

Modeling Wintertime Particulate Matter Formation in Central California

Betty K. Pun, Rochelle T.F. Balmori, Christian Seigneur

Atmospheric and Environmental Research, Inc.

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Abstract

A wintertime episode during the 2000 California Regional PM Air Quality Study (CRPAQS) was simulated with the air quality model CMAQ-MADRID. Model performance was evaluated with 24-hour average measurements available from CRPAQS. Modeled organic matter (OM) was dominated by emissions, which were probably significantly underrepresented, especially in urban areas. In one urban area, modeled daytime nitrate concentrations were low and evening concentrations were high. This diurnal profile was not explained by the partition of nitrate between the gas and particle phases, because gaseous nitric acid concentrations were low compared to PM nitrate. Both measured and simulated nitrate concentrations aloft were lower than at the surface. Heterogeneous reactions involving NO_3 and N_2O_5 accounted for significant nitrate production in the model, resulting in a nighttime peak. The sensitivity of PM nitrate to precursor emissions varied with time and space. Nitrate formation was on average sensitive to NO_x emissions. However, for some periods at urban locations, reductions in NO_x caused the contrary response of nitrate increases. Nitrate was only weakly sensitive to reductions in anthropogenic VOC emissions. Nitrate formation tended to be insensitive to the availability of ammonia at locations with high nitrate, although the spatial extent of the nitrate plume was reduced when ammonia was reduced. Reductions in PM emissions caused OM to decrease, but had no effect on nitrate despite the role of heterogeneous reactions. A control strategy that focuses on NO_x and PM emissions would be effective on average. Reductions in VOC and NH_3 emissions would also be beneficial for certain times and locations.

Introduction

The California San Joaquin Valley (SJV) (see Figure 1), home to more than three million people, is associated with some of the highest particulate matter (PM) concentrations measured in the United States (EPA, 2007). High concentrations occur in the wintertime, driven by a regional distribution of particulate nitrate and organic matter (OM) concentrations that tend to elevate around urban areas (Watson and Chow, 2002). The 2000 (December 1999 – January 2001) California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) was designed to monitor annual concentrations of PM and to collect detailed information during PM episodes. Analyses using available data have led to some insights on the distribution and formation of PM and its various components (CARB, 2007). Key conclusions so far include the confirmation that carbon concentrations were highest in cities during winter, and that wood smoke constituted a large fraction of the carbonaceous PM. Dense sampling confirmed the widespread nature of nitrate concentrations within the SJV. The concentrations were observed not only at the surface, but also above the mixing layer. Vertical exchange was thought to play a role in replenishing surface concentrations when the mixed layer increases after sunrise. Measurements showed that ammonia (NH₃) concentrations typically exceeded nitric acid (HNO₃) concentrations; hence, nitrate formation was not limited by NH₃. The role of fog had been clarified by CRPAQS to cause a net removal of PM. During CRPAQS, wintertime transport often flowed from the SJV towards the San Francisco Bay Area, reversing the source / receptor relationship assumed before CRPAQS.

The last stage of CRPAQS is the application of air quality models to simulate PM concentrations and to evaluate their performance compared to measurements. The availability of measurement data benefited model application because a thorough model performance evaluation allowed the model to be used with confidence as a tool to understand key processes and the response of PM components to emission control strategies. Here we describe the modeling performed using the Community Multiscale Air Quality model with the Model of Aerosol Dynamics, Reaction, Ionization, and Dissolution (CMAQ-MADRID), including sensitivity studies to investigate the efficacies

of common control strategies for ammonium nitrate and OM, the two key components of PM in the SJV. Using these simulations, we analyze the formation of PM nitrate and confirm or qualify key conclusions drawn based on previous data analyses. We conclude with a discussion of the key challenges in our understanding PM formation for wintertime episodes in the SJV.

Methods

The model used here is CMAQ version 4.6 (Byun and Schere, 2006), with MADRID (Zhang et al., 2004; Pun et al., 2005). The following options are used: the Statewide Air Pollution Research Center (SAPRC) mechanism for gas-phase chemistry, the asymmetric convective model (ACM) for cloud, the asymmetric convective model version 2 (ACM2) for vertical diffusion, the multiscale algorithm for horizontal diffusion, and the Yamatino scheme for mass-conserving advection in the horizontal and vertical directions. The particle size distribution is represented by two sections (fine and coarse).

