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Ozone Modeling and Data Analysis During CCOS

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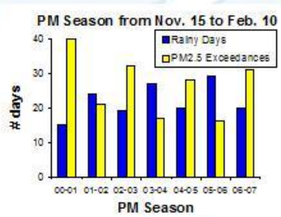

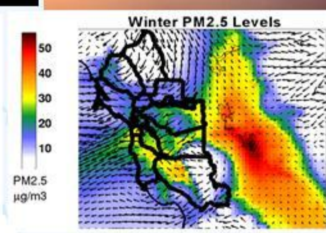

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1. Introduction

Ozone concentrations in central California frequently exceed the federal 8-hr (75 ppb) and California State 1-hr (94 ppb) ozone standards. The 2000 Central California Ozone Study (CCOS) was established to investigate the causes of ozone formation in the region. CCOS was a multi-year program of meteorological and air quality monitoring, emissions inventory development, data analysis, and air quality modeling. The CCOS domain (Figure 1) included all of central California and portions of northern California, extending from the Pacific Ocean to east of the Sierra Nevada and from north of Redding to the Mojave Desert.

The formation of ozone in central California is influenced by the unique characteristics of meteorology and emissions of the region. During a typical ozone episode, the 500 mb Eastern Pacific High Pressure System causes a sinking motion that produces low-level divergence, warm temperatures, and a shallow mixing depth over central California. It also produces a predominately northwesterly airflow along the California coast (Bridger et al., 1993). During the day, a sea breeze develops. The flow over the land is strongly influenced by topography. The marine air that reaches the Central Valley through the San Francisco Bay Area is often directed southward into the San Joaquin Valley (SJV) and northward into the Sacramento Valley. During the night, shallow drainage flows are observed along the slopes and a northwesterly low-level jet forms along the long axis of the SJV (Burk and Thompson, 1996). By the morning, a cyclonic eddy appears near Fresno (Lin and Jao, 1995; Seaman et al., 1995).

Various anthropogenic emission sources exist in the region. In the San Francisco Bay Area (SFBA), the dominant ozone producing emissions are from motor vehicles (including light and heavy duty trucks), airports, shipping, refineries, power-generating facilities, construction equipment and other industrial activities. In the SJV and the Sacramento area, the dominant emission sources include motor vehicles (including light and heavy duty trucks), urban development, and agricultural activities (including harvesting, shipping and pump operated irrigation).

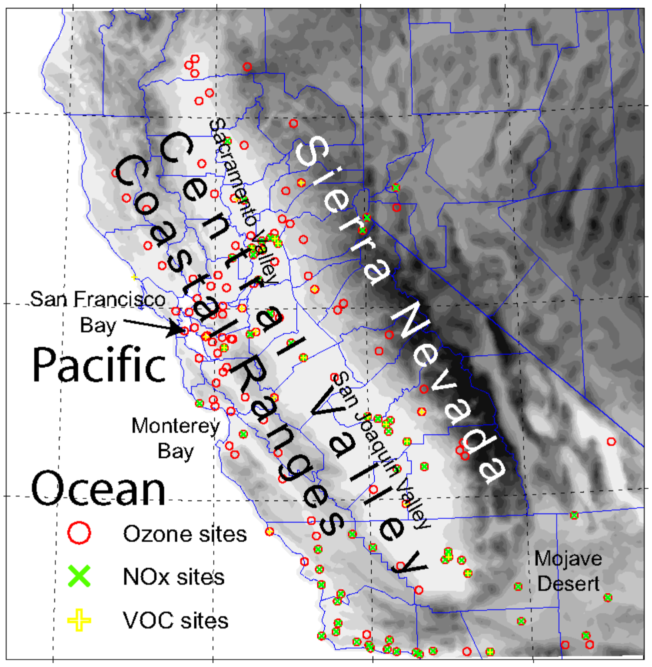


Figure 1: The modeling domain for the 2000 CCOS study and air quality measurement sites.

Biogenic hydrocarbons and soil NOx are also important contributors to ozone precursors in the region. The estimated amount of biogenic hydrocarbons for 2000 was about three times larger than the total anthropogenic hydrocarbons in the study domain. However, more than half of the biogenic hydrocarbons were emitted away from high ozone areas.

Ozone exceedances are usually observed in the SJV (downwind of both Fresno and Bakersfield), Sacramento, and SFBA (Livermore and San Martin). During a typical summer, ozone concentrations exceed the 8-hr federal standard about 100 times in the SJV, 20 times in Sacramento and 8 times in the SFBA (California Air Resources Board, 2006b).

This report briefly describes the CCOS field program, and key findings of data analysis and modeling for one of the captured ozone episodes.

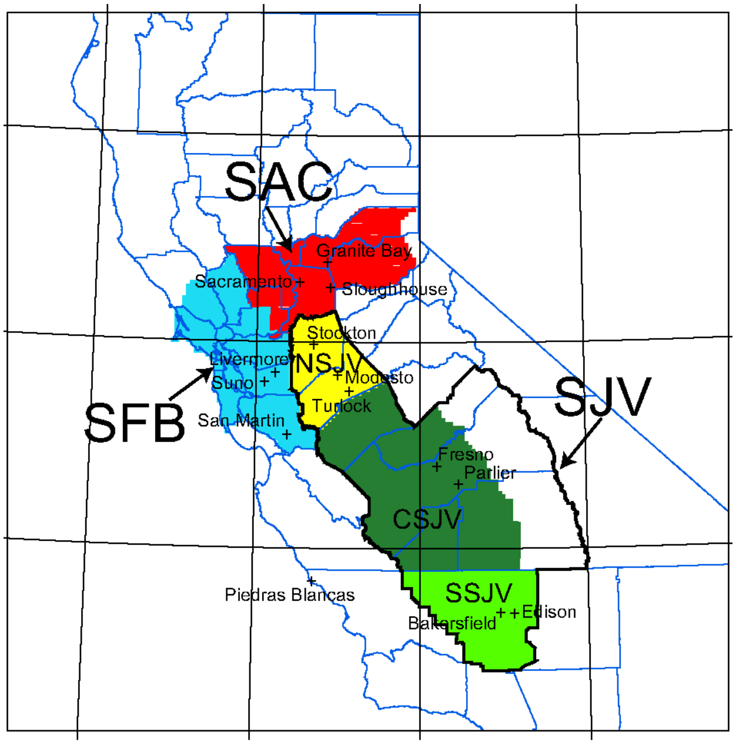


Figure 2: Three regions of the modeling domain (SFB, SAC, and SJV). The SJV region is further subdivided into three sub-regions: Northern (NSJV), Central (CSJV), and Southern (SSJV). The elevated sites in eastern SJV were not included in the performance analysis.

2. The CCOS field program

There are about one hundred existing air quality monitoring sites (mainly measuring ozone and nitrogen dioxide) and three hundred surface meteorological stations in the CCOS region. The air quality and meteorological stations are concentrated near San Francisco, Sacramento, Fresno and Bakersfield, where ozone exceedances are frequently observed. Routine upper air meteorological measurements are made at Oakland, Sacramento, Fairfield, Monterey, Visalia (near Fresno) and Vandenberg. There are eleven Photochemical Assessment Monitoring Stations in the Central Valley (four in the Sacramento area, four in the Fresno area and three in the Bakersfield area). In addition to these existing monitoring stations, the annual field program of the California Regional Particulate Air Quality Study (CRPAQS) provided measurements of surface and upper air meteorology and surface air quality during the CCOS period (Watson et al., 1998). The CRPAQS stations were mainly concentrated in the SJV.

Field program guidelines for CCOS were established based upon technical, logistical and cost considerations, and lessons learned from previous studies in the region (Fujita et al., 1999). Twenty existing surface air quality stations were supplemented with additional instruments for measurements. Thirteen new surface air quality and fifteen upper air meteorological stations were established. Six aircraft were utilized to monitor meteorology and air quality aloft. Two ozonesonde and one ozone-lidar stations were established. Day-specific emissions were monitored. About 300 stations for traffic count were added to supplement the existing traffic count stations. Four stations for remote sensing of exhaust emissions were also established.

The CCOS field program consisted of four categories of measurement sites with increasing levels of chemical speciation and time resolution measurements. The first level sites (S0) were intended to fill in key areas of the modeling domain where ozone and nitrogen oxide were not routinely monitored. Surface meteorological stations were also established at S0 sites. The next level sites (S1) were intended to establish boundary and initial conditions for input into air quality models. In addition to meteorological measurements, S1 sites also measured: ozone, nitrogen oxide, NOy, hydrocarbons, and carbonyls. The S2 sites were located along the inter-basin transport routes and near the downwind edge of urban centers. The S2 sites measured: meteorology, ozone, nitrogen oxide, nitrogen dioxide, NOy, peroxyacylnitrate, formaldehyde, hydrocarbons, and carbonyl. The research sites (R) were intended to measure a representative urban mix of pollutants and to provide the maximum extent of high-quality, time-resolved chemical and emissions inventory estimates. The R sites included S2 type measurements as well as continuous measurements of hydrocarbons (using Gas Chromatography and Mass Spectrometry), CO, CO_2, actinic flux, particulate nitrate, total light absorption, and H_2O_2.

The locations of upper air meteorological stations were selected carefully to capture the main features of the meteorological fields that may play a role in the development of increased ozone concentrations. Special attention was given to pollutant transport routes, terrain orientation, terrain elevation, and flow features such as slope flows, low-level jet, divergence and convergence zones, return flows, and flow bifurcations. A field coherence technique developed by Stauffer et al. (1999) was applied by Tanrikulu et al. (2000) to provide objective guidance in locating the stations.

Aircraft measurements were intended to provide aloft initial and boundary conditions as well as temporal and spatial ozone patterns in layers aloft. Two aircraft were operated from Davis, California covering the San Francisco Bay Area, the Livermore Valley, Sacramento, and the Sacramento Valley. One aircraft was operated from Bakersfield covering the central and southern SJV. Two aircraft were operated (one from Fresno and the other from Petaluma) covering the northern SJV and California coastal waters (western boundary conditions). One aircraft operated from the San Francisco Bay Area making power plant plume measurements. All aircraft made eight hours of measurements a day (four in the morning from 6:00 am to 10:00 am and four in the afternoon from 2:00 pm to 6:00 pm) during the intensive measurement period.

The field study was conducted during a four-month period from 6/1/2000 to 10/2/2000. However, the measurements had a phased-in schedule. Surface and upper air meteorological measurements as well as existing air quality measurements were made during the entire period. Supplemental air quality measurements for ozone, NO, NOx, and NOy were made continuously from 6/26/2000 to 10/2/2000 at all sites. The remaining species at S1 and S2 sites as well as aircraft operations were made during ozone episodes. The majority of the species at research sites were continuously measured from 7/5/2000 to 10/2/2000. Additional information on the CCOS field program can be found in Fujita et al. (2001), Lehrman et al. (2004), and Fujita et al. (2005).

