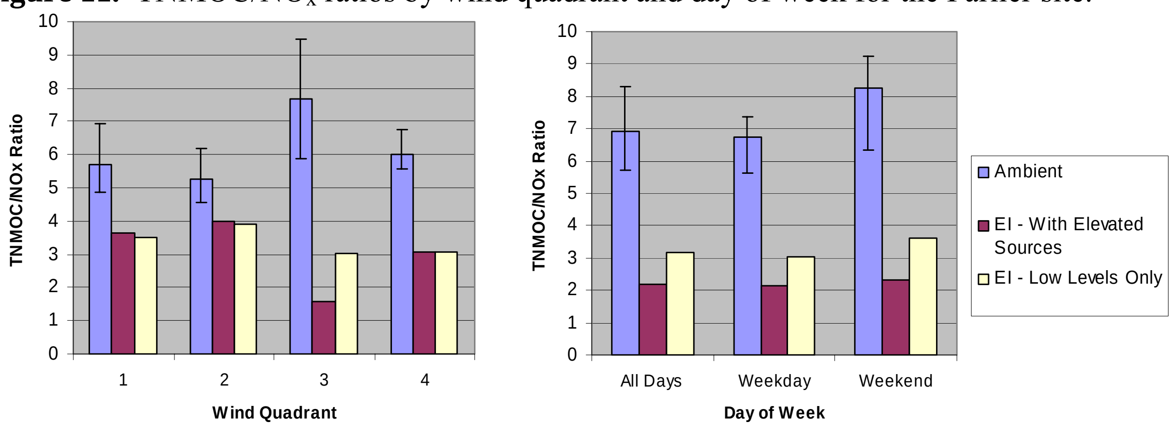


**Figure 12.** Unidentified winery in wind quadrant 3 of the Parlier site.


Figures 13 through 15 show TNMOC/$NO_x$ ratios by wind quadrant for sites in Kern County. At the Bakersfield Golden State site, ambient-derived TNMOC/$NO_x$ ratios are 3 to 4 times higher than emission inventory-derived ratios for all wind quadrants and days of the week. The emission inventory is similar in magnitude and source composition for all wind quadrants, though point source emissions are somewhat higher in quadrant 4, where an oil refinery and other industrial sources are located.

At the two rural sites in Kern County (Arvin and Shafter), significant differences also exist between ambient- and emission inventory-derived TNMOC/$NO_x$ ratios. At the Arvin site, the ratios agree closely for all wind quadrants except quadrant 2, which is dominated by biogenic emissions. At the Shafter site, ambient-derived TNMOC/$NO_x$ ratios are 2 to 3 times higher than emission inventory-derived ratios for all wind quadrants and days of the week. However, emission densities are very low for both these sites, so it is likely that the sites are influenced primarily by transported pollutants rather than local sources.

**Figure 13.** TNMOC/$NO_x$ ratios by wind quadrant and day of week for the Bakersfield Golden State site.

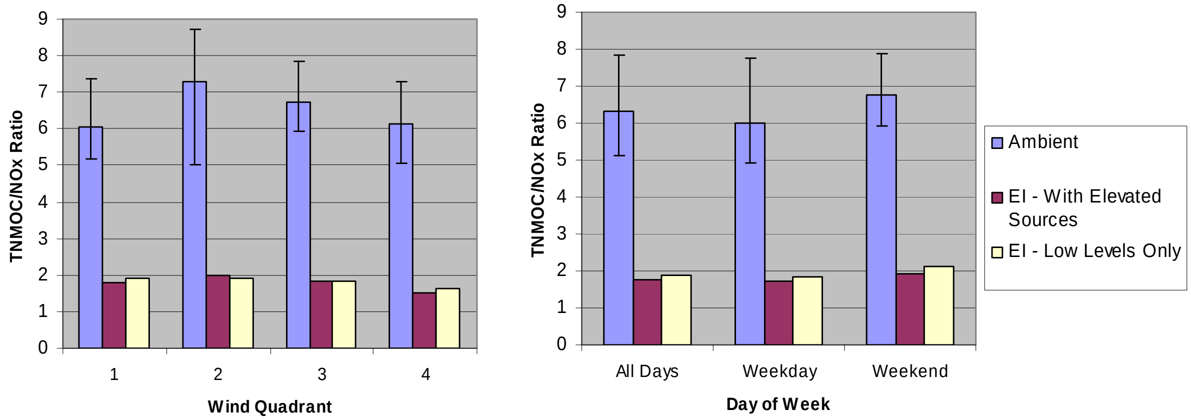



**Figure 14.** TNMOC/$NO_x$ ratios by wind quadrant and day of week for the Arvin site.

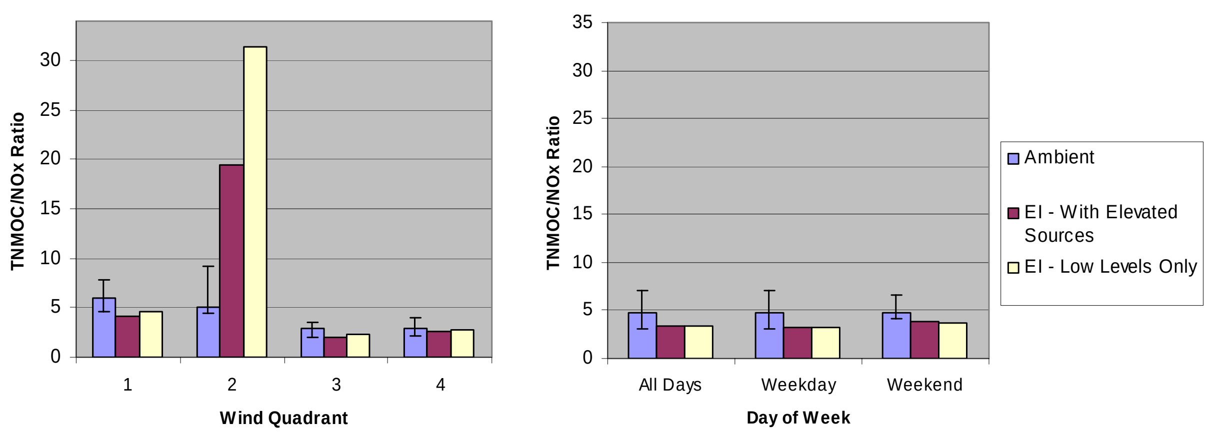
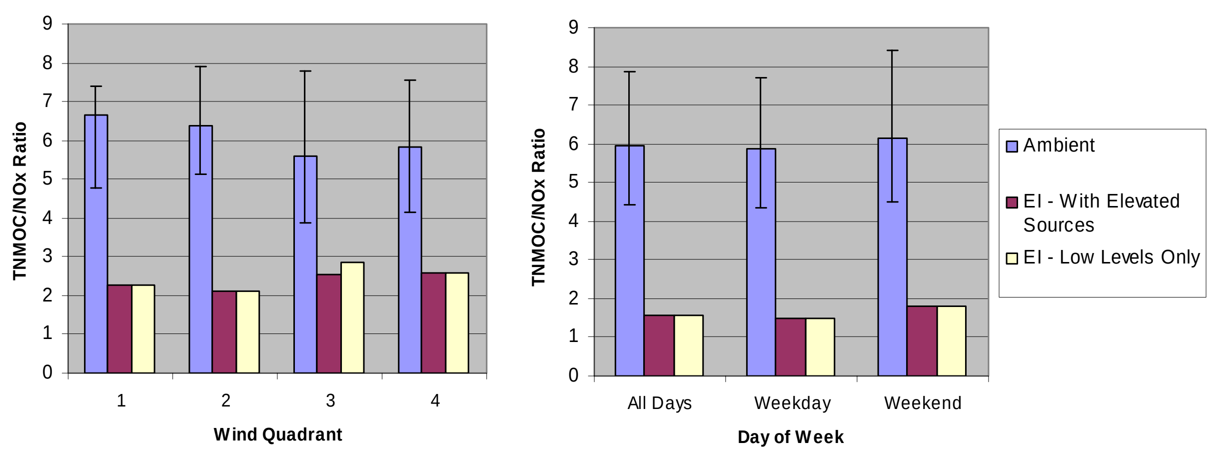



