TECHNICAL MEMORANDUM

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TO: Dr. Patricia Velasco, California Air Resources Board

FROM: Lyle R. Chinkin, President
Stephen B. Reid, Manager, Emissions Assessment Group

RE: Emissions Reconciliation Findings and Recommendations – Comparison of Ambient Measurements to Emissions Representations for Modeling

SUMMARY OF FINDINGS AND RECOMMENDATIONS

Key findings and recommendations that resulted from the Central California Ozone Study (CCOS) emissions reconciliation are summarized below:

- When compared with previous emissions reconciliation studies, the emissions data used in this project are generally in better agreement with ambient data than previous emission inventories.
- At some sites, the emissions data correlate with ambient data as closely as could be expected given the limitations of the comparison techniques used.
- For urbanized areas in the northern part of the CCOS modeling domain (the Sacramento area), the gridded emissions data are in good agreement with data from ambient monitoring sites on weekdays, but show poorer agreement on weekend days.
- For urbanized areas in the central part of the CCOS modeling domain (the Fresno area), the gridded emissions data are in good agreement with data from ambient monitoring sites on both weekdays and weekend days.
- For urbanized areas in the southern part of the CCOS modeling domain (Bakersfield), the gridded emissions 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 emissions 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, Sonoma Technology, Inc. (STI) recommends 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 emissions-derived data).
- Further investigate the poor agreement between ambient and emissions data in Kern County. Given that the comparison between ambient and emissions 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)[1] 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 emissions-derived data were very limited in this project given the availability of data from Bay Area sites.

A detailed description of the analysis techniques and results that served as the basis for these conclusions and recommendations are provided in the sections that follow.

[1] Limited PMF analyses are scheduled to be done as part of the current study with assistance from the Bay Area Air Quality Management District. No source apportionment results were ready at the time this document was prepared.

INTRODUCTION

This memorandum is a deliverable for the "CCOS—Comparison of Ambient Measurements to Emissions Representations for Modeling" project. The CCOS is a multi-year program of meteorological and air quality monitoring, emission inventory development, data analysis, and air quality simulation modeling carried out for the purpose of improving the scientific understanding of ozone air quality problems in northern and central California. The goals of CCOS are being met through analysis of existing data; a large-scale field study conducted in summer 2000 to acquire a comprehensive database to support modeling and data analysis; analysis of the data collected during the field study; and the development, evaluation, and application of an air quality simulation model for northern and central California. The "CCOS—Comparison of Ambient Measurements to Emissions Representations for Modeling" project complements these other activities by investigating why preliminary CCOS photochemical modeling results differ from ambient observations by comparing emissions and ambient data.

The purpose of this technical memorandum is to provide the CCOS Technical Committee (TC) an assessment of the emission inventories being used for CCOS photochemical modeling efforts and to provide recommendations for meaningful improvements to the emission inventories that will improve subsequent photochemical ozone modeling results. The results of CCOS modeling will provide much of the technical basis for State Implementation Plan (SIP) updates for ozone nonattainment areas of the San Francisco Bay Area, Sacramento Valley, and San Joaquin Valley (SJV). Therefore, it is crucial that the modeling system improve its ability to predict the spatial and temporal patterns of observed ozone.

BACKGROUND

Comparisons between emission inventory- and ambient-derived data (often called "emissions reconciliation") can identify components of an emission inventory that warrant further investigation and improvement. Such analyses commonly reveal omissions or inaccuracies, which can be iteratively investigated and remedied until the emission inventory and ambient data reconcile with one another. Recognizing potential issues and implementing needed improvements *before* continuing air quality planning activities represent opportunities for appreciable benefits, such as improved plan effectiveness, defensibility, cost savings, and/or time efficiency. Real-world examples of inventory reconciliation analyses that have produced such successes have been published by Haste et al. (1998), Korc et al. (1995), and Fujita et al. (1992).

An inventory reconciliation analysis is a selective, quantitative comparison of emission inventory- and ambient-derived molar pollutant ratios (e.g., volatile organic compounds [VOC]/oxides of nitrogen [NO_x] or carbon monoxide [CO]/NO_x) and chemical speciation profiles. Inventory reconciliation analyses are considered "top-down" evaluations because they begin with a global overview of the emission inventory and then drill down to the details by targeting selected, high-priority source types for further investigation. (In contrast, "bottom-up" evaluations begin with specific, individual emissions source categories, which are synthesized to construct a comprehensive inventory from many elements of information.) Typically, inventory reconciliation analyses attempt to address the following questions:

- How well do emission inventory-derived pollutant ratios of VOC/NO_x and CO/NO_x compare with ambient-derived pollutant ratios?
- How well does the chemical composition reported in the emission inventory compare with the chemical composition of the ambient air?
- How do the ratio comparisons and chemical species comparisons vary by hour, wind quadrant, and source influence?
- What sectors (point, area, mobile) of the emission inventory, if any, need improvement and what changes are recommended?
- How do the ratio comparisons in this study compare with past emission inventory reconciliation studies?
- Are the emission inventory estimates getting better?

Comparisons of ambient- and emission inventory-derived primary pollutant ratios are confounded by the fact that ambient concentrations are influenced not only by pollutants emitted in the near vicinity of a monitor, but also by the carryover of aged (i.e., transported or chemically changed) pollutants. The influence of aged pollutants on the comparison can be minimized (though not eliminated) by selecting ambient data collected at times when emission rates are high and chemical reaction rates are low, such as the morning hours. Emissions are generally high during morning hours, mixing depths are low, and long-range transport and chemical reactions are minimized. It should be recognized, however, that emissions from elevated sources may be injected above the mixed layer and, hence, may not affect surface-level ambient concentrations. Evaluations with and without elevated emissions sources were performed to understand the potential effects of this phenomenon.

OVERVIEW OF APPROACH

Using ambient measurements collected 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 has 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 here.

Site Selection and Ambient Data Processing

During the first phase of this project, 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 speciated VOC measurements
- Availability of NO_x measurements
- Availability of wind direction measurements
- Sufficient density of total organic gas (TOG) and NO_x emissions around the site
- Availability of CO or TNMOC measurements
- Number of distinct counts of VOC, NO_x, and CO above the monitor detection limit and background thresholds (for this analysis, we used VOC > 50 ppbC, NO_x > 10 ppb, and CO > 0.150 ppm)
- Visual inspection of monitoring sites using imagery from "Google™ Earth". Sites were examined for visual evidence of local emissions

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. These were the most suitable sites for comparisons with emission inventory data. Only six 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. 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.

Table 1. Monitoring sites selected for emissions reconciliation analyses.

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

Emission Inventory Acquisition and Processing

Staff at the California Air Resources Board (ARB) provided STI with the latest gridded emission inventories prepared for the July/August 2000 modeling episode. These inventories reflect recent updates to emission estimates, including the use of new versions of EMFAC, the ARB's on-road mobile source emissions model, and OFFROAD, the ARB's off-road mobile source emissions model. Emissions were gridded to the 190 x 190 cell CCOS modeling domain at a resolution of 4 km. Specific emission inventory files provided by ARB include

- 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
- Temporal profiles used by ARB to distribute daily emission estimates across the hours of the day

STI applied ARB's temporal profiles to the area, off-road mobile, and point source emissions to generate hourly estimates for those source types. For on-road mobile and biogenic sources, average weekday and weekend day emission estimates were produced from the day-specific files provided by ARB. STI then applied ARB'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.

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 data and emission inventory, 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 1** 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 inner wind quadrant grid extents are larger at sites where wind speeds are greater and smaller where wind speeds are light. The center point of the grid represents the ambient monitoring site, the hollow grid represents the entire analysis zone, and the colored regions represent the wind quadrant definitions and quadrant analysis zones.

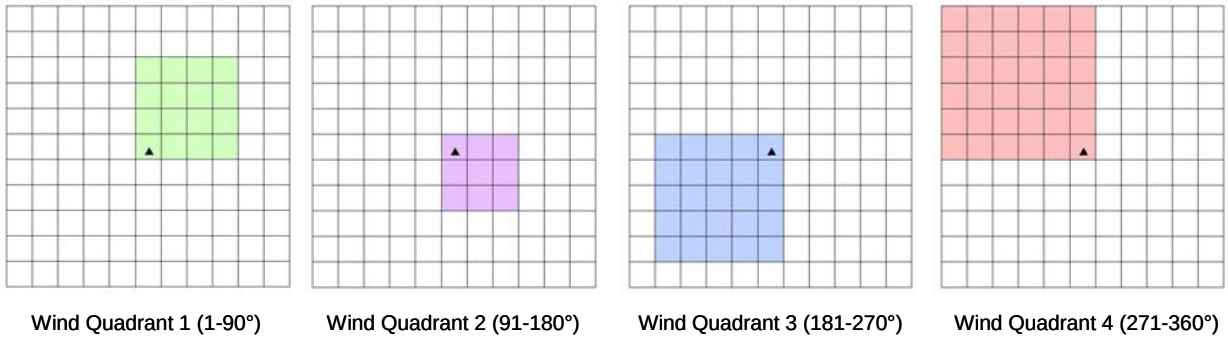

Figure 1. Example illustration of the spatial configuration of grid cells for which ambient- and emission inventory-derived ratios comparisons were calculated.

For ambient data, both average and median pollutant ratios were calculated, and for the emission inventory, 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 to 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 to the data measured at ambient monitoring sites. Hydrocarbon compositions were based on species groupings defined by ARB's modeling emissions data system (MEDS) (Allen, 2001). **Table 2** shows the 35 group definitions used by ARB, and the species measured at each monitoring site were assigned to one of these groups for purposes of comparison.

Table 2. ARB 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		

Site Characterization

To help characterize land use patterns and emission sources surrounding each ambient monitoring site, digital images of the 20 km x 20 km[2] area around each site were generated using Google Earth™ (see Appendix A). In addition, emission totals for 0500-1000 PDT were calculated for the full grid extent around each monitoring site and for each wind quadrant using the gridded emission inventory data provided by ARB. An overview of the characteristics of key monitoring sites appears below.

San Jose – 4th Street (SJ4)

The SJ4 site is located in the center of a heavily populated urban area, with heavily-traveled freeways occupying all wind quadrants. The emission inventory for the grid cells surrounding this site shows that light-duty motor vehicles are the most significant source of TNMOC, CO, and NO_x emissions for each wind quadrant, while non-road mobile sources and point sources also contribute significantly to the TNMOC and NO_x emissions in quadrant 4 (see **Figure 2**). Overall emission densities[3] are highest in quadrant 4.

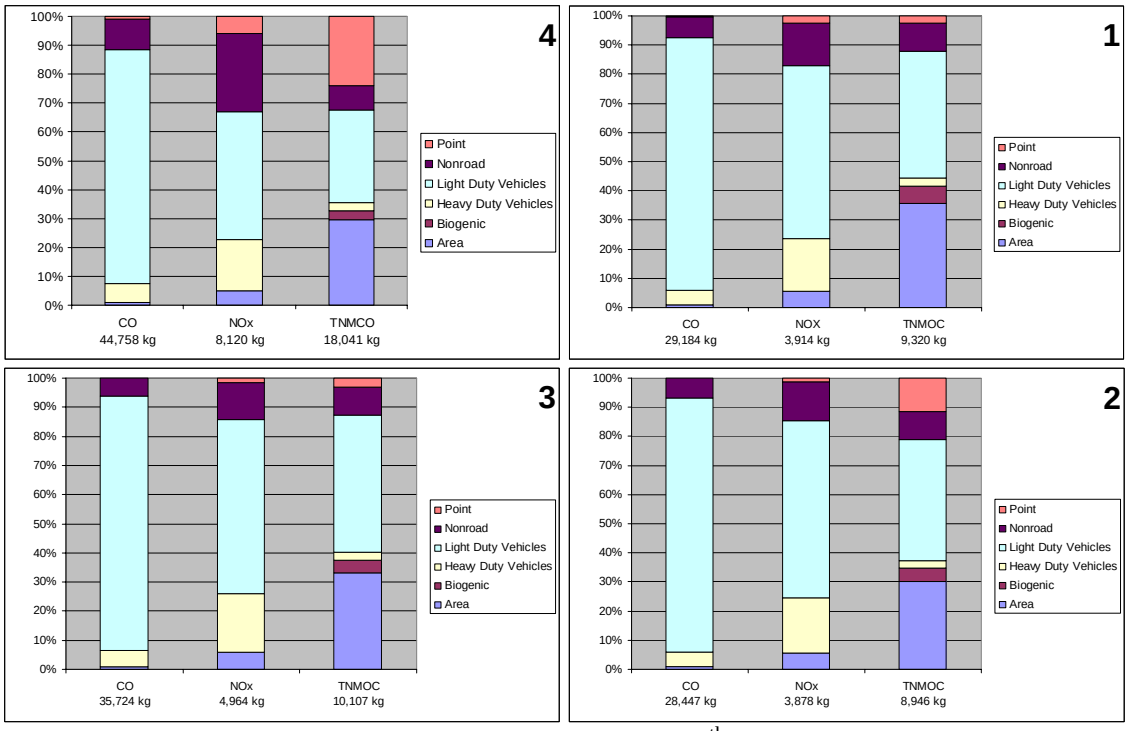

Figure 2. Emissions by wind quadrant for the San Jose 4th Street Station (0500-1000 PDT).

[2] In general, the full grid extent around individual monitoring sites was 5 x 5 grid cells, or 20 km x 20 km.
[3] The emission totals in kg shown on all bar charts represent emissions for 0500-1000 PDT for the full grid extend around each site.

Elk Grove (ELK)

The Elk Grove site is located in a rural area about 30 km south of downtown Sacramento. The emission inventory for the grid cells surrounding this site shows that CO and NO_x emissions are dominated by on-road mobile sources in all quadrants, while TNMOC emissions are also significantly influenced by area sources, particularly in quadrants 1 and 2 (see **Figure 3**). Overall emissions densities are highest in quadrants 1 and 2.

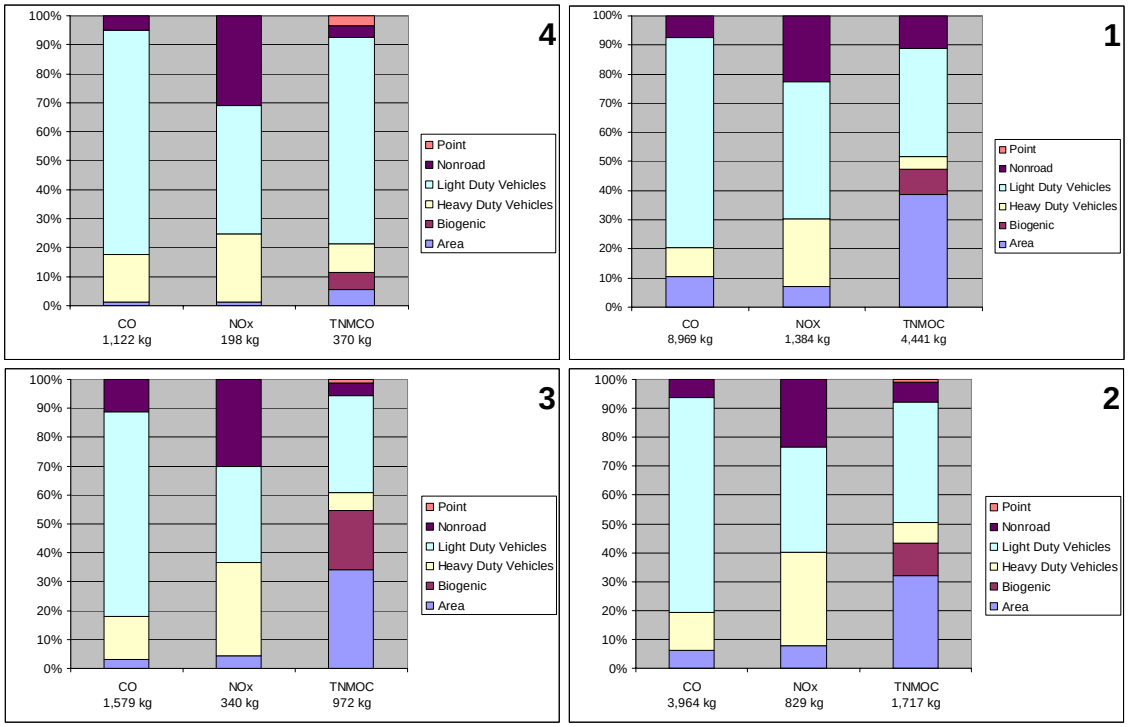

Figure 3. Emissions by wind quadrant for the Elk Grove Station (0500-1000 PDT).

Folsom (FLN)

The Folsom site is located in a suburban area to the south of Folsom Lake and about 30 km east of downtown Sacramento. The emission inventory for the grid cells surrounding this site shows that CO and NO_x emissions are dominated by on-road mobile sources in all quadrants, while TNMOC emissions are also significantly influenced by area sources in all quadrants. Overall emissions densities are highest in quadrant 4 (see **Figure 4**).

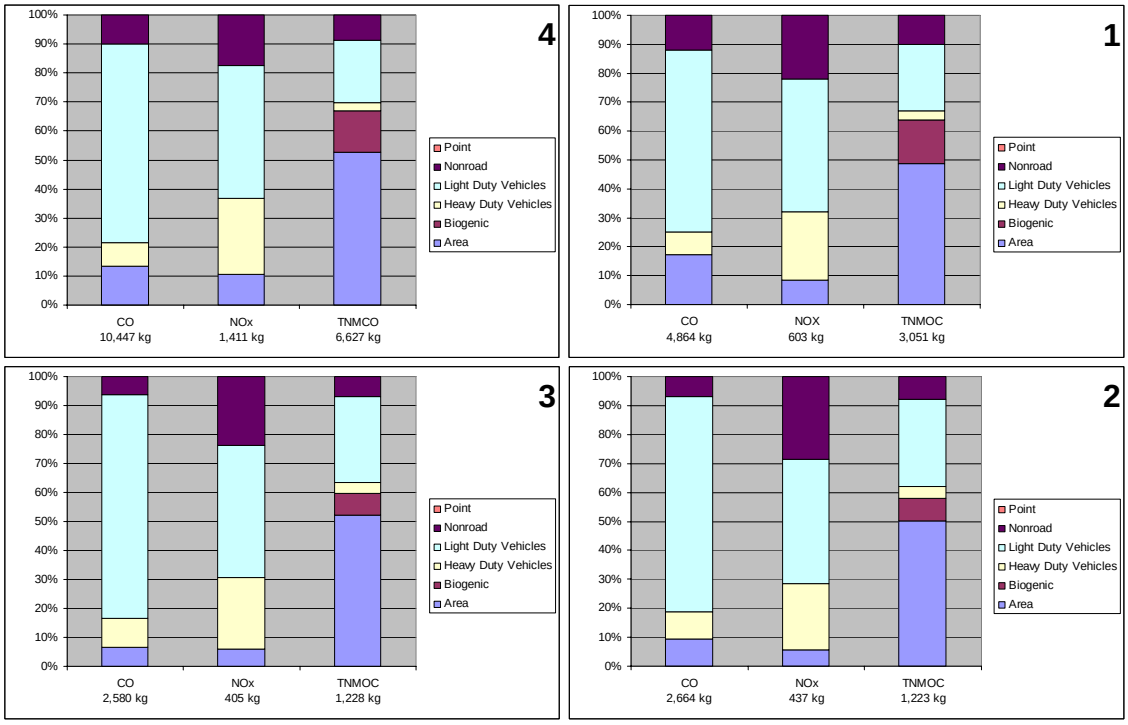

Figure 4. Emissions by wind quadrant for the Folsom Station (0500-1000 PDT).

Sacramento – Natomas (NAT)

The Natomas site is located about 6 km north of downtown Sacramento, near the intersection of Highways 5 and 80. The emission inventory for the grid cells surrounding this site shows significant on-road mobile source emissions in each quadrant, with non-road mobile sources also contributing significantly to the NO_x emissions in quadrants 3 and 4 (which contain large areas of agricultural land). Overall emissions densities are highest in quadrant 2, which is the most urbanized quadrant (see **Figure 5**).

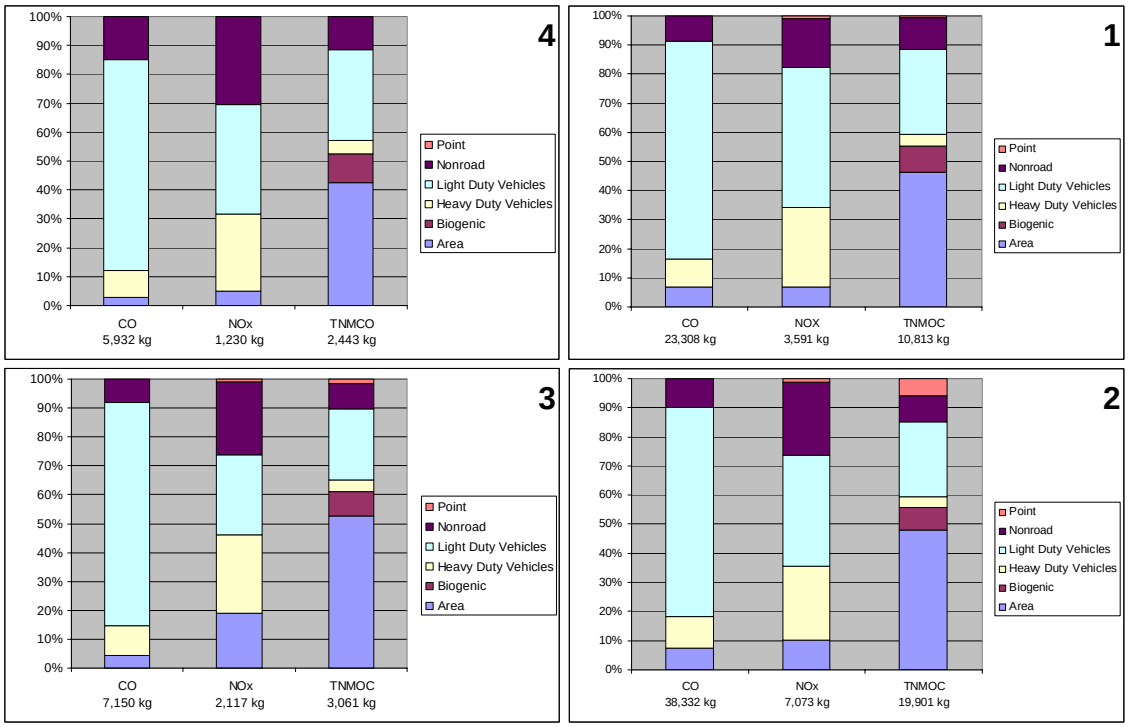

Figure 5. Emissions by wind quadrant for the Sacramento/Natomas Station (0500-1000 PDT).