A domain that covered central California with a 4-km horizontal resolution was used in this study. The California Air Resources Board (CARB) provided meteorological simulation results for the period between 25 December 2000 and 7 January 2001. Version 3.6.3 of the Fifth-generation PSU/NCAR Mesoscale Model (MM5) was used, and the Meteorology-Chemistry Interface Processor (MCIP) version 3.1 was used to process the meteorological data for these air quality simulations. For California, prognostic meteorological models are known to have limitations for air quality modeling (Jackson et al., 2006). Previous analysis at CARB indicated that the quality of the meteorological fields deteriorated after 31 December (Kaduwela, 2006); therefore, we focused on the first half of the episode between 25 December and 31 December 2000 in these simulations.

The latest emission inventories were not available from CARB at a 4-km resolution. We updated an earlier 4-km resolution inventory with information available from an up-to-date emission inventory with a 12-km resolution. Both sets of emissions were obtained from CARB. Adjustments were made to the 4-km resolution emission inventory by

scaling the emissions of 11 key VOC and PM species that were significantly different between the two inventories to match the 12-km resolution inventory. The terpene species was speciated into five surrogate monoterpene species (α -pinene, β -pinene, limonene, terpinene, and ocimene) and one sesquiterpene surrogate species (humulene) for compatibility with MADRID's secondary organic aerosol (SOA) module. A chemical speciation profile from Helmig et al. (1999) was used to distribute the biogenic VOC emissions among the of individual terpene and sesquiterpene surrogate species. Following Henze and Seinfeld (2006), isoprene was treated explicitly in the model. Emissions of the anthropogenic SOA precursors that were not explicitly treated in the SAPRC mechanism, i.e., long-chain alkanes and polycyclic aromatic hydrocarbons (PAH), were added. Based on information from CARB (Allen, 2006), emissions of long-chain alkanes and PAHs were estimated as fractions of higher alkanes (ALK5) and aromatics. Five components of fine PM emissions (elemental carbon [EC], organic aerosols [OA], sulfate [SO₄], nitrate [NO₃], and other [PMFINE]) were assigned to the corresponding MADRID species for the fine section: EC_1, OO_1, SO4_1, NO3_1, and OI_1. The PMCOARSE component, representing emissions of coarse PM, was assigned to OI_2. Seasalt emissions of fine and coarse chloride, sodium, and sulfate, were added to the corresponding PM size sections.

CARB also provided initial and boundary conditions. These files were modified for use in the two-section MADRID simulation by mapping the Aitken and fine mode PM to the first size section and the coarse mode PM to the second size section.

Model performance is evaluated using 24-hour average concentrations observed during CPRAQS (<http://arb.ca.gov/airways/ccaqsnets/> or by direct request). We focus on PM_{2.5} mass, sulfate, nitrate, ammonium, OM, and EC.

Sensitivity simulations were performed to investigate possible strategies for reducing wintertime PM concentrations in the SJV. To investigate the potential effectiveness of control strategies for ammonium nitrate, NO_x, VOC, and NH₃ emissions were reduced. NO_x is viewed as a direct precursor to nitrate, which is formed mainly when HNO₃

combines with NH_3 . VOC reductions can also affect nitrate formation due to the effects of VOC on oxidants (Pun and Seigneur, 2001). Reductions in anthropogenic VOC were investigated because biogenic VOC cannot be controlled. Because OM emissions were expected to be important during wintertime episodes, reducing primary PM emissions was expected to be an effective strategy for reducing PM especially in the urban areas. In addition, because of the importance of heterogeneous nitrate formation, the effects, if any, of the availability of surface area from primary PM on secondary nitrate formation was also investigated. The effects of across-the-board emission reductions on PM concentrations were analyzed in both urban and rural areas.

Results

Model Performance

The base case modeling results were evaluated against 24-hour average concentrations measured during CRPAQS. Key performance statistics are shown in Table 1. MADRID tended to underpredict $\text{PM}_{2.5}$ mass. The model was able to predict 70% of the variability in the daily $\text{PM}_{2.5}$ mass samples. On average, the two main components of $\text{PM}_{2.5}$ were OM and nitrate. The model overpredicted the concentrations of nitrate by about $4.5 \mu\text{g}/\text{m}^3$ (about 35%) on average, but underpredicted OM by $9 \mu\text{g}/\text{m}^3$ (about 60%). Therefore, the $\text{PM}_{2.5}$ predictions contained some compensating errors. Nonetheless, MADRID was able to explain 50% or more of the variability of the two key PM components. Ammonium and EC were the next most abundant components of $\text{PM}_{2.5}$. The average ammonium concentration was slightly overpredicted, possibly due to its association with nitrate, which was overpredicted. EC concentrations were underpredicted on average, although the degree of underprediction was not as severe as that for OM. For EC and ammonium, MADRID was able to represent 50% and 46%, respectively, of the variability of daily concentrations. Sulfate was a fairly small component of $\text{PM}_{2.5}$ during this episode, and its average concentrations were quite well predicted. The model did not represent the variability in sulfate as well as for the more abundant components.

