Photochemical Modeling Investigation of an Extended Winter PM Episode Observed in Central California

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1. INTRODUCTION

We conducted a number of 22-day simulations using Community Multiscale Air Quality (CMAQ) model (USEPA, 1999; www.cmascenter.org, September, 2005) with prognostic meteorology inputs generated with a mesoscale model (MM5; Grell et al., 1995; www.mmm.ucar.edu/mm5, 2005), to investigate an extended winter PM episode captured in the California San Joaquin Valley during the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS) conducted from December 1999 to February 2001 (Magliano and McDade, 2005; www.arb.ca.gov/airways). PM modeling for the CRPAQS episode using updated CMAQ (Liang et al., 2005), CMAQ-UCD (Zhang et al., 2005a), and UCD/CIT model (Ying and Kleeman, 2006) were described previously by Zhang et al. (2005b). Liang et al. (2005) presented the setup and updates to CMAQ model code as well as preliminary results of sensitivity simulations. Zhang et al. (2005a) compared sectional representation of aerosol size distribution vs. modal representation. Corroborative analysis of CMAQ simulations using matrix factorization methods was presented by Liang et al. (2006). The emission inventory has been updated since an earlier study that used Chemical Mass Balance method as a corroborative analysis tool (Magliano et al., 1999).

We focus here on the evaluation of simulated chemistry and meteorology with extensive observations, based on guidelines for ozone model performance evaluation in central California (DaMassa et al., 1996). Our primary focus is on secondary aerosols that are important in Central California from a regulatory perspective.

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2. EVALUATION OF SIMULATED TEMPERATURE AND WIND

MM5 model results were evaluated with extensive observations collected during the CRPAQS study. The observed meteorological data were collected at 365 stations situated at surface and aloft throughout central and northern California between December 25, 2000 and January 7, 2001, as shown in Figure 1. Simulated temperature, wind speed, and wind direction were compared against hourly observations. First, spatial comparisons of 2-D horizontal cross sections of wind and temperature near the surface were plotted at every hour using all surface stations. Second, temporal comparisons of wind and temperature at each surface station for the duration of the model run were plotted. Third, the simulated upper air soundings were compared against the observed radiosonde data at the time of observations. An effort was also made to compare the progression of temperature and wind at other levels above the surface using available upper air observations. The mean bias (MB) and mean gross error (MGE) of modeled wind speed, wind direction, and temperature at all stations during the episode is listed in Table 1. It is shown that modeled wind speed and temperature agreed with observations within 1.5 m s^{-1} and 2.5 K, and modeled wind direction was off by ~60°, partly because of the low wind speed during the modeling period. Since the observed humidity was not always available, we did not evaluate relative humidity. Instead, air-quality simulations were conducted to evaluate the effect of using observed relative humidity, when available, on PM components and precursors.

3. Evaluation of PM Components and Precursors

We evaluated simulated PM components and their organic and inorganic precursor species with extensive observations collected during the CRPAQS study. Observations of organic and

inorganic precursor species as well as $PM_{2.5}$ components and PM masses were made at 162 stations in central and northern California during the modeling period (Figure 1). Note that not all pollutants were measured at all stations.

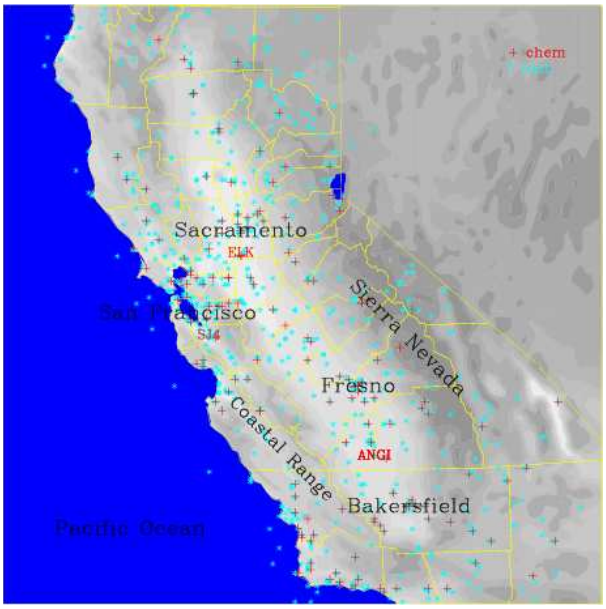

Figure 1. Observational stations for meteorology (*) and chemistry (+) over the model domain.