Sacramento – Del Paso Manor (SDP)

The Del Paso Manor site is located in a residential area about 11 km northeast of downtown Sacramento. The emission inventory for the grid cells surrounding this site shows significant on-road mobile source emissions in each quadrant, with non-road mobile sources also contributing significantly to the NO_x emissions in quadrants 2 and 3. Area sources contribute about half of the total TNMOC emissions in each wind quadrant (see **Figure 6**). Overall emissions densities are highest in quadrants 1 and 4, which are intersected by Highway 80.

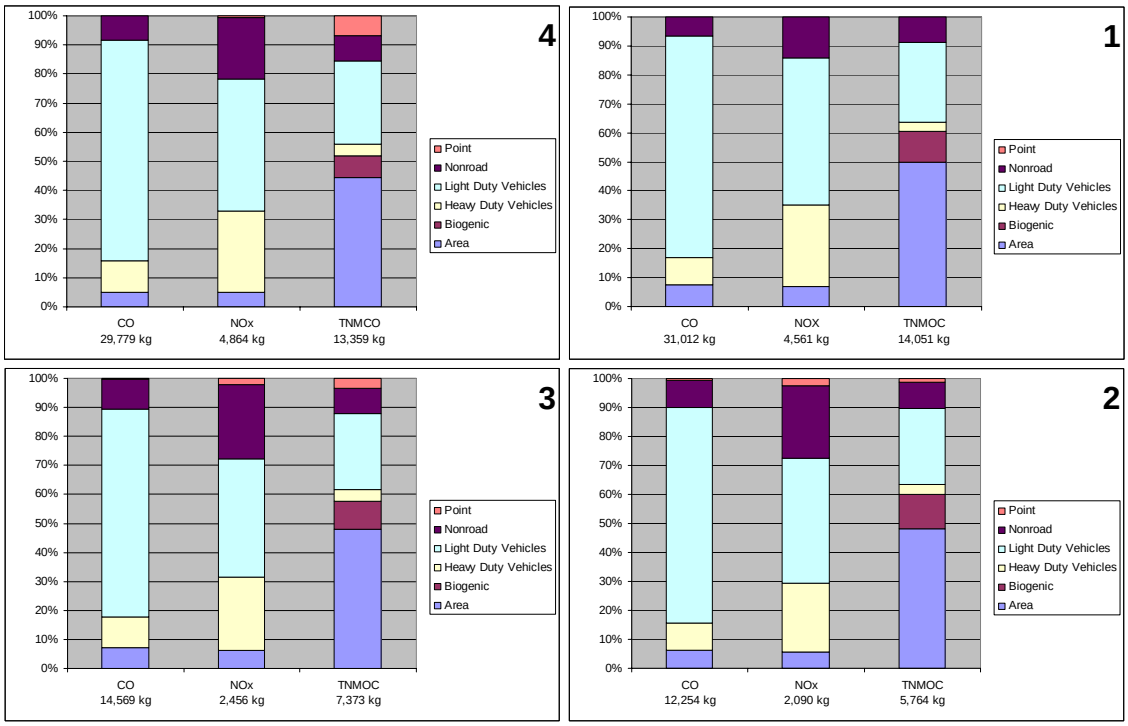

Figure 6. Emissions by wind quadrant for the Sacramento Del Paso Manor Station (0500-1000 PDT).

Clovis (CLO)

The Clovis site is located in a residential area about 10 km northeast of Fresno. The emission inventory for the grid cells surrounding this site shows significant on-road mobile source CO and NO_x emissions in each quadrant, with area sources contributing over 80% of the TNMOC emissions in each quadrant (see **Figure 7**). Overall emissions densities are somewhat lower in quadrant 1 than the remaining wind quadrants.

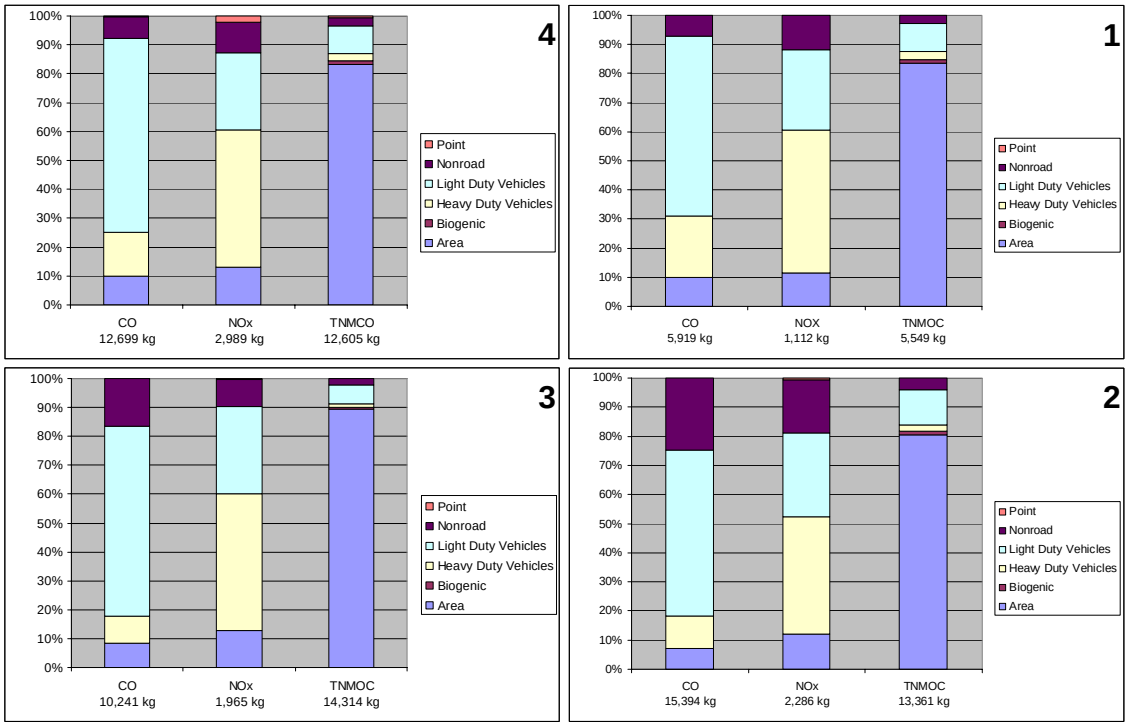

Figure 7. Emissions by wind quadrant for the Clovis Station (0500-1000 PDT).

Fresno – First Street (FSF)

The First Street site is located in a residential area about 4 km northeast of downtown Fresno. The emission inventory for the grid cells surrounding this site shows significant on-road mobile source CO and NO_x emissions in each quadrant, with area sources contributing about 90% of the TNMOC emissions in each quadrant (see **Figure 8**). Overall emissions densities are highest in quadrants 1 and 2.

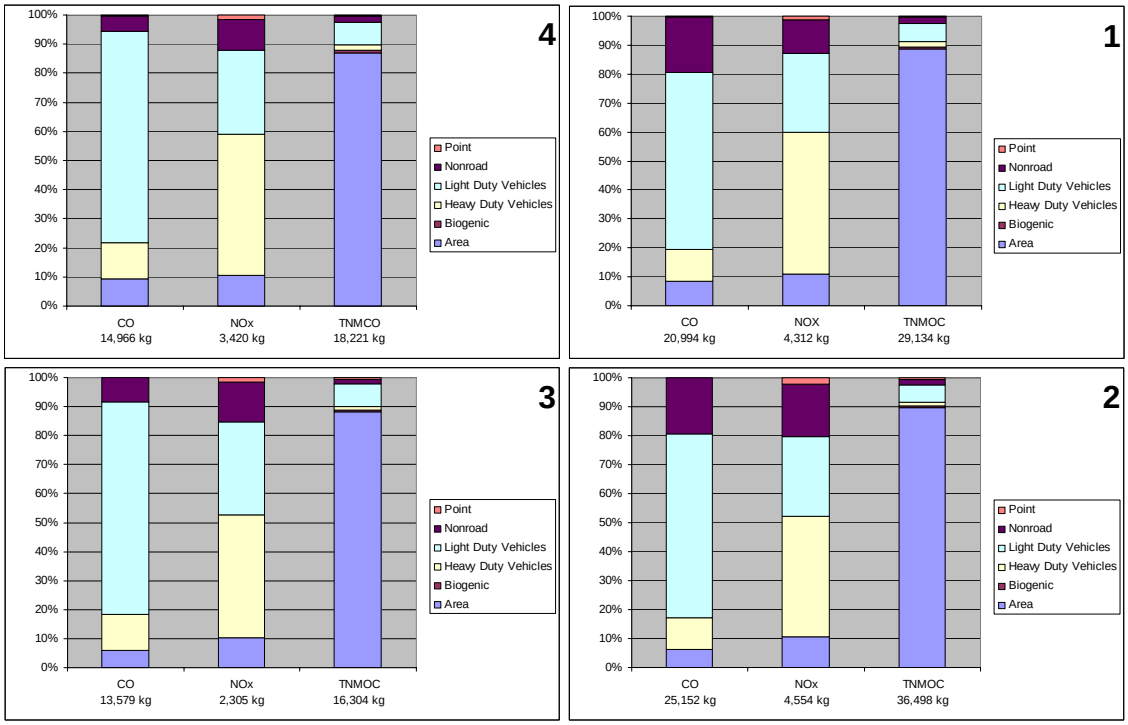

Figure 8. Emissions by wind quadrant for the Fresno First Street Station (0500-1000 PDT).

Madera (M29)

The Madera site is located in a rural area about 25 km northwest of Fresno. The emission inventory for the grid cells surrounding this site shows significant area source TNMOC emissions in each quadrant, and area sources also contribute over half of the NO_x emissions in quadrant 3. Point sources contribute almost 40% of the NO_x emissions in quadrant 4 (see **Figure 9**). Overall emissions densities are highest in quadrants 1 and 2.

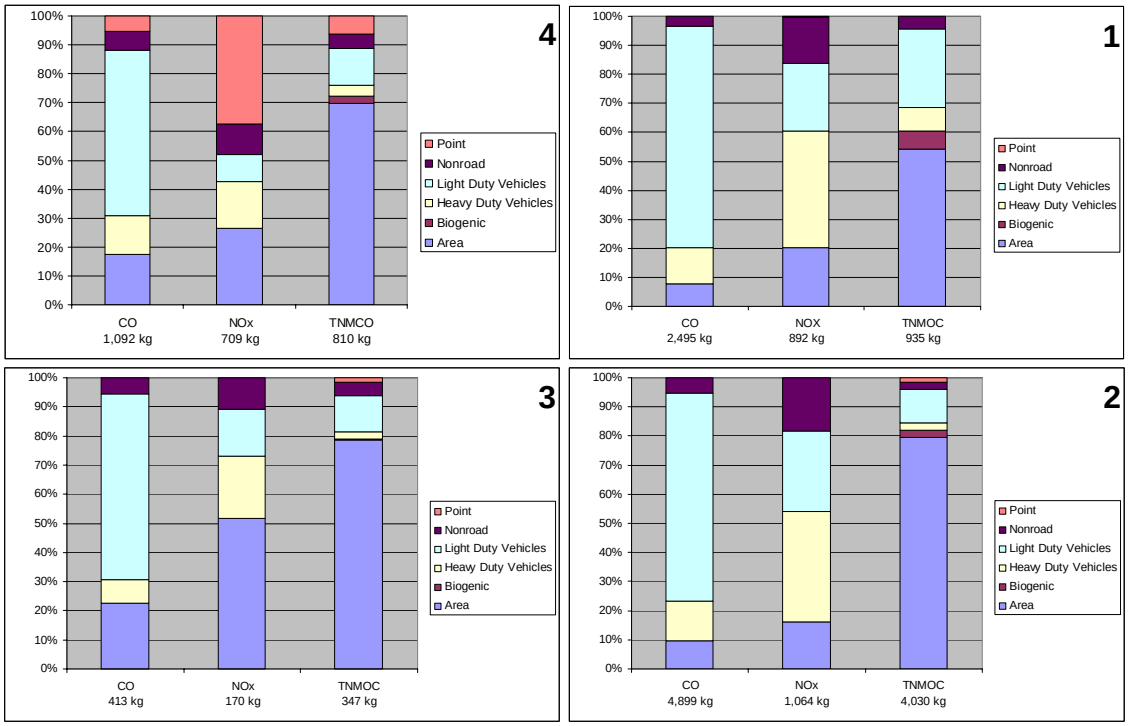

Figure 9. Emissions by wind quadrant for the Madera Station (0500-1000 PDT).

Parlier (PLR)

The Parlier site is located in a rural area about 30 km southeast of Fresno. The emission inventory for the grid cells surrounding this site shows that area sources contribute over 90% of the total TNMOC emissions in each quadrant, and point sources contribute almost half of the NO_x emissions in quadrant 3. Non-road mobile sources are a significant source of NO_x in quadrants 1 and 2 (see **Figure 10**). Overall emissions densities are highest in quadrant 2.

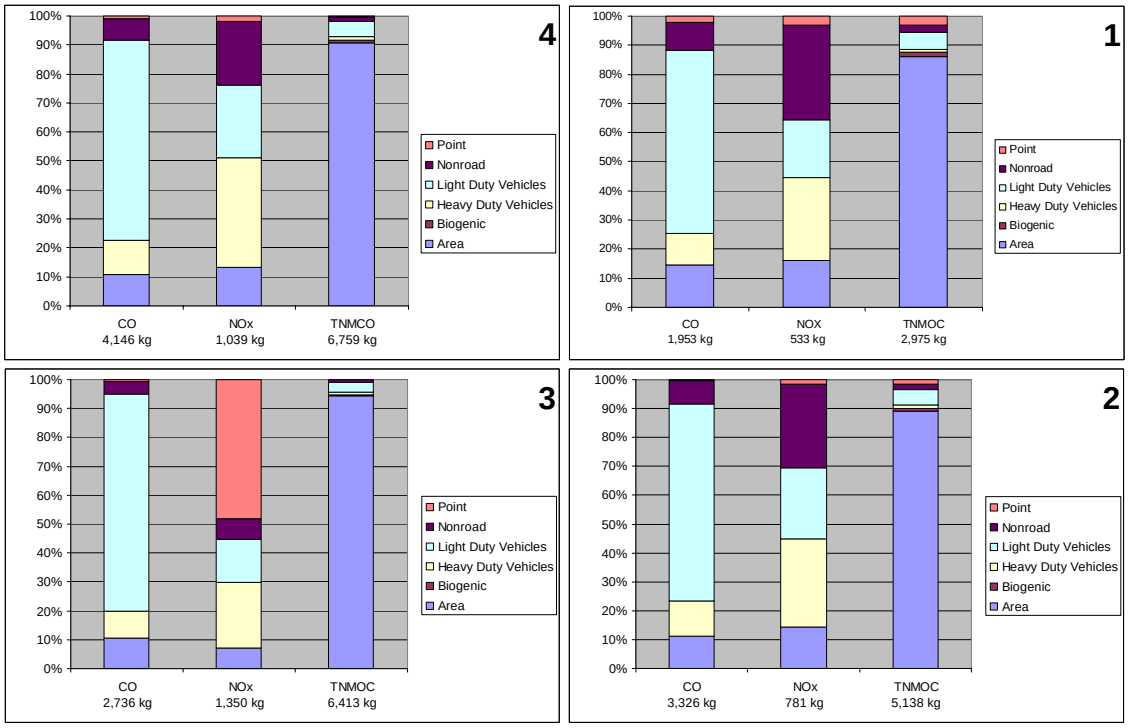

Figure 10. Emissions by wind quadrant for the Parlier Station (0500-1000 PDT).

Bakersfield – Golden State (BGS)

The Golden State site is located in a commercial area near downtown Bakersfield. The emission inventory for the grid cells surrounding this site shows that emission densities are similar in magnitude and source composition in each wind quadrant. Mobile sources are the most significant source of CO and NO_x in all quadrants, while area sources contribute about 70% of the TNMOC emissions in all quadrants (see **Figure 11**).

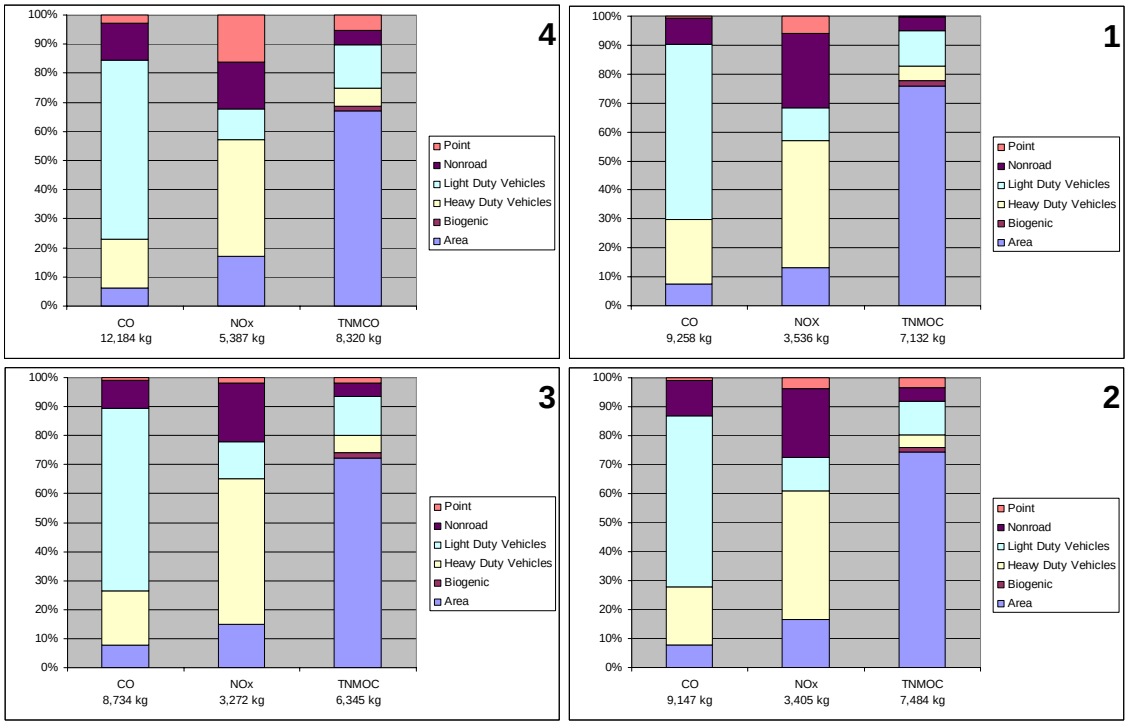

Figure 11. Emissions by wind quadrant for the Bakersfield Golden State Station (0500-1000 PDT).

Bakersfield – California Avenue (BAC)

The California Avenue site is located just south of the Kern River in a mixed commercial/residential area of Bakersfield. Across the river is an oil refinery, about 2 km northwest of the site. The emission inventory for the grid cells surrounding this site shows that area sources make up at least 65% of the TNMOC emissions in all quadrants, with point sources contributing about 10% of the TNMOC emissions in quadrants 1, 3, and 4. On-road mobile sources are the most significant source of CO and NO_x in all quadrants, and overall emission densities are highest in quadrants 1 and 2 (see **Figure 12**).

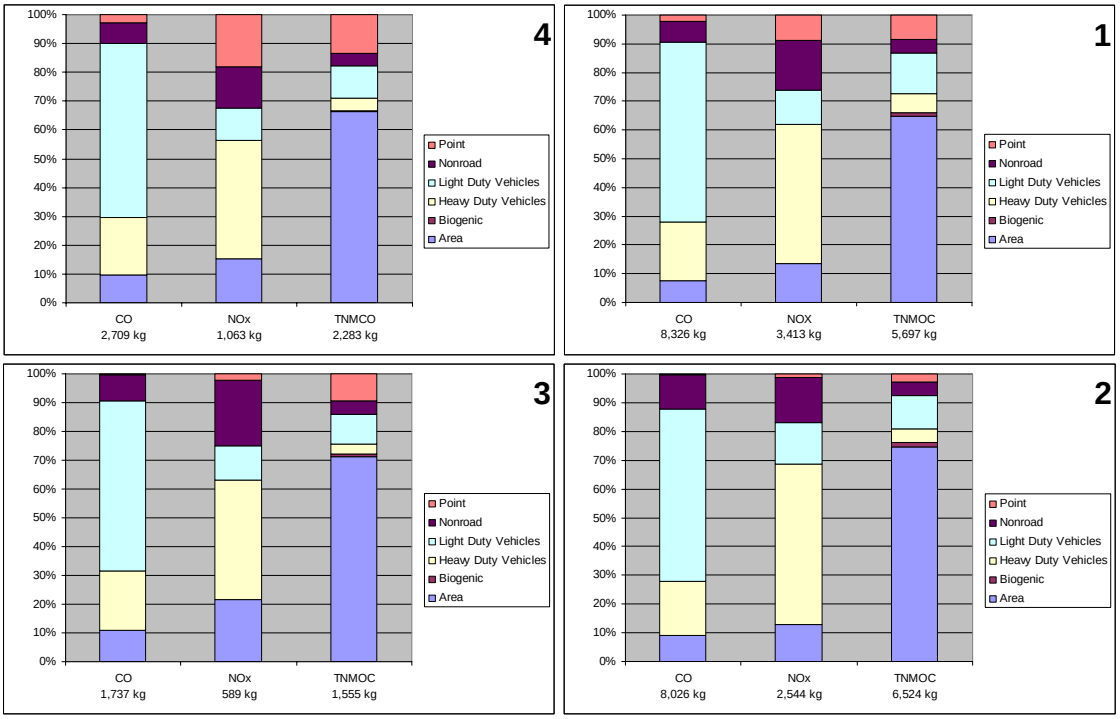

Figure 12. Emissions by wind quadrant for the Bakersfield California Avenue Station (0500-1000 PDT).

Arvin (ARV)

The Arvin site is located in a rural part of Kern County about 25 km southeast of Bakersfield. The emission inventory for the grid cells surrounding this site shows that biogenic sources contribute about 90% of the TNMOC emissions in quadrants 1 and 2, while area sources are the most significant source of TNMOC in quadrants 3 and 4. Area sources also contribute significantly to the NO_x emissions inventory in quadrants 1 and 3 (see **Figure 13**).