During the CCOS program, seven ozone episodes (former federal 1-hr exceedances) were captured. Among them, the three-day episode of 31 July – 2 August was selected for modeling. Intensive Operational Measurements were made during the first two days of this episode. Meteorological conditions leading to high ozone in the region during this three-day episode are described by Wilczak et al., 2007. Ozone exceeded the federal 1-hr ozone standard in the SFBA on 31 July, in the Sacramento area on 1 August, and in the SJV on 2 August (Table 1). The ozone exceedance in the SFBA occurred at Livermore (126 ppb) at 16:00 PST, in the Sacramento area at Sloughhouse (133 ppb) at 14:00 PST, and in SJV at Edison (151 ppb) at 13:00 PST (Figure 2).

3. Air Quality Modeling

3.1 Preparation of emissions inventory

Emissions inventory for this episode was prepared by the California Air Resources Board (CARB) and reviewed and evaluated by a consortium of local air districts, transportation management agencies, and consultants (CARB, 2005). Five major source categories of emissions were included in the inventory: on-road light-duty gasoline-powered motor vehicles, on-road heavy-duty diesel vehicles, area sources (including off-road motor vehicles, architectural coatings, and consumer products), point sources, and biogenic sources.

County-level emissions from on-road motor vehicles, including light-duty gasoline vehicles and heavy-duty diesel vehicles, were calculated using version 2.2 of CARB's EMFAC model. This version of the EMFAC model used truck survey results and global positioning system techniques to estimate vehicle miles traveled (VMT). This methodology is more realistic than previous EMFAC versions (EMFAC, 2002). Emissions were spatially distributed within counties using CalTran's DTIM model (Ireson and Fieber, 1994) and the California Integrated Transportation Network (Wilkinson, 2006). The hourly distribution of on-road emissions, on both weekdays and weekends, was estimated using weigh-in-motion vehicle traffic count data from state highways. Separate hourly distributions were obtained for light-duty vehicles and heavy-duty diesel vehicles.

Area source emissions were estimated statewide at the county level by CARB and distributed spatially using spatial surrogates based on land use and population data (Funk et al., 2001). The

OFFROAD model estimated emissions from off-road mobile equipment such as agricultural, construction, lawn and garden, and off-road recreational vehicles (OFFROAD, 2006).

Biogenic VOC emissions were estimated using CARB's Biogenic Emissions Inventory Geographic Information System (BEIGIS) model (Scott and Benjamin, 2003). BEIGIS uses California solar insolation, temperature and wind estimates, as well as land use-land cover, leaf mass, and emissions rate databases within a geographic information system to estimate day-specific hourly emissions of isoprene, monoterpenes, and methylbutenol. Biogenic soil NOx emissions were estimated outside of BEIGIS using a modified Guenther method (Guenther et al., 1994).

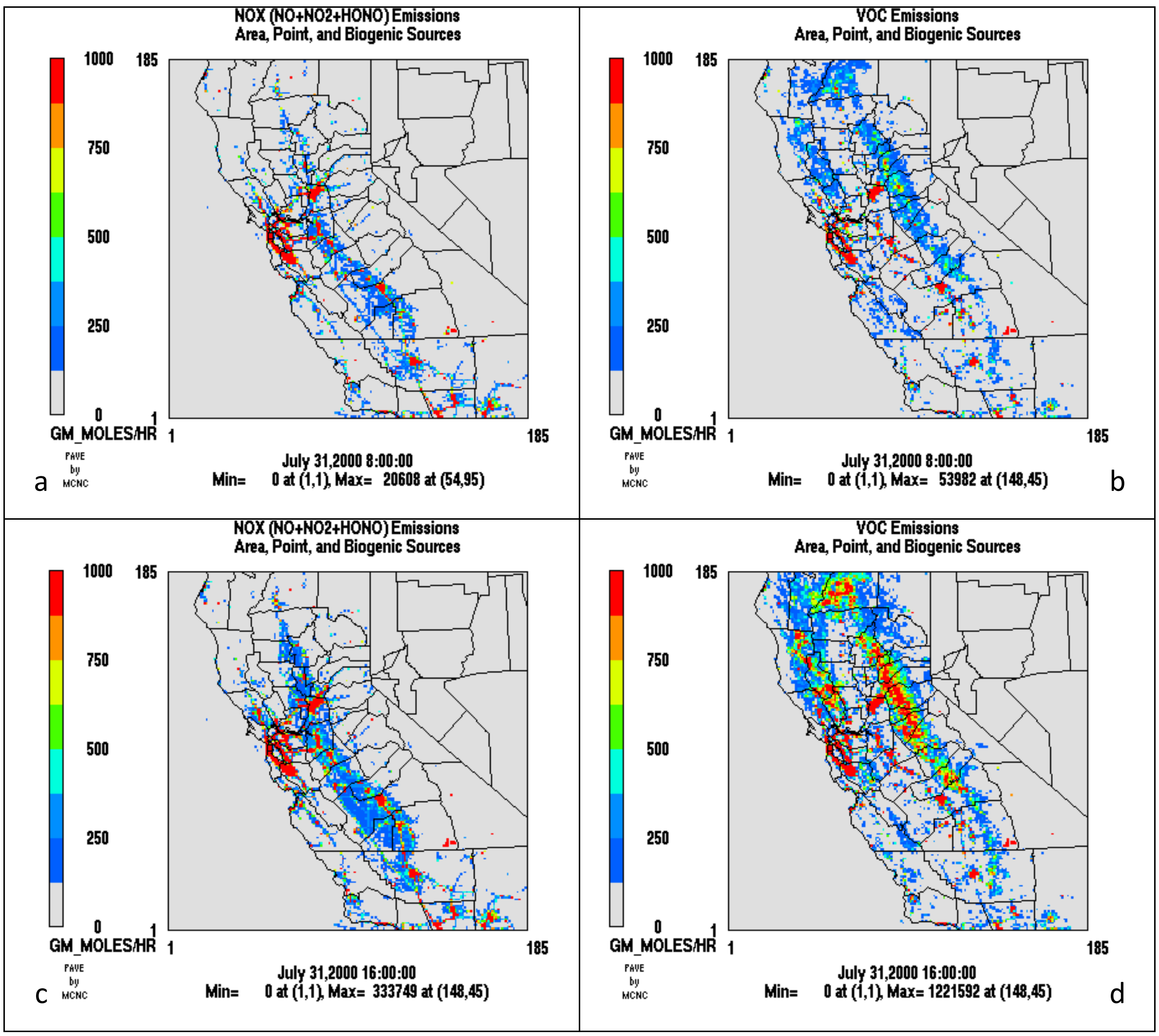


Figure 3: NOx and VOC emissions (g-moles/hr) over the CCOS domain on 31 July 2000. Panels (a,b) show traffic rush hour (7:00 PST), and (c,d) the time of observed peak ozone for SFBA (15:00 PST).

In the SFBA, the largest anthropogenic source of NOx emissions was motor vehicles, followed by area and point sources (Table 2). Biogenic VOC emissions were comparable to anthropogenic VOC emissions there. In the Sacramento area and the SJV, biogenic VOC emissions were the largest followed by NOx and VOC emissions from motor vehicles, area, and point sources, respectively. Figure 3 shows the spatial distribution of emissions for both NOx and VOC over the modeling domain. NOx emissions generally reached their peak values during morning commute hours and leveled off throughout the day, but their maximum spatial coverage was reached in the late afternoon. Anthropogenic VOC emissions had a spatial distribution similar to that of NOx (Figure 3c,d). Biogenic VOC were low at night and reached a maximum, both in magnitude and spatial extent, in the early afternoon. In the early afternoon, biogenic VOCs dominated in the mountainous areas of the Sierra Nevada and the Coastal Ranges, whereas anthropogenic sources were largest in the SJV, around the SFBA, and generally near urban centers.

3.2 Preparation of meteorological inputs

The MM5 model (Grell et al., 1994) was used for preparing meteorological inputs to the air quality model. A nested grid with 36-12-4 km horizontal resolutions was used. The model had 50 vertical layers with expanding layer thicknesses. The lowest 30 layers were below 2 km and the lowest model layer was about 24 m deep. The 4 km domain coincides with the CCOS field study area in Figure 1. Boundary and initial conditions were obtained from the 40 km NCEP Eta analysis. The simulations began at 12 UTC on 29 July (2 days before the first day of the episode) and ended at 12 UTC on 3 August.

Analysis nudging on the 36 km domain for winds and temperatures and observational nudging on the 4 km domain for winds were utilized. The 36 and 12 km domains were run using the two-way nest and the 4 km domain with the one-way nest options.

3.3 Ozone simulations

The CAMx (ENVIRON, 2004) was used to simulate ozone. The simulations started on 29 July 2000 at 12:00 UTC (two days before the first day of the episode as done with MM5 simulation) and ended on 3 August at 12:00 UTC. In the horizontal direction, the modeling domain had 185 x 185 grids with 4 km resolution. This domain matched the innermost domain of MM5, ignoring 2 cells along the edges. A telescoping vertical grid structure was also utilized in CAMx with 20 layers. The two lowest CAMx layers coincided with the two lowest MM5 layers. Above these layers, however, the resolution of CAMx layers was coarser than MM5: two MM5 layers were collapsed into one CAMx layer for CAMx layers 3-5 and 18-20 and three MM5 layers were collapsed for CAMx layers 6-17.

In all simulations, the SAPRC-99 chemical mechanism (Carter, 2000) was used. Initial and boundary conditions were specified based on interpolated data from aircraft measurements during the CCOS field program. The interpolation resulted in 40 ppb ozone near the surface at lateral boundaries over land and 25 ppb over water (Table 3). It also resulted in a profile with ozone concentrations increasing with height to 70 ppb at 1500 m. The names of species that need to be specified along the boundaries for the SAPRC-99 chemical mechanism and their values are given in Table 3.

4. Results

4.1 Horizontal distribution of surface ozone and precursors

In the morning hours of the first day of the episode (31 July 2000), simulated ozone concentrations were low (below 40 ppb) in much of the Central Valley and near the coast, and moderate (60-80 ppb) in mountainous regions such as the Sierra Nevada Figure 4a. Throughout the day, ozone concentrations increased in the region, especially in the downwind areas of large cities.

Figure 4b depicts observed and simulated 1-hr ozone concentrations at 16:00 PST on 31 July, when the peak ozone was observed in the SFBA at Livermore and exceeded the former federal 1-hr standard. This was the only 1-hr exceedance in the region. Ozone in the Sacramento area was generally low at this time. Some observed 1-hr ozone values were above 100 ppb in the SJV.