Table 1. Mean bias (MB) and mean gross error (MGE) of wind and temperature

	MB	MGE
Wind speed (m s^{-1})	0.49 (0.5)	1.53 (0.5)
Wind direction (º)	3.54 (10)	57.21 (30)
Temperature (K)	0.76 (0.5)	2.5 (2)

Note: Numbers in parenthesis are the upper limits recommended by US EPA.

Observed inorganic compounds include NO, NO_2, O_3, SO_2, NH_3, HNO_3, and CO. Observed organic compounds consist of α-pinene and detectable Volatile Organic Compounds (VOC) measured at the Photochemical Assessment Monitoring Stations (PAMS), with the total of 57 compounds. Observed organic compounds were mapped into 11 primary organic species in SAPRC99 chemical mechanism (cert.ucr.edu/~carter/SAPRC99/s99files.htm), namely, ALK1-5, OLE1-2, ARO1-2, Isoprene, and Terpene. Simulated isoprene is not presented here since observed values were rarely above the detection limit during the episode. Observed $PM_{2.5}$ components used for model evaluation include sulfate, nitrate, ammonium, elemental carbon, organic carbon, and pyrolyzed carbon. Other components, such as metals and water, were either not simulated in model or not reliable in observations. Size-resolved PM components were not used for evaluation here (Watson *et al.*, 2002; Herner *et al.*, 2005). We pooled all carbons together for evaluation, owing to possible differences in the measurement methods for ambient air (Chow et al., 2006) and emission samples (Kleeman et al., 1999). Hourly averaged model results were compared with observations for the above model species, in the form of diurnal pattern, vertical profile, scatter plot, and time series at each station. Separate scatter plot was made with data from all stations for each species mentioned above.

To evaluate modeled results with an observation, we considered modeled results for grids within n-grid distances from the corresponding station, where n ranged from 0 to 3, to assess the effect of spatial disparity (DaMassa et al., 1992; Ching et al., 2006) and to diagnose outstanding problems. When n>0, we made two comparisons. First, we compared the measured value with the average modeled value for $(2n+1)^2$ grid cells centered at the cell with the monitor. The statistics from this comparison may be compared with other modeling efforts with coarser grid resolutions. Second, we compared the measured value with the closest simulated value found within the $(2n+1)^2$ grid cells. When n=3, the second method is comparable to the 15-km-radius best-match method for summer time O_3 modeling (USEPA, 2006).

We show below some sample evaluation results of PM precursors and components in forms of scatter plots, diurnal patterns, and time series. Detailed comparisons of simulated and observed mixing ratios will be presented elsewhere.

3.1 Scatter Plots for Central and Northern California

We evaluated correlations of modeled results against observations at 162 stations over central and northern California for $PM_{2.5}$ mass and components, inorganic, and organic precursors when n=0, 1, 2, and 3, respectively. We found that the inconsistency between model and observations at n=0 was rather large for all species except terpene. Other studies with coarser resolution also found large inconsistency between modeled components and inorganic precursors, though no information was available for organic species (Boylan and Russell, 2006; Zhang et al., 2006). The relatively good representation of terpene in the model suggests

that biogenic emissions were fairly uniform around the stations.

Table 2 lists mean fractional error (mFE), mean fractional bias (mFB), and correlation coefficient (R) for 23 species when n=0 and n=3, respectively. Here we use the "best-match" method when n>0. Except for ALK2, NO, and HNO_3, for all other species the (mFE, mFB, R) ranged from (0.37, 0.05, 0.06) to (1.1, 1.0, 0.71) when n=0, and from (0.05, 0.02, 0.54) to (0.59, 0.52, 0.99) when n=3. It appears that, as n increased from 0 to 3, better agreement between model and observations was reached, as illustrated in Figure 2 for $PM_{2.5}$ mass. This indicates that significant spatial gradients existed in the model grids around stations. This is also supported by the fact that a 49-cell average was not a significant improvement over the n=0 case, as shown in the second panel of Figure 2. In such a situation, model performance is sensitive to spatial resolution of emissions, volume representation of stations, and the wind field from source grids to stations, among others.

