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Mobile Source and Livestock Feed Contributions to Regional Ozone Formation in Central California

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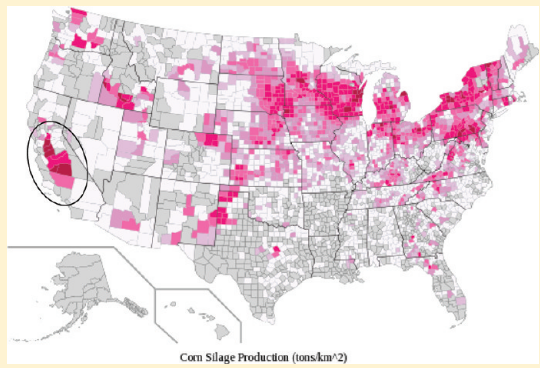
S Supporting Information

ABSTRACT: A three-dimensional air quality model with 8 km horizontal resolution was applied to estimate the summertime ozone (O_3) production from mobile sources and fermented livestock feed in California's San Joaquin Valley (SJV) during years 2000, 2005, 2010, 2015, and 2020. Previous studies have estimated that animal feed emissions of volatile organic compounds (VOCs) have greater O_3 formation potential than mobile-source VOC emissions when averaging across the entire SJV. The higher spatial resolution in the current study shows that the proximity of oxides of nitrogen (NO_x) and VOC emissions from mobile sources enhances their O_3 formation potential. Livestock feed VOC emissions contributed 3−4 ppb of peak O_3 (8-h average) in Tulare County and 1−2 ppb throughout the remainder of the SJV during the CCOS 2000 July−August episode. In total, livestock feed contributed ~3.5 tons of the ground level peak O_3 (8 h average) in the SJV region, and mobile VOC contributed ~12 tons in this episode. O_3 production from mobile sources is declining over time in response to emissions control plans that call for cleaner fuels and engines with advanced emissions controls. Projecting forward to the year 2020, mobile-source VOC emissions are predicted to produce ~3 tons of the ground level peak O_3 (8-h average) and livestock feed VOC emissions are predicted to contribute ~2.5 tons making these sources nearly equivalent.



■ INTRODUCTION

California's San Joaquin Valley (SJV) experiences the highest ozone (O_3) pollution in the United States and the region has been designated as a severe nonattainment area for the National Ambient Air Quality Standards (NAAQS) for O_3.[1] The SJV Air Pollution Control District has implemented various emissions reduction plans to control O_3 precursors over the past decade, but these efforts have produced only slight reductions in O_3 concentrations.[2] Emissions of O_3 precursors (oxides of nitrogen, NO_x; volatile organic compounds, VOC) from agricultural sources have come under scrutiny in the SJV because of the large agricultural industry in the region. Measured in financial terms, the SJV produces almost 10% of the U.S. agricultural output, with half of this production associated with livestock and poultry operations.[3] As recently as five years ago, the California Air Resources Board (CARB) estimated that waste from dairy cattle was the second largest source of VOCs that produce O_3 in the SJV (with the largest VOC source being motor vehicles).[4] However, Shaw et al.[5] demonstrated that VOC fluxes from dairy cattle waste were 6−10 times lower than the estimates used by CARB, and Howard et al.[6,7] confirmed that the O_3 formation potential (OFP) for the animal waste VOC was overestimated. Combining the two factors, the total O_3 production from animal waste sources was ~9 times lower than the original estimates based on the historical regulatory profiles;[7] CARB has adjusted their inventories accordingly.

Recent studies identified animal feeds as one possible important source of O_3 formation[8−10] that has not been included in official inventory estimates to date. Alanis et al.[8] found that the VOC flux measured from silage and total mixed ration (TMR) was 2 orders of magnitude higher than comparable fluxes from animal waste. Malkina[9] confirmed that animal feed VOC emissions are significantly higher than animal waste VOC emissions and found that several of the animal feed VOC compounds have high OFP. VOC emissions are produced from animal feed during the anaerobic fermentation process as well as during subsequent exposure to air during unsealed storage and eventual handling immediately prior to consumption. Howard et al.[10] directly measured the OFP of seven commonly used animal feeds using a transportable smog chamber and estimated that the total O_3 production from all feed source VOC is roughly 2 times larger than O_3 production from light duty vehicle VOC emissions in the SJV. The compounds emitted from corn silage (