**Figure 15.** TNMOC/$NO_x$ ratios by wind quadrant and day of week for the Shafter site.




## CO/$NO_x$ Ratios

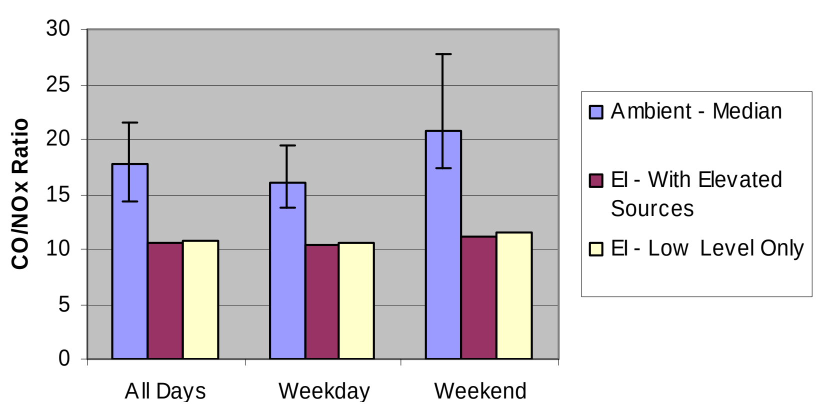
Ambient- and emission inventory-derived CO/$NO_x$ ratios were calculated for eight sites. Table 4 shows calculated ratios for the full grid extent around each monitoring site, and the data show that median ambient ratios are 1.1 to 3.9 times higher than emission inventory ratios calculated with elevated sources excluded. The emission inventory ratios show the best comparison at urbanized sites in San Jose, Sacramento, and Fresno, with sites in Bakersfield (BAC and BGS) comparing less favorably.

**Table 4.** $CO/NO_x$ ratios by site (emission inventory-derived ratios for full grid extent around each site).

| Station | Tier | Ambient Data | | Emission Inventory | | Median/EI Low Level Only | Average/EI Low Level Only |
|---|---|---|---|---|---|---|---|
| | | Median | Average | Low Level + Elevated | Low Level Only | | |
| Bay Area | | | | | | | |
| San Jose – 4th Street (SJ4) | 3 | 17.6 | 18.9 | 10.5 | 10.8 | 1.6 | 1.8 |
| Sacramento Area | | | | | | | |
| Sacramento – Natomas (NAT) | 1 | 14.3 | 15.8 | 8.8 | 8.9 | 1.6 | 1.8 |
| Sacramento – Del Paso Manor (SDP) | 1 | 11.5 | 12.4 | 10.1 | 10.2 | 1.1 | 1.2 |
| Fresno Area | | | | | | | |
| Clovis (CLO) | 1 | 18.9 | 19.8 | 8.7 | 8.7 | 2.2 | 2.3 |
| Fresno – First St. (FSF) | 1 | 14.3 | 15.2 | 8.2 | 8.3 | 1.7 | 1.8 |
| Bakersfield Area | | | | | | | |
| Bakersfield – California Ave. (BAC) | 4 | 10.0 | 11.4 | 4.1 | 4.4 | 2.3 | 2.6 |
| Bakersfield – Golden State (BGS) | 1 | 18.2 | 19.9 | 4.2 | 4.7 | 3.9 | 4.2 |
| Other | | | | | | | |
| Turlock Station (TSM) | 3 | 17.6 | 18.2 | 7.2 | 7.4 | 2.4 | 2.5 |

Figure 16 shows $CO/NO_x$ ratios by day of week for the San Jose-4th Street site (ratios by wind quadrant were not calculated due to a lack of wind data). The emission inventory-derived ratios closely approximate ambient-derived ratios overall, with weekday ratios showing closer agreement than ratios for weekend days.

**Figure 16.** $CO/NO_x$ ratios by day of week for the San Jose-4th Street site.




Figures 17 and 18 show $CO/NO_x$ ratios by wind quadrant and day of week for Sacramento sites. At the Natomas site, emission inventory-derived $CO/NO_x$ ratios reasonably approximate ambient-derived ratios (i.e., within 40-80%) for all wind quadrants except quadrant 3, where the ambient-derived ratio is 2.5 times higher than the emission inventory-derived ratio. According to emission inventory data, light-duty motor vehicles emit almost 90% of the CO emissions in quadrant 3, where urbanized west Sacramento gives way to large areas of agricultural land.

At the Del Paso Manor site, emission inventory-derived $CO/NO_x$ ratios agree very closely with ambient-derived ratios (i.e., within 10-60%) for all wind quadrants and days of the week (see Figure 18). At this site, the emission inventory-derived ratios correlate with ambient-derived ratios as closely as could be expected given the limitations of the comparison techniques used.

**Figure 17.** $CO/NO_x$ ratios by wind quadrant and day of week for the Sacramento Natomas site.

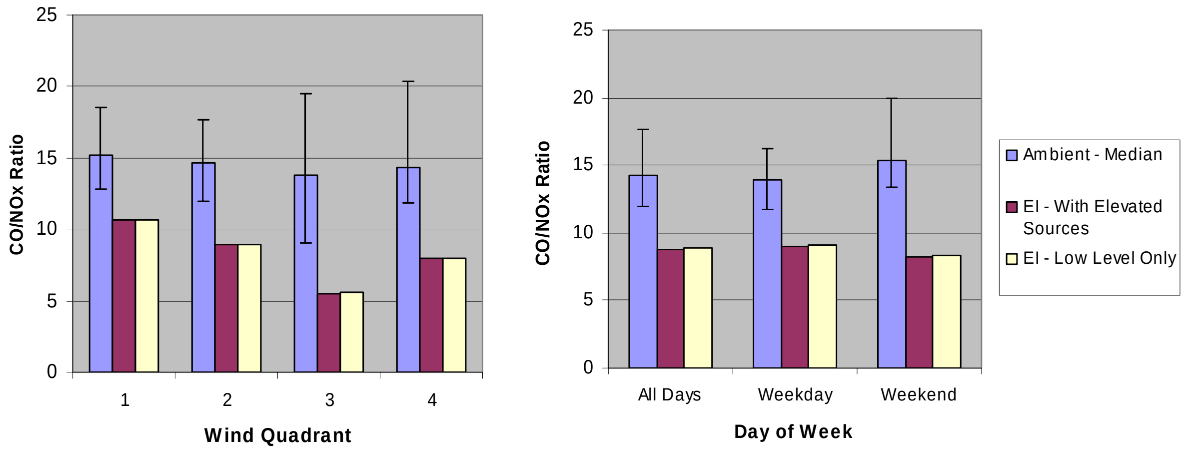
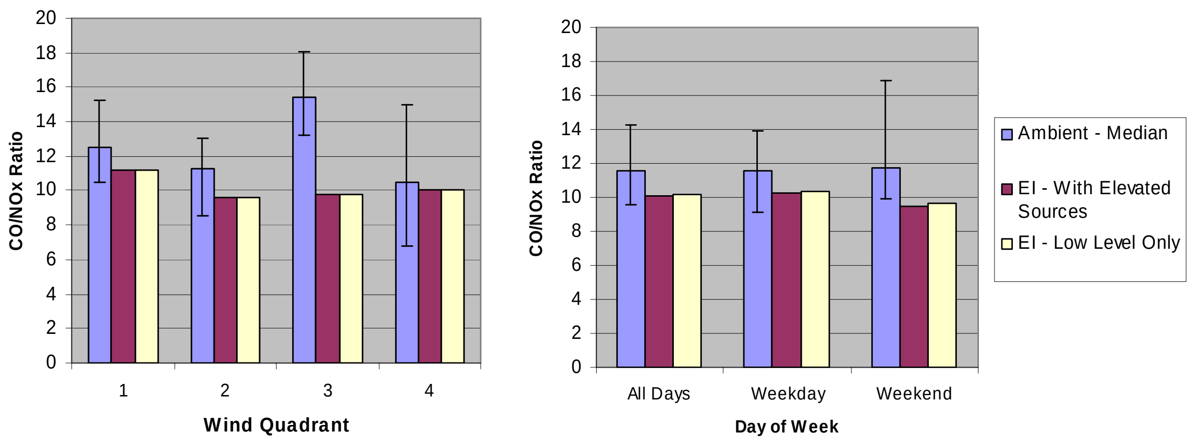



**Figure 18.** $CO/NO_x$ ratios by wind quadrant and day of week for the Sacramento Del Paso Manor site.




Figures 19 and 20 show $CO/NO_x$ ratios by wind quadrant and day of week for Fresno area sites. At the Clovis site, ambient-derived $CO/NO_x$ ratios are approximately two times higher than emission inventory-derived ratios for all wind quadrants except quadrant 2, where the ambient-derived ratio is only 60% higher than the emission inventory-derived ratio. Ambient- and emission inventory-derived $CO/NO_x$ ratios show slightly closer agreement on weekend days than weekdays at the Clovis site (see Figure 19).