Table 2. Mean fractional error (mFE), mean fractional bias (mFB), and correlation coefficient (R) of selected model species

	mFE		mFB		R	
	n=0	n=3	n=0	n=3	n=0	n=3
PM mass and key components						
NH_4^+	0.73	0.44	-0.19	-0.14	0.44	0.59
NO_3^-	0.79	0.49	0.05	0.09	0.44	0.63
PM_{10}	0.78	0.53	-0.21	-0.18	0.55	0.78
PM_{25}	0.68	0.37	-0.26	-0.09	0.41	0.74
$SO_4^=$	0.77	0.45	-0.54	-0.33	0.18	0.63
TC	0.83	0.45	-0.71	-0.37	0.71	0.82
Inorganic gas precursor species						
CO	0.85	0.59	-0.73	-0.48	0.39	0.57
HNO3	***0.90***	***0.75***	***-0.63***	***-0.61***	***0.14***	***0.33***
NH_3	0.94	0.54	0.07	0.10	0.23	0.84
NO_2	0.77	0.33	-0.37	-0.16	0.46	0.80
NO	***1.30***	***0.90***	***-0.90***	***-0.67***	***0.23***	***0.55***
O_3	0.79	0.49	0.50	0.33	0.49	0.76
SO_2	0.96	0.39	-0.57	-0.20	0.06	0.76
Organic gas precursor species						
ALK1	0.75	0.26	0.23	0.09	0.42	0.77
ALK2	***1.60***	***1.30***	***-1.60***	***-1.30***	***0.44***	***0.54***
ALK3	1.10	0.53	-1.00	-0.52	0.56	0.71
ALK4	0.87	0.33	-0.73	-0.31	0.42	0.59
ALK5	0.67	0.23	-0.12	-0.04	0.54	0.84
ARO1	0.90	0.37	-0.78	-0.36	0.48	0.65
ARO2	0.94	0.40	-0.82	-0.38	0.53	0.68
OLE1	0.81	0.24	-0.27	-0.15	0.68	0.95
OLE2	1.10	0.36	-0.65	-0.32	0.40	0.61
TERP	0.37	0.05	-0.24	-0.02	0.64	0.99

Note: mFE and mFB are arithmetic means of FE and FB, where FE = 2|M-O|/(M+O), and FB = 2(M-O)/(M+O). M and O denote modeled and observed values, respectively.

Observed propane and ethyne were several times larger than model species (ALK2), but sensitivity tests showed that its effects on PM components were small. Since NO_2 and PM nitrate were major components of NO_x and total nitrate, respectively, poor performances of NO and HNO_3 had little effect on model performance.

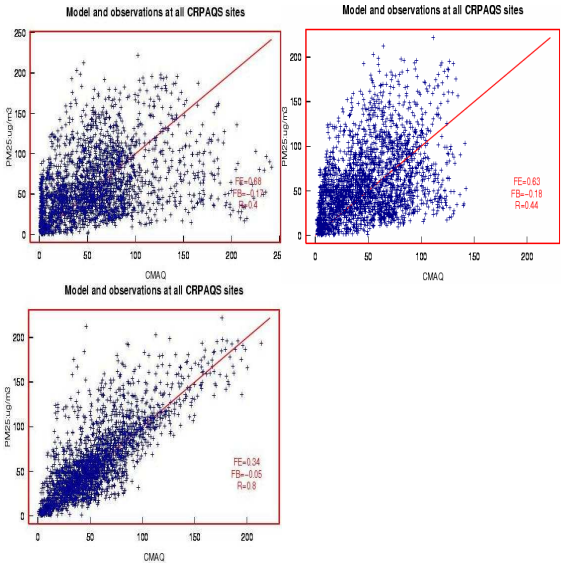

Figure 2. $PM_{2.5}$ mass in observations and simulations when n=0 (upper-left) and 3 (upper-right, average of 49 cells) and lower (best-match within 49 cells).

3.2 Diurnal Patterns in San Joaquin Valley

We evaluated diurnal patterns of ozone, O_x (defined as $[O_3]+[NO_2]$), and PM nitrate in model and observations at three anchor sites (ANGI, BAC, and FSF) in the domain. BAC and FSF are two urban sites at Bakersfield and Fresno, respectively, and ANGI is a rural site at Angiola between BAC and FSF, as shown in Figure 1. At ANGI station, measurements were also made at a tower of 100 m above the ground. We found that ozone peaked in early afternoon and decrease until daylight in both model and observations at these stations, except that, on one day, it dropped to near zero at FSF around 3 pm. O_x showed the similar pattern as ozone, but had no drop on that day, which indicates that the drop of O_3 was caused by the titration with NO. PM nitrate concentrations were different from that for ozone in terms of diurnal variation. We found that PM nitrate had comparable peaks at night and during the day, which reflects that the nighttime production pathway (NO_2+O_3) was as important as the daytime production pathway (NO_2+OH) for PM nitrate during the wintertime PM episode. This phenomenon can be explained by the abundant

particle liquid water at night and relatively low hydroxyl radical concentration during the day (~20% of the summertime value) in San Joaquin Valley during the episode. Figure 3 shows the diurnal pattern of PM nitrate at BAC during the episode.