For fractional error and bias, Boylan and Russell (2006) proposed performance criteria for major PM components based on a review of recent modeling applications. They recommended criteria of 75% for the fractional error and $\pm 60\%$ for the fractional bias when the observed concentrations are above $2.25 \mu\text{g}/\text{m}^3$. MADRID met these performance criteria for fractional error and bias for 24-hour average $\text{PM}_{2.5}$, nitrate, ammonium, sulfate, and EC, but failed to meet the performance criteria for OM.

Primary emissions dominated the modeled concentrations of OM during this winter episode. In the model results, SOA accounted for only 9% and 3% of the OM in Angiola and Bakersfield, respectively. Photochemistry and secondary formation were expected to be limited under cold temperature conditions during the model episode. Therefore, the underprediction of OM most likely resulted from an underestimation of emissions throughout the day.

The model predicted high nighttime and early morning nitrate concentrations at Bakersfield and low daytime concentrations. Although nitrate volatilizes to gaseous HNO_3 during the day in response to the temperature cycle, the modeled daytime concentration of HNO_3 at Bakersfield was generally less than 1 ppb ($2.8 \mu\text{g}/\text{m}^3$ at STP) during this episode. This amount was small compared to the modeled daytime nitrate concentrations and did not explain the daytime decrease from the nighttime peak concentrations. Therefore, the simulated conditions in SJV were NH_3 -rich, and the gas/particle partitioning of nitrate was pushed towards the PM phase by excess NH_3 .

Based on measurements taken on two towers, the average aloft nitrate concentrations at the Angiola (100 m) and Walnut Grove (244 m) were 66% and 62%, respectively, of the surface concentrations. Because the mixing layer was frequently less than 100 m deep at night (Herner et al., 2006), the aloft measurements were expected to be representative of the valleywide decoupled layer, rather than the surface layer. At these two locations, upper air concentrations were not a significant source of nitrate at the surface during the episode. The model significantly overestimated average nitrate concentrations at the surface (by a factor of 2.6) and aloft (by a factor of 3.3) at Angiola, due to a continued

increase in nitrate concentrations predicted in the latter part of the episode that was not observed. The model showed more realistic results at the Walnut Grove tower, which is north of Fresno and Bakerfield. It underestimated nitrate by 8% at the surface of the Walnut Grove tower and overestimated by 14% at 244 m. The model predicted surface and aloft concentrations to be more similar than indicated by measurements. Based on the fractional statistics, the model showed more skill in predicting surface nitrate concentrations than aloft concentrations.

Nitric acid is formed via a homogeneous reaction in the gas-phase involving the oxidation of NO_2 by OH or in a sequence of reactions involving $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3$; $\text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5$; $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3$. In addition, heterogeneous oxidation reactions of NO_3 and N_2O_5 to HNO_3 can also take place at the surface of particles and droplets. By deactivating heterogeneous reactions in a sensitivity simulation, it was determined that these reactions were a key source of nitrate in the MADRID simulations, accounting for about two-thirds of the nitrate production in rural locations and more in urban locations at peak periods. Such production routes involved NO_3 and N_2O_5 , which had short live times during the day, and occurred primarily at night.

Emission Sensitivity Results

Emissions of PM, NO_x , NH_3 , and anthropogenic VOC were reduced by 50% in the emission sensitivity simulations. Figure 2 shows the time series of EC, nitrate, and OM in the base case and emission sensitivity cases. As expected of a primary PM component, EC concentrations were not affected by changes in gaseous pollutants to any significant extent, and their response to reductions in primary PM emissions was linear.