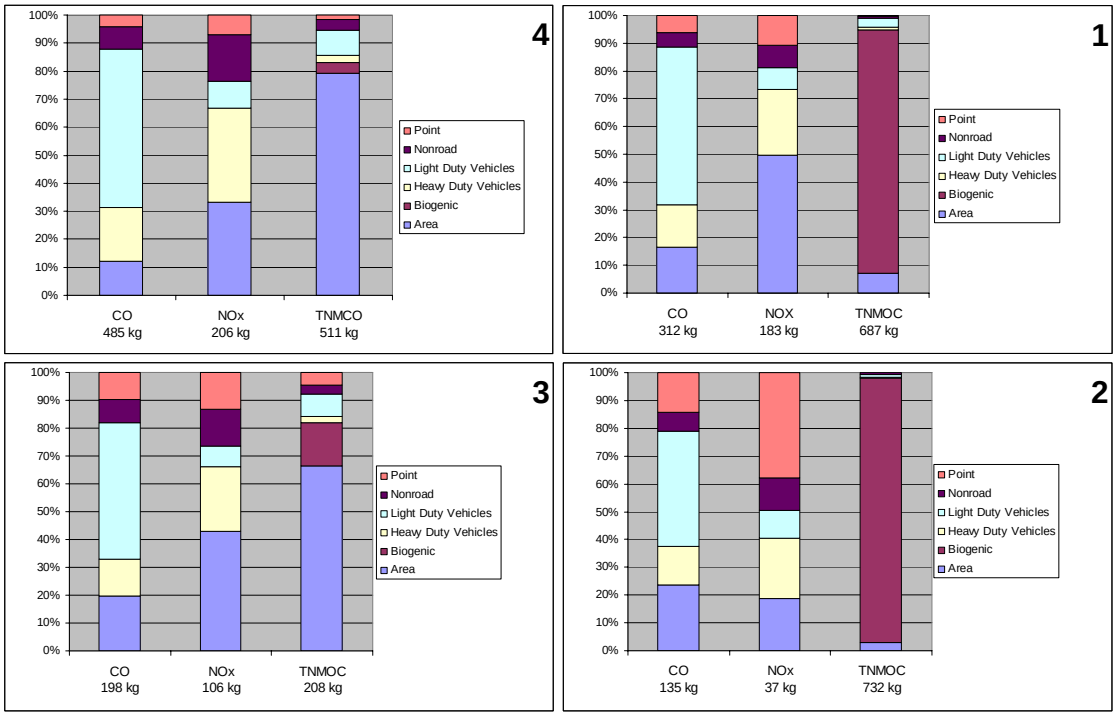

Figure 13. Emissions by wind quadrant for the Arvin Station (0500-1000 PDT).

Shafter (SHA)

The Shafter site is located in Kern County about 25 km northwest of Bakersfield. The immediate vicinity of the site is a mixed commercial/residential area, but these land use types give way to agricultural lands within about 2 km of the monitoring site. The emission inventory for the grid cells surrounding this site shows that area sources contribute about 70% of the TNMOC and about 30% of the NO_x emissions in quadrants 1 and 2, while non-road mobile sources are also a significant NO_x source in quadrants 1 and 4 (see **Figure 14**). Overall emission densities are highest in quadrants 1 and 2.

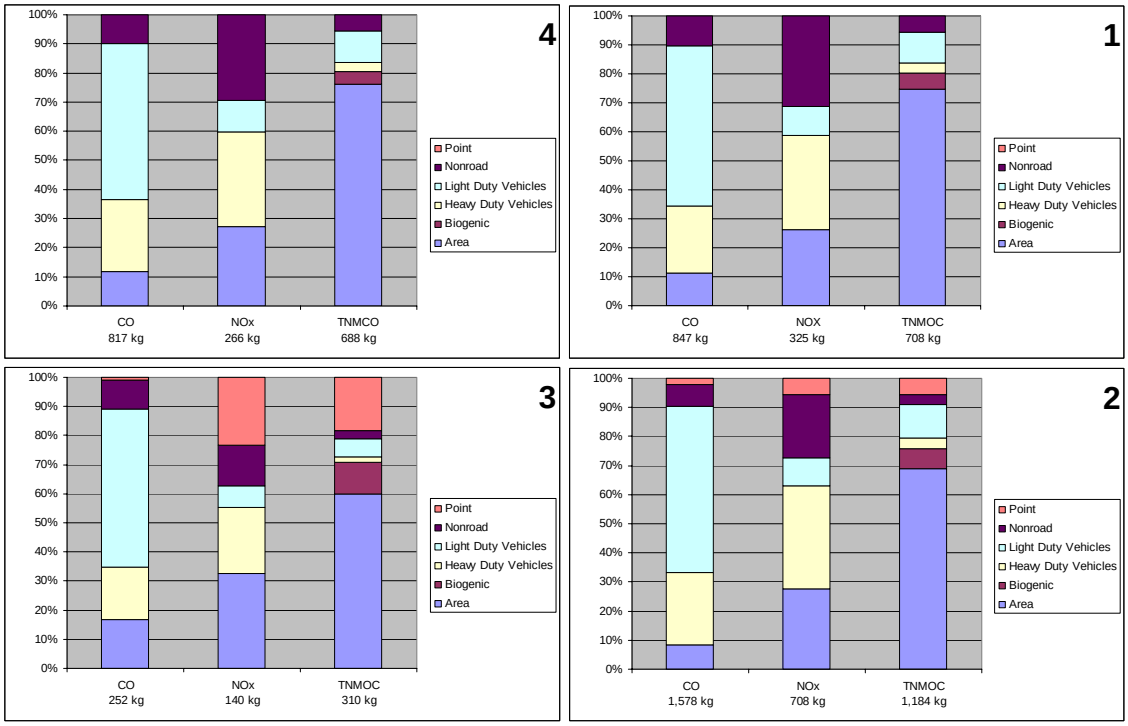

Figure 14. Emissions by wind quadrant for the Shafter Station (0500-1000 PDT).

Turlock (TSM)

The Turlock site is located in an urbanized area of the northern San Joaquin Valley about 20 km southeast of Modesto. The immediate vicinity of the site is a largely residential area, giving way to agricultural lands within a few kilometers of the monitoring site. The emission inventory for the grid cells surrounding this site shows that area sources contribute at least 80% of the TNMOC emissions in all quadrants, while on-road and non-road mobile sources are the most significant NO_x source in all quadrants (see **Figure 15**). Overall emission densities are highest in quadrants 1 and 4, which contain the city of Turlock.

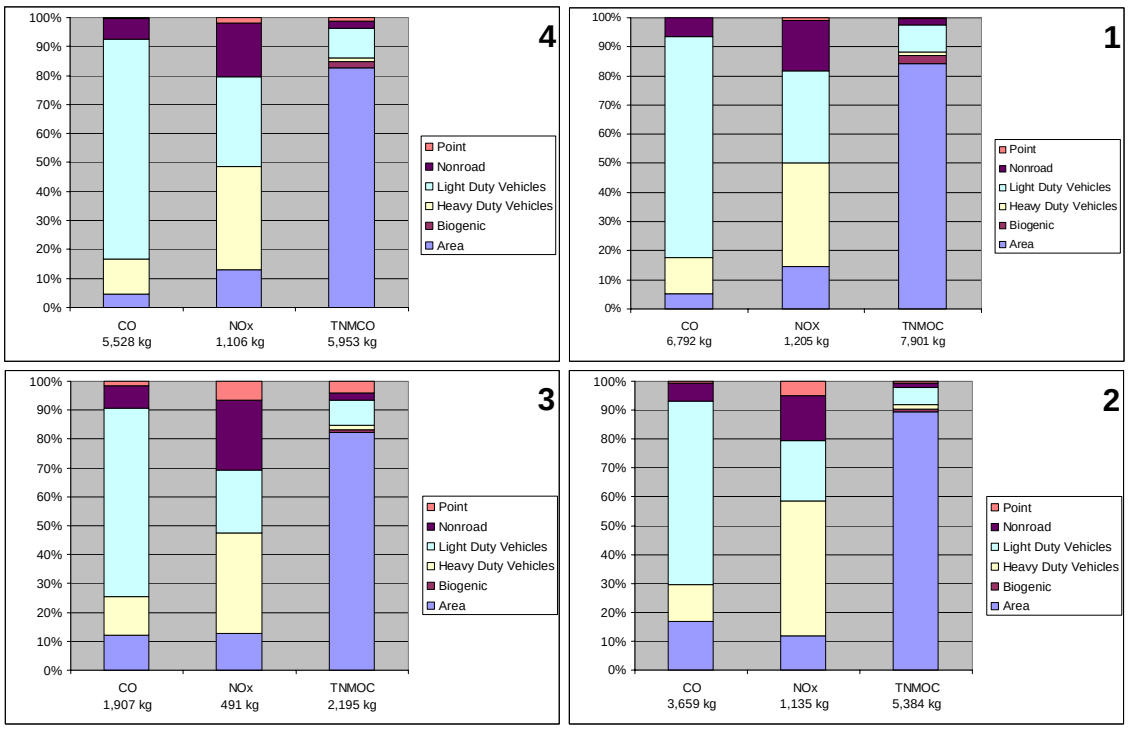

Figure 15. Emissions by wind quadrant for the Turlock Station (0500-1000 PDT).

Uncertainty Issues

Understanding the uncertainties associated with comparisons of ambient- and emission-inventory-derived pollutant ratios is essential to assess the suitability of top-down evaluation analyses. Three general categories of uncertainty issues are associated with top-down emissions reconciliation analyses: (1) accuracy of the emission inventory, (2) accuracy of the ambient concentration measurements, and (3) suitability of comparisons.

Emission Inventory Uncertainties

To compare ambient pollutant ratios to emission inventory ratios, it is important to accurately characterize, to the extent possible, the magnitude, spatial distribution, chemical composition, and diurnal pattern of emissions. Uncertainties and inaccuracies associated with

emission inventory data generally stem from (1) emissions estimation techniques and (2) emissions processing techniques. Inaccuracies and uncertainties associated with emissions estimation techniques include misclassification or exclusion of major emissions sources, the use of incorrect emissions activity data, the use of incorrect emission factors, and the use of incorrect chemical speciation profiles.

To perform an emission inventory evaluation, emissions estimates must be spatially and temporally resolved for the region surrounding the ambient monitoring sites. The methods used to disaggregate annual average countywide total emissions estimates into gridded, hourly data can introduce inaccuracies in the emission inventory data. Spatial surrogate data that are not representative of the locations of emissions sources, and temporal profiles that are not representative of the monthly, weekly, and diurnal distribution of emissions source activity can result in misrepresentation of the geographic location of emissions sources and diurnal activity patterns for sources within the vicinity (grid cells) of the ambient monitor.

Ratios of individual chemical species can be used to estimate the chemical composition of the emission inventory and specifically the different source types. Incorrect assignments of speciation profiles to emissions sources and/or speciation profiles that do not represent the chemical source composition can create emission inventory uncertainties.

Ambient Measurement Uncertainties

Uncertainties associated with ambient measurements include the influence of instrument detection limits, precision of measurements, sampling and handling losses, and reporting errors. Prior to conducting an emission inventory evaluation, the ambient data measurement methods should be assessed to ensure that the collection methods yield adequate data for this type of analysis. Furthermore, the ambient data sets intended for use must be quality-assured to eliminate invalid samples. For this study, ambient data were validated as part of an earlier project conducted by STI (Chinkin et al., 2006).

Uncertainties Associated with the Comparisons

Uncertainties associated with the comparison of ambient and emission inventory data arise from the spatial and temporal matching of ambient and emission inventory data, meteorological factors, and atmospheric reactions. To minimize differences between ambient- and emission inventory-derived ratios due to a mismatch in time and space, it is best to use emissions estimates as close to the vintage of the ambient data as is practical. For this study, emissions estimates representative of summer 2000 were compared to ambient data for the same time period.

A major premise of the top-down evaluation is that only monitoring sites and sampling periods dominated by fresh emissions are considered in the analysis. Temporal uncertainties may be caused by early morning ambient ratios that include carryover emissions in which TNMOC and/or NO_x have been preferentially removed by chemical conversion overnight. Spatial uncertainties may arise due to different influences of surface and aloft emissions. For example, TNMOC, CO, and NO_x emissions from nearby elevated sources may be injected aloft

and, as a result, may not mix into the surface air sample containing TNMOC, CO, and NO_x emissions.

Meteorological factors such as wind speed, direction, and mixing depth determine the spatial distribution of emissions and, thus, which emissions are sampled. For example, emissions from non-homogenous area and/or motor vehicle sources might be incompletely sampled at a given site. Atmospheric reactions modify the species distributions and mass of midday and afternoon ambient samples. Thus, comparisons from midday and afternoon periods are likely to be less reliable than morning comparisons.

OVERVIEW OF KEY FINDINGS

Detailed results by analysis method and ambient monitoring site are provided in the sections that follow.

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 urbanized areas. For two 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), two are "Tier 3" sites with relatively low emission densities in the area around the monitoring site.

Figures 16 through 19 show TNMOC/NO_x ratios by wind quadrant[4] and day of week[5] for sites in the Sacramento area. Overall, agreement between ambient- and emissions-derived ratios at these sites is significantly better on weekdays than weekend days. Since the Sacramento area sites are heavily influenced by on-road mobile source emissions, this 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 16), ambient-derived TNMOC/NO_x ratios are slightly (20-30%) higher than emissions-derived ratios in wind quadrants 1 and 3, while the emissions-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 17), ambient- and emissions-derived TNMOC/NO_x ratios agree to within 60% at all wind quadrants. For wind quadrants with at least 5 ambient data

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

points, agreement is closest in quadrant 4, which has the highest overall emission density. At the Sacramento Natomas site (see Figure 18), ambient- and emissions-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 emissions-derived TNMOC/NO_x ratios is poorest at the Sacramento Del Paso Manor site (see Figure 19), though the ratios agree to within 80% at all wind quadrants except quadrant 3. Further investigation showed that there are two large shopping centers about 1 km southwest of the SDP site (see **Figure 20**), so the low TNMOC/NO_x ratio in the emission inventory may be the result of a failure to capture hot soak emissions[6] from vehicles parked in this shopping area.

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

[6] CCOS on-road mobile source emissions are spatially allocated with the Direct Travel Impact Model (DTIM), which assigns hot soak emissions to the grid cell containing the centroid of a given travel analysis zone (TAZ).

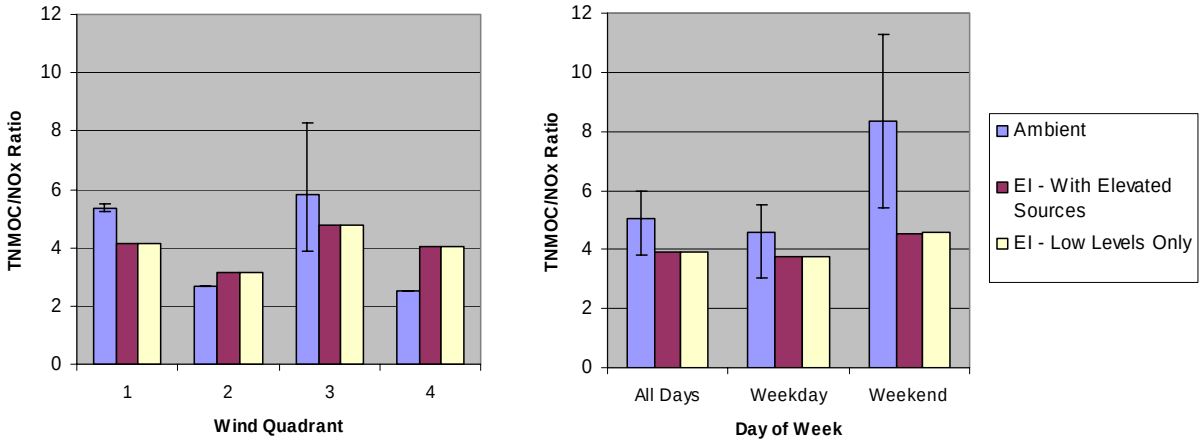

Figure 16. TNMOC/NO_x ratios by wind quadrant and day of week for the Elk Grove site.

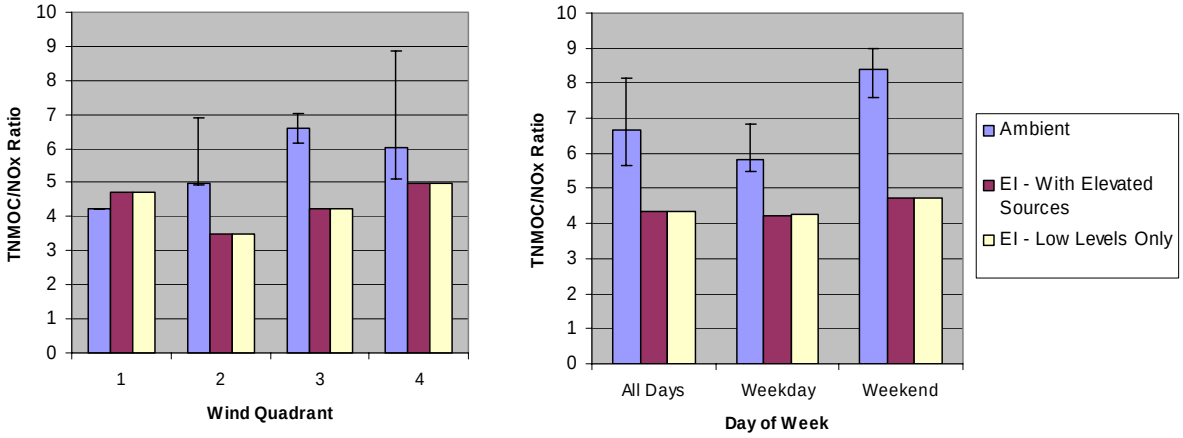

Figure 17. TNMOC/NO_x ratios by wind quadrant and day of week for the Folsom site.

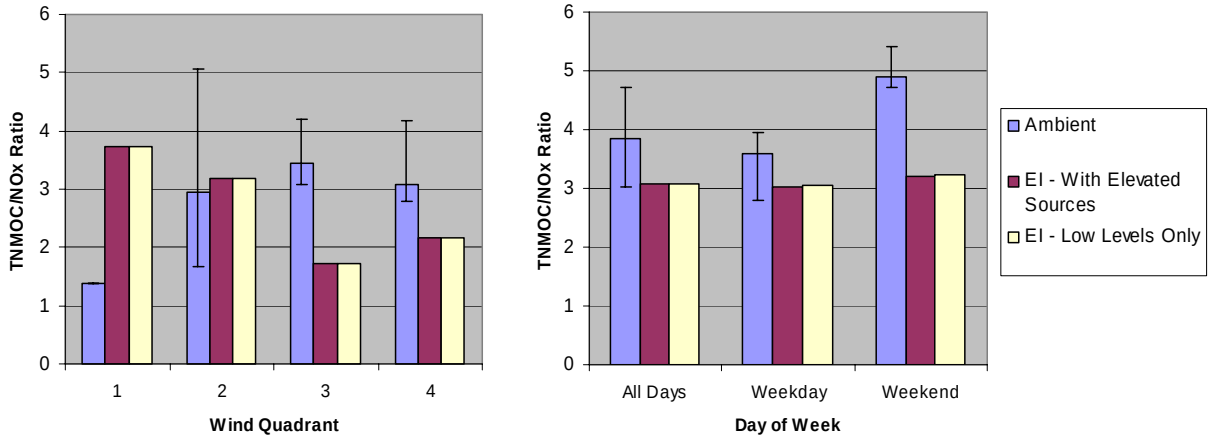

Figure 18. TNMOC/NO_x ratios by wind quadrant and day of week for the Sacramento Natomas site.

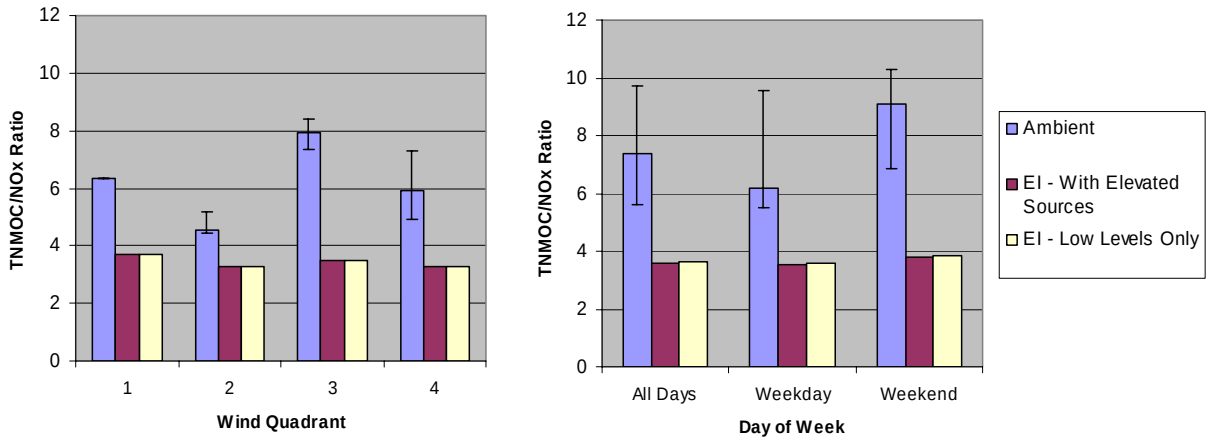

Figure 19. TNMOC/NO_x ratios by wind quadrant and day of week for the Sacramento Del Paso Manor site.