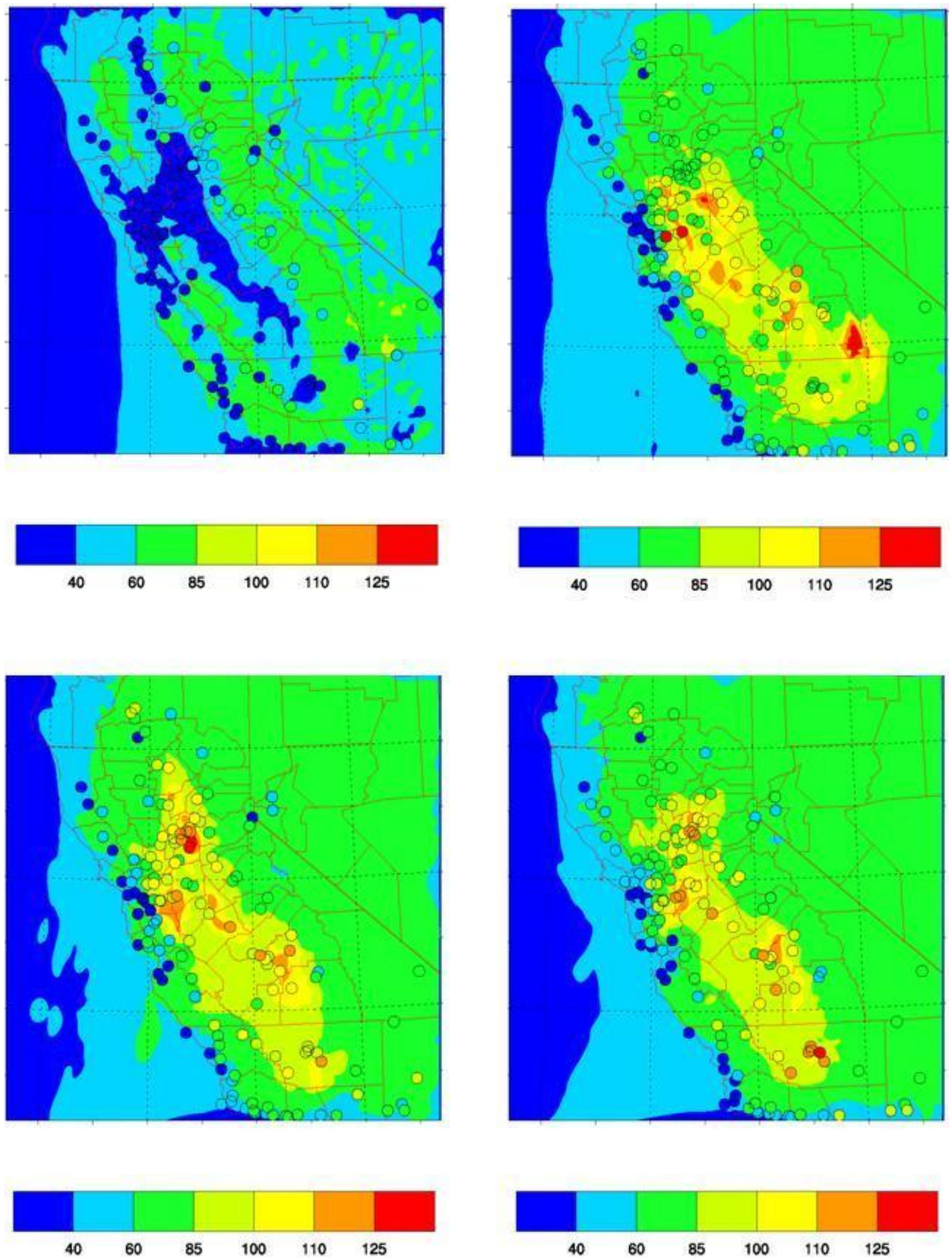


Figure 4: Ozone concentrations (ppb) simulated by CAMx and observed at station locations (filled circles) (a) at 2:00 PST on 31 July (upper left panel) and (b) at 16:00 PST on 31 July (upper right panel), time of the maximum observed ozone over SFB, (c) at 14:00 PST on 1 August, time of the maximum observed ozone over Sacramento and (d) at 14:00 PST on 2 August, time of the maximum observed ozone over SJV.

The observed high ozone at Livermore occurred in an isolated region, surrounded by stations with maximum observed 1-hr ozone less than 85 ppb. This isolated high value makes it challenging to accurately simulate the observed ozone peak. However, isolated high ozone at Livermore is not uncommon. Between 1995 and 2002, there were 36 days that exceeded the 1-hr ozone standard in the SFBA. Out of these 36 days, the highest ozone in the entire SFBA was observed at Livermore on 20 days. Livermore was the only station that exceeded the federal 1-hr ozone standard on 15 of the 36 days (Bay Area Air Quality Management District, 2007).

In general the simulated and observed high ozone areas coincided over much of the modeling domain on this first day of the episode. Ozone concentrations were overestimated along the coast, especially over the San Francisco and the Monterey Bays, where simulated ozone peaked 1-2 hours before observations. The location of the simulated ozone plume over the SFBA was about 20 km east of observations (Figure 4b). Near Sacramento, ozone concentrations were underestimated and peaked later than observations. Similarly, ozone concentrations were also underestimated in Fresno and Bakersfield and peaked 1-3 hours later than observations.

In the Central Valley, observed ozone concentrations decreased rapidly in the late afternoon compared to simulations. For example, near Bakersfield and Fresno, observed ozone was below 85 ppb at 16:00 PST (Figure 4b), whereas simulated values were still above 100 ppb.

During the second day of the episode, August 1, 2000, ozone concentrations exceeded the former federal 1-hr standard in the Sacramento area. This was the only exceedance region in the study domain. Figure 4c shows that the magnitude, timing and location of simulated ozone concentrations were very close to observations there. In the SFBA, ozone concentrations were slightly underestimated but the timing of simulated peak coincided with observations. In the SJV, especially near Bakersfield, the ozone was underestimated by 10-15 ppb.

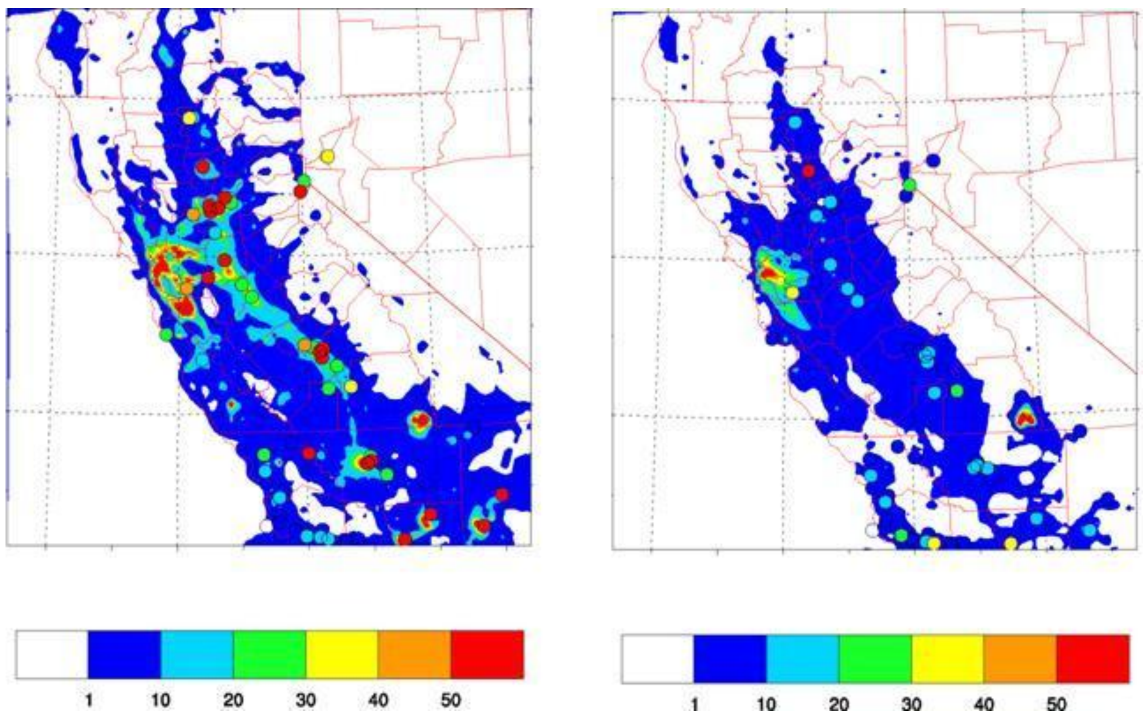
On August 2, 2000, observed ozone concentrations reached 151 ppb in the SJV at Edison. This was the only exceedance region in the study domain. On this day, ozone concentrations were underestimated (by about 25-30 ppb in Fresno and 40 ppb in Bakersfield) and the peak ozone was simulated 2-3 hours after observations. Ozone maxima were simulated accurately in terms of both timing and location in the Sacramento area (Figure 4d), although the simulated ozone plume did not extend far enough north. In SFBA, similarly to the first day of the episode, simulated ozone was slightly overestimated and was located 10-15 km east of observations, but the timing was accurate.

Simulated and observed concentrations of NOx (NO + NO2 + HNO2) are shown in Figure 5a,b. During rush hours, NOx concentrations were highest, especially around the major metropolitan areas. In general, CAMx reproduced the location of NOx maxima correctly at this time (Figure 5a). Underestimates were found along the coast, near cities in the SJV, and along the southern boundary. The latter was possibly caused by the proximity to the Los Angeles area, not well represented in the boundary conditions. On August 2, 2000, the day that ozone was significantly underestimated in the southern SJV, simulated concentrations of NOx were in very good agreement with observed values near Bakersfield (not shown).

Two different VOC concentration patterns were found in simulations. The first one, associated with anthropogenic activity, was dominant during the night (Figure 6a). VOC maxima were found along the main axis of the Central Valley, especially near major urban areas, around the city of Sacramento, in the southern SFBA (near the city of San Jose), and in the Sacramento River delta area. High concentrations over the Sierra Nevada, southeast of Fresno, were due to emissions from the Manter wild fire. The second pattern dominated during the daytime and was clearly associated with biogenic emissions (Figure 6b).

VOC maxima were found in the Sierra Nevada, in the Cascade Range near Mount Shasta, and on the mountain ranges between the Pacific Ocean and the Sacramento Valley. High anthropogenic VOC concentrations were found during the afternoon at only a few isolated locations, such as the

Livermore area, and to the south of Modesto in the northern SJV. In the early morning and in the evening, a combination of the two patterns was present (not shown).



Figures 5: NOx (ppb) 1-hr concentrations simulated by CAMx and observed (filled circles) at station locations at: (a) 7:00 PST on 31 July, representative of rush hour conditions (left panel); and (b) 15:00 PST on 31 July, one hour prior to the time of the maximum observed ozone over SFBA.