As discussed above, OM concentrations were dominated by primary emissions. Therefore, OM also responded strongly to reductions in primary emissions. A 50% reduction in primary OM led to less than 50% reduction in OM concentrations because a small portion of the OM is secondary. Since the percentage of SOA was higher in rural areas than urban areas, the percentage reduction in rural areas was smaller than in urban areas. A 50% reduction in NO_x emissions caused a minute increase (0.2%) of OM in

Bakersfield and Angiola. This increase was attributed to the response of SOA to increased oxidant levels in both urban and rural areas when NO_x emissions are reduced. (Because of low photochemical activity during this wintertime episode, O_3 production tended to occur on the regional scale and background ozone concentrations contribute to local concentrations. The titration of ozone by NO is an important reaction controlling ozone levels in the winter.) Reductions in anthropogenic VOC led to decreased ozone concentrations at both urban and rural sites. However, there was virtually no effect on OM concentrations. There was a small decrease in SOA concentration at the rural site; caused by a decrease in anthropogenic SOA and a negligible decrease in biogenic SOA, which dominated over anthropogenic SOA. Since biogenic VOC emissions were not reduced, the small change in biogenic SOA would be caused indirectly by a decrease in oxidants as VOC is decreased. Therefore, in this case, the formation of SOA in rural areas was sensitive to VOC but less sensitive to oxidants. In urban areas, reductions in anthropogenic VOC emissions by 50% translated into slightly larger than 50% reductions in anthropogenic SOA from xylene and toluene. Biogenic SOA showed a negligible decrease. But the overall decrease in OM was small because of the dominance of primary OM. Overall, reductions in anthropogenic VOC have limited effects on OM.

Under wintertime conditions, gas-phase HNO_3 concentrations were small (< 2 ppb) within the SJV, and nitrate formation was generally limited by the availability of nitric acid rather than ammonia. Not surprisingly, therefore, nitrate concentrations responded less than linearly to changes in ammonia emissions in general. However, at the rural site Angiola, nitrate concentrations decreased by 10 to 25% on 5 days during the 7-day episode. A particularly strong response was simulated during early morning on 31 December, indicating that NH_3 was not present in sufficient excess throughout the valley to be irrelevant in the design of emission control strategies for rural areas.

Figure 3 shows the 24-hour average particulate nitrate concentrations on 31 December 2001. An important observation is that the spatial distributions of nitrate changed even when the concentrations changed in the sensitivity cases. In the ammonia sensitivity case, the formation of total nitrate was not affected by changes in ammonia emissions.

However, because nitric acid was removed more effectively by dry deposition than ammonium nitrate, the reduced formation of ammonium nitrate at locations with less excess ammonium in the sensitivity case increased the concentration of HNO₃ relative to nitrate, and enhancements in the removal of total nitrate resulted from the reduction in NH₃ emissions.

The reduction in NO_x emissions induced a strong response in nitrate concentrations. At the rural site, nitrate reductions approached 50% on average, and the time series in Figure 2 shows a consistent decrease throughout the episode. At Bakersfield, reductions were of the order of 30-45% and were less than linear. Fresno, located in the heart of the nitrate plume (Figure 3) tended to be less responsive to NO_x reductions than Bakersfield. In fact, there were a couple brief periods at night in Fresno when a 50% reduction in NO_x caused nitrate to increase above the base case values by up to 40% (not shown). This response was predicted earlier by Pun and Seigneur (2001) for the vicinity of Fresno using a box model. The increase was shown to be due to an increase in O₃ in a VOC-sensitive area when NO_x is reduced. Increase oxidant availability can enhance the formation of N₂O₅ at night. Since the N₂O₅ pathway was important for nitrate formation in the SJV, nitrate formation increases in those instances.

As discussed previously, the reduction of anthropogenic VOC emissions reduced O₃ concentrations in both urban and rural locations. However, nitrate concentrations were less sensitive to anthropogenic VOC emissions than to NO_x emissions on average. Reductions in anthropogenic VOC emissions consistently caused small reductions in nitrate in the urban areas, even when nitrate increases resulted from reductions in NO_x emissions. Rural nitrate concentrations were quite insensitive to anthropogenic VOC emissions on some days.

Although nitrate formation depended on heterogeneous reactions, there was no significant sensitivity of nitrate concentrations to primary emissions of PM. This indicated that the surface area required for heterogeneous reactions was supplied mostly by secondary aerosols (including nitrate).