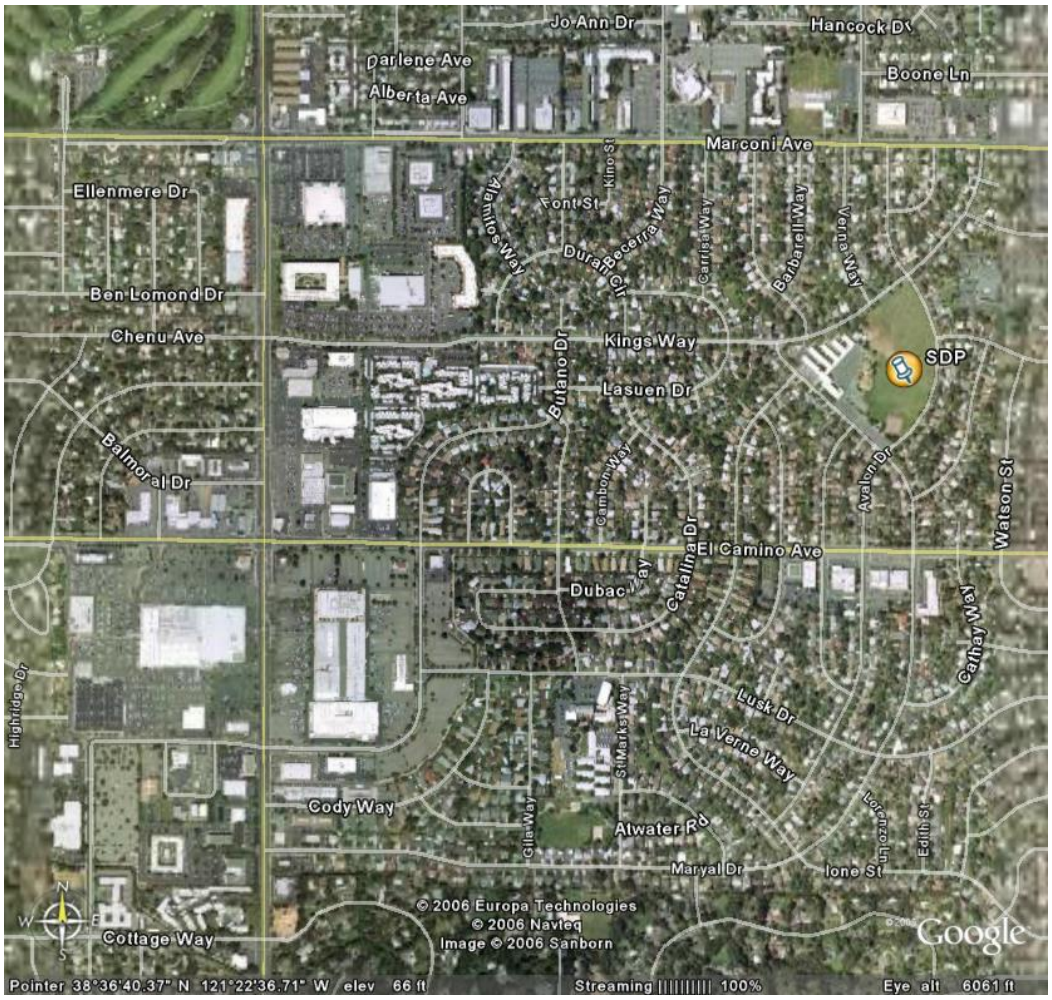

Figure 20. Wind quadrant 3 of the Sacramento Del Paso Manor site.

Figures 21 through 24 show TNMOC/NO_x ratios by wind quadrant for the Fresno area. Unlike the Sacramento area sites, agreement between ambient- and emissions-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), emissions-derived TNMOC/NO_x ratios are within 50% of emissions-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 emissions-derived ratio (see Figures 21 and 22). 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 emissions-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 emissions-derived ratios. Quadrant 3 has the poorest agreement between ambient- and emissions-derived ratios, and this quadrant contains the town of Selma and a large winery (see **Figure 25**) that could not be identified in the point source inventory provided by ARB.

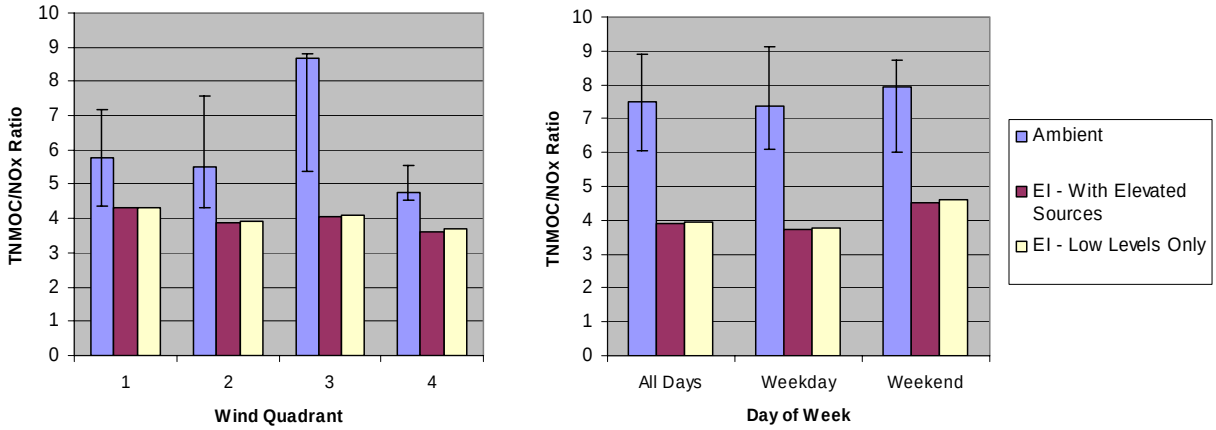

Figure 21. TNMOC/NO_x ratios by wind quadrant and day of week for the Clovis site.

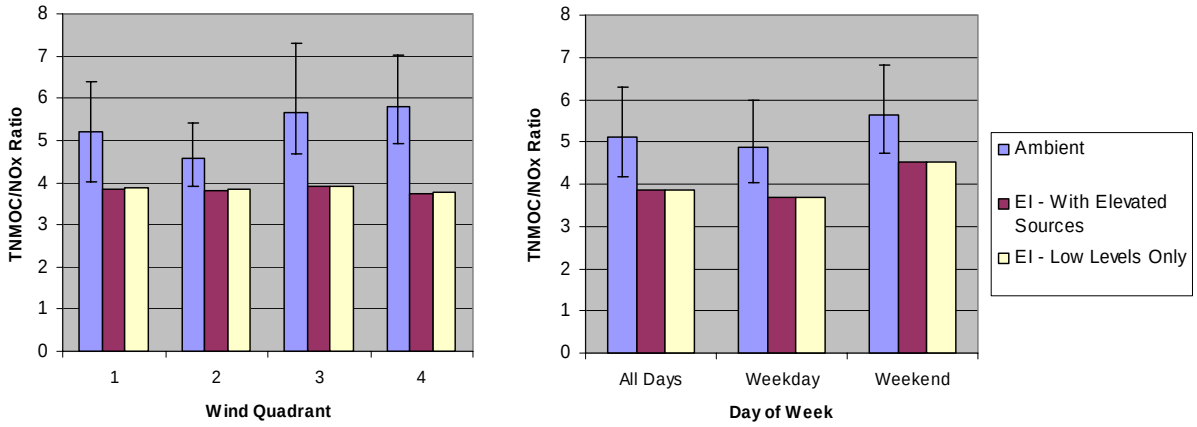

Figure 22. TNMOC/NO_x ratios by wind quadrant and day of week for the Fresno First Street site.

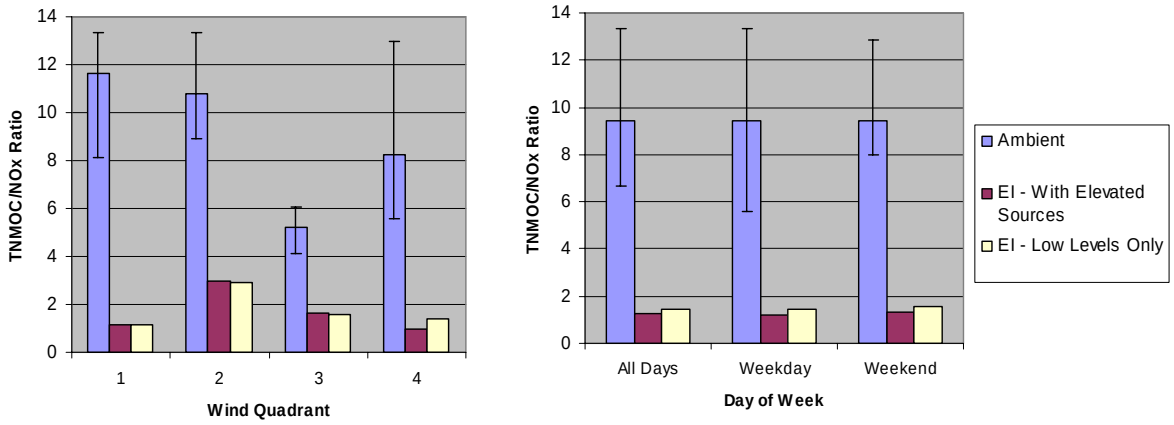

Figure 23. TNMOC/NO_x ratios by wind quadrant and day of week for the Madera site.

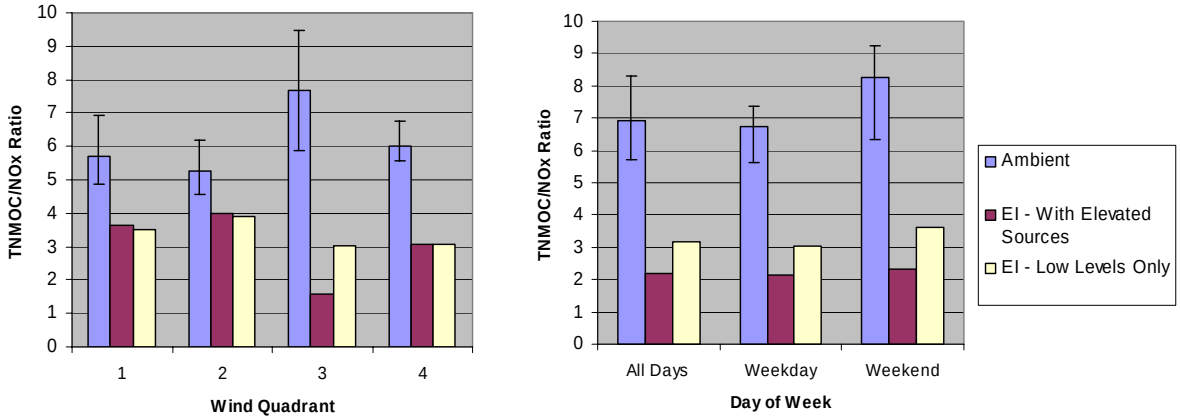

Figure 24. TNMOC/NO_x ratios by wind quadrant and day of week for the Parlier site.

Figure 25. Unidentified winery in wind quadrant 3 of the Parlier site.

Figures 26 through 28 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 emissions-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 sources emissions are somewhat higher in quadrant 4, where there is an oil refinery and other industrial sources.

At the two rural sites in Kern County (Arvin and Shafter), significant differences also exist between ambient- and emissions-derived TNMOC/NO_x ratios. At the Arvin site, the ratios agree closely for all wind quadrants except for 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 emissions-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 being influenced primarily by transported polluants rather than local sources.

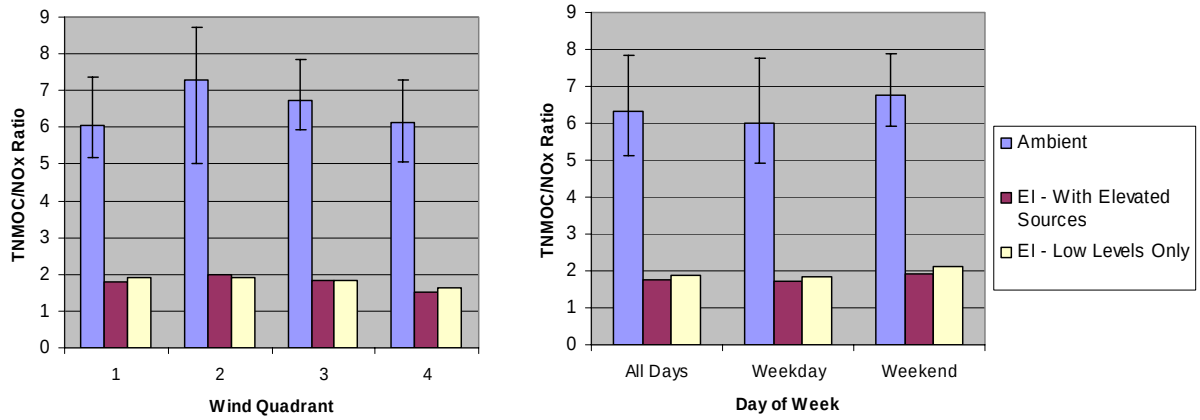

Figure 26. TNMOC/NO_x ratios by wind quadrant and day of week for the Bakersfield Golden State site.

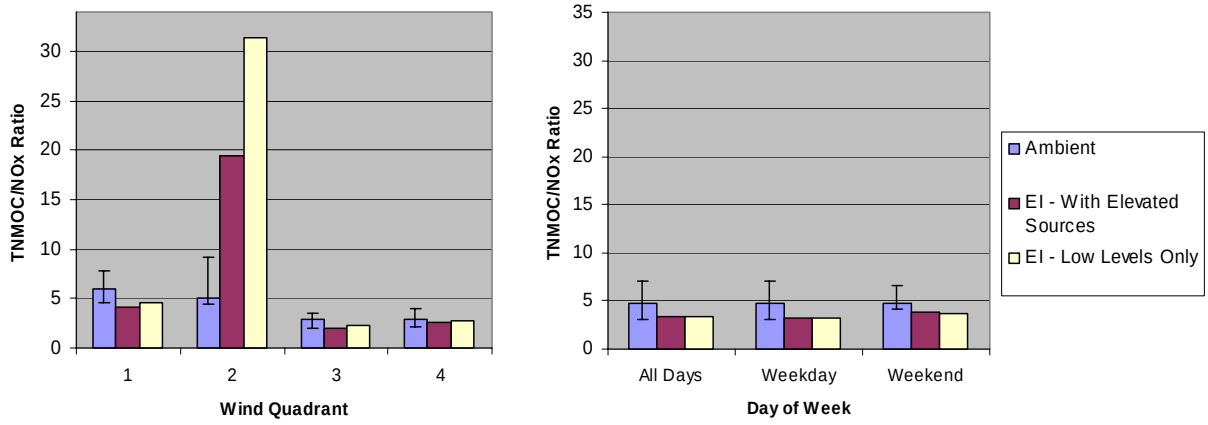

Figure 27. TNMOC/NO_x ratios by wind quadrant and day of week for the Arvin site.

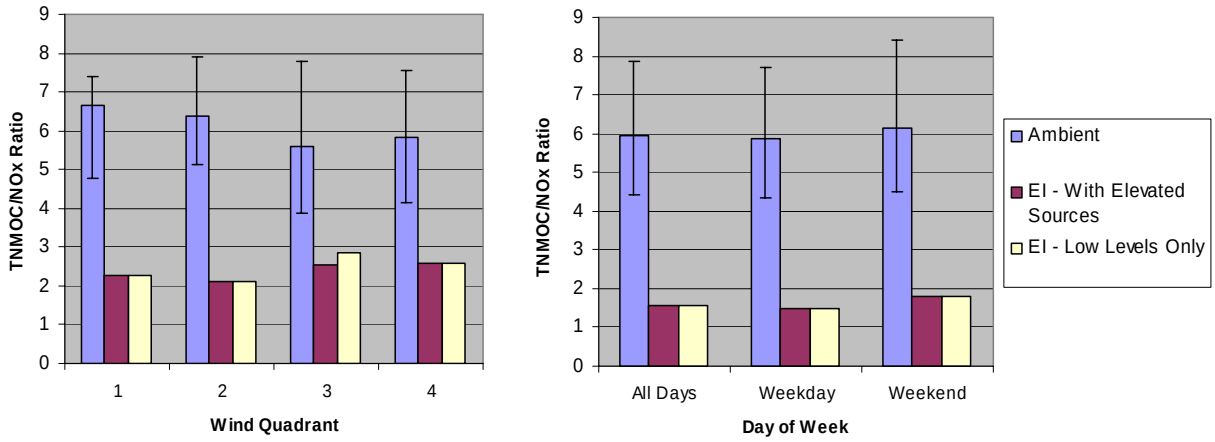

Figure 28. TNMOC/NO_x ratios by wind quadrant and day of week for the Shafter site.

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 ratios calculated with elevated sources excluded. The emission 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 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 29 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-derived ratios closely approximate ambient-derived ratios overall, with weekday ratios showing closer agreement than ratios for weekend days.

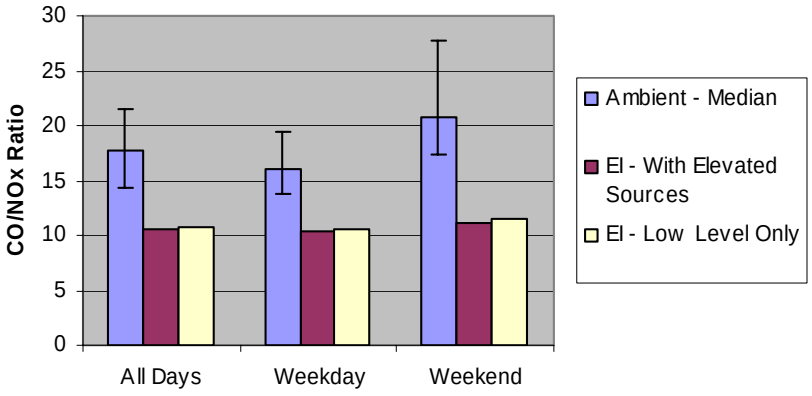

Figure 29. CO/NO_x ratios by day of week for the San Jose 4th Street site.

Figures 30 and 31 show CO/NO_x ratios by wind quadrant and day of week for Sacramento sites. At the Natomas site, emissions-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 emissions-derived ratio. According to the emissions inventory, 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, emissions-derived CO/NO_x ratios agree very closely with ambient-derived ratios (i.e., within 10-60%) for all wind quadrants and days of week (see Figure 30). At this site, the emissions-derived ratios correlate with ambient-derived ratios as closely as could be expected given the limitations of the comparison techniques used.

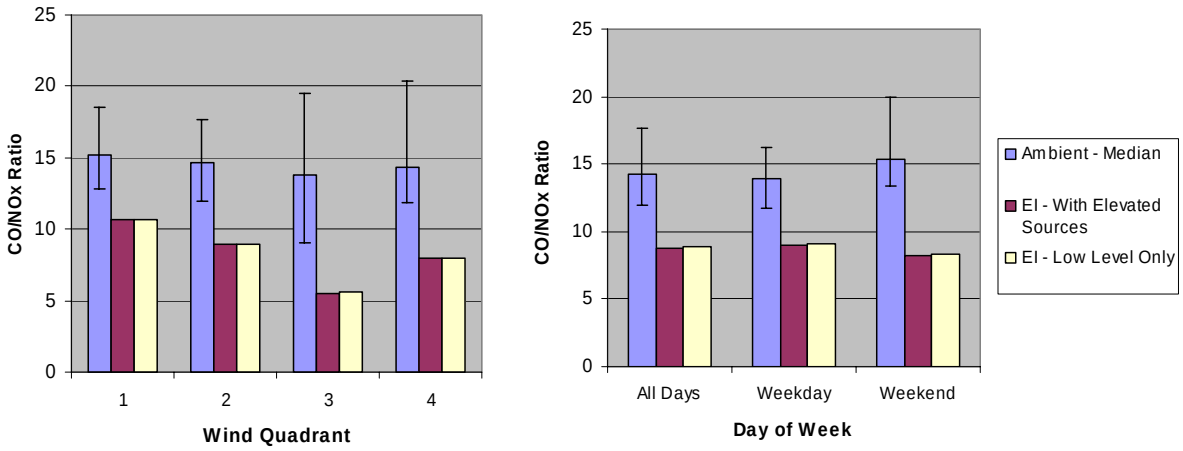

Figure 30. CO/NO_x ratios by wind quadrant and day of week for the Sacramento Natomas site.

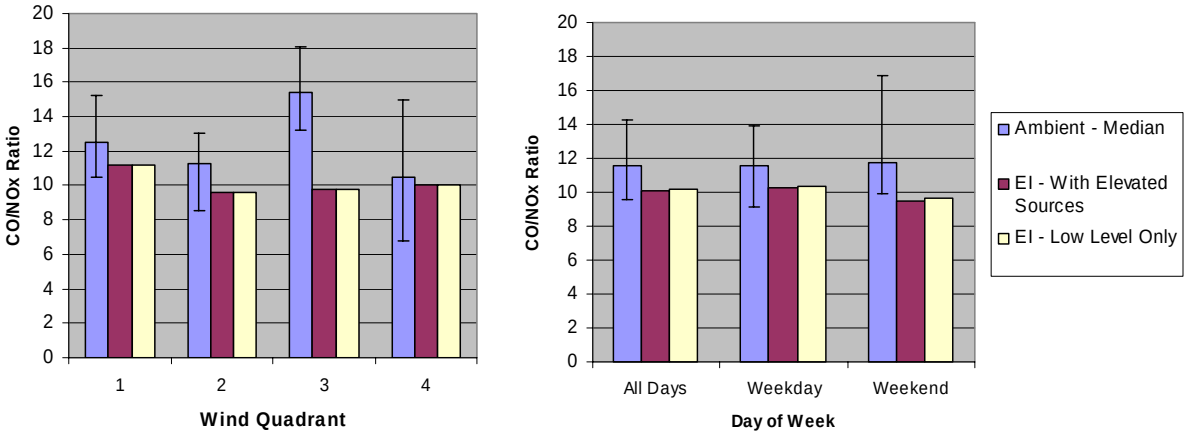

Figure 31. CO/NO_x ratios by wind quadrant and day of week for the Sacramento Del Paso Manor site.

Figures 32 and 33 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 emissions-derived ratios for all wind quadrants except quadrant 2, where the ambient-derived ratio is only 60% higher than the emissions-derived ratio. Ambient- and emissions-derived CO/NO_x ratios show slightly closer agreement on weekend days than weekdays at the Clovis site (see Figure 32).

At the Fresno First Street site, emissions-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 emissions-derived ratio. Ambient- and emissions-derived CO/NO_x ratios show slightly closer agreement on weekend days than weekdays at the First Street site (see Figure 33).