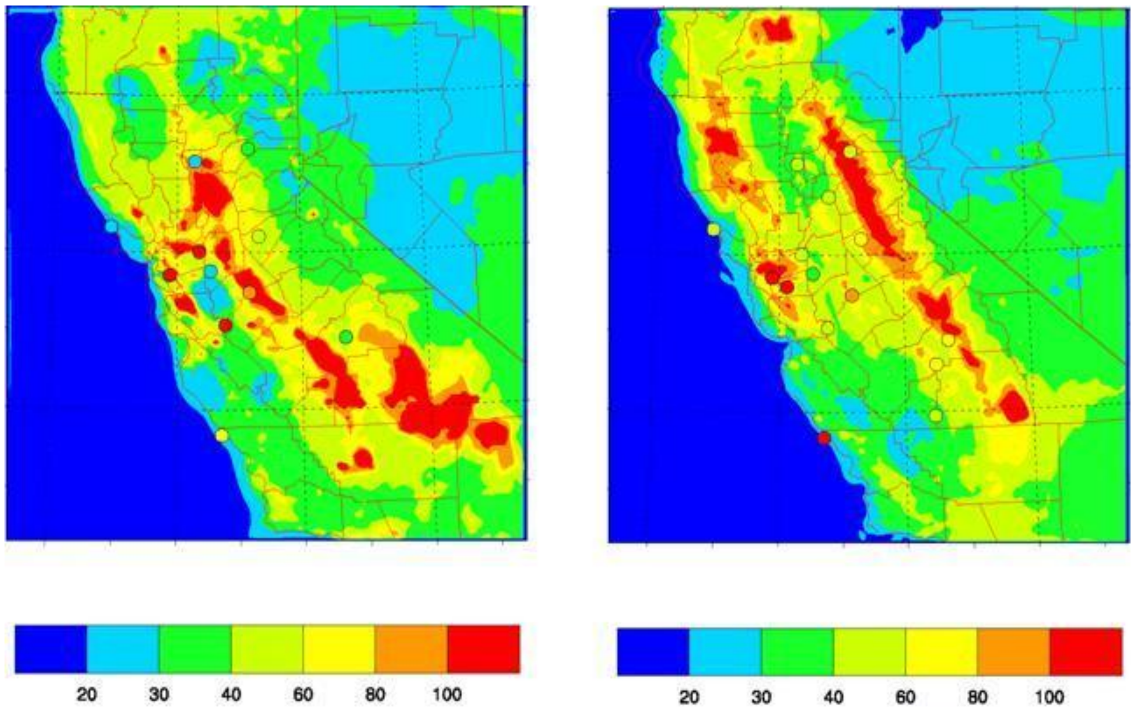


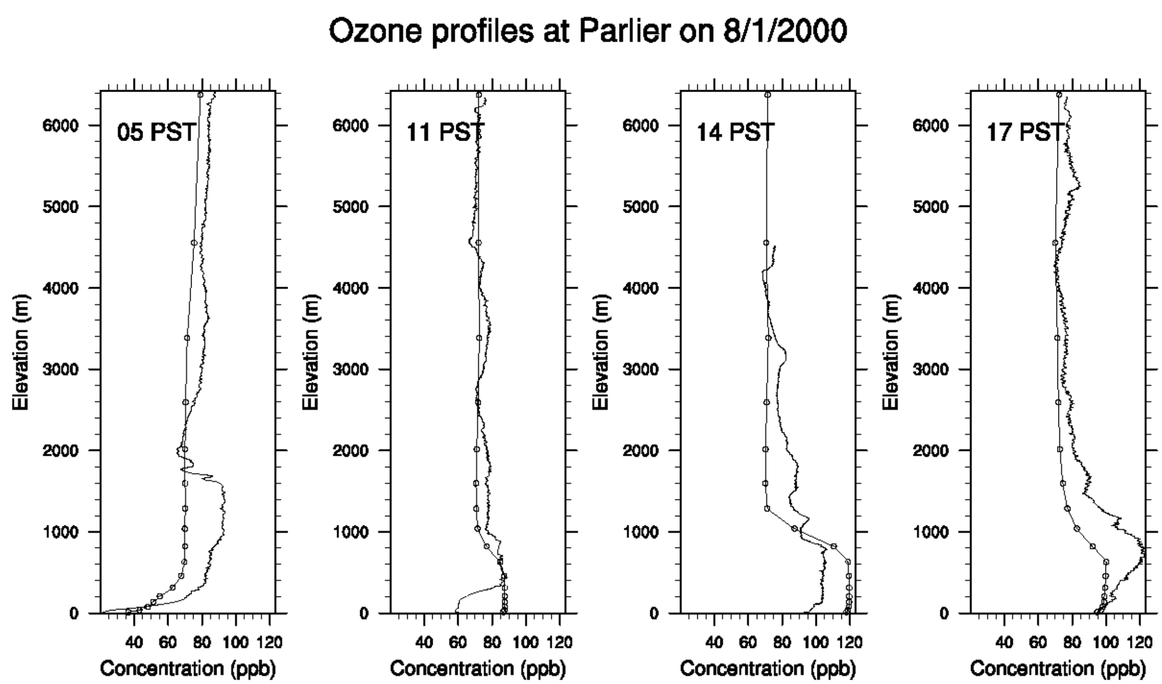
Figure 6: VOC (ppbC) 3-hour concentrations simulated by CAMx and observed (filled circles) at station locations at: (a) 0:00 PST on 31 July, representative of nocturnal conditions (left panel); and (b) 13:00 PST on 31 July, representative of daytime conditions.

4.2 Ozone in aloft layers

Ozone data were collected with the use of ozonesondes at Parlier and Granite Bay on the first two days of the episode. Observed and CAMx simulated ozone are shown, for August 1, in Figure 7a,b.

At Parlier (Figure 7a), concentrations were near uniform with height above 2000 m and approximately equal to 80 ppb. This behavior was well reproduced by the model. Below 2000 m, the ozone profile transitioned from a sheared profile in the morning, with less than 10 ppb of ozone near the ground and about 90 ppb at 1000 m, to a uniform profile of about 100 ppb during the time of maximum vertical mixing in the early afternoon. This behavior was generally reproduced by CAMx, but the uniform profile was reached earlier in the day (at 11:00 PST) compared to observations. In the late afternoon, a local ozone maximum of 120 ppb was observed at about 800 m. Above that level, ozone decreased to 80 ppb near 2000 m. CAMx did not reproduce this sheared profile but simulated a uniform profile, similar to that simulated in the early afternoon but with lower ozone (100 vs. 120 ppb).

At Granite Bay (Figure 7b), the same uniform profile of 80 ppb was produced as in Parlier, but above 4000 m. Between 2000 and 4000 m ozone was not uniform but increased slightly with height. CAMx showed a uniform simulated profile from 2000 m up. In the lowest 2000 m, the transition from a sheared pattern in the morning to a uniform and well mixed layer in the afternoon was observed. CAMx showed the same transition pattern, but the timing was again off by a few hours, as a uniform layer of 100 ppb was reached as early as 11:00 PST, whereas the observed profile at that time was only about 65 ppb.