At the Fresno First Street site, emission inventory-derived $CO/NO_x$ ratios reasonably approximate ambient-derived ratios (i.e., within 30-80%) for all wind quadrants except quadrant 4, where the ambient-derived ratio is 2.3 times higher than the emission inventory-derived ratio. Ambient- and emission inventory-derived $CO/NO_x$ ratios show slightly closer agreement on weekend days than weekdays at the First Street site (see Figure 20).

**Figure 19.** $CO/NO_x$ ratios by wind quadrant and day of week for the Clovis site.

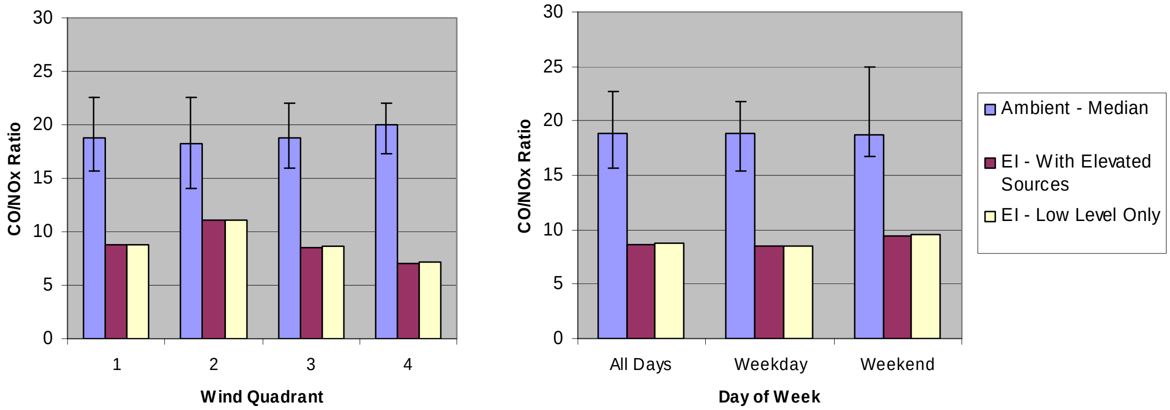
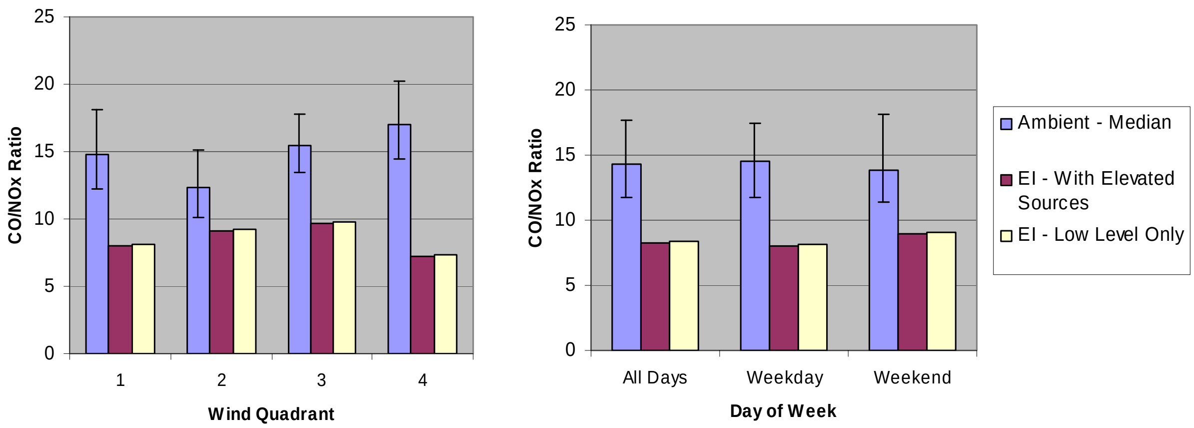



**Figure 20.** $CO/NO_x$ ratios by wind quadrant and day of week for the Fresno First Street site.




Figures 21 and 22 show $CO/NO_x$ ratios by wind quadrant and day of week for the two Bakersfield sites (California Avenue and Golden State). At the California Avenue site, emission inventory-derived $CO/NO_x$ ratios reasonably approximate ambient-derived ratios (i.e., within 60-80%) for wind quadrants 1 and 2, while the ambient-derived ratios are more than two times higher than the emission inventory-derived ratios in quadrants 3 and 4 (see Figure 21). These differences may be partly attributable to the fact that overall emission densities are significantly higher in quadrants 1 and 2 than in the other two quadrants. At the Golden State site, emission inventory-derived $CO/NO_x$ ratios compare poorly with ambient-derived ratios, being 3.5 to 5 times lower than ambient-derived ratios for all wind quadrants and days of the week (see Figure 22).

Figure 23 shows $CO/NO_x$ ratios by wind quadrant and day of the week for the Turlock site in Stanislaus County. Ambient-derived $CO/NO_x$ ratios are consistently two to three times higher than emission inventory-derived ratios for this site.