Discussion

For wintertime episodes, physical processes such as emissions and transport (horizontal dispersion and vertical mixing) played a very important role in the distribution of PM and components. For example, EC concentrations in urban areas were linearly dependent on emissions. In addition, regional accumulation of key secondary components was driven by synoptic systems. A misprediction in the timing and coverage of the meteorological phenomenon can cause PM accumulation to cease in key areas of the SJV. Therefore, weaknesses in the meteorological models for simulating calm wintertime conditions would necessarily translate into performance issues pertaining to the air quality simulation.

The simulation of the December 2000 episode illustrated that the response of key PM components nitrate and OM to emission controls was a function of time and space. Although OM is predominately primary, reductions in NO_x can cause a small increase in SOA due to increased oxidants. Urban locations with the highest concentrations of nitrate (e.g., around Fresno) tended to respond to reductions in NO_x emissions. However, nitrate can be oxidant-sensitive at times, during which NO_x control alone could have the contrary effect of increasing nitrate. Urban and rural locations with moderate to high nitrate concentrations responded well to NO_x controls. Controls of anthropogenic VOC emissions tended to reduce oxidant concentrations but had only small effects on nitrate, indicating that nitrate concentrations were not generally limited by the availability of oxidants during this episode. Rural locations with low to moderate nitrate levels displayed some NH₃ sensitivity. The conclusion that NO_x controls are more effective than VOC and NH₃ was consistent with results from the modeling of a previous episode in 1995 (Kleeman et al., 2005). However, an effective control strategy for PM_{2.5} in the SJV that is comprehensive in time and location may require controls of multiple precursors rather than a single key precursor.

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Table 1. Key measures of statistical performance for 24-hour average PM concentrations during 25-31 December 2000.

Species	Num. obs.	Mean obs. ($\mu\text{g}/\text{m}^3$)	Mean sim. ($\mu\text{g}/\text{m}^3$)	Frac. error	Frac. bias	R ²
PM _{2.5}	134	31.68	24.76	0.59	-0.40	0.70
Nitrate	94	12.08	16.63	0.59	0.24	0.50
Ammonium	92	4.32	4.79	0.54	0.00	0.46
Sulfate	93	1.44	1.45	0.54	-0.18	0.14
OM*	95	14.69	5.72	0.94	-0.82	0.53
EC	96	3.83	2.71	0.64	-0.28	0.50