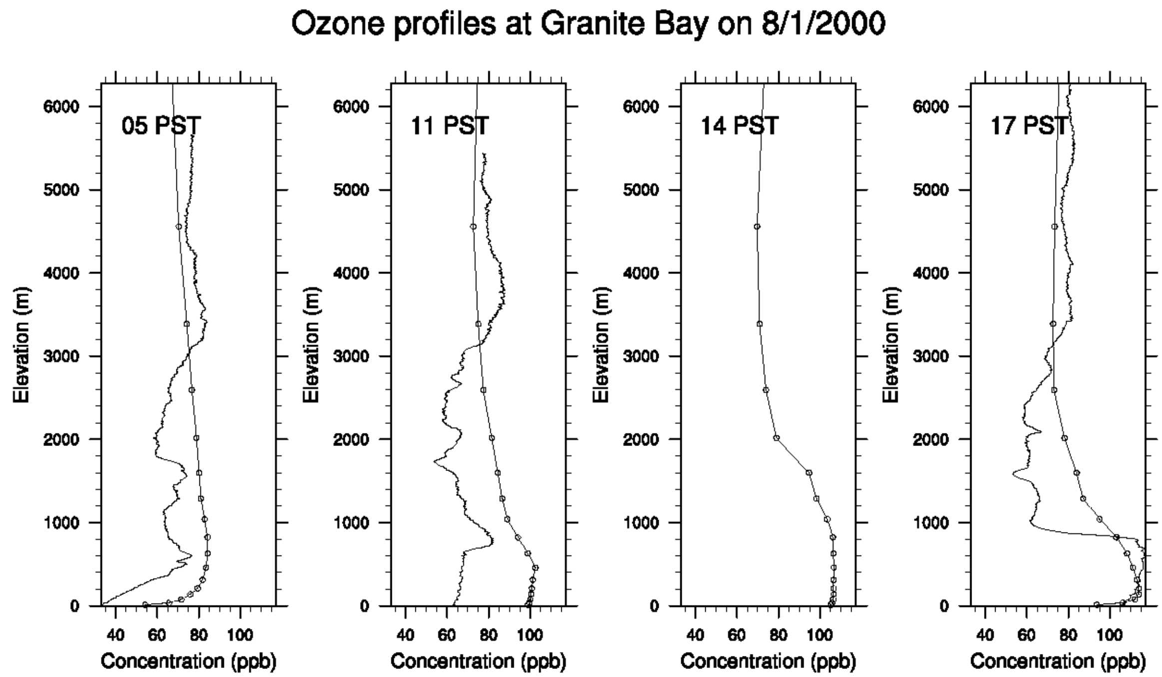


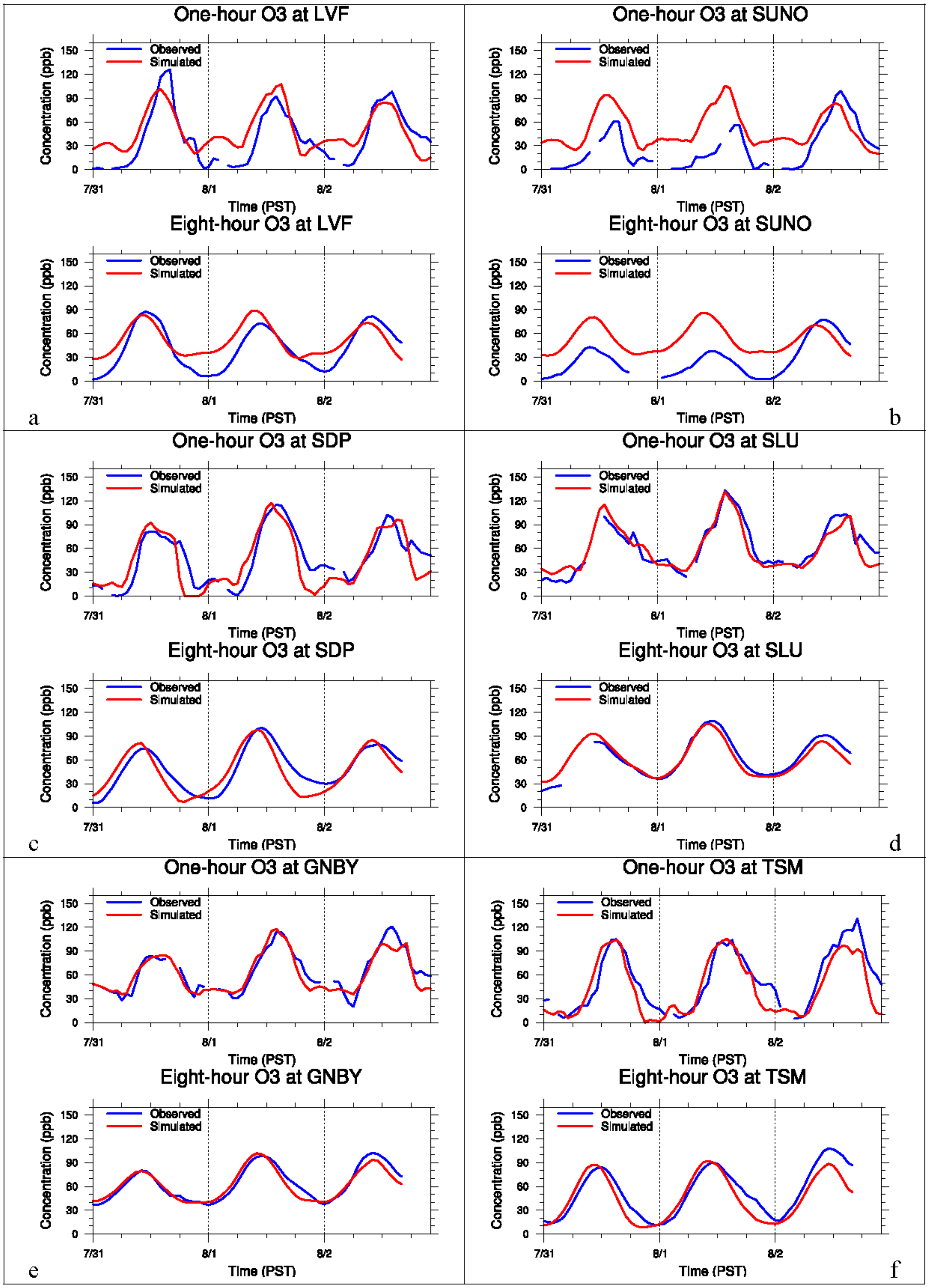
Figure 7: Observed (solid line) versus simulated (solid line with circles) ozone profiles at selected times on 1 August 2000 at (a) Parlier (upper panel), and (b) Granite Bay (lower panel).

4.3 Model performance

We evaluated model performance for ozone and its precursors over the modeling domain as well as over the three major regions SFBA, Sacramento, and SJV. To facilitate the discussion, the SJV region was further subdivided into three regions: northern (NSJV), central (CSJV), and southern (SSJV), as shown in (Figure 2). We selected several stations in the three regions based on representativeness of their respective region and availability of measurements with multiple chemical species, such as O3, NOx, and VOC, from the same site. Sites meeting these criteria are: Livermore (LVF) and Sunol (SUNO) in SFBA; Sacramento (SDP), Sloughhouse (SLU), and Granite Bay (GNBY) in the Sacramento region; Turlock (TSM) in NSJV; Parlier (PLR) in CSJV; and Bakersfield (BGS) and Edison (EDS) in SSJV (Figure 1). Hourly time series of 1-hr and 8-hr observed and simulated ozone concentrations at these sites are shown in (Figure 8).

In the SFBA, Livermore had the only exceedance of the former federal 1-hr ozone standard on 31 July, with observed and simulated 1-hr peaks of 126 and 101 ppb, respectively (Figure 8a). The diurnal pattern was reproduced well by CAMx, but nocturnal values were generally higher than observed by up to 30 ppb. The timing of the simulated ozone peak was off by a couple of hours, with the simulated maximum occurring earlier than observed on all days. Similar results were found at Sunol (Figure 8b).

Maximum 8-hr ozone concentrations, calculated from the moving averages of 1-hr concentrations, were reached at about 10:00 PST. Simulated 8-hr concentrations were generally too high in Livermore, mostly due to the combination of two effects: the overestimates in 1-hr ozone at night and the fact that the observed peak was generally narrower than the simulated one. A consequence of the latter is that the standard deviations of observed ozone concentrations σ^{OBS} were in general larger than the standard deviations of simulated concentrations σ^{SIM}. The normalized standard deviation $\sigma^{NORM} = \sigma^{SIM}=\sigma^{OBS}$ was therefore lower than 1 in general, especially for 8-hr ozone. At Sunol, simulated concentrations were generally higher than observed, both during the day and night. Also, the simulated ozone peak occurred earlier than observed by 1-3 hours.



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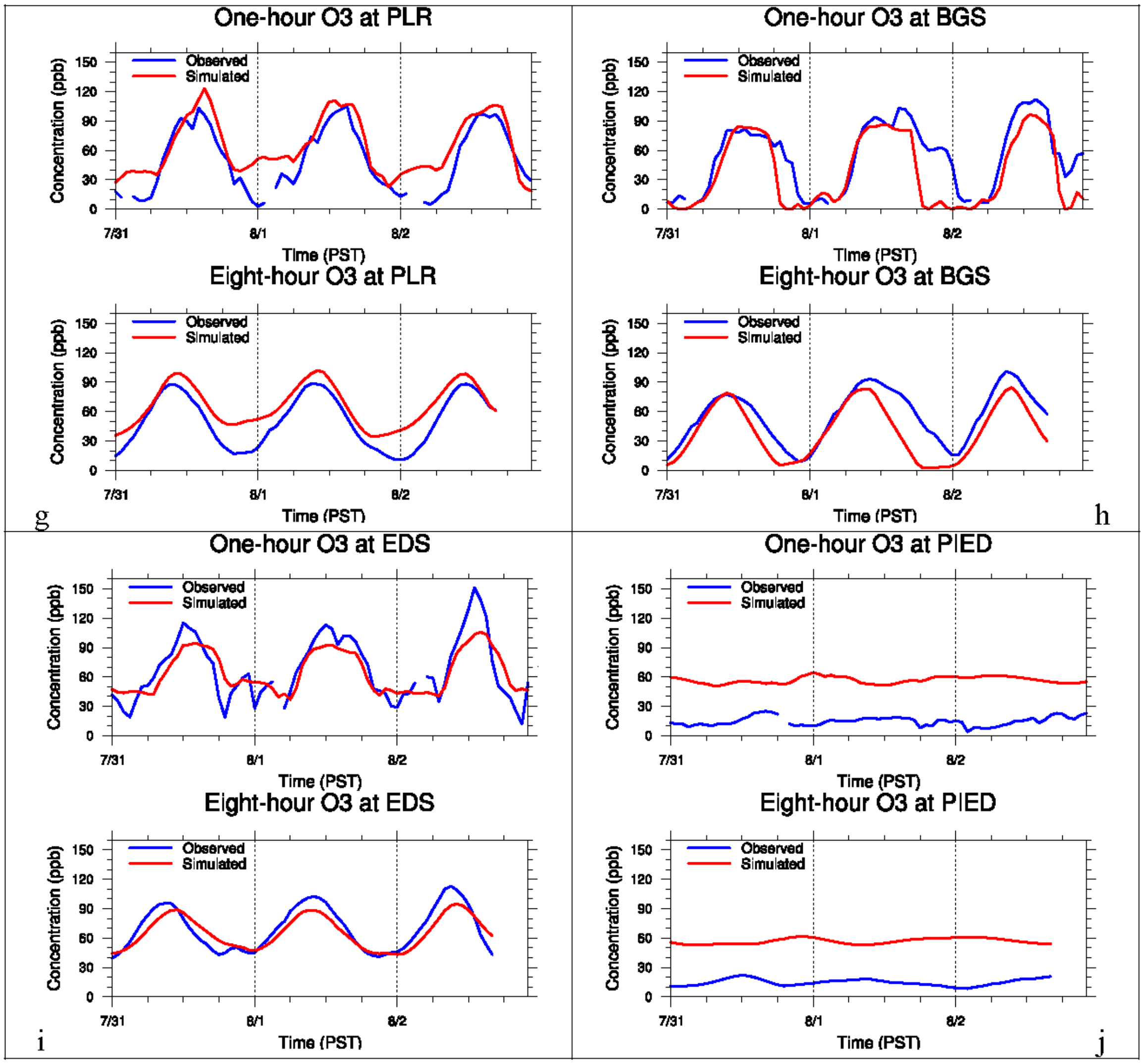

Figure 8: Observed versus simulated 1-hr and 8-hr ozone concentrations at: Livermore (a) and Sunol (b) in SFBA; Sacramento (c), Sloughhouse (d), and Granite Bay (e) in the Sacramento area; Turlock (f) in NSJV; Parlier (g) in CSJV; Bakersfield (h) and Edison (i) in SSJV; and Piedras Blancas (j), a costal site.

In Figure 9a-c, Taylor diagrams (Taylor, 2001) for 1- and 8-hr ozone, and NOx for the 3-day CCOS episode are shown. Each point on the diagram corresponds to simulated results at a site. Three statistical parameters are represented: the correlation coefficient ρ, as the clockwise angle from the y-axis, the normalized standard deviation σ^{NORM}, as the radial distance from the origin, and the normalized centered RMSE (root mean square error) divided by σ^{OBS}, as the distance from the point marked as "OBSERVED" on the diagram. This point represents all observed values, since, by definition, they all have ρ = 1 and σ^{NORM} = 1. The color scale indicates the subregion.