**Figure 21.** CO/$NO_x$ ratios by wind quadrant and day of week for the Bakersfield California Avenue site.

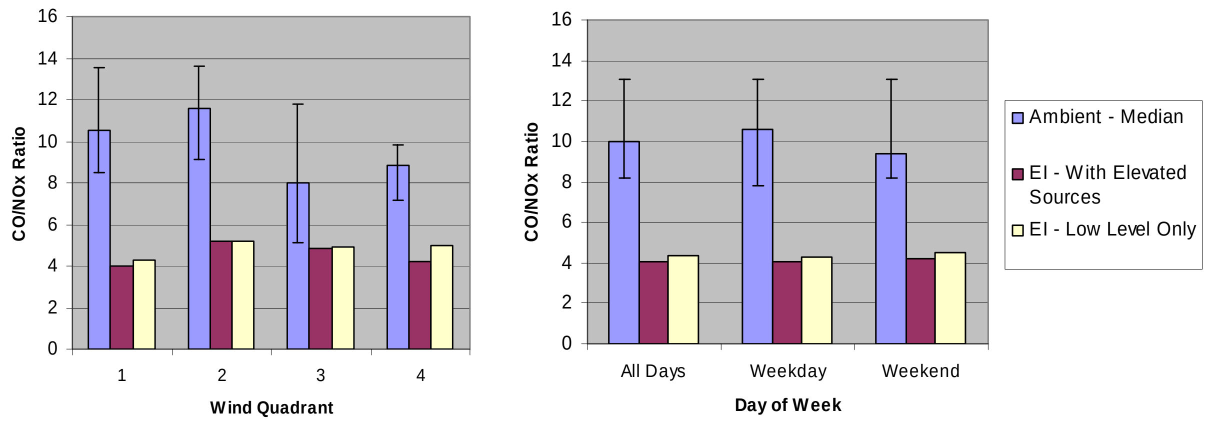



**Figure 22.** CO/$NO_x$ ratios by wind quadrant and day of week for the Bakersfield Golden State site.

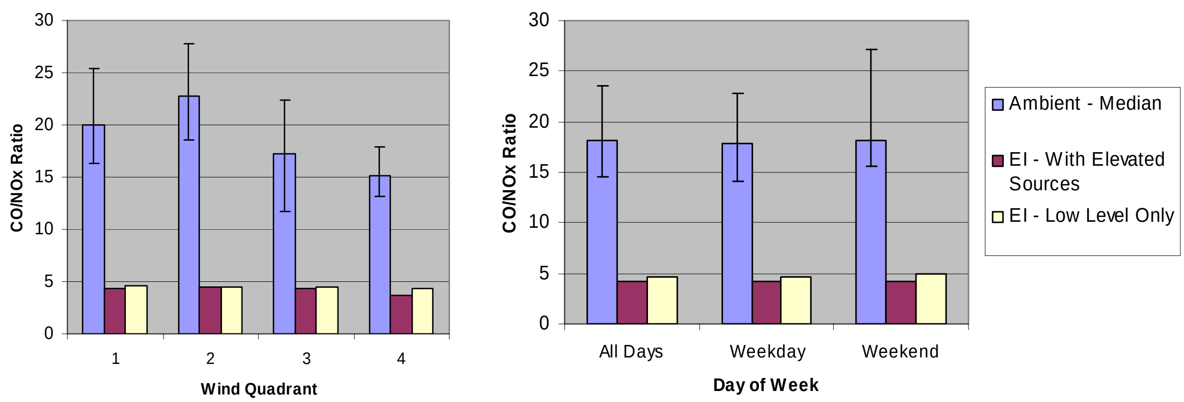
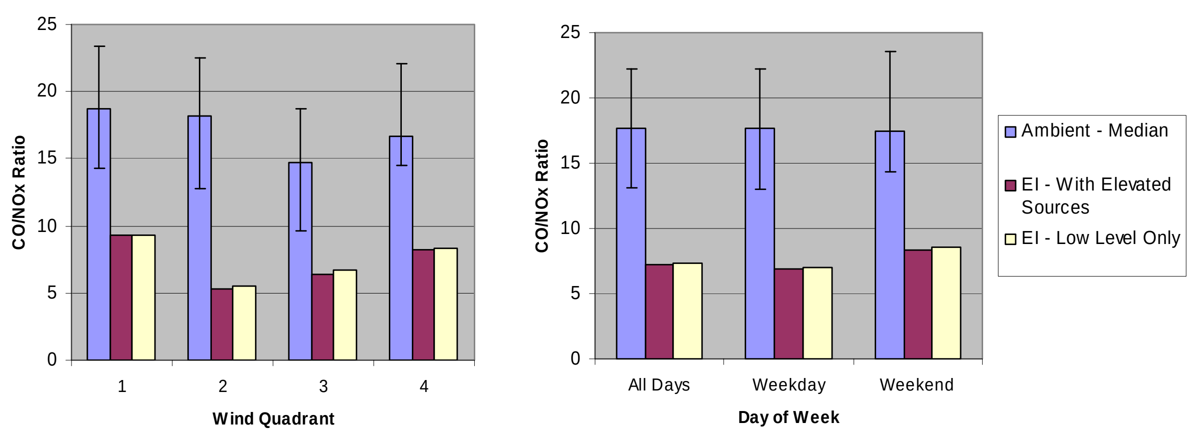



**Figure 23.** CO/$NO_x$ ratios by wind quadrant and day of week for the Turlock site.




## Ratios of Individual Hydrocarbon Species

Further investigations of the CCOS emission inventory were conducted by comparing relative amounts of individual hydrocarbons in the ambient data and in the CCOS emission inventory. Individual species ratios were computed for 11 sites for a select number of chemical compounds: acetylene/benzene, acetylene/propylene, benzene/m- and p-xylene, benzene/o-xylene, benzene/toluene, toluene/m- and p-xylene, and toluene/o-xylene.

Table 5 shows ambient- and emission inventory-derived pollutant ratios for 13 monitoring sites in the CCOS modeling domain. Overall, the emission inventory-derived ratios show good agreement with the ambient-derived ratios, though a few significant discrepancies do exist. The emission inventory-derived acetylene/benzene ratios were in poor agreement with the ambient-derived ratios at the Sunol and Granite Bay sites. The emission inventory-derived benzene/o-xylene ratio was also in poor agreement with the ambient-derived ratios at the Granite Bay site, and the pollutant ratios at the Parlier site compared poorly in almost all cases.

In general, these results suggest that the relative proportions of individual hydrocarbon species in the emissions data are reasonably representative of ambient data. Further investigation of the composition of hydrocarbon emissions was undertaken through the fingerprint analyses described in the following section.

**Fingerprint Comparisons**

Comparisons of the ambient- and emission inventory-derived relative hydrocarbon compositions were performed for 10 sites. In general, the fingerprint analyses showed that

- The speciation of the emission inventory is representative of the TNMOC composition detected by ambient monitoring sites for most species groups.
- The contribution of ethane to the overall TNMOC composition is consistently higher in the emission inventory than in the ambient data. Further analysis of the emission inventory showed that this overprediction is attributable to emissions from livestock waste. (In a related CCOS study [Chinkin and Reid, 2006], STI discovered that significant amounts of livestock waste emissions are spatially distributed across the CCOS modeling domain using the human population as a spatial surrogate.)
- The contribution of propane to the overall TNMOC composition is consistently lower in the emission inventory than in the ambient data. These differences may be due to the fact that propane has a low reactivity and tends to persist in the atmosphere. However, these differences may also indicate an underprediction of emissions from oil and natural gas extraction and production activities, which are a significant source of propane. This conclusion is bolstered by the fact that other species emitted by oil and gas production activities, such as butanes and pentanes, also tend to be underpredicted in the emission inventory (though these more highly reactive compounds are underpredicted by a smaller amount than propane).
- The contribution of isoprene to the overall TNMOC composition is consistently higher in the emission inventory than in the ambient data. However, these differences are likely due to the fact that isoprene, a highly reactive species, is being removed from the ambient air by photochemistry before it can be detected at monitoring sites.

Figures 24 through 27 show ambient- and emission inventory-derived hydrocarbon compositions for Sacramento area sites. In addition to the already identified issues with propane, ethane, and isoprene, note that emission inventory-derived fractions of C6+ alkanes, C4+ alkenes, C8+ aromatics, and pentanes are lower than the ambient-derived fractions at the Elk Grove site (see Figure 24). The toluene fraction is somewhat higher in the emission inventory-derived compositions than the ambient-derived compositions at the remaining three Sacramento sites (Folsom, Natomas, and Del Paso Manor), but otherwise, the hydrocarbon compositions show very close agreement at those sites.

**Table 5.** Individual species ratios by site (emission ratios for full grid extent around each site).

| Station | Acetylene/Benzene | | | Acetylene/Propylene | | | Benzene/mp-Xylene | | | Benzene/o-Xylene | | | Benzene/Toluene | | | Toluene/mp-Xylene | | | Toluene/o-Xylene | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | A[a] | EI [b] | A/EI | A | EI | A/EI | A | EI | A/EI | A | EI | A/EI | A | EI | A/EI | A | EI | A/EI | A | EI | A/EI |
| Bay Area | | | | | | | | | | | | | | | | | | | | | |
| Sunol (SUN) | 6.8 | 1.1 | 6.1 | – | 1.1 | – | 0.7 | 0.6 | 1.2 | 2.0 | 1.3 | 1.6 | 0.4 | 0.2 | 1.7 | 1.7 | 2.4 | 0.7 | 4.6 | 5.3 | 0.9 |
| Sacramento Area | | | | | | | | | | | | | | | | | | | | | |
| Elk Grove (ELK) | 1.1 | 1.2 | 0.9 | 0.7 | 1.1 | 0.6 | 0.7 | 0.6 | 1.2 | 1.3 | 1.7 | 0.8 | 0.4 | 0.4 | 1.1 | 1.8 | 1.7 | 1.1 | 3.6 | 4.7 | 0.8 |
| Folsom (FLN) | 1.1 | 1.0 | 1.1 | 1.0 | 0.8 | 1.2 | 0.4 | 0.5 | 0.8 | 1.1 | 1.0 | 1.1 | 0.3 | 0.2 | 1.4 | 1.7 | 2.4 | 0.7 | 4.2 | 4.7 | 0.9 |
| Granite Bay (GNBY) | 3.6 | 0.9 | 3.9 | – | 0.8 | – | 0.4 | 0.5 | 0.8 | 2.7 | 1.0 | 2.6 | 0.3 | 0.2 | 1.5 | 1.2 | 2.6 | 0.5 | 8.9 | 5.0 | 1.8 |
| Sacramento - Natoma (NAT) | 1.2 | 1.0 | 1.2 | 1.2 | 0.9 | 1.3 | 0.5 | 0.5 | 1.0 | 1.1 | 1.1 | 1.0 | 0.3 | 0.2 | 1.3 | 1.6 | 2.2 | 0.7 | 4.2 | 4.6 | 0.9 |
| Sacramento - Del Paso Manor (SDP) | 1.4 | 1.0 | 1.4 | 1.0 | 0.9 | 1.1 | 0.4 | 0.5 | 0.8 | 1.0 | 1.0 | 1.0 | 0.2 | 0.2 | 0.9 | 1.5 | 2.2 | 0.7 | 4.1 | 4.6 | 0.9 |
| Fresno Area | | | | | | | | | | | | | | | | | | | | | |
| Clovis (CLO) | 1.3 | 1.3 | 1.0 | 1.2 | 1.1 | 1.1 | 0.4 | 0.5 | 0.8 | 1.0 | 1.1 | 0.9 | 0.2 | 0.2 | 1.0 | 1.6 | 2.6 | 0.6 | 4.8 | 5.2 | 0.9 |
| Fresno - First Street (FSF) | 1.3 | 1.2 | 1.0 | 1.1 | 0.9 | 1.2 | 0.4 | 0.5 | 0.8 | 1.0 | 1.1 | 0.9 | 0.2 | 0.2 | 1.0 | 2.0 | 2.6 | 0.8 | 4.7 | 5.4 | 0.9 |
| Madera (M29) | 1.3 | 1.8 | 0.7 | 0.9 | 1.2 | 0.8 | 0.5 | 0.7 | 0.8 | 1.3 | 1.7 | 0.8 | 0.3 | 0.3 | 1.1 | 1.9 | 2.4 | 0.8 | 4.5 | 6.1 | 0.7 |
| Parlier (PLR) | 2.2 | 1.5 | 1.5 | – | 1.2 | – | 8.4 | 0.6 | 14.7 | 4.4 | 1.0 | 4.3 | 20.8 | 0.2 | 130.0 | 1.4 | 3.5 | 0.4 | 2.7 | 6.4 | 0.4 |
| Bakersfield Area | | | | | | | | | | | | | | | | | | | | | |
| Arvin (ARV) | 1.0 | 1.0 | 1.0 | 1.0 | 1.1 | 0.9 | 0.5 | 1.1 | 0.5 | 1.0 | 2.6 | 0.4 | 0.3 | 0.5 | 0.7 | 2.1 | 2.4 | 0.9 | 4.2 | 5.8 | 0.7 |
| Bakersfield - Golden State (BGS) | 1.6 | 1.1 | 1.5 | 2.7 | 1.0 | 2.6 | 0.4 | 0.7 | 0.6 | 1.0 | 1.4 | 0.7 | 0.2 | 0.3 | 0.7 | 1.5 | 2.4 | 0.6 | 4.2 | 4.9 | 0.9 |
| Shafter (SHA) | 1.0 | 1.2 | 0.8 | 1.5 | 1.3 | 1.2 | 0.5 | 1.0 | 0.5 | 1.3 | 2.3 | 0.6 | 0.3 | 0.4 | 0.7 | 1.7 | 2.2 | 0.8 | 5.1 | 5.3 | 1.0 |