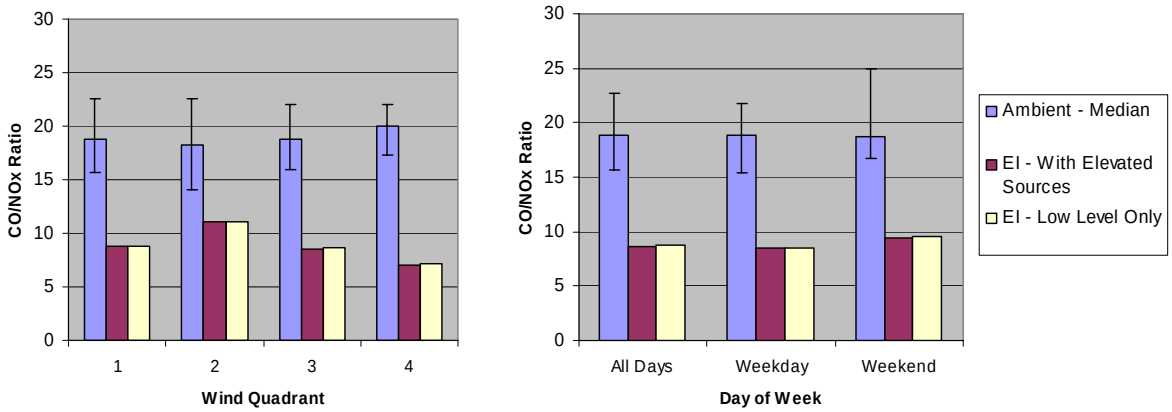

Figure 32. CO/NO_x ratios by wind quadrant and day of week for the Clovis site.

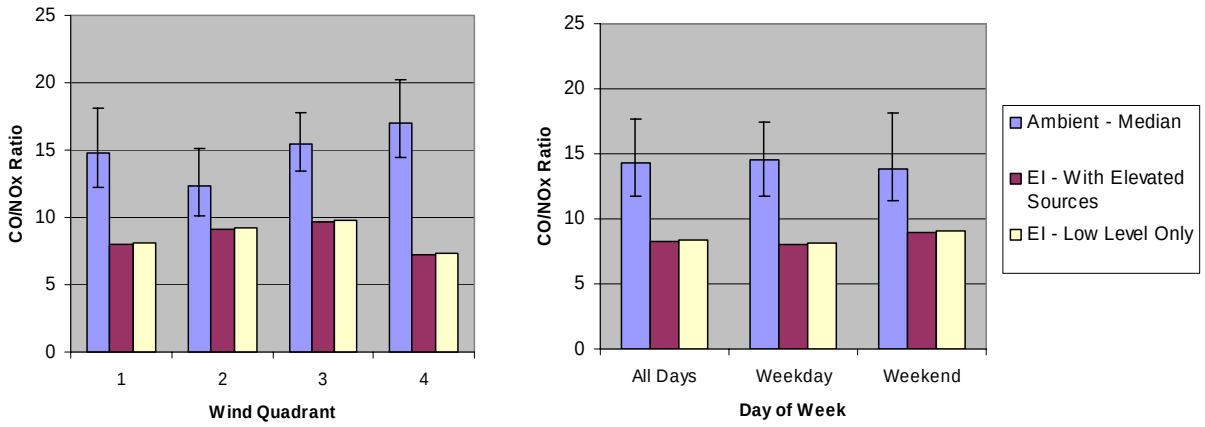

Figure 33. CO/NO_x ratios by wind quadrant and day of week for the Fresno First Street site.

Figures 34 and 35 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, emissions-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 emissions-derived ratios in quadrants 3 and 4 (see Figure 34). 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, emissions-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 35).

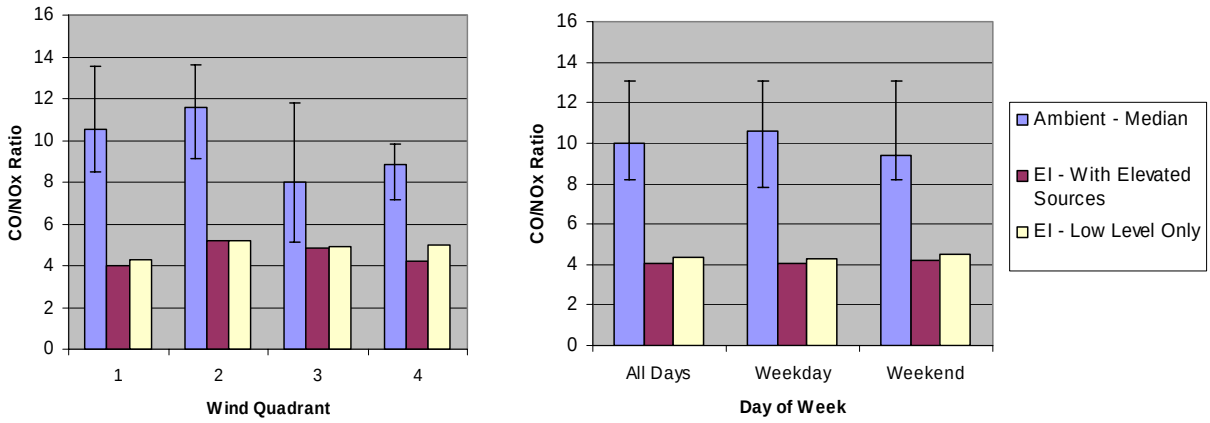

Figure 34. CO/NO_x ratios by wind quadrant and day of week for the Bakersfield California Avenue site.

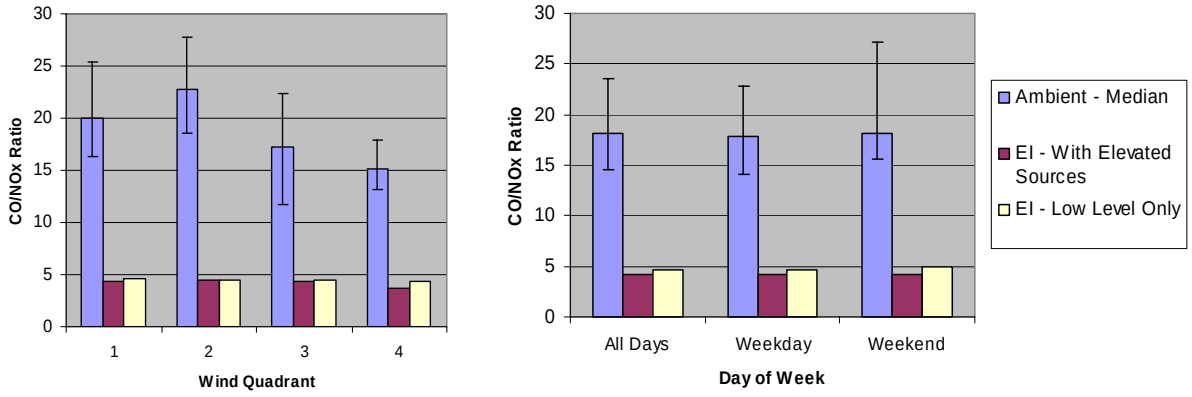

Figure 35. CO/NO_x ratios by wind quadrant and day of week for the Bakersfield Golden State site.

Figure 36 shows CO/NO_x ratios by wind quadrant and day of week for the Turlock site in Stanislaus County. Ambient-derived CO/NO_x ratios are consistently two to three times higher than emissions-derived ratios for this site.

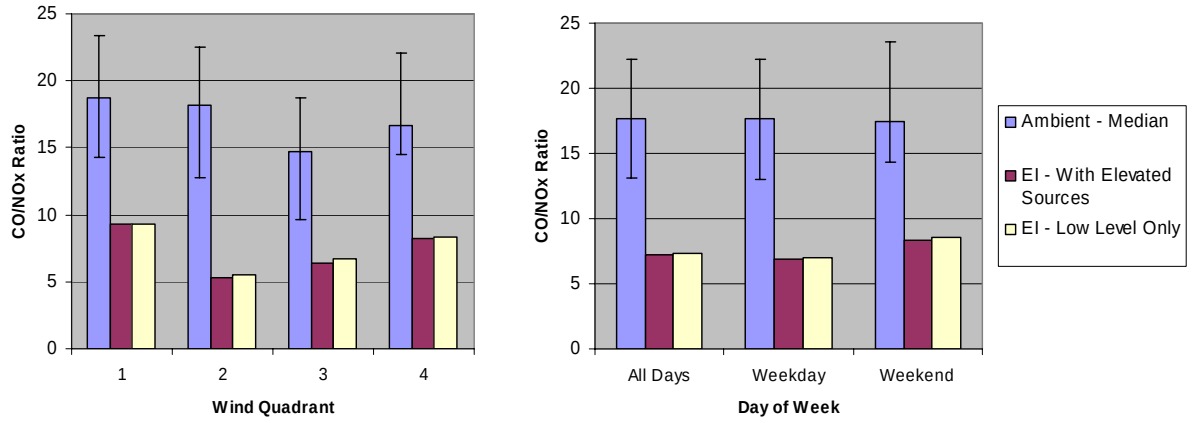

Figure 36. CO/NO_x ratios by wind quadrant and day of week for the Turlock site.

Individual Species Ratios

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 emissions-derived pollutant ratios for 13 monitoring sites in the CCOS modeling domain. Overall, the emissions-derived ratios show good agreement with the ambient-derived ratios, though a few significant discrepancies do exist. The emissions-

derived acetylene/benzene ratios were in poor agreement with the ambient-derived ratios at the Sunol and Granite Bay sites. The emissions-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.

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.

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 over prediction is attributable to emissions from livestock waste. (In a related CCOS study, STI has discovered that significant amounts of livestock waste emissions are being spatially distributed across the CCOS modeling domain using 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 under-prediction 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 under-predicted in the emission inventory (though these more highly reactive compounds are under-predicted 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 37 through 40 show ambient- and emissions-derived hydrocarbon compositions for Sacramento area sites. In addition to the already identified issues with propane, ethane, and isoprene, note that emissions-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 37). The toluene fraction is somewhat higher in the emissions-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.

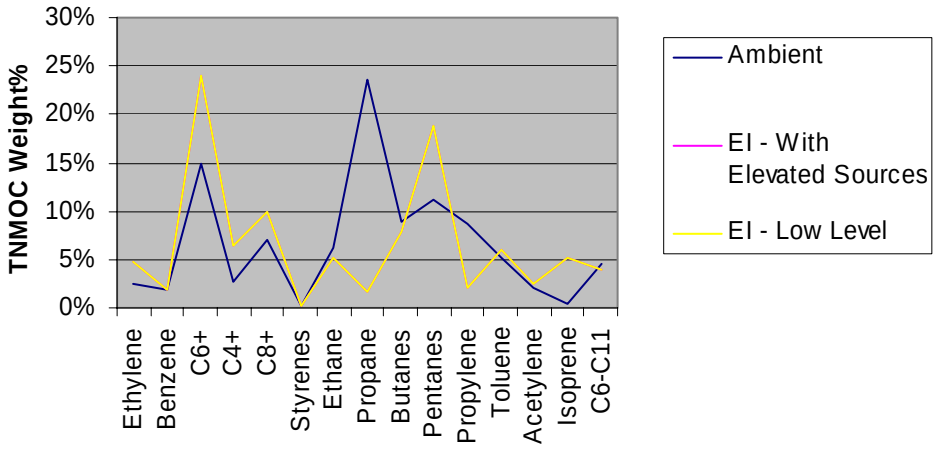

Figure 37. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Elk Grove site.

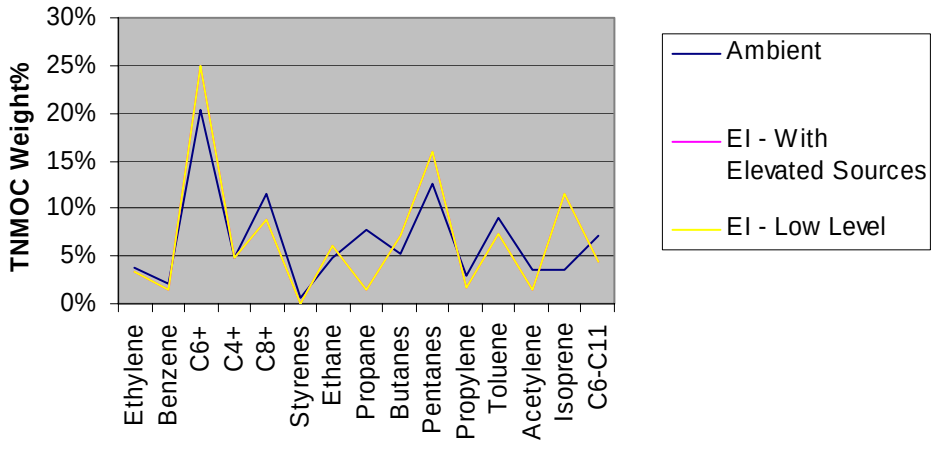

Figure 38. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Folsom site.

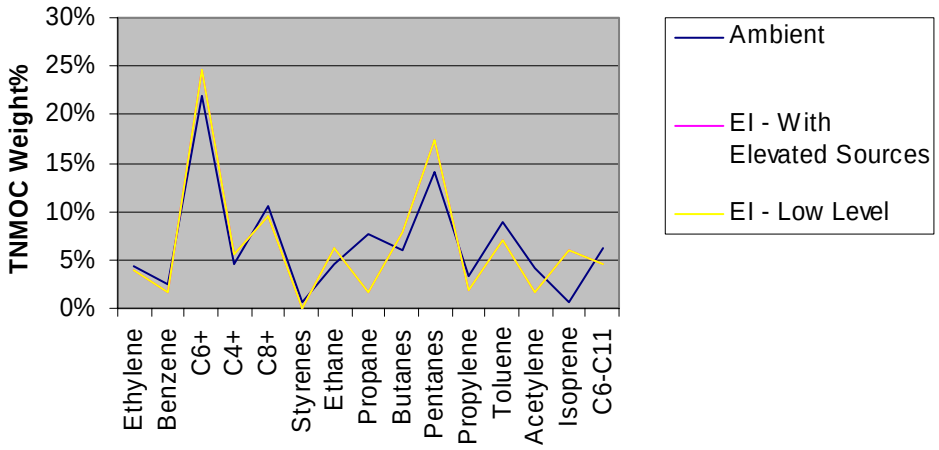

Figure 39. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Sacramento Natomas site.

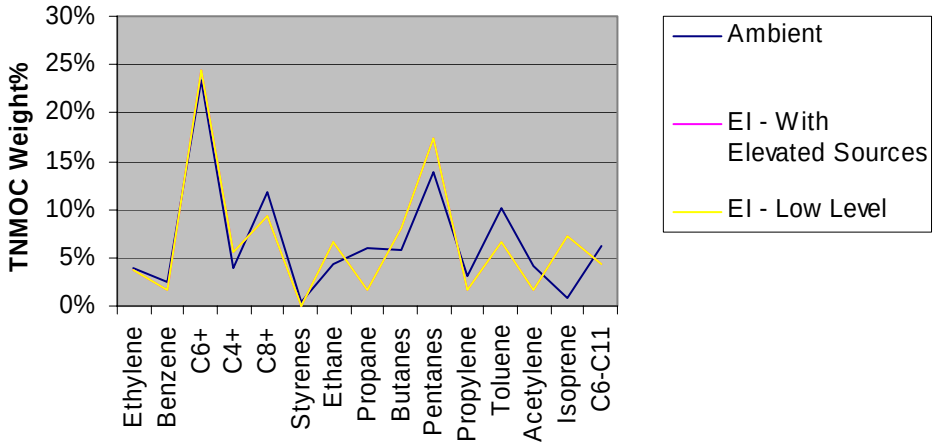

Figure 40. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Sacramento Del Paso Manor site.

Figures 41 through 43 show ambient- and emissions-derived hydrocarbon compositions for Fresno area sites. Again, agreement between the ambient- and emissions-derived data is excellent apart from the already-identified issues with ethane and propane, though C8+ aromatics and toluene are under-predicted in the emissions data at the Clovis site (see Figure 41).

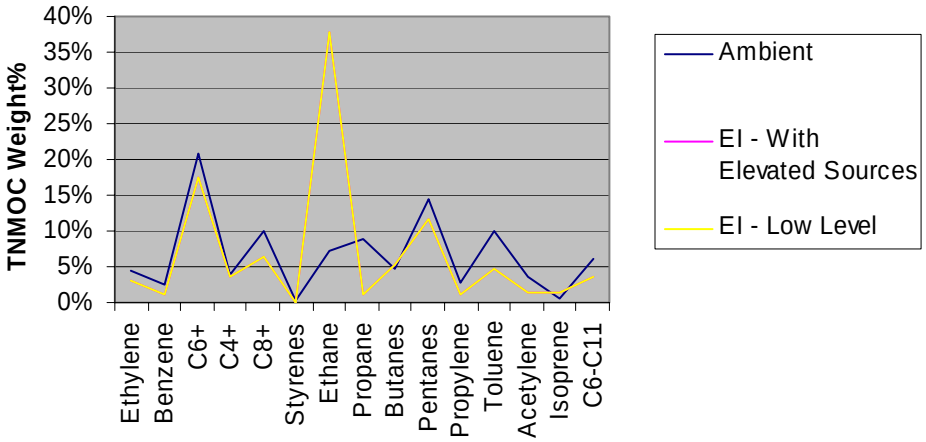

Figure 41. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Clovis site.

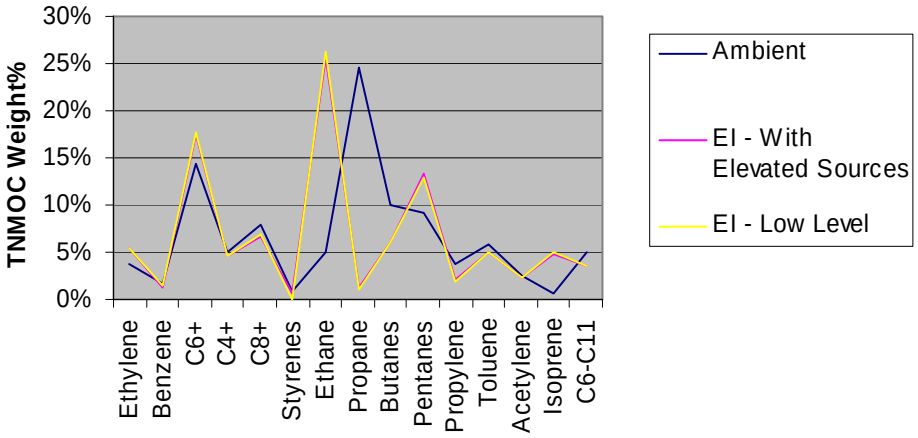

Figure 42. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Madera site.

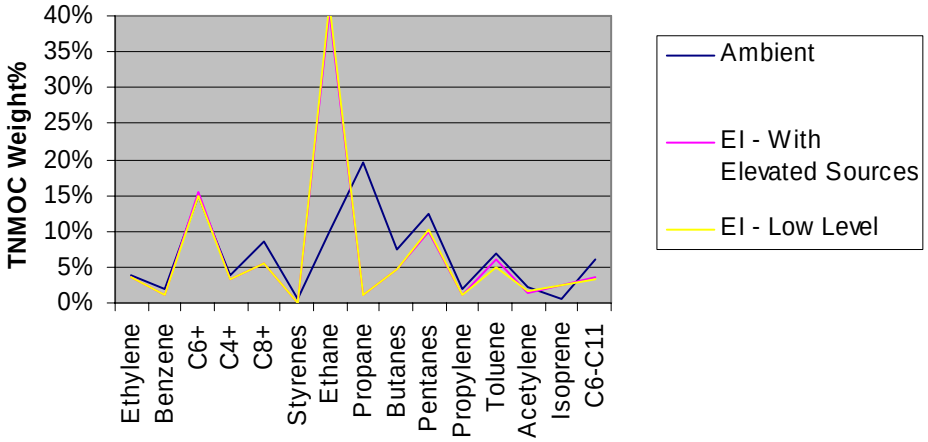

Figure 43. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Parlier site.

Figures 44 through 46 show ambient- and emissions-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 emissions-derived data show a spike in the fraction of isoprene and an under-prediction of several species groups, including C6+ alkanes, ethane, and pentanes (see Figure 44). The discrepancy between emissions- and ambient-derived isoprene fractions is more significant at Arvin than 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 are not crossing the ridgeline and impacting the monitoring site).

At the Bakersfield Golden State site, the emissions-derived fraction of pentanes is lower than the ambient-derived fraction, while the emissions-derived fraction of C6+ alkanes is lower than the ambient-derived fraction (see Figure 45). At the Shafter site, the emissions-derived fraction of butanes is higher than the ambient-derived fraction (see Figure 46).

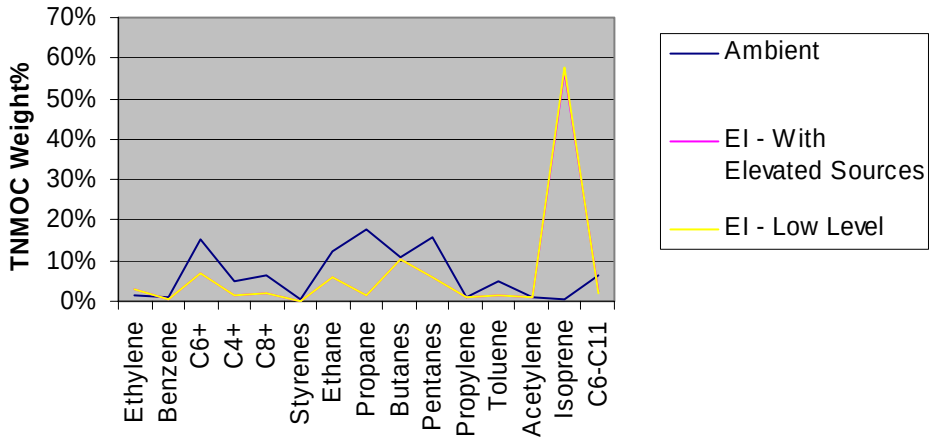

Figure 44. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Arvin site.

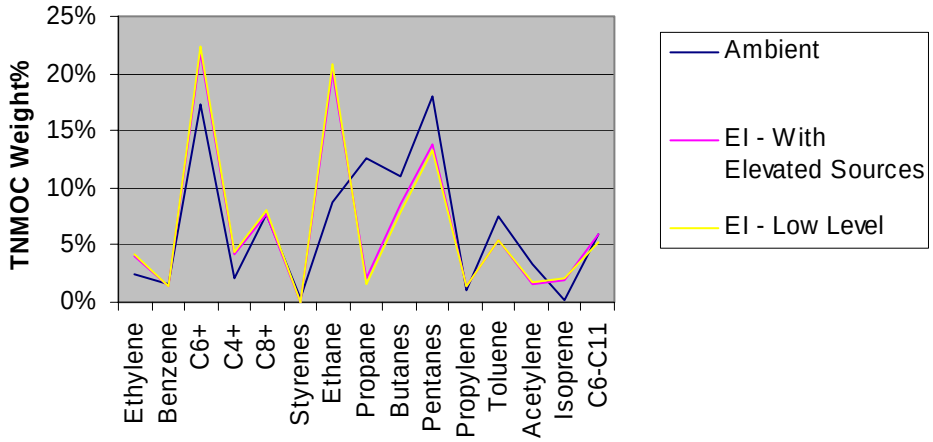

Figure 45. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Bakersfield Golden State site.