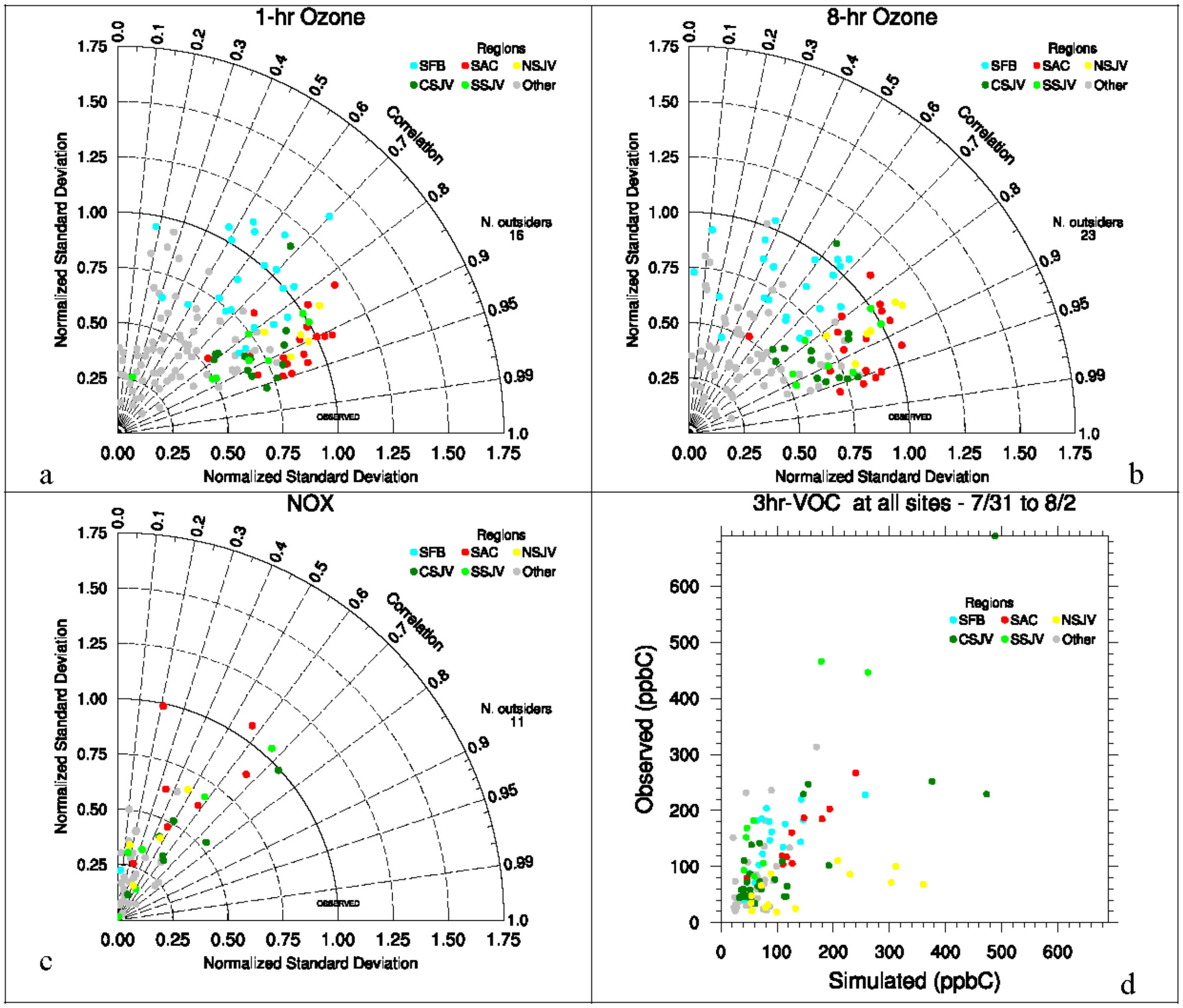

Figure 9: Taylor diagrams for: (a) 1-hr ozone; (b) 8-hr ozone; (c) NOx for the 3-day episode. Each point on the diagram corresponds to simulated results at a station. The angle from the y-axis is the correlation with observed values ρ and the distance from the origin is the ratio of the simulated to the observed standard deviation ($\sigma^{NORM} = \sigma^{SIM}/\sigma^{OBS}$). All observed values are collapsed at a single point, marked as "OBSERVED", with ρ =1 and σ^{NORM} =1. The distance between each point and "OBSERVED" is proportional to the centered square error. For VOC, the scatter plot of observed vs. simulated 3hr-averages is shown in (d) for the three days.

For the SFBA, CAMx performance was acceptable for both 1-hr and 8-hr ozone concentrations (Figure 9a,b). Correlation coefficients were about 0.60 and normalized standard deviations were 0.75. Additional statistical parameters are shown in Table 1 for 1-hr ozone and in Table 4 for 8-hr. Ozone peaks were generally underestimated, as peak ratios varied between 0.88 and 0.93. Also, the mean bias was positive. This is consistent with previous findings in that ozone was generally overestimated by CAMX. Coastal locations showed large overestimates at night, despite small underestimates at peak ozone time.

Among the selected subregions, the best CAMx performance for ozone was achieved in the Sacramento area, with an average ρ of 0.90 and σ-norm close to one (Figure 9 and Tables 1, 4). Ozone time series plots for Sacramento, Sloughhouse and Granite Bay (Figure 8c-e) confirm this. Sloughhouse and Granite Bay had an almost perfect match between observed and simulated 1-hr and 8-hr ozone, whereas at Sacramento ozone peaks were slightly early and nocturnal values were slightly underestimated for both 1-hr and 8-hr ozone concentrations.

In NSJV, represented by Turlock in (Figure 8f), the simulated hourly trend of 1-hr ozone matched the observations well in terms of peak timing, magnitude, and width. Overall, this subregion had very good performance (Figures 9a,b and Tables 1, 4).

In CSJV, the model consistently overestimated ozone concentrations. Parlier was one of the few sites with overestimated ozone in the modeling domain (Figure 8g). At this site, the simulated 1-hr and 8-hr ozone values were higher than observed during both day and night, although the peak width was close to observations. In general, simulated peaks occurred after the observed ones in CSJV, a timing issue that was frequently encountered throughout the modeling domain. Results were good for this region for both 1-hr and 8-hr ozone, with average correlation coefficients of 0.61-0.83, and 0.67-0.81, respectively (Figures 9a,b and Tables 1, 4).

In SSJV, large underestimates of 1-hr ozone concentrations were found during the day, especially at Edison on August 2 (Figure 8i), where the maximum observed value was 151 ppb, but the simulated peak was only 106 ppb. Note that only the Edison site reported an exceedance on that day, with Arvin having the second highest reading of 120 ppb and Bakersfield 112 ppb. A spike like this at a sole station is always difficult to replicate. Overall model performance for this subregion was also acceptable, as shown by the average correlation coefficient of 0.73 and 0.84 (for 1-hr and 8-hr ozone, respectively) in Tables 1 and 4 and by the Taylor diagrams (Figures

9a,b). However, the average bias was negative and relatively high on all three days (between -8 and -11 ppb).

In summary, the CAMx performance for ozone was rather good in the CCOS domain, particularly in the Sacramento area. The model had the tendency to overestimate ozone at night, possibly due to the boundary conditions, vertical mixing and the thickness of the first layer of the model. Tracer runs (not shown) indicated that concentrations were especially sensitive to the northern boundary values in the SFBA and to the southern boundary in SSJV, the latter perhaps related to emissions in the Los Angeles basin. Improvements in the southern boundary conditions would likely improve the model performance there.

Despite the good performance achieved by CAMx for ozone, simulated NOx concentrations were generally lower than observed (Figure 10). The morning peak was often underestimated by up to 60% (e.g., Granite Bay site in Sacramento and Parlier site in SSJV on 31 July), whereas the evening peak was overestimated. The sites with the best model performance for NOx in the morning had also the best ozone performance during the day.

The Taylor diagram (Figure 9c) shows that the best performance site location in the SFBA had a correlation coefficient of about 0.70 for NOx and 0.95 for ozone. Also most site locations for NOx had a normalized standard deviation lower than 0.4. This indicates that the amplitude of simulated diurnal trends for NOx was generally underestimated by CAMx.

VOCs were sampled over 3 hours at 26 sites, but the sampling frequency varied from site to site. For example, only two 3-hr measurements were made at Sunol during the 3-day episode, but over 10 measurements were made at Turlock. Because of the small sample size, statistical evaluation was not possible at individual sites.

We created a scatter plot of observed vs. simulated 3-hr VOC to evaluate model performance (Figure 9d). The average correlation coefficient was 0.61 and the bias was -12 ppbC, suggesting that CAMx performance was acceptable for VOC, with a tendency towards underestimation. The best performance was achieved at site locations in the SFBA and Sacramento area, all aligned along the 1:1 slope line. The largest overestimates occurred in NSJV and CSJV.

Time series plots of VOC at selected stations are shown in Figure 11. At all sites, CAMx simulations show VOC minima occurring in the middle of the day or in the early afternoon, and high VOC concentrations are found in the early morning and in the evening, which suggests a strong correlation with the timing of motor vehicle emissions. Observations at some sites do not support this pattern.

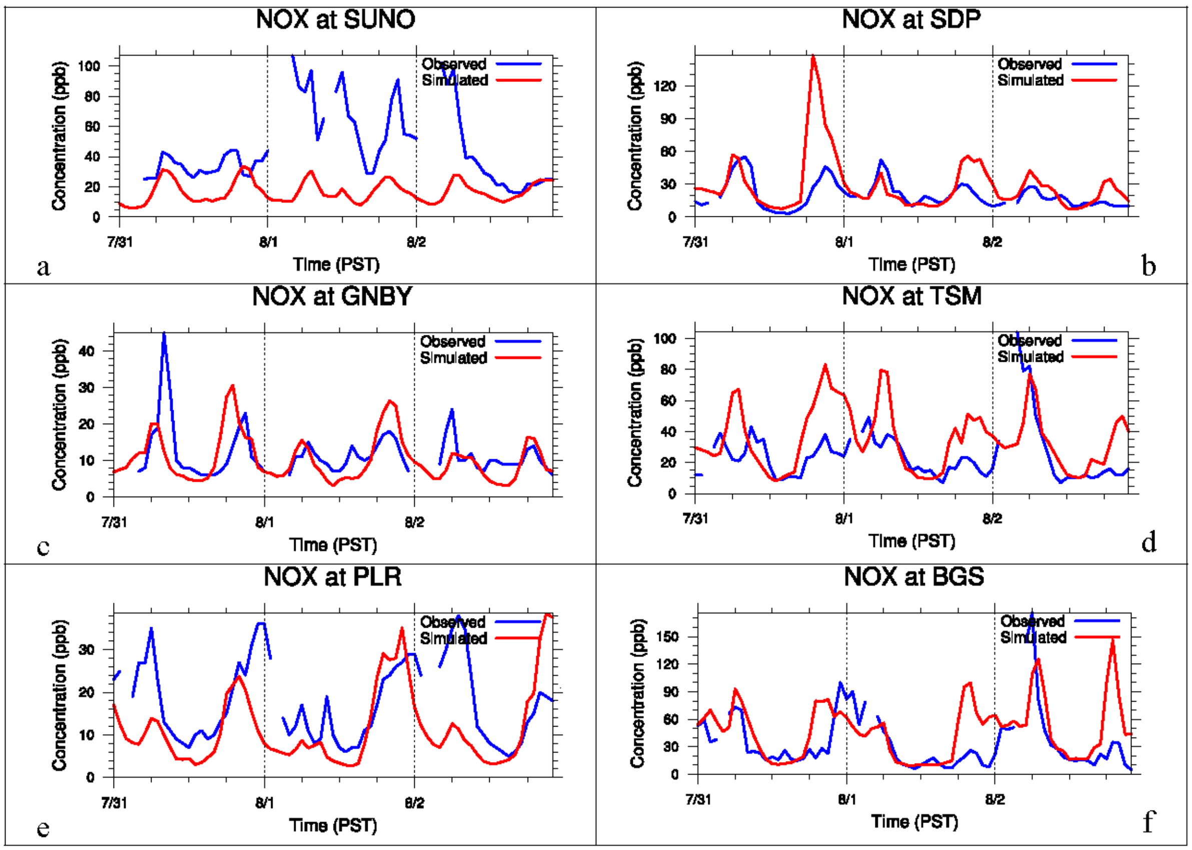

Figure 10: Observed versus simulated NOx concentrations at: Sunol (a), Sacramento (b), Granite Bay (c), Turlock (d), Parlier (e), and Bakersfield (f).