[a] "A" = ratios derived from ambient data.
[b] "EI" = ratios derived from emission inventory data.

**Figure 24.** Comparison of 0500-1000 PDT ambient- and emission inventory-derived TNMOC compositions for the Elk Grove site.

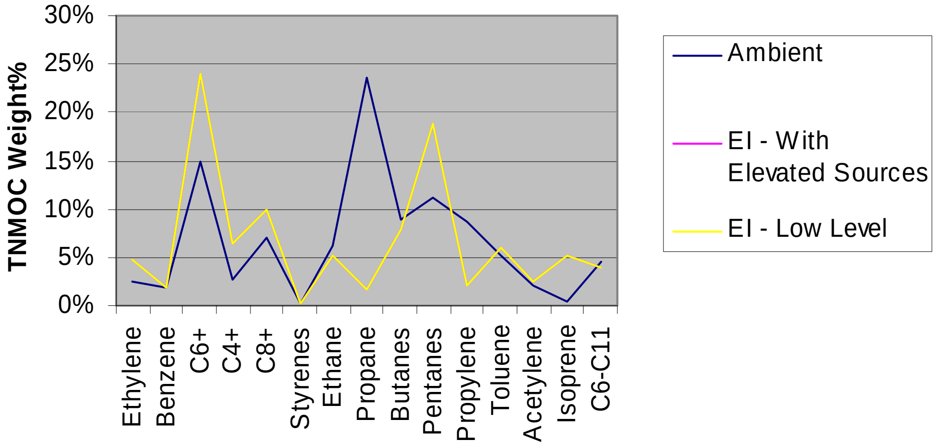



**Figure 25.** Comparison of 0500-1000 PDT ambient- and emission inventory-derived TNMOC compositions for the Folsom site.

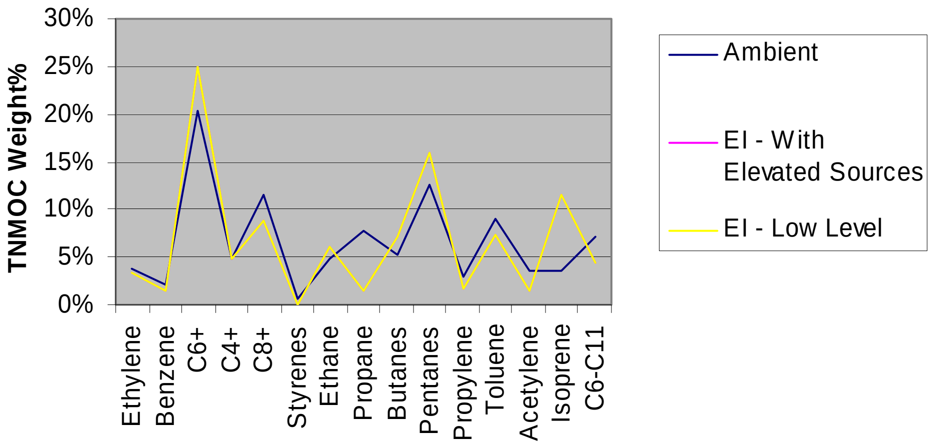



**Figure 26.** Comparison of 0500-1000 PDT ambient- and emission inventory-derived TNMOC compositions for the Sacramento Natomas site.

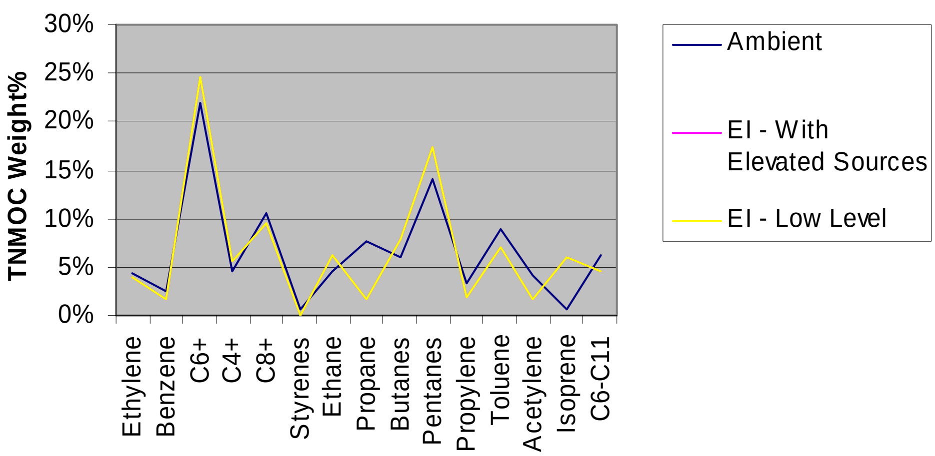
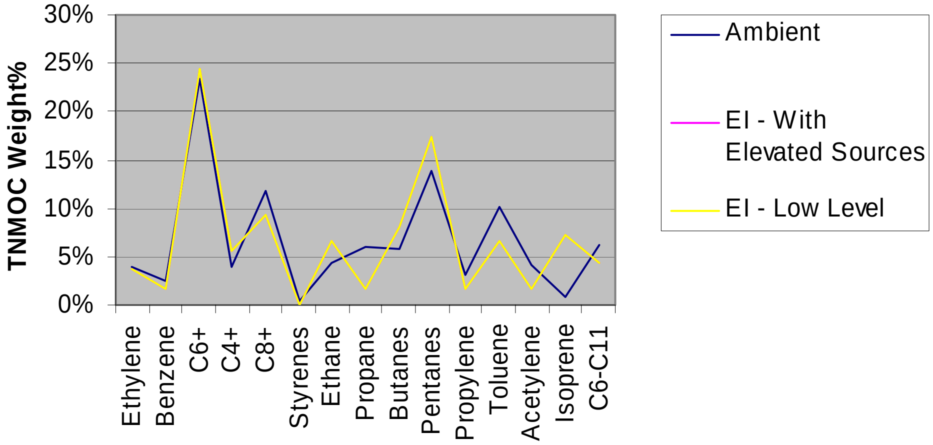


**Figure 27.** Comparison of 0500-1000 PDT ambient- and emission inventory-derived TNMOC compositions for the Sacramento Del Paso Manor site.