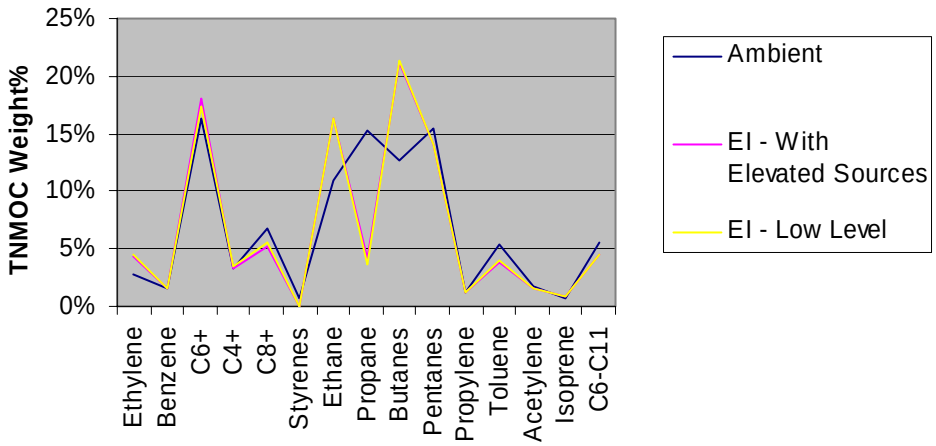

Figure 46. Comparison of 0500-1000 PST ambient- and emission inventory-derived TNMOC compositions for the Shafter site.

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 47** presents a series of comparisons between ambient- and emissions-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 emissions-derived ratios agree much more closely with the ambient data than in past years.

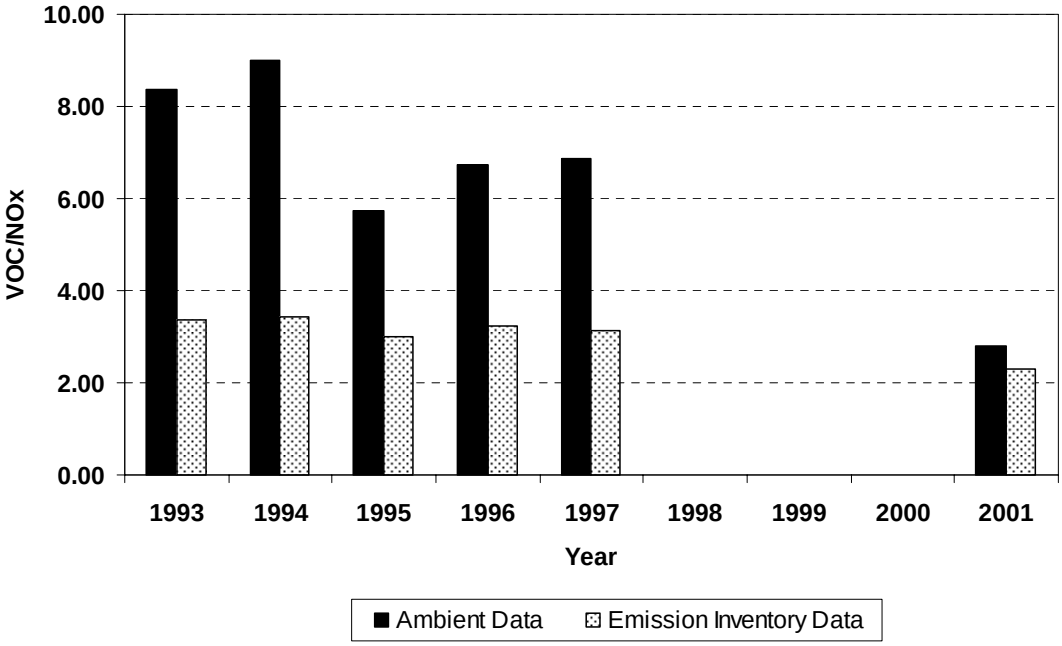

Figure 47. Emission inventory- and ambient-derived VOC/NO_x ratios at Los Angeles North Main during summer mornings.

A similar pattern can be seen in emissions reconciliation work that has been conducted in Central California, with emissions-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 emissions-derived TNMOC/NO_x ratios. While the techniques used in this study differ from those employed in the current project (i.e., basinwide emission estimates were used instead of a spatially-resolved modeling inventory), the overall trends do show an improvement in the agreement between emissions estimates and ambient data. **Table 6** shows the ratios of ambient- and emissions-derived TNMOC/NO_x ratios from the previous and current CCOS studies.

Table 6. Comparison of ambient- and emissions-derived TNMOC/NO_x ratios.

Air Basin	Ambient ratio/Emissions 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 that compared emission inventories to ambient data in central California include:

- 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 the summer of 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 emissions inventory. Comparisons were made for sites in the 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 49 through 52**.

Figures 49 and 50 compare pollutant ratios for sites in the Sacramento area. Figure 49 shows that the ratio between ambient- and emissions-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 emissions-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 50).

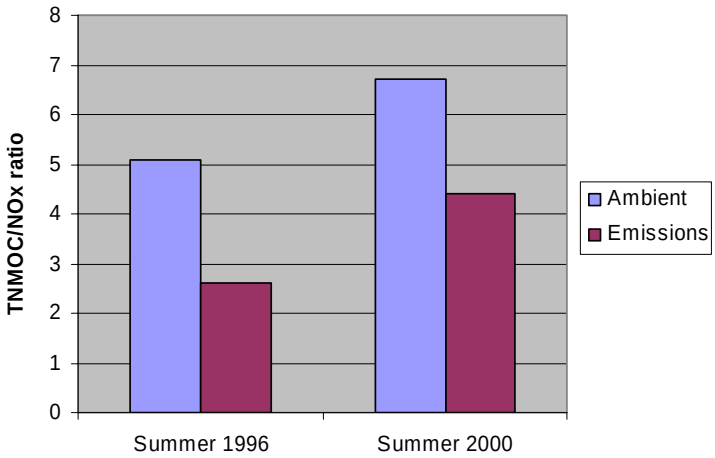

Figure 49. Trends in ambient- and emissions-derived $TNMOC/NO_x$ ratios at the Folsom site.

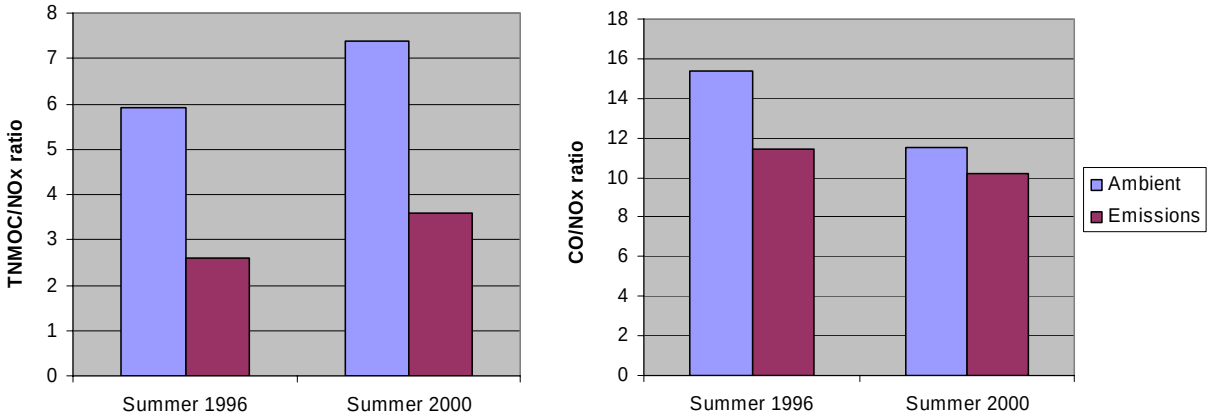

Figure 50. Trends in ambient- and emissions-derived $TNMOC/NO_x$ (left plot) and CO/NO_x (right plot) ratios at the Sacramento Del Paso site.

Figures 51 and 52 compare pollutant ratios for sites in the Fresno area. Figure 51 shows that the ratio between ambient-and emissions-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 emissions-derived ratios improved from 2.7 in 1996 to 1.3 in the current study).

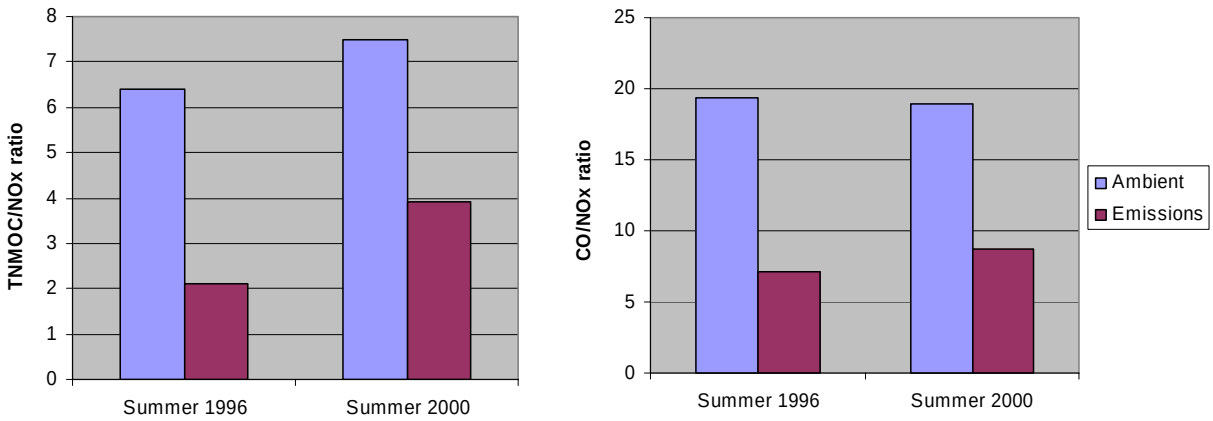

Figure 51. Trends in ambient- and emissions-derived TNMOC/NO_x (left plot) and CO/NO_x (right plot) ratios at the Clovis site.

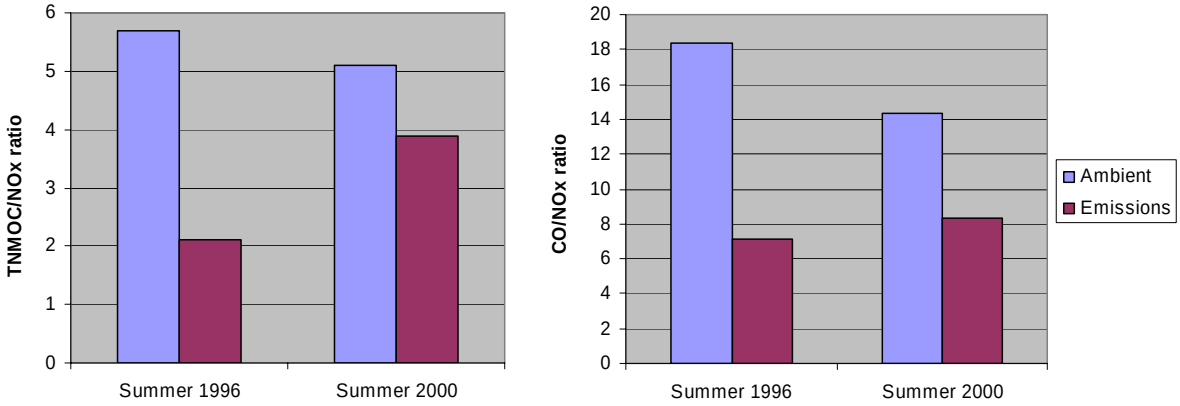

Figure 52. Trends in ambient- and emissions-derived TNMOC/NO_x (left plot) and CO/NO_x (right plot) ratios at the Fresno First Street site.

SUMMARY AND RECOMMENDATIONS

Overall findings for the CCOS emissions reconciliation are summarized below:

- When compared with previous emissions reconciliation studies, the emissions data used in this project are generally in better agreement with ambient data than previous emission inventories.
- At some sites, the emissions data correlate with ambient data as closely as could be expected given the limitations of the comparison techniques used.
- For urbanized areas in the northern part of the CCOS modeling domain (the Sacramento area), the gridded emissions data are in good agreement with data from ambient monitoring sites on weekdays, but show poorer agreement on weekend days.

- For urbanized areas in the central part of the CCOS modeling domain (the Fresno area), the gridded emissions data are in good agreement with data from ambient monitoring sites on both weekdays and weekend days.
- For urbanized areas in the southern part of the CCOS modeling domain (Bakersfield), the gridded emissions 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 emissions 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 recommends 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 emissions-derived data).
- Further investigate the poor agreement between ambient and emissions data in Kern County. Given that the comparison between ambient and emissions 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 PMF[7] 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 emissions-derived data were very limited in this project given the availability of data from Bay Area sites.

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[7] Limited PMF analyses are scheduled to be done as part of the current study with assistance from the Bay Area Air Quality Management District. No source apportionment results were ready at the time this document was prepared.

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APPENDIX A

GOOGLE™ EARTH IMAGES OF KEY MONITORING SITES

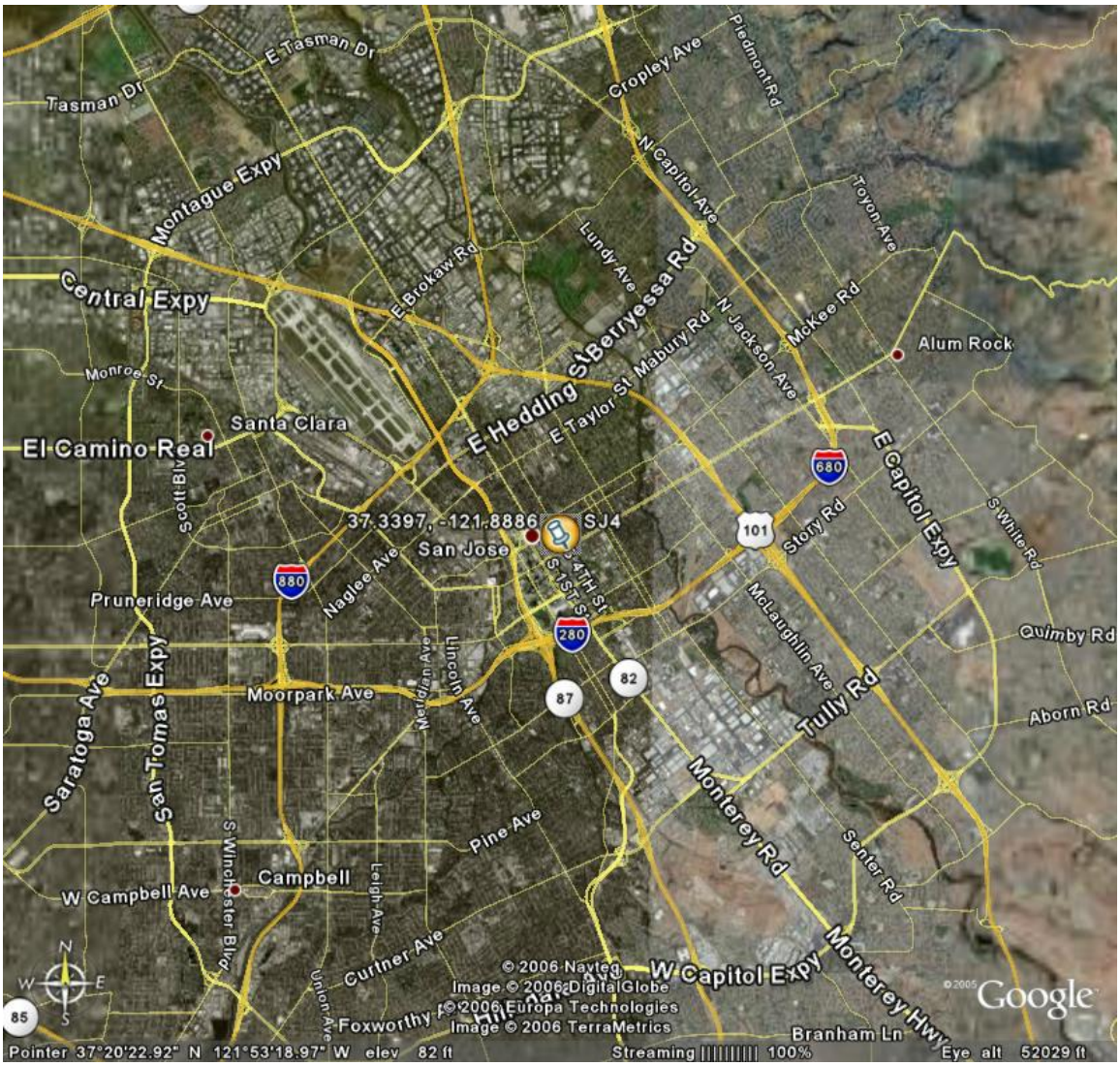

Figure A-1. San Jose 4th Street Station (SJ4), 20-km width.

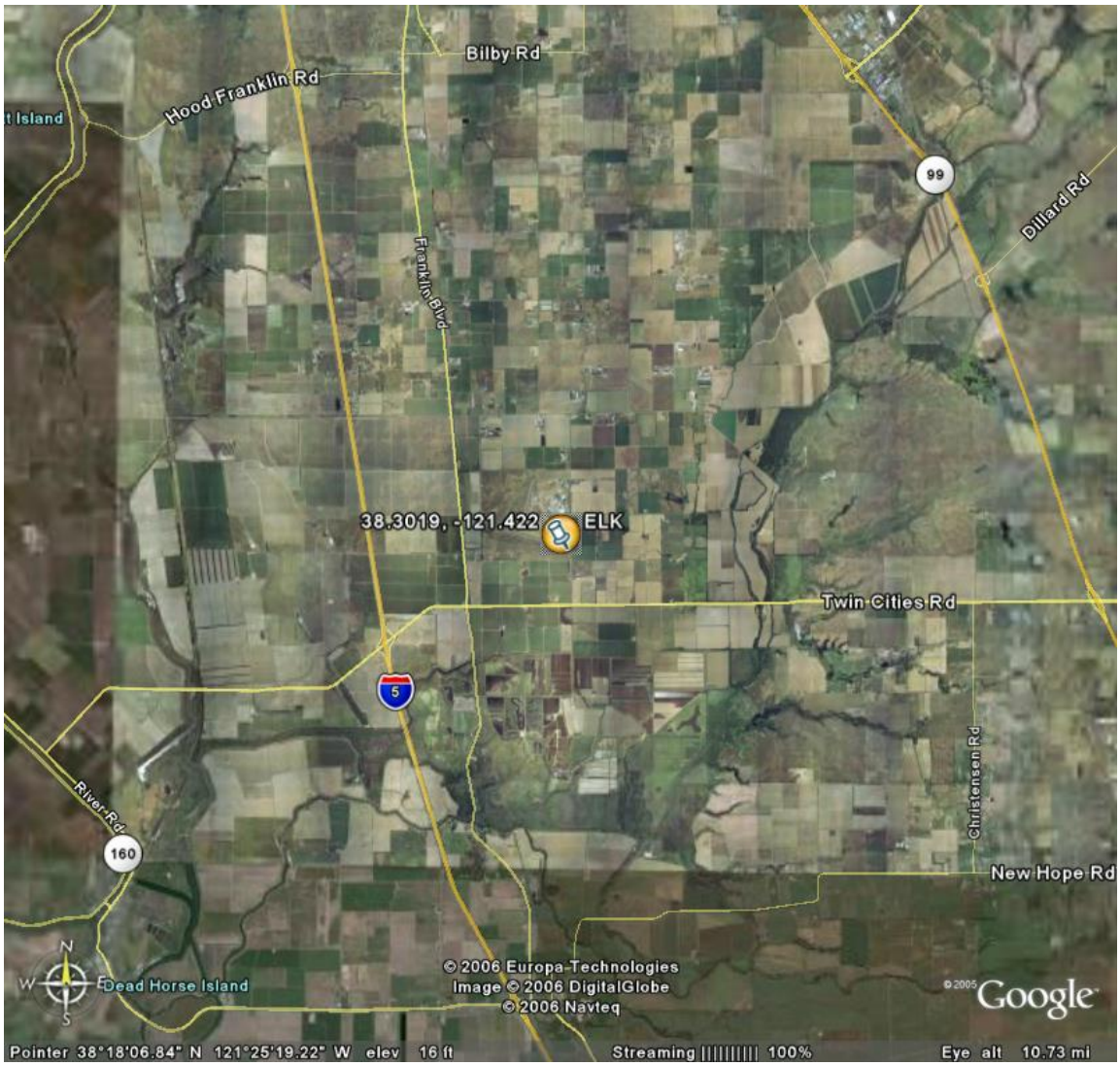

Figure A-2. Elk Grove Station (ELK), 20-km width.