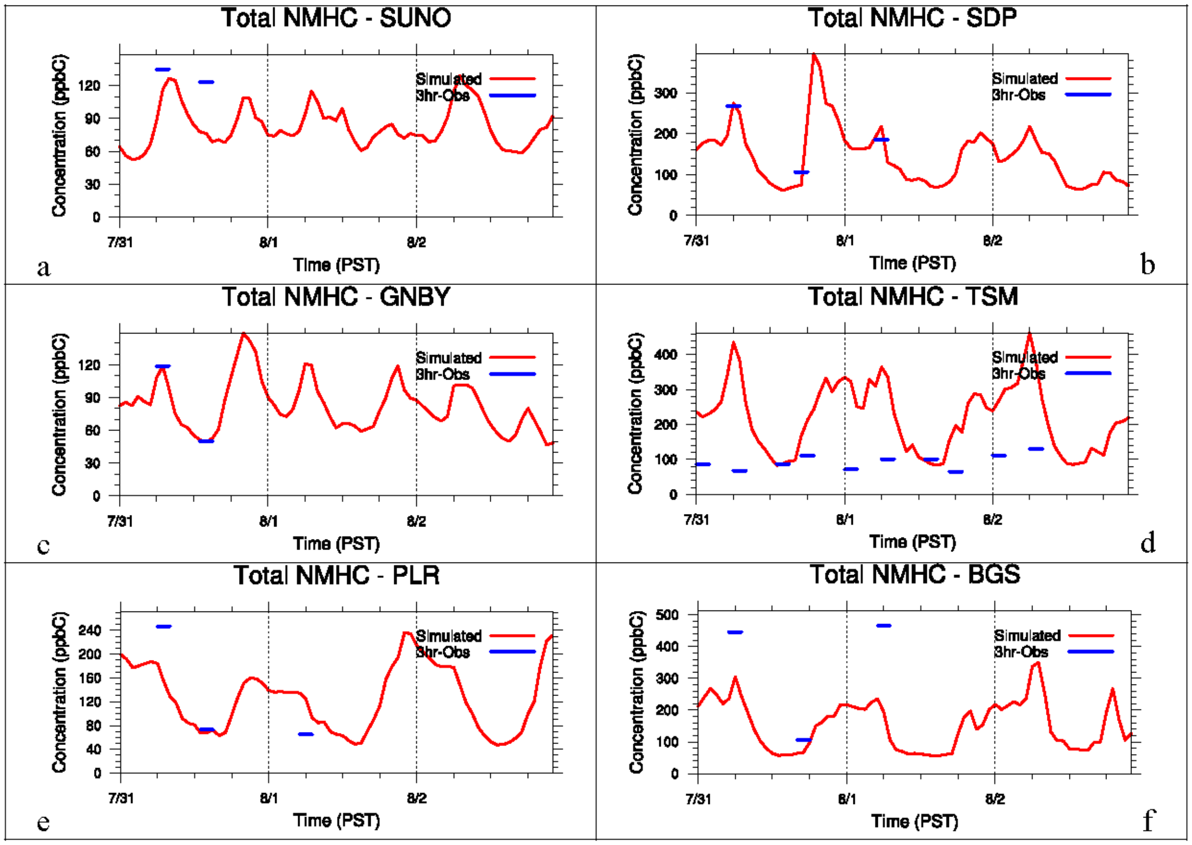

Figure 11: Observed versus simulated NMHC concentrations at: Sunol (a), Sacramento (b), Granite Bay (c), Turlock (d), Parlier (e), and Bakersfield (f).

4.4 Sensitivity Analysis

To evaluate the sensitivity of simulated ozone to reductions in NOx and VOC, we produced a set of ozone isopleths at several stations of interest. Simulations were conducted by reducing anthropogenic emissions uniformly across the modeling domain by 20%, 40%, and 60%. Figure 12 shows ozone isopleths diagrams for each region when they had 1-hr ozone exceedance (31 July for SFBA, 1 August for Sacramento, and 2 August for SJV). Emissions from the Manter forest fire were not included in the sensitivity analysis.

The SFBA region, represented by Livermore and Sunol (Figure 12a,b), appears to be VOC limited. When anthropogenic NOx emissions were reduced by 20% while keeping VOC emissions unaltered, the maximum 8-hr ozone at Livermore increased by about 3 ppb. This increase, however, appears to be episode-specific since it was not supported by other episodes. When NOx was further reduced (40% and above), ozone concentrations were reduced. Reducing VOC emissions always reduce 8-hr ozone.

In the Sacramento region, three sites, Sacramento, Sloughhouse, and Granite Bay were selected for sensitivity analysis. From the ozone isopleths in Figures 12c-e, the Sacramento region appeared to be NOx-limited.

The sub regions in the SJV did not respond uniformly to emission reductions during this episode. In CSJV, ozone production was NOx limited (Parlier, Figure 12g). In SSJV, it was VOC limited (Bakersfield and Edison, Figures 12h,i).

To verify the simulated sensitivities against observations, we calculated trends in emissions and ambient ozone concentrations from 1995 through 2005 and compared them against isopleths.

The 1995-2005 trends in NOx and ROG emissions and in design value ozone concentrations in the SFBA, Sacramento, and SJV areas are shown in Table 5. Both emissions and ozone went down in all regions. In the SFB area, more reductions were achieved in ROG than in NOx (-24 vs. -21 tons/day per year), resulting in 1 ppb ozone reduction. Model somewhat agrees qualitatively with these ambient trends. In the SJV, NOx was reduced more than ROG (-21 vs. -12 tons/day per year). This is also consistent with the model findings. In the SAC area, both NOx and ROG were reduced equally. Trend in ambient ozone is steeper in the Sacramento area compared to other regions for the same amount of emission reduction. Overall, observed and modeled sensitivities appeared to be in qualitative agreement.

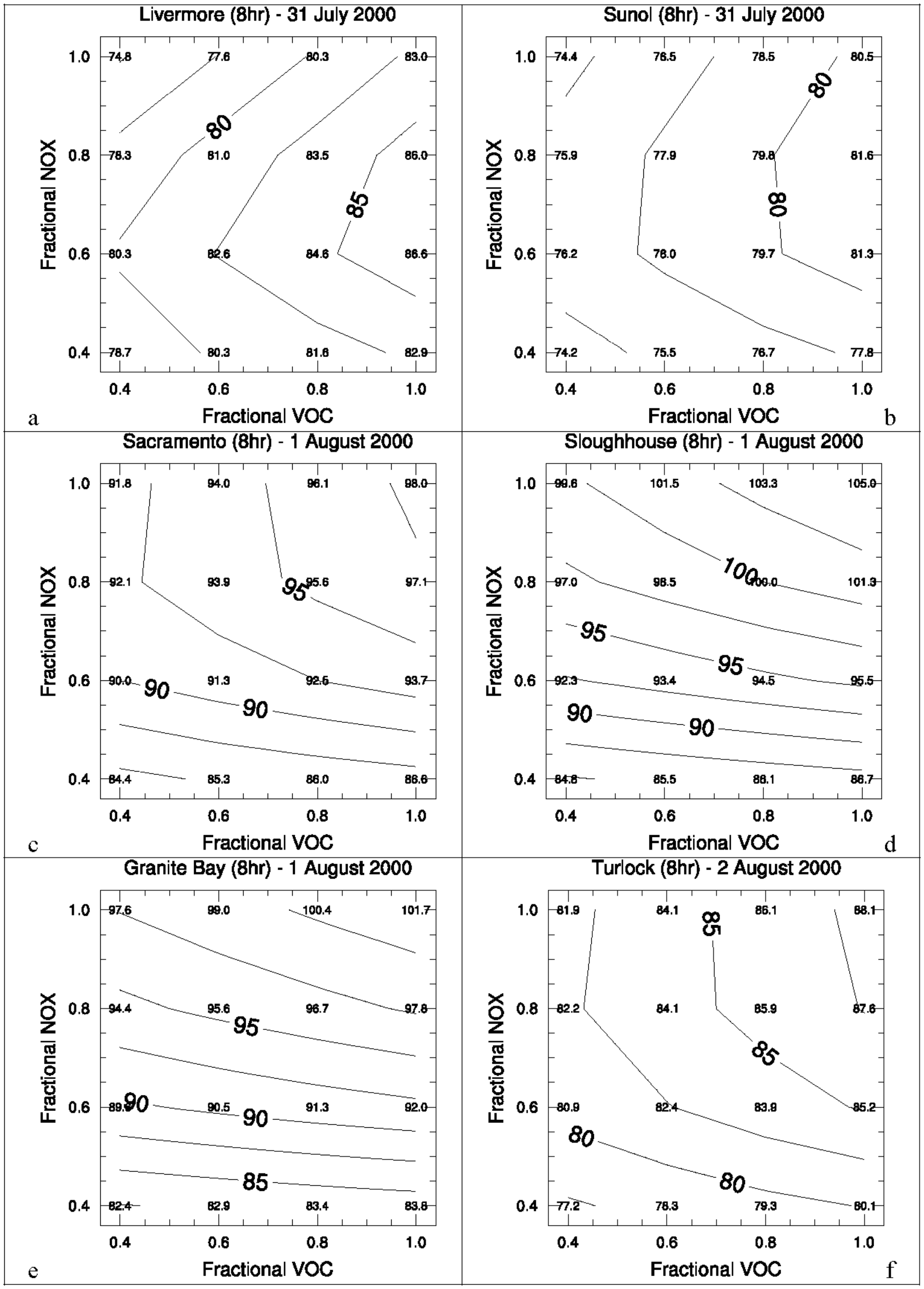

Figure 12: Continued on the next page.