Figures 28 through 30 show ambient- and emission inventory-derived hydrocarbon compositions for Fresno area sites. Again, agreement between the ambient and emission inventory data is excellent apart from the already identified issues with ethane and propane, though C8+ aromatics and toluene are underpredicted in the emission inventory data at the Clovis site (see Figure 28).

**Figure 28.** Comparison of 0500-1000 PDT ambient- and emission inventory-derived TNMOC compositions for the Clovis site.

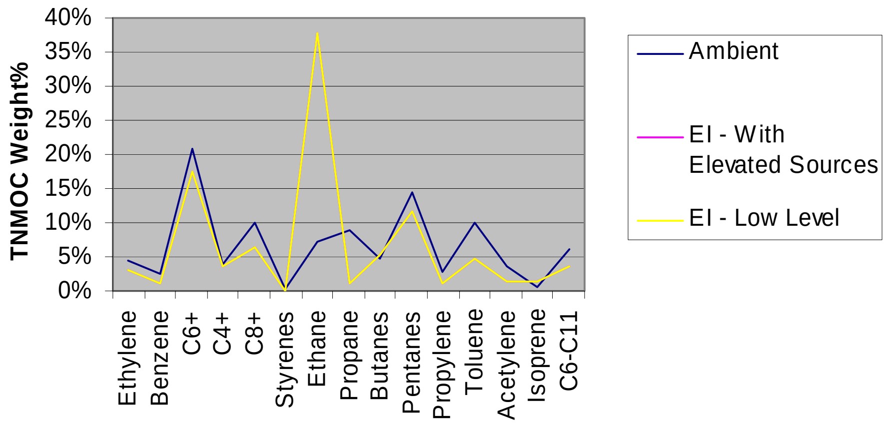


**Figure 29.** Comparison of 0500-1000 PDT ambient- and emission inventory-derived TNMOC compositions for the Madera site.

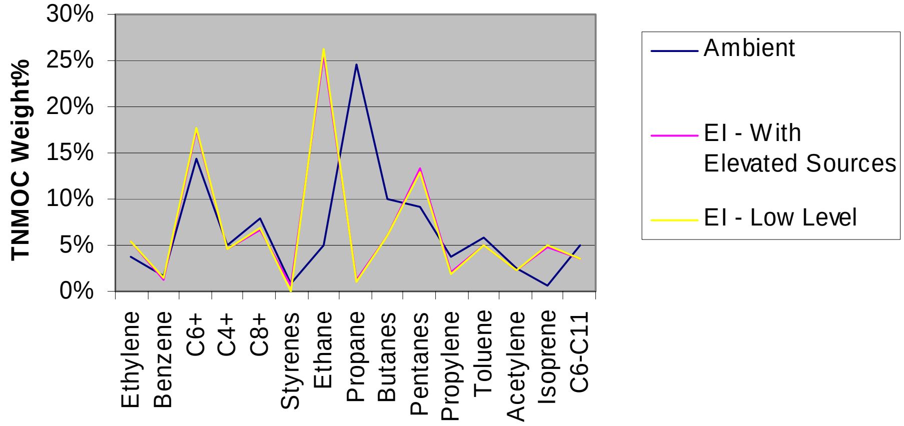
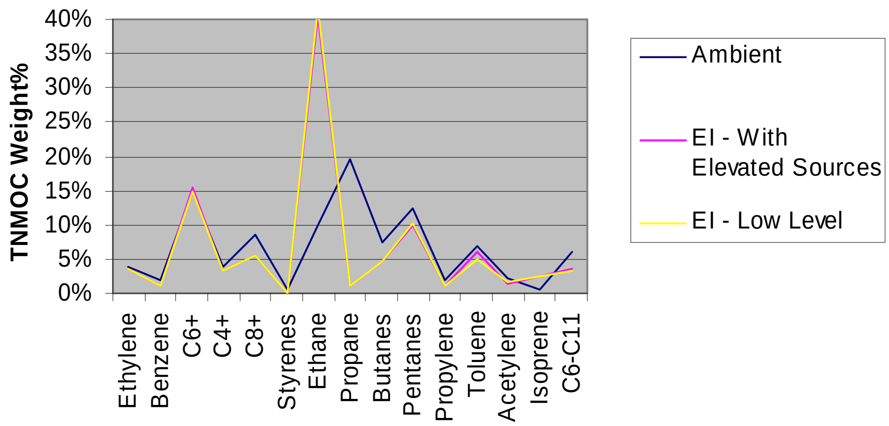



**Figure 30.** Comparison of 0500-1000 PDT ambient- and emission inventory-derived TNMOC compositions for the Parlier site.




Figures 31 through 33 show ambient- and emission inventory-derived hydrocarbon compositions for Kern County sites, where more significant differences exist than was the case at the Sacramento and Fresno area sites. At the Arvin site, the emission inventory data show a spike in the fraction of isoprene and an underprediction of several species groups, including C6+ alkanes, ethane, and pentanes (see Figure 31). The discrepancy between ambient- and emission inventory-derived isoprene fractions is more significant at Arvin than at any other site, and this difference could be caused by issues related to the reactivity of isoprene, an over-estimation of biogenic emissions in the region around the monitoring site, or terrain factors (i.e., biogenic emissions from the Sierra foothills to the east of the site do not cross the ridgeline and impact the monitoring site).

At the Bakersfield Golden State site, the emission inventory-derived fraction of pentanes is lower than the ambient-derived fraction, while the emission inventory-derived fraction of C6+ alkanes is lower than the ambient-derived fraction (see Figure 32). At the Shafter site, the emission inventory-derived fraction of butanes is higher than the ambient-derived fraction (see Figure 33).

**Figure 31.** Comparison of 0500-1000 PDT ambient- and emission inventory-derived TNMOC compositions for the Arvin site.

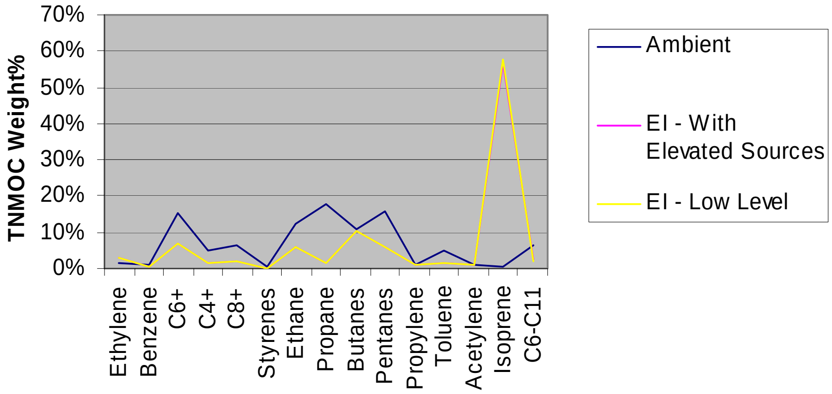



**Figure 32.** Comparison of 0500-1000 PDT ambient- and emission inventory-derived TNMOC compositions for the Bakersfield Golden State site.