3.3 Time Series

We compared the simulated and observed hourly concentrations of PM components and their organic and inorganic precursors at 162 stations in the model domain during the episode for n=0, 1, 2, and 3. We found that the model captured observed trends at most stations, while discrepancy existed in terms of exact magnitudes. The discrepancy decreased noticeably when n increased from 0 to 3 at most stations, which reflects that spatial gradients were significant for PM components and precursors. Figure 4 illustrates the hourly history of PM nitrate in observation and model at a Fresno station during the episode.

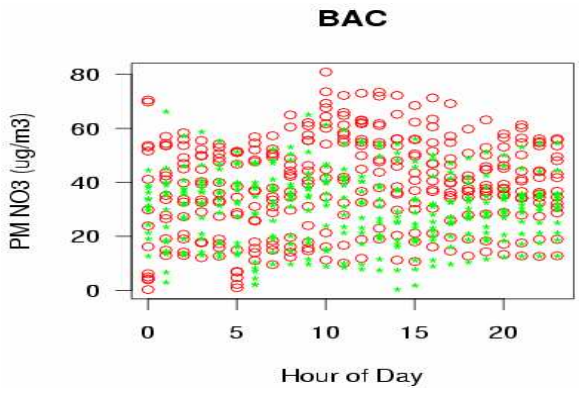

Figure 3. Diurnal patterns of simulated PM nitrate ('*') and observations ('o') at a Bakersfield station from December 25, 2000 to January 7, 2001.

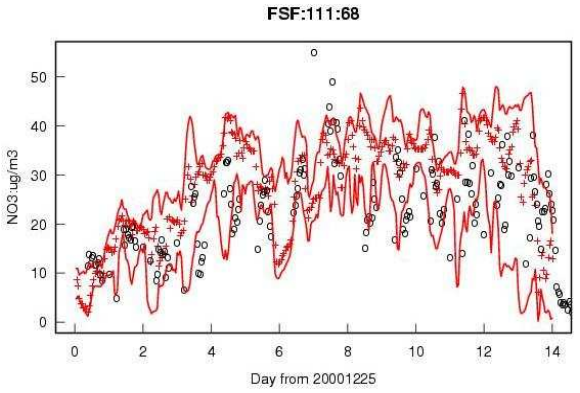

Figure 4. Time series of PM nitrate at a Fresno station ('o') and model. '+' denotes values at n=0, and lines for the extremes within 49 cells at n=3.

We evaluated bar-plots of daily average $PM_{2.5}$ in model and observations at three anchor sites in SJV when n=0. On the daily average basis, model captured observed trends well, especially in the first week of the episode. In the second week, the recovery of PM mass after a weather perturbation appeared satisfactory in Fresno and Angiola. In Bakersfield, the simulated perturbation was too strong in MM5. When the weather perturbation was removed, simulated results were in close agreement with observations, as shown in Figure 5. In the latter case, PM nitrate was also closely simulated at Bakersfield.

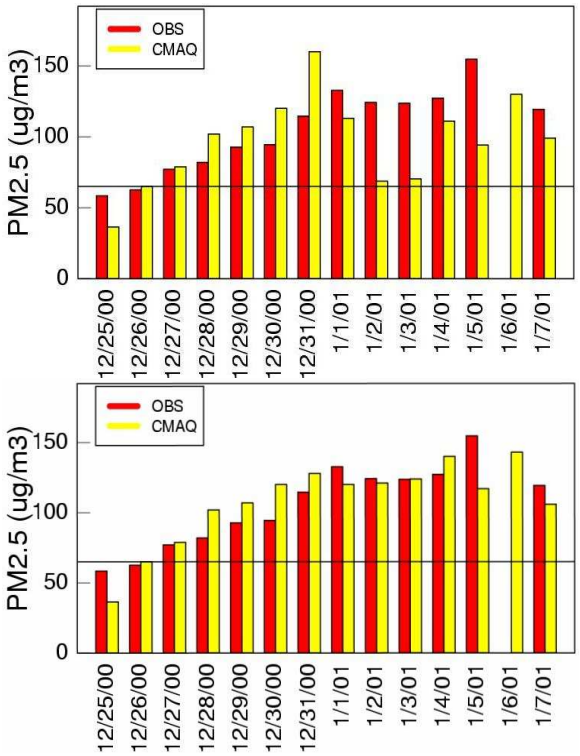

Figure 5. Daily average $PM_{2.5}$ in observation and model at a Bakersfield station, with (upper) and without (lower) the simulated weather perturbation.