* A factor of 1.4 was used to convert organic carbon (OC) measurements to OM

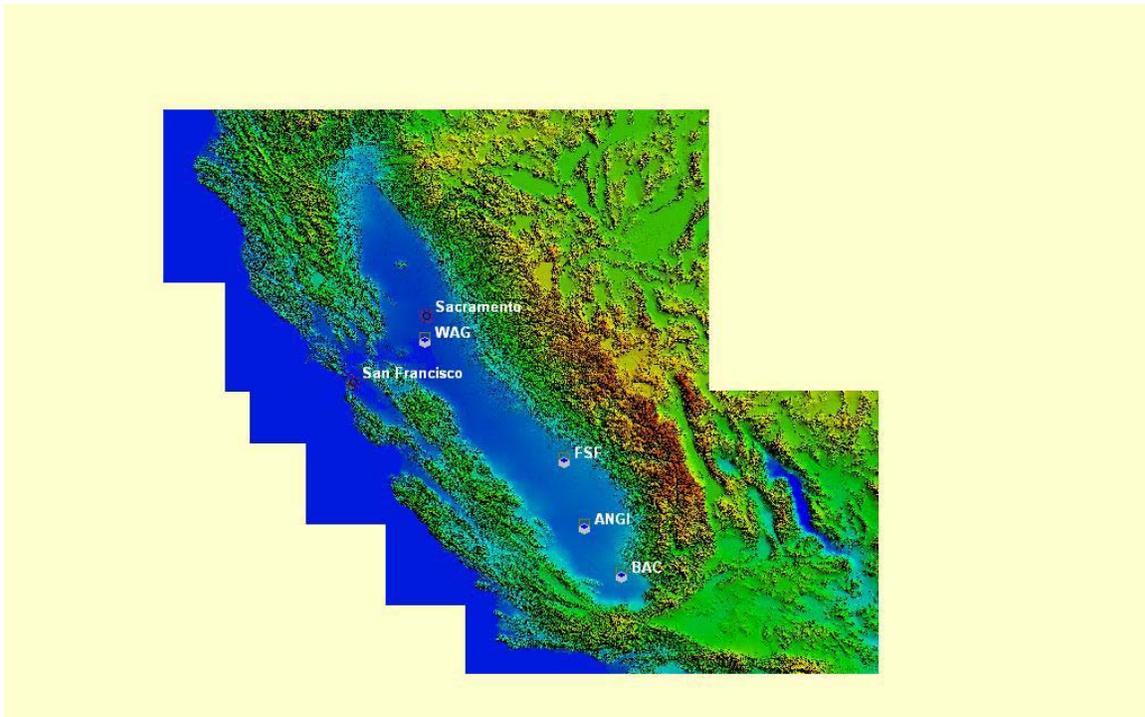


Figure 1. Map of the California Central Valley (including the Sacramento Valley and the San Joaquin Valley). WAG is Walnut Grove; FSF is Fresno, ANGI is Angiolo, and BAC is Bakersfield.

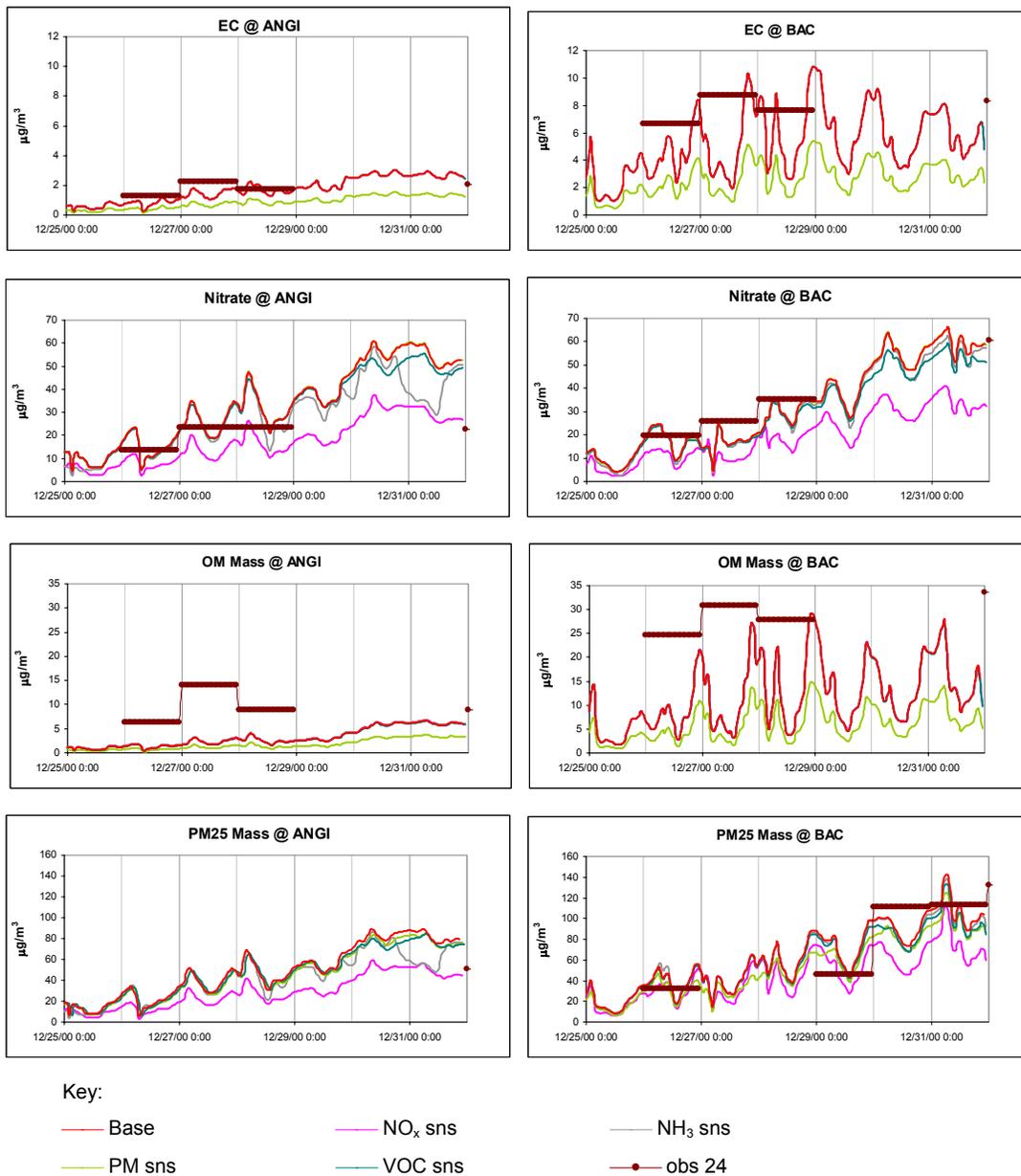
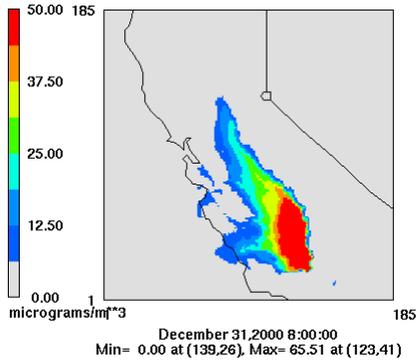
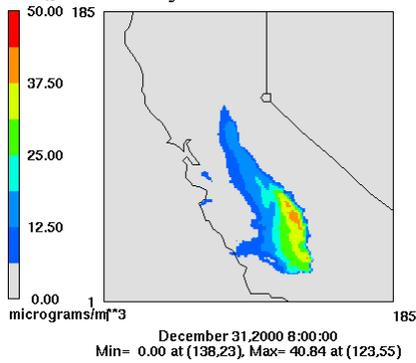