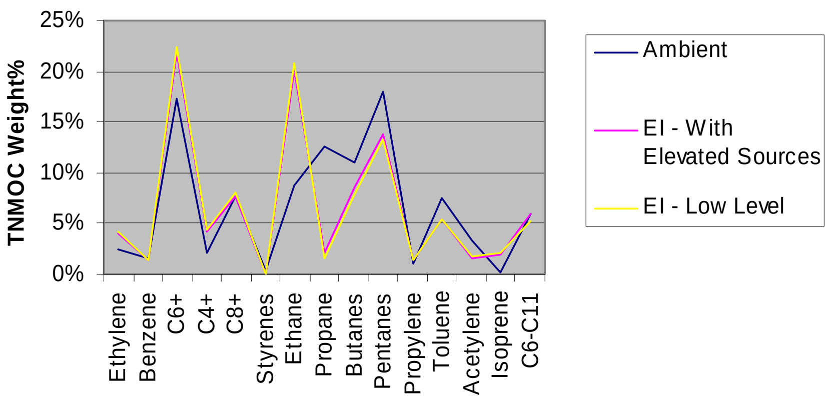
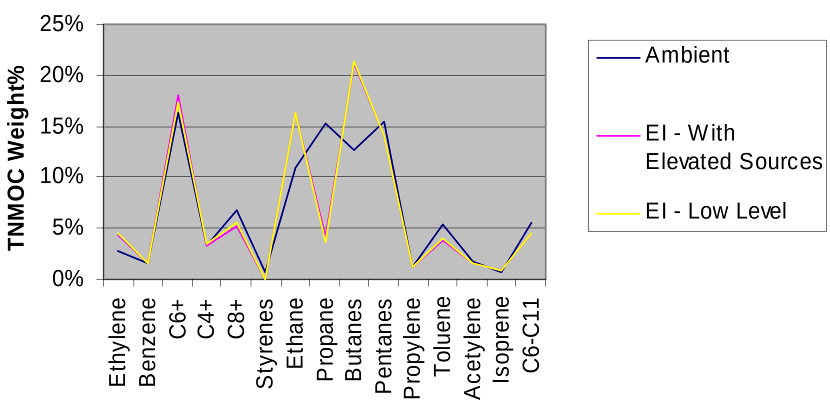



**Figure 33.** Comparison of 0500-1000 PDT ambient- and emission inventory-derived TNMOC compositions for the Shafter site.




## Integration of Previous Research

In general, trends show that emission inventories have been moving toward closer agreement with ambient monitoring data over time. For example, Figure 34 presents a series of comparisons between ambient- and emission inventory-derived VOC/$NO_x$ ratios at the Los Angeles North Main monitoring site during summer mornings (Chinkin et al., 2005). This figure shows that ambient

$VOC/NO_x$ ratios have declined over time and that recent emission inventory-derived ratios agree much more closely with the ambient data than in past years.

A similar pattern can be seen in emissions reconciliation work that has been conducted in Central California, with emission inventory-derived pollutant ratios calculated for this project generally comparing more favorably with ambient-derived ratios than was the case with previous emission inventories. In a previous CCOS study performed by the Desert Research Institute (DRI) (Fujita et al., 2005), trends in the consistency between emission inventory estimates and ambient measurements were analyzed by calculating ambient- and emission inventory-derived $TNMOC/NO_x$ ratios. While the techniques used in DRI's study differ from those employed in the current project (i.e., basin-wide emission estimates were used instead of a spatially resolved modeling inventory), the overall trends show an improvement in the agreement between emission inventory estimates and ambient data. Table 6 shows the ratios of ambient- and emission inventory-derived $TNMOC/NO_x$ ratios from the previous and current CCOS studies.

**Figure 34.** Ambient- and emission inventory-derived $VOC/NO_x$ ratios at Los Angeles North Main during summer mornings.

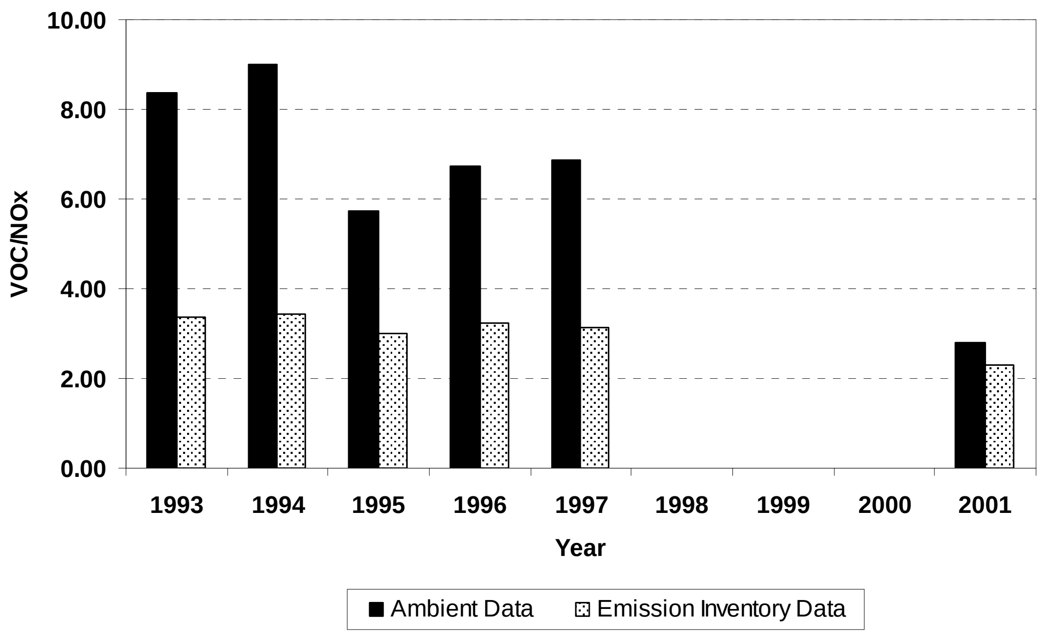



**Table 6.** Comparison of ambient- and emission inventory-derived $TNMOC/NO_x$ ratios.

| Air Basin | Ambient/Emission Inventory Ratio | | | |
|---|---|---|---|---|
| | DRI 1990 | DRI 1995 | DRI 2000 | STI 2000[a] |
| Sacramento | 2.2 | 1.6 | 1.7 | 1.4 – 2.4 |
| Fresno | 3.6 | 2.6 | 1.9 | 1.4 – 7.2 |
| Kern | — | 3.9 | 2.9 | 2.6 – 4.3 |

[a]This column shows the range of results from all sites evaluated in a given air basin, including both urban and rural sites.

Other studies compared emission inventory data with ambient data in Central California:

- A comparison of ambient data collected during the Integrated Monitoring Study (IMS95) conducted during fall and winter of 1995-96 (Haste et al., 1998). This study compared ambient weekday data collected at sites in Fresno and Kern County from December 9, 1995, through January 6, 1995, to a gridded emissions inventory.
- A comparison of Photochemical Assessment Monitoring Stations (PAMS) monitoring data collected during summer 1996 with county-level emissions data from Fresno and Sacramento counties (Haste and Chinkin, 1999).
- A comparison of ambient data collected during the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS) from December 18, 2000, through January 18, 2001, to a gridded emission inventory. Comparisons were made for sites in the San Francisco Bay Area, Sacramento, Fresno, and Bakersfield.

Comparisons of results from the analysis of PAMS data in summer 1996 and in the current project are shown in Figures 35 through 38.

Figures 35 and 36 illustrate pollutant ratio comparisons for sites in the Sacramento area. Figure 35 shows that the ratio between ambient- and emission inventory-derived TNMOC/$NO_x$ ratios for the Folsom site improved from 2 to 1.5 between the summers of 1996 and 2000. A slight improvement can also be seen in the ratio between ambient- and emission inventory-derived TNMOC/$NO_x$ ratios at the Del Paso Manor site over that same period (with the ratio decreasing from 2.3 to 2.1), and a significant improvement can also be seen in the CO/$NO_x$ ratios at that site (see Figure 36).

Figures 37 and 38 compare pollutant ratios for sites in the Fresno area. Figure 37 shows that the ratio between ambient-and emission inventory-derived TNMOC/$NO_x$ ratios for the Clovis site improved from 3 to 1.9 between the summers of 1996 and 2000, while the ratio of CO/$NO_x$ ratios improved from 2.7 to 2.2. Improvement can also be seen at the Fresno First Street site, particularly for TNMOC/$NO_x$ ratios (the ratios between ambient- and emission inventory-derived ratios improved from 2.7 in 1996 to 1.3 in the current study).

**Figure 35.** Trends in ambient- and emission inventory-derived TNMOC/$NO_x$ ratios at the Folsom (Sacramento) site.

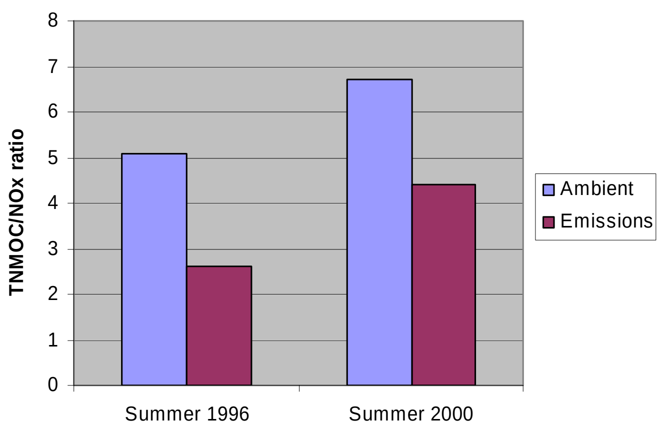


**Figure 36.** Trends in ambient- and emission inventory-derived TNMOC/$NO_x$ (left plot) and CO/$NO_x$ (right plot) ratios at the Sacramento Del Paso site.