4. MODEL RESULTS OF SECONDARY AEROSOLS

We present below results for secondary organic and inorganic aerosols.

4.1 Secondary Organic Aerosol (SOA)

SOA was produced from both anthropogenic and biogenic VOC emissions in the model, assuming ideal mixing of condensable organic components. We found that SOA concentration was < 2 µg m^{-3} in California Central Valley, and could reach 5 µg m^{-3} in coastal area. SOA

accounted for ~5% total organic aerosol in urban Bakersfield and Fresno, and ~15% in rural Angiola where primary organic aerosol was low. We found that anthropogenic SOA peaked in Bakersfield, though its magnitude was small, and biogenic SOA exceeded anthropogenic SOA in California Central Valley and adjacent area. For comparison, a recent study in a coniferous forest, ~50 km downwind of Sacramento, found that biogenic SOA accounted for ~40% of identified OC (Cahill et al., 2006). We understand that aqueous oxidation of soluble organic compounds could increase SOA in the nature. However, sufficient information was not available for including such effects in the model. Figure 6 shows the distribution of simulated SOA in the middle of the episode.

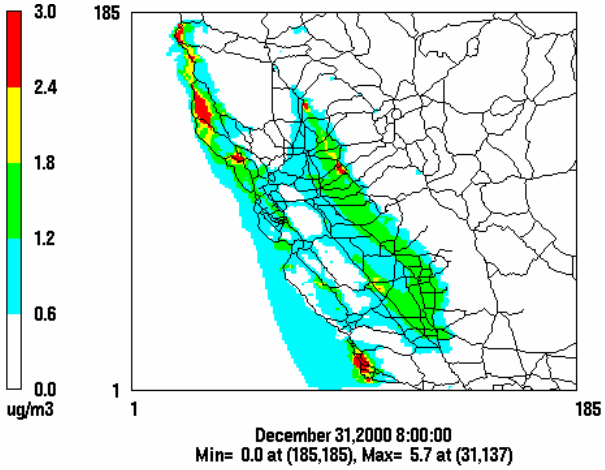

Figure 6. Surface distribution of 24-hour average SOA in the model on December 31, 2000.

4.2 Secondary Inorganic Aerosol

Secondary inorganic aerosol, especially ammonium nitrate, was the major component of $PM_{2.5}$ in California Central Valley in both model and observations. To help understand the limiting factors of ammonium nitrate we conducted simulations with 50% emission reductions of its precursors, namely, NH_3, NO_x, total VOC, and anthropogenic VOC (AVOC). We found that the Cental Valley was ammonia rich, which is consistent with findings of Blanchard et al. (2000), and the production of ammonium nitrate during the episode was least sensitive to ammonia, less sensitive to AVOC, and most sensitive to NO_x and occasionally to biogenic VOC. Therefore, controls of ammonia and AVOC in SJV may be less desirable. A more in depth investigation will be carried out to in the future to access the detailed response of PM to emission reductions of its precursors.

5. SUMMARY

We simulated an extended winter PM episode captured in the California San Joaquin Valley during the 2000-2001 CRPAQS, using fine-grid CMAQ and MM5. We evaluated models with extensive surface and aloft observations at hundreds of stations across central and northern California. Modeled temperature, wind speed and direction were compared against hourly observations at 239 surface and 16 aloft stations. Modeled $PM_{2.5}$ components and their 7 inorganic and 10 organic precursor species were compared with observations at 162 stations. Total 58 organic compounds were used in the evaluation. We found that model captured diurnal and spatial patterns of temperature and the relatively low wind speed in California Central Valley. Except for ALK2, for other species, model performance improved significantly when 3-grid radius best-match method was used. The spatial and diurnal patterns of PM components were well reproduced in the model. The accumulation of PM mass during the episode was captured in the model, especially after a simulated weather perturbation, which was unrealistic, was removed. Simulated SOA was <2 µg m^{-3} in SJV during the winter episode, and could reach 5 µg m^{-3} in coastal area. Ammonium nitrate was most sensitive to reductions of NO_x emissions and least sensitive to NH_3 emissions during this episode.

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7. DISCLAIMER

This paper has been reviewed by the staff of the California Air Resources Board and has been approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the California Air Resources Board, nor does mention of trade names or commercial

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