Figure 2. Time series with daily observations, base case simulation results and results from four sensitivity cases of EC, nitrate, OM, and PM_{2.5} at Angiola (left) and Bakersfield (right).

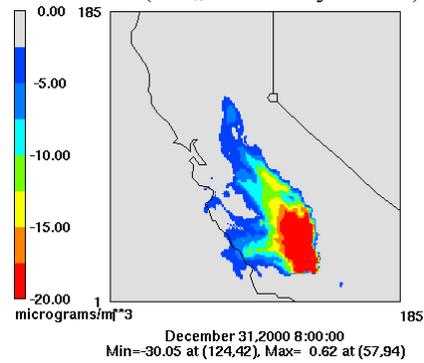
base case



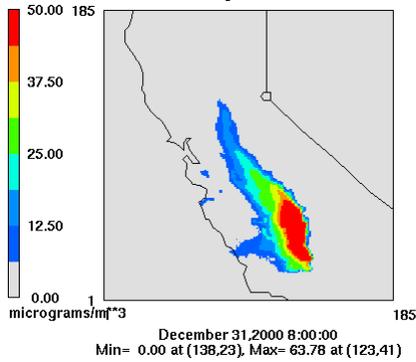
NO_x sensitivity



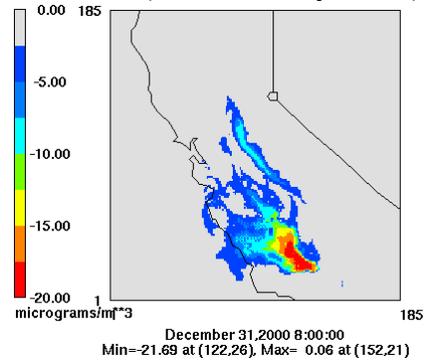
Difference (NO_x sensitivity – base)



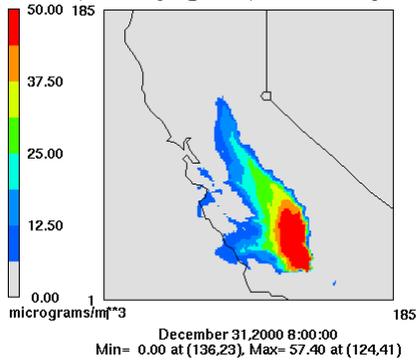
ammonia sensitivity



Difference (NH₃ sensitivity – base)



VOC (anthropogenic) sensitivity



Difference (VOC sensitivity – base)

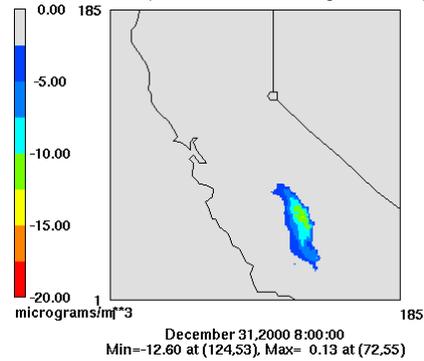


Figure 3. Spatial distribution of PM nitrate in the base and sensitivity cases.

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