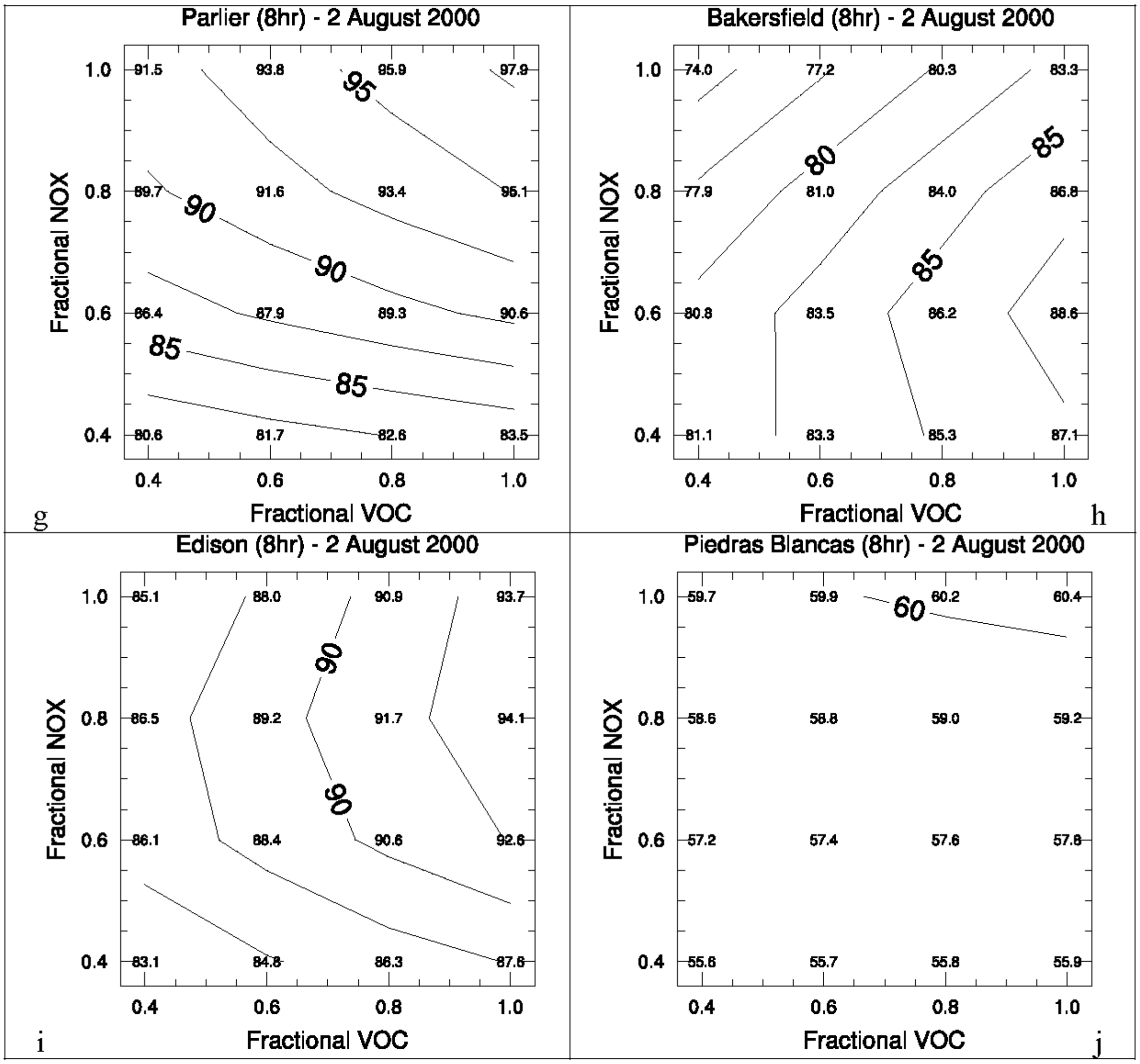

Figure 12: Eight-hour ozone isopleths (or ozone sensitivity maps) corresponding to uniform reductions of NOx and/or VOC over the entire CCOS domain at: Livermore (a) and Sunol (b) in SFBA; Sacramento (c), Sloughhouse (d), and Granite Bay (e) in Sacramento; Turlock (f) in NSJV; Parlier (g) in CSJV; Bakersfield (h) and Edison (i) in SSJV; and Piedras Blancas (j), a costal site. The day with the highest observed 1-hour ozone is shown for each site.

6. Conclusions

The MM5 and CAMx models were used to study meteorology and formation of ozone in central California. The three-day ozone episode of 31 July – 2 August 2000 was chosen for modeling because of the availability of rich database from the 2000 CCOS field program. CAMx performed well for ozone and satisfactorily for NOx and VOC. The model appeared to be adequate for photochemical modeling to prepare the State Implementation Plans.

Response of model to emission reductions was studied by reducing NOx and VOC emissions over the modeling domain. Simulated sensitivities varied across the domain. The SFBA appeared to be VOC limited. The Sacramento and the northern SJV areas appeared to be NOx-limited. The rest of the SJV appeared to be VOC-limited or sensitive to NOx and VOC reductions equally. Qualitatively, model sensitivities were in agreement with observed emission and ozone trends in recent years.

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Table 1: Statistical evaluation of CAMx performance for 1-hr ozone in the five sub-regions on each day of the CCOS episode. All concentrations are in ppb and time is in PST. Correlation coefficient ρ was calculated only if at least 3 observations were above 60 ppb in a sub-region. Maximum simulated ozone at any site within each sub-region is shown in column "Simulated (sites)", whereas maximum simulated ozone in the entire sub-region (even where no sites were available) is shown in "Simulated (regional)".

Sub-Region	N. Obs.	Peak Concentrations								Statistical Parameters			
		Observed		Simulated (sites)			Simulated (regional)						
		Value	Time	Value	Time	Peak Ratio	Value	Time	Peak Ratio	Mean Bias	Mean Error	Mean ρ	ρ
31 July 2000													
SFB	59	126.0	16	110.9	16	0.88	125.3	14	0.99	5.1	16.8	0.84	0.43
SAC	142	103.0	13	115.5	13	1.12	132.5	15	1.29	1.0	9.2	0.49	0.43
NSJV	47	125.0	16	119.6	15	0.96	130.4	15	1.04	5.4	15.6	0.89	0.63
CSJV	111	119.0	16	122.9	15	1.03	123.3	15	1.04	0.3	10.6	0.61	0.59
SSJV	94	115.0	12	109.2	15	0.95	110.5	15	0.96	-3.3	7.8	0.65	0.71
1 August 2000													
SFB	82	109.0	14	107.4	15	0.99	123.3	15	1.13	-3.9	15.8	0.67	0.53
SAC	158	133.0	14	131.7	14	0.99	142.5	15	1.07	-0.2	9.9	0.85	0.70
NSJV	58	119.0	15	117.6	15	0.99	129.4	16	1.09	4.7	12.5	0.70	0.66
CSJV	150	120.0	13	110.7	14	0.92	119.3	15	0.99	-6.1	13.2	0.83	0.62
SSJV	109	116.0	13	101.6	14	0.88	105.4	13	0.91	-11.1	12.2	0.89	0.74
2 August 2000													
SFB	112	100.0	11	92.3	14	0.92	112.9	15	1.13	-12.4	16.0	0.62	0.52
SAC	153	121.0	14	120.4	15	0.99	122.2	13	1.01	-2.6	12.8	0.52	0.63
NSJV	64	131.0	17	113.3	15	0.86	117.6	15	0.90	-14.9	18.6	0.80	0.79
CSJV	149	120.0	18	115.7	13	0.96	125.1	14	1.04	-8.7	15.7	0.65	0.58

SSJV	87	151.0	13	105.8	14	0.70	106.7	14	0.71	-14.6	16.5	0.73	0.77

Table 2: Total NOx and VOC emissions (tons/day) from area, motor vehicles, biogenic, and point sources over each of the three sub regions of the CCOS domain for the 31 July - 2 August 2000 episode.

		NOx				VOC			
Day	Region	Area	Motor Vehicles	Biogenic	Point	Area	Motor Vehicles	Biogenic	Point
31 July	SFB	236	282	6	91	240	194	305	69
(Monday)	SAC	87	106	9	5	76	71	446	4
	SJV	325	262	52	51	421	126	695	24
	CCOS	920	898	146	268	1070	555	5075	126
1 August	SFB	236	273	6	92	240	195	283	74
(Tuesday)	SAC	87	102	9	5	76	71	409	4
	SJV	325	247	59	52	421	131	793	24
	CCOS	920	858	155	271	1070	560	4995	131
2 August	SFB	236	275	6	90	240	192	262	73
(Wednesday)	SAC	87	101	9	5	76	69	418	4
	SJV	325	252	58	51	421	130	800	24
	CCOS	920	867	150	270	1070	551	4900	131

Table 3: Boundary conditions (ppb) at the surface over land and over water. The values in parentheses are aloft values, if different from the surface.

Species	Land	Water
NO	0.05	0.05
NO2	1	1
O3	40 (70)	25 (70)
CO	200	200
HCHO	2	2
RCHO	0.5	0.5
PAN	0.005	0.005
ALK1	10	6
ALK2	2.5	1
OLE1	0.5	0
OLE2	0.2	0
ARO1	0.35	0
ARO2	0.25	0
ISOP	0.1	0
ACET	1	1

Table 4: Same as Table 1, but for 8-hr ozone. Only 8-hr concentrations above 50 ppb were used.

Sub Region	Nmbr. of Obs.	Peak Concentrations								Statistical Parameters			
		Observed		Simulated at Sites			Simulated at Region						
		Value	Time	Value	Time	Peak Ratio	Value	Time	Peak Ratio	Mean bias	Mean error	Mean ρ	ρ
July 30, 2000													
SFB	69	89.5	11	97.0	10	1.08	102.2	10	1.14	5.6	10.2	0.71	0.60
SAC	167	89.5	10	94.3	10	1.05	109.3	11	1.22	2.6	7.8	0.67	0.61
NSJV	65	96.6	12	96.8	11	1.00	109.5	11	1.13	3.3	14.0	0.72	0.58
CSJV	147	103.6	11	98.7	10	0.95	100.5	11	0.97	2.8	9.0	0.67	0.71
SSJV	113	95.6	9	97.0	13	1.01	101.2	11	1.06	-1.4	7.2	0.89	0.72
August 1, 2000													
SFB	107	90.4	13	88.7	13	0.98	105.2	11	1.16	-2.6	12.3	0.77	0.49
SAC	212	108.8	11	105.1	10	0.97	111.1	11	1.02	0.1	7.3	0.90	0.82
NSJV	77	93.3	12	99.8	10	1.07	106.7	11	1.14	0.8	11.4	0.86	0.68
CSJV	191	109.9	11	101.9	10	0.93	109.6	10	1.00	-3.1	12.0	0.67	0.64
SSJV	136	104.6	10	94.7	10	0.90	99.0	11	0.95	-8.2	10.0	0.91	0.73
August 2, 2000													
SFB	136	89.6	10	73.5	9	0.82	93.1	11	1.04	-11.2	12.9	0.78	0.53
SAC	210	107.3	11	101.3	11	0.94	102.9	11	0.96	-0.9	8.2	0.95	0.78
NSJV	71	107.8	11	91.1	10	0.85	98.7	11	0.92	-13.6	15.6	0.93	0.69
CSJV	154	112.4	12	103.9	10	0.92	111.5	11	0.99	-3.3	10.5	0.81	0.56
SSJV	111	112.9	9	94.9	10	0.84	97.7	10	0.87	-10.4	12.6	0.84	0.82

Table 5: Observed trends in NOx and ROG emissions (tons/day per year) and observed change in 3-year average of 4th highest 8-hr ozone concentrations (ppb per year) in the three sub regions of interest from 1995 to 2005.

Region	ΔNOx	ΔROG	ΔO_3
SFB	-21	-24	-1.0
SAC	-9	-9	-0.6
SJV	-21	-12	-0.4