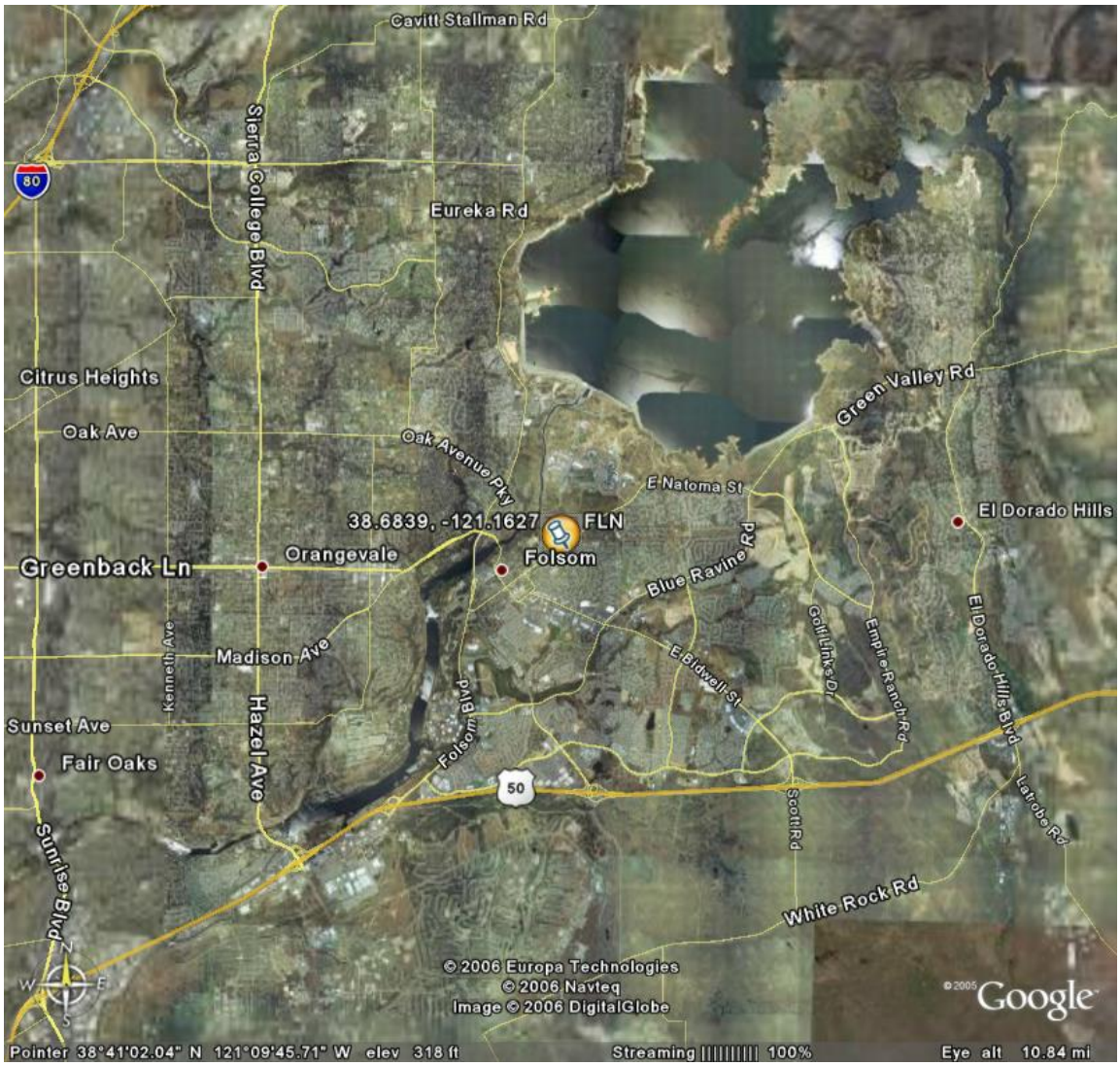

Figure A-3. Folsom Station (FLN), 20-km width.

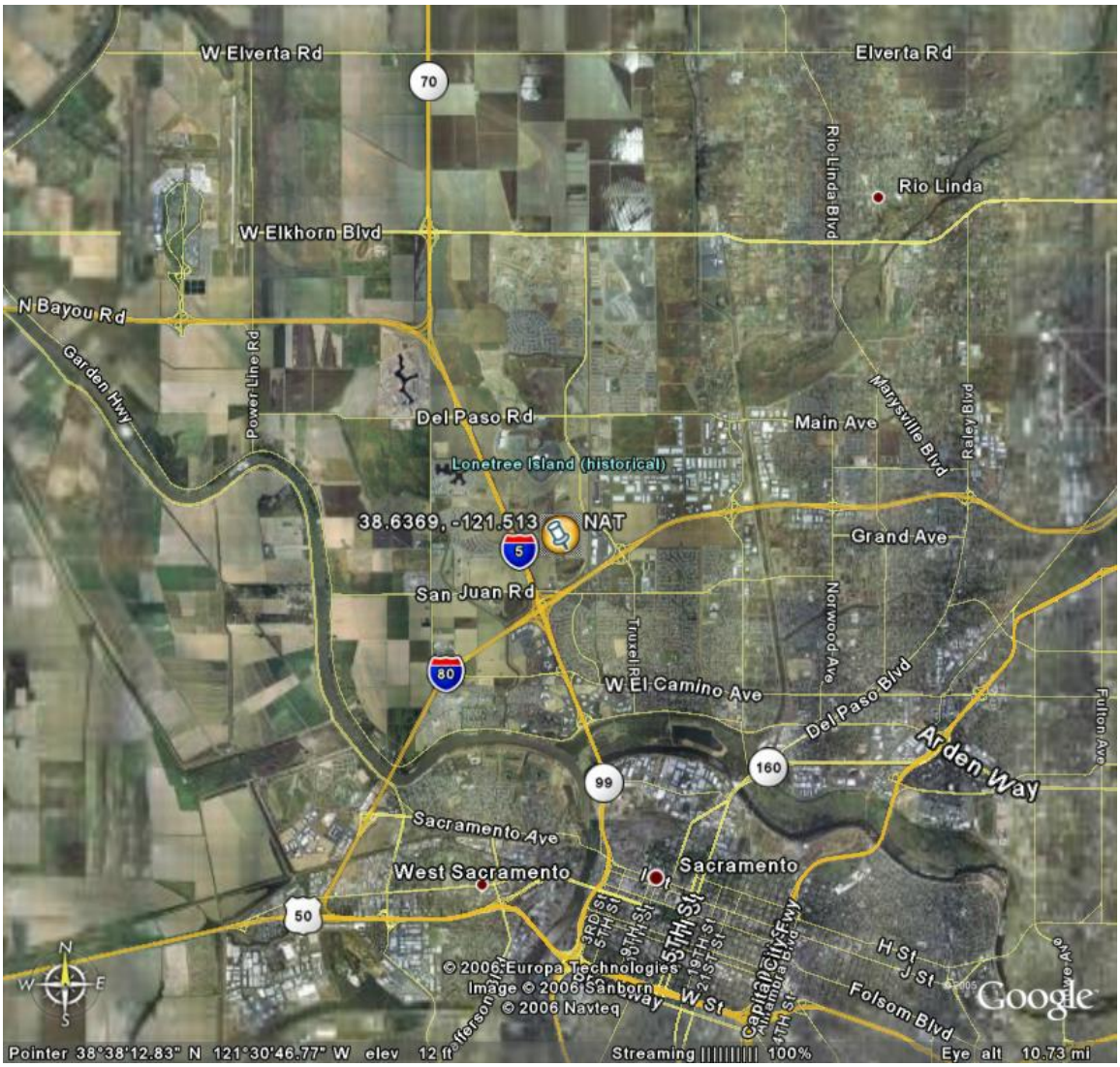

Figure A-4. Sacramento/Natomas Station (NAT), 20-km width.

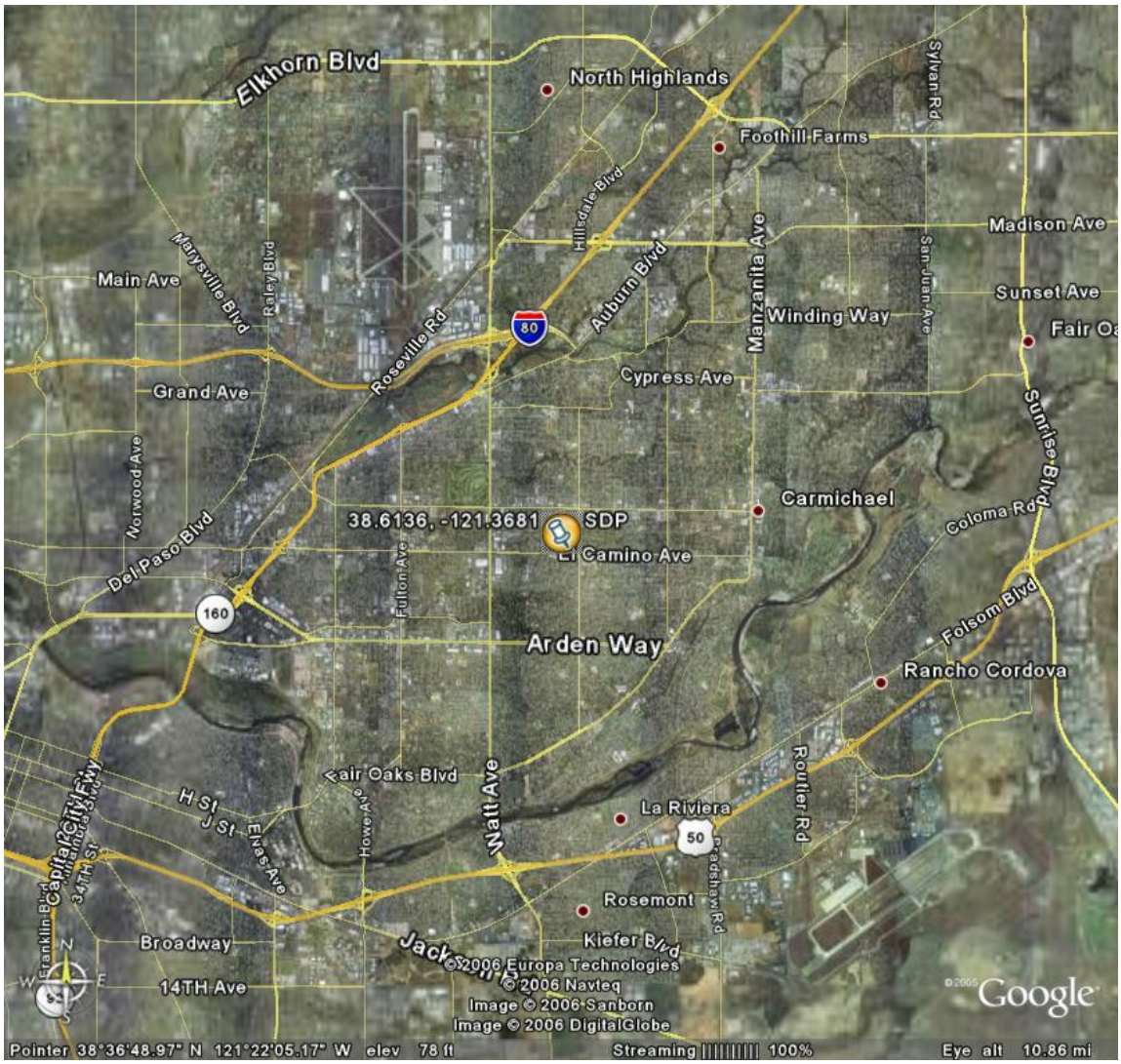

Figure A-5. Sacramento Del Paso Manor Station (SDP), 20-km width.

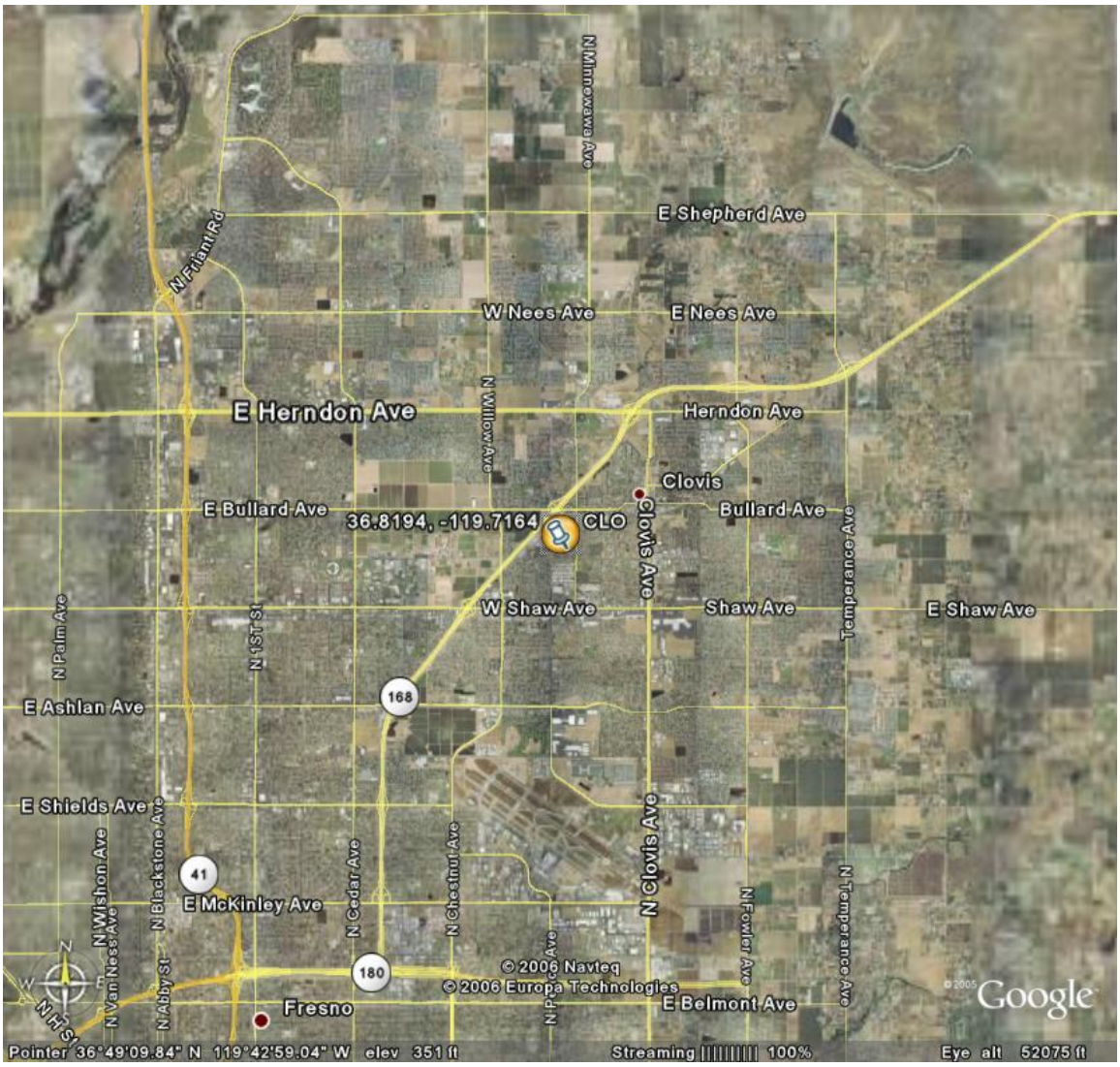

Figure A-6. Clovis Station (CLO), 20-km width.

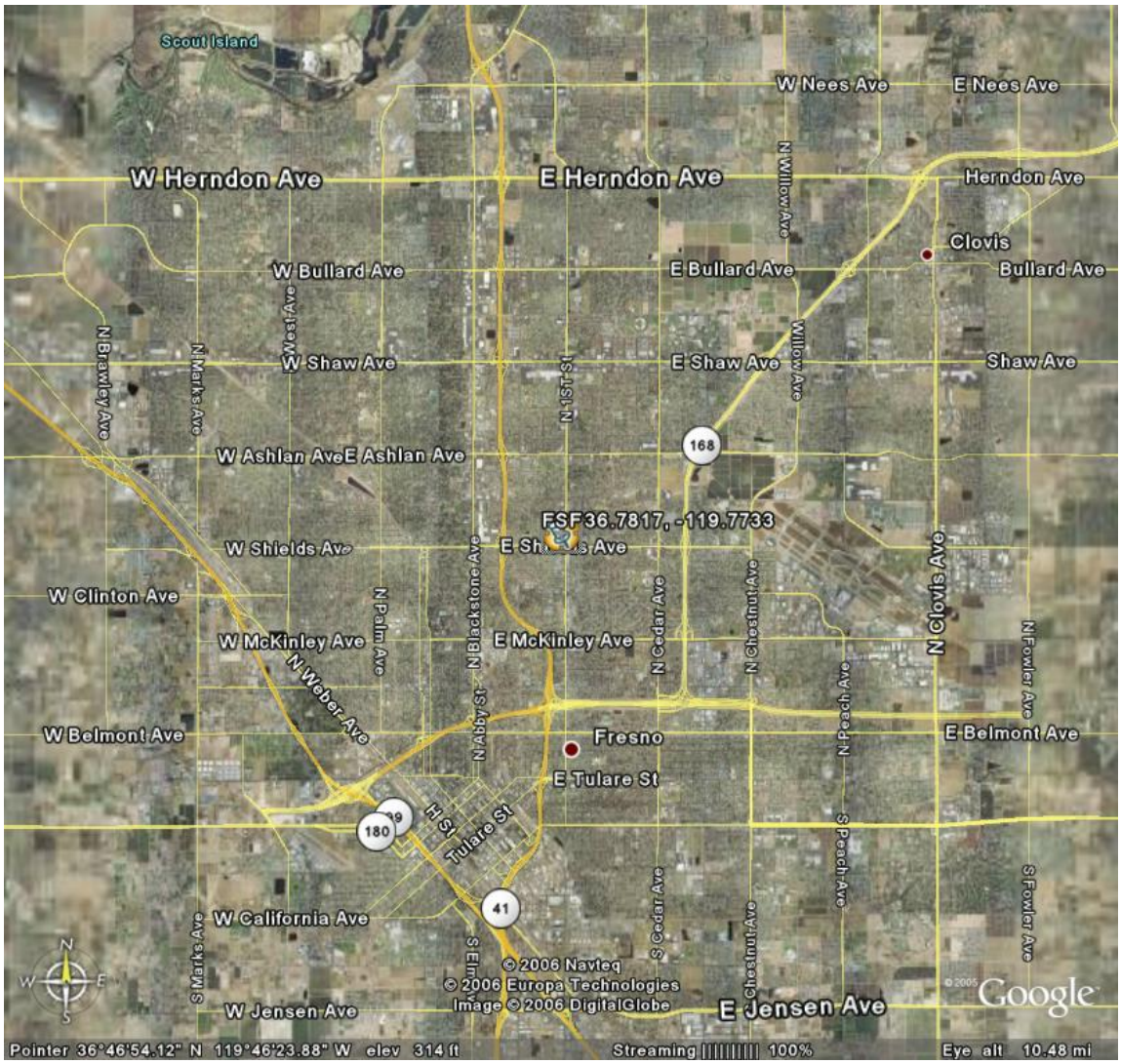

Figure A-7. Fresno First Street Station (FSF), 20-km width.

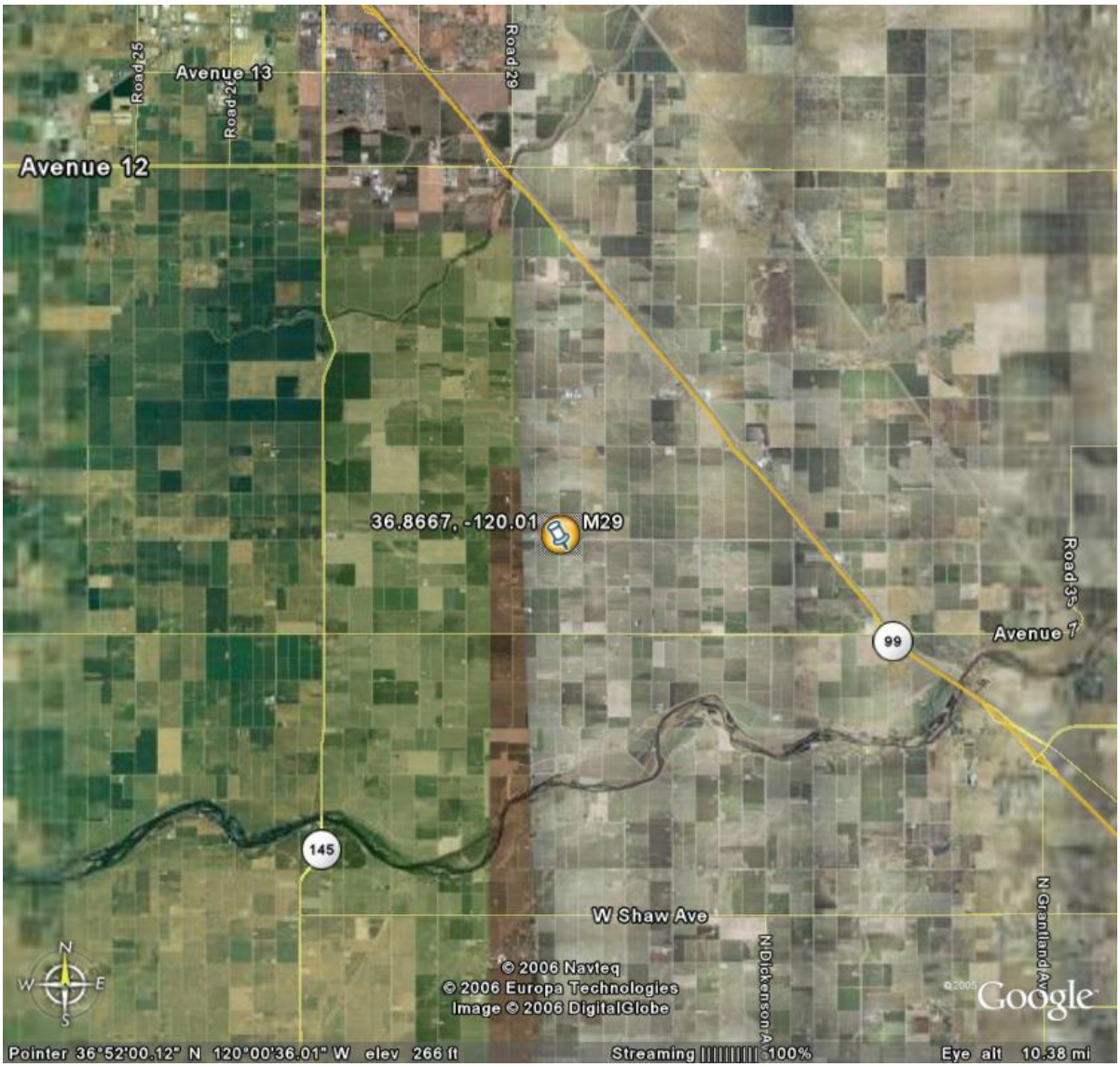

Figure A-8. Madera Station (M29), 20-km width.