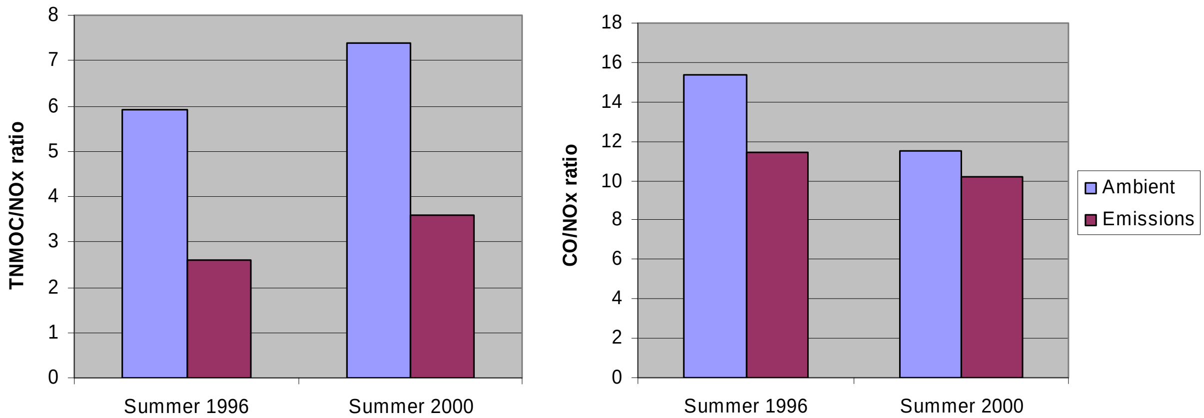



**Figure 37.** Trends in ambient- and emission inventory-derived TNMOC/$NO_x$ (left plot) and CO/$NO_x$ (right plot) ratios at the Clovis site.

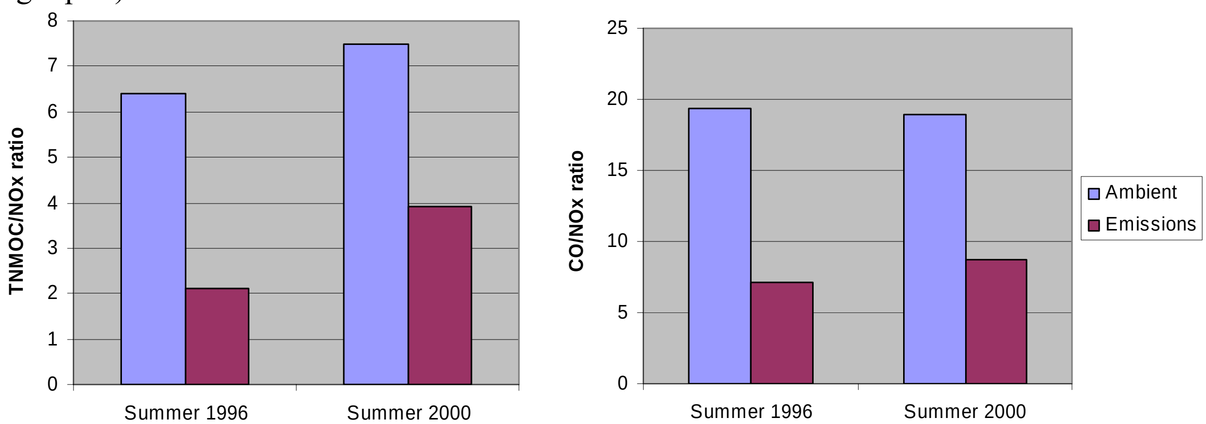
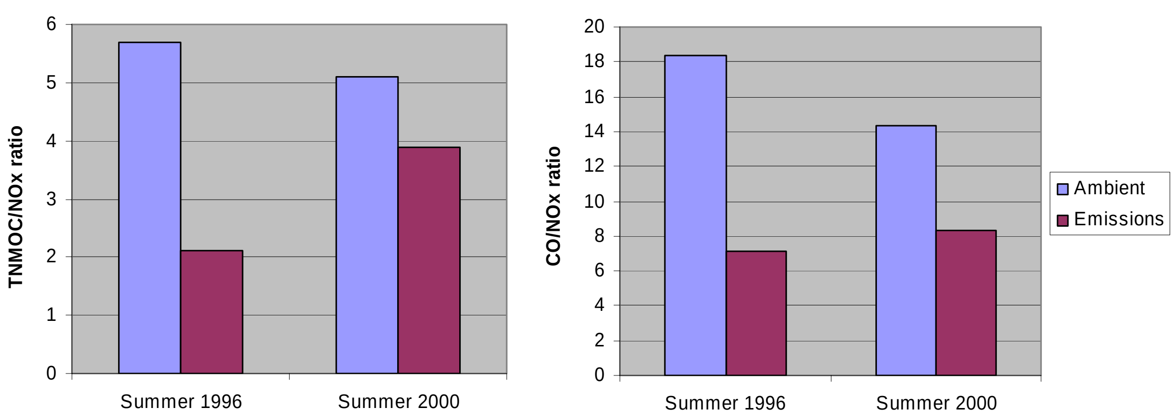



**Figure 38.** Trends in ambient- and emission inventory-derived TNMOC/$NO_x$ (left plot) and CO/$NO_x$ (right plot) ratios at the Fresno First Street site.



## CONCLUSIONS

Overall findings for the CCOS emissions reconciliation are summarized below:

- When compared with other emissions reconciliation studies, the emission inventory data used in this project are generally in better agreement with ambient data than data in previous emission inventories.
- At some sites, the emission inventory data correlate with ambient data as closely as could be expected given the limitations of the comparison techniques used.[3]
- For urban areas in the northern part of the CCOS modeling domain (the Sacramento area), the gridded emission inventory data are in good agreement with data from ambient monitoring sites on weekdays, but show poorer agreement on weekend days.
- For urban areas in the central part of the CCOS modeling domain (the Fresno area), the gridded emission inventory data are in good agreement with data from ambient monitoring sites on both weekdays and weekend days.
- For urban areas in the southern part of the CCOS modeling domain (Bakersfield), the gridded emission inventory data do not show good agreement with ambient monitoring data on either weekdays or weekend days.
- For most rural areas in the CCOS modeling domain, the gridded emission inventory data do not show good agreement with ambient monitoring data on either weekdays or weekend days. However, these sites do not fully meet the underlying assumptions of the analysis techniques used (i.e., significant local emissions around the monitoring site).

Based on the findings from this study, STI recommended that the following steps be taken to further investigate the CCOS modeling emission inventories and to make specific improvements to those inventories:

- Improve the accuracy of weekend emission estimates in the Sacramento area. Because monitoring sites in Sacramento are likely to be primarily influenced by on-road mobile source emissions, weekend vehicle activity data should be collected and used to better characterize differences in weekday and weekend-day travel.
- A correction should be made to the spatial distribution of emissions from livestock waste in the existing emission inventory. (This update should resolve the discrepancies between the ethane fractions observed in the ambient and emission inventory data).
- Further investigate the poor agreement between ambient and emission inventory data in Kern County. Given that the comparison between ambient and emission inventory data is generally good at urban sites dominated by mobile sources, it may be that other source types are poorly characterized in Kern County. Source apportionment techniques, such as positive matrix factorization (PMF) or chemical mass balance (CMB)[4] or bottom-up efforts to "ground truth" the Kern County inventory could be used to identify specific areas of improvement.
- Collect more ambient data at Bay Area sites. The possible comparisons between ambient and emission inventory data were very limited in this project given the availability of data from Bay Area sites.

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[3] For the types of comparisons performed in this study, emissions-derived pollutant ratios that are within ± 25-50% of ambient-derived ratios are considered to be in good agreement (California Air Resources Board, 1997).

[4] Both PMF and CMB analyses are scheduled to be conducted during 2007. However, no source apportionment results were ready at the time this document was prepared.

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