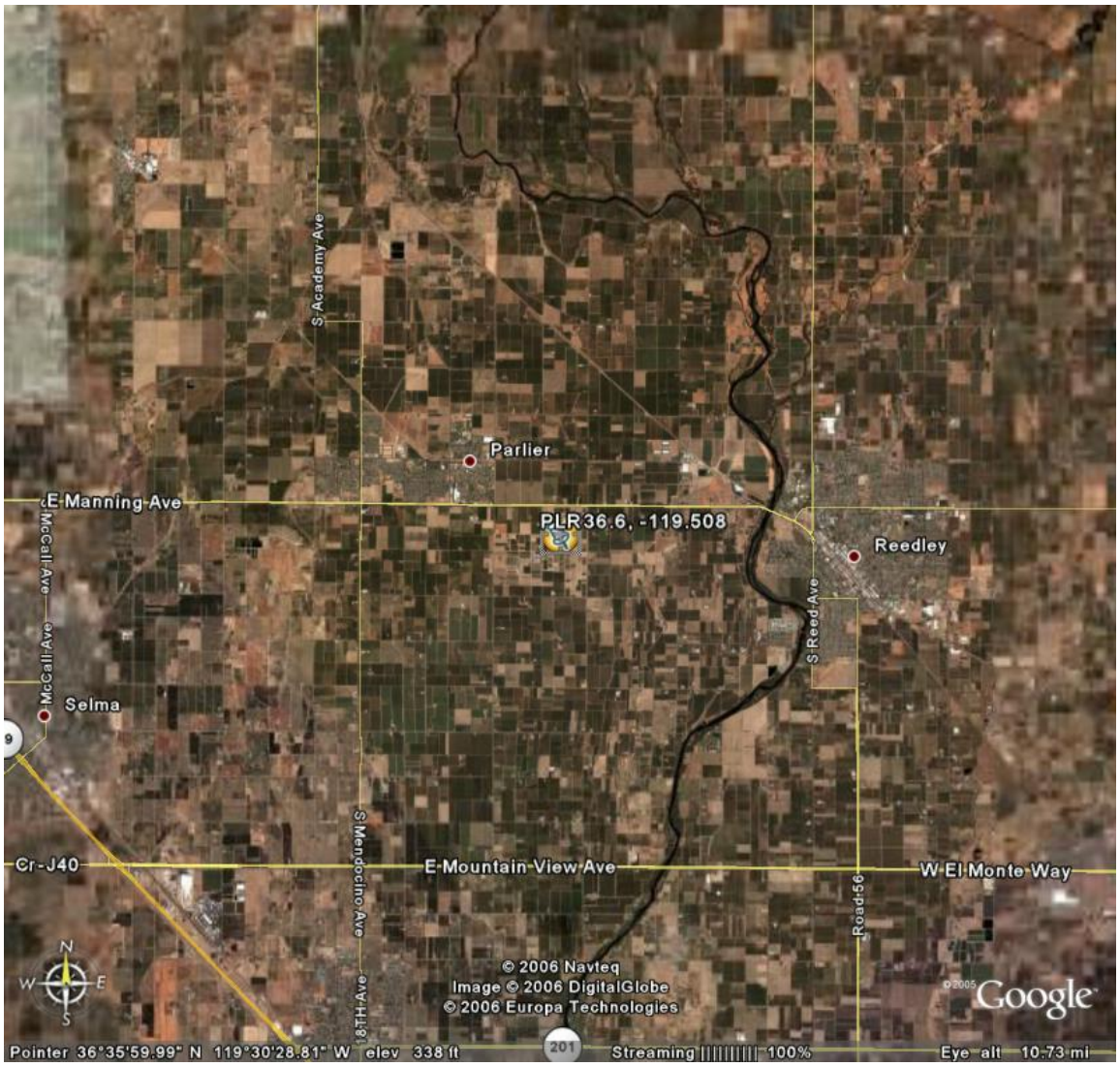

Figure A-9. Parlier Station (PLR), 20-km width.

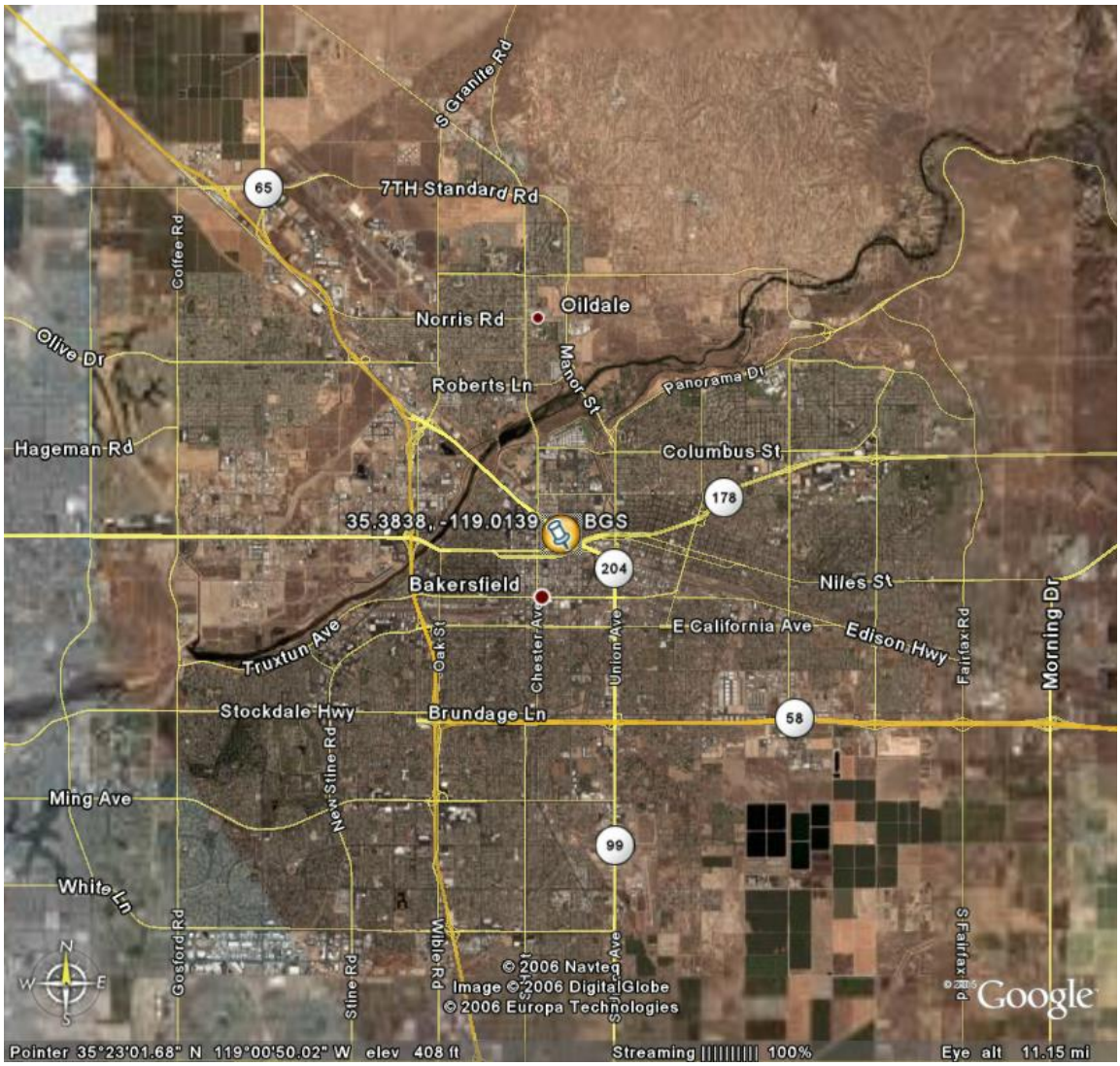

Figure A-10. Bakersfield Golden State Station (BGS), 20-km width.

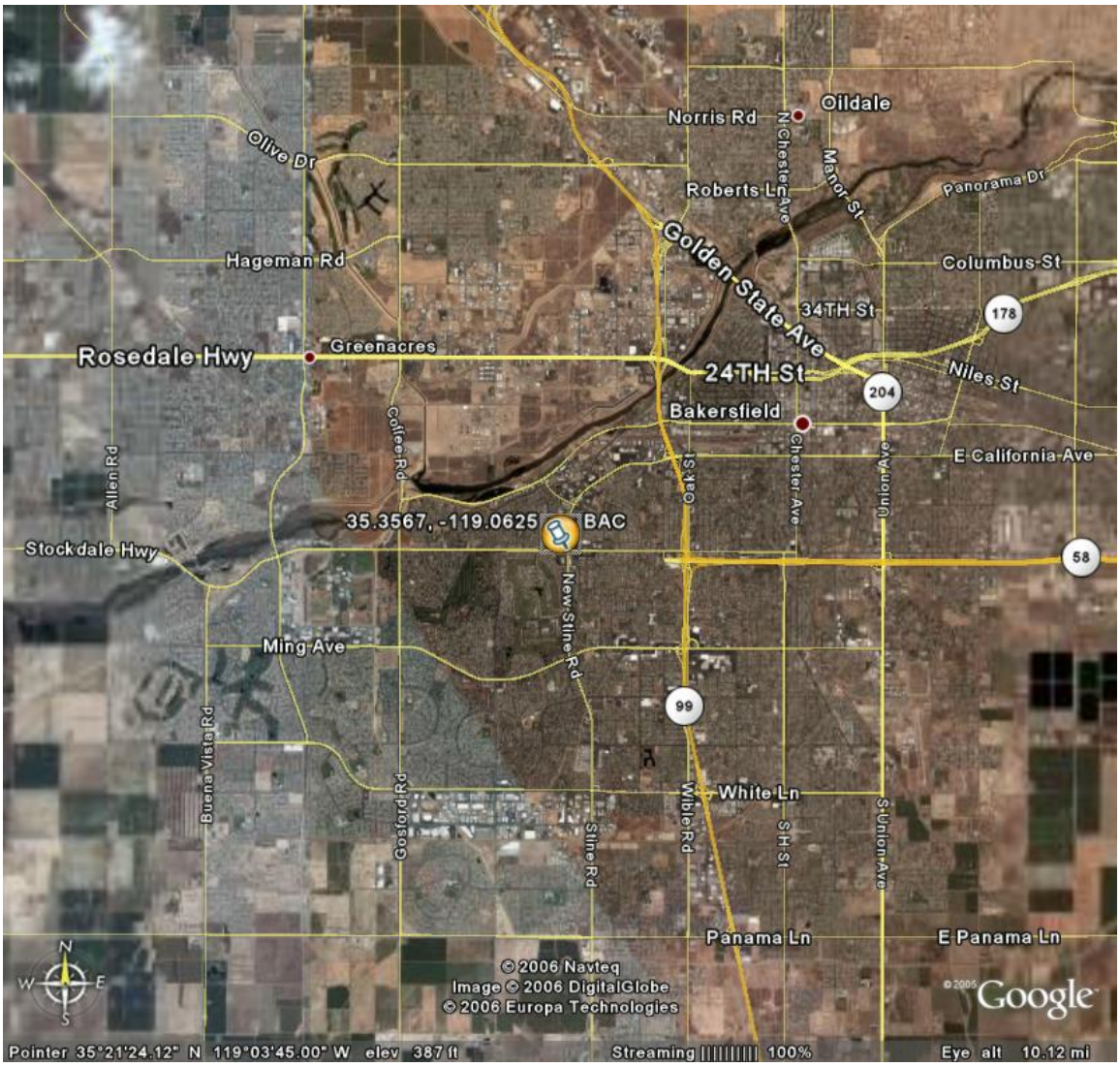

Figure A-11. Bakersfield California Avenue Station (BAC), 20-km width.

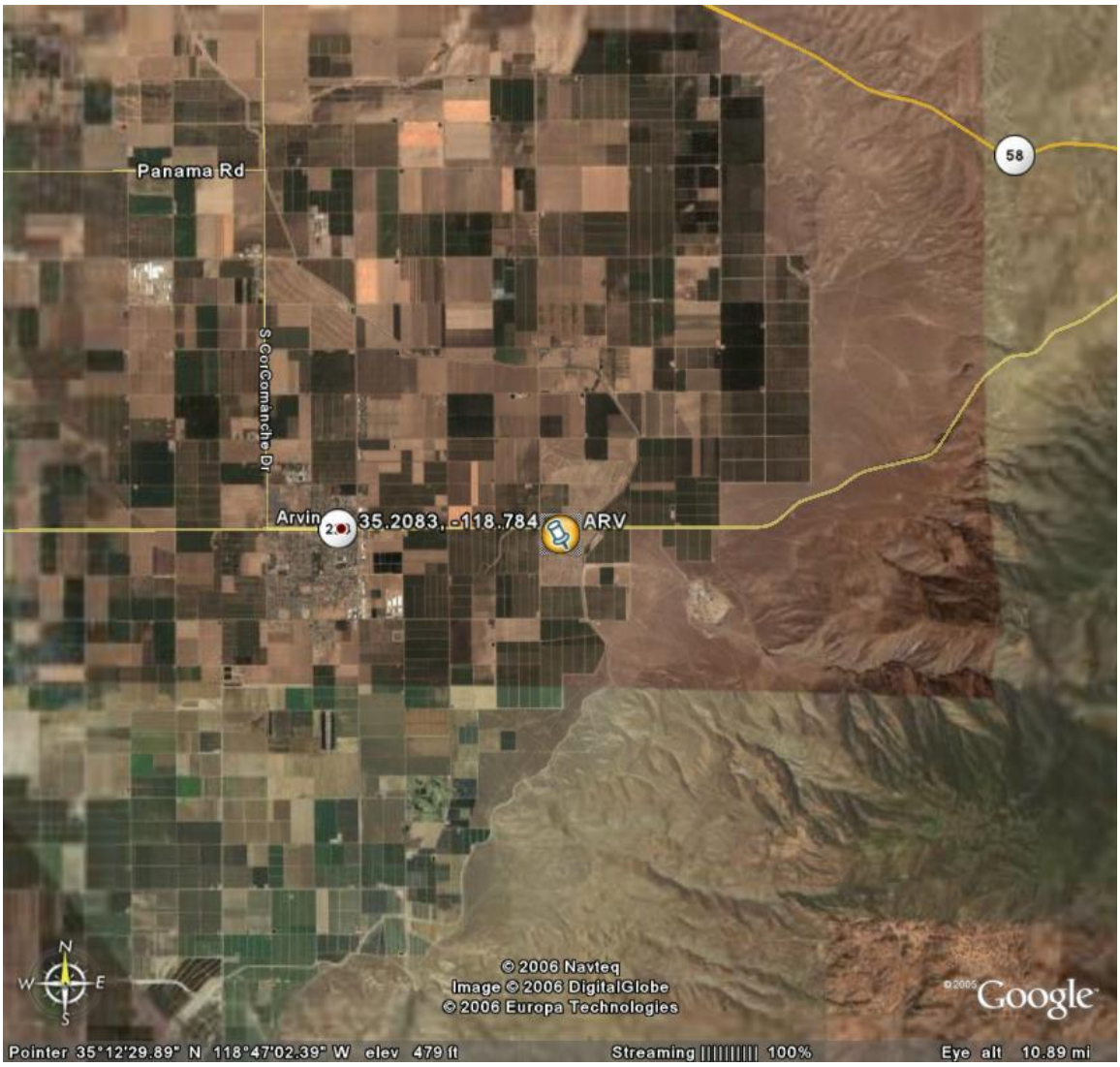

Figure A-12. Arvin Station (ARV), 20-km width.

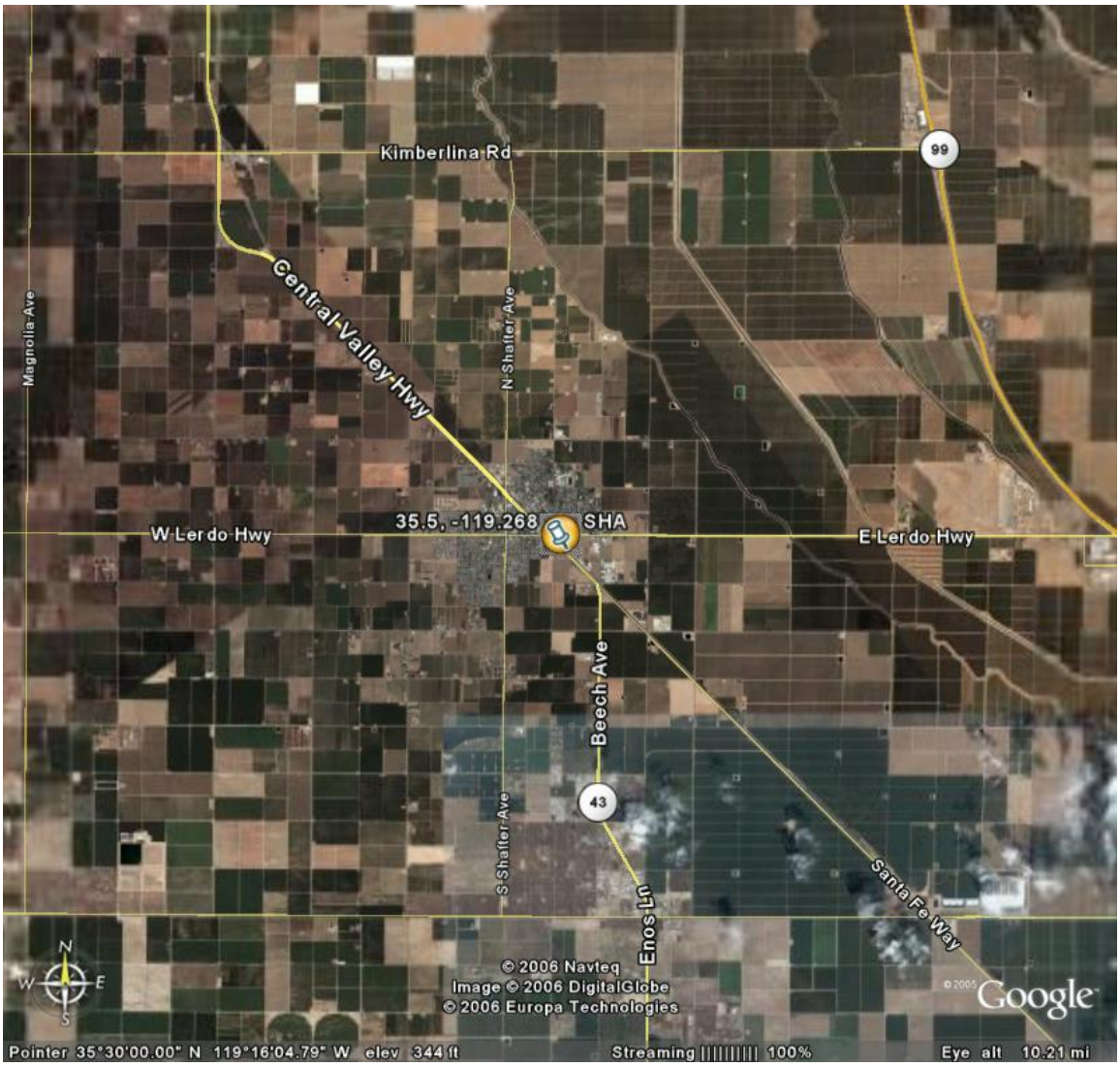

Figure A-13. Shafter Station (SHA), 20-km width.

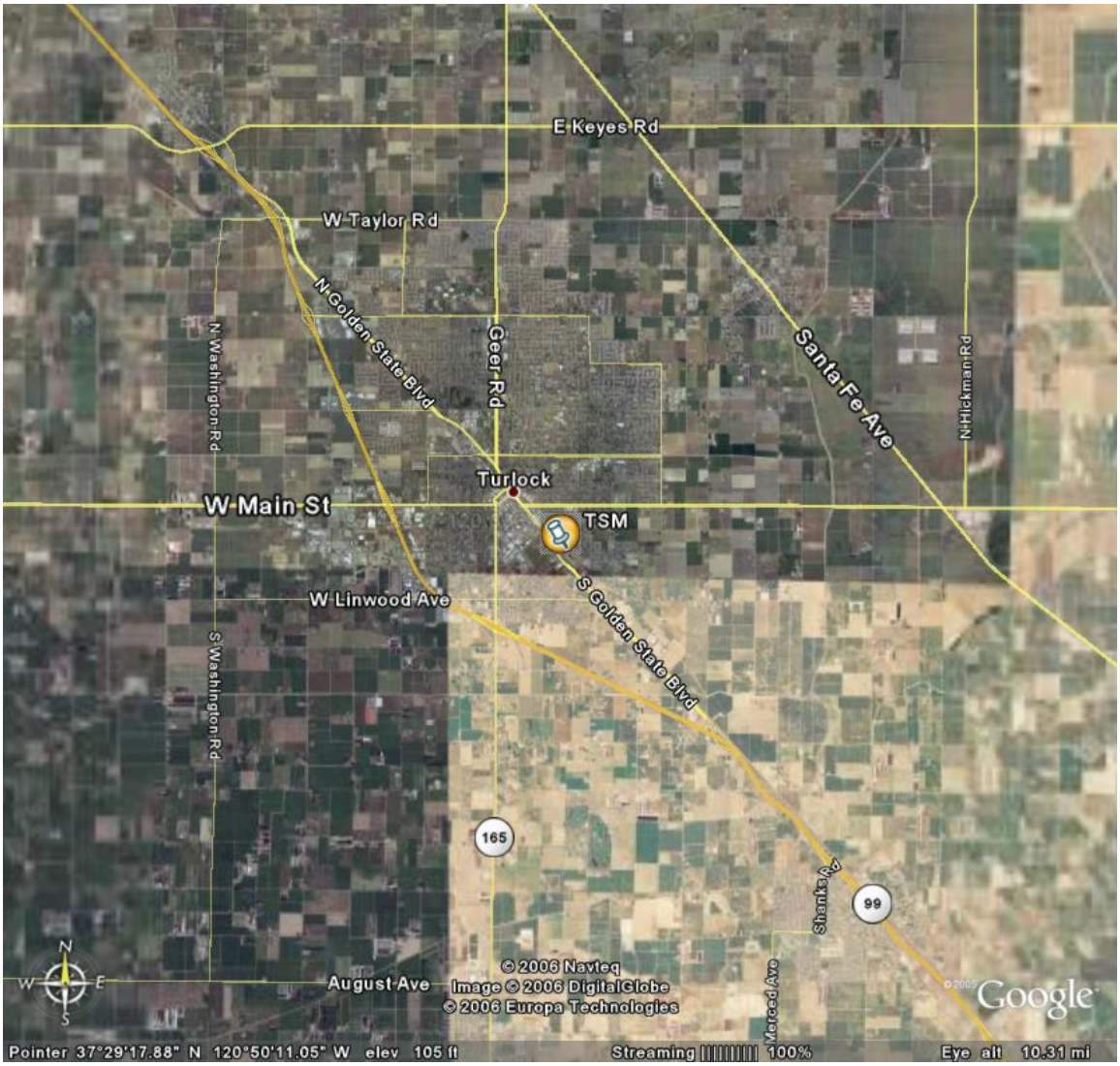

Figure A-14. Turlock Station (TSM), 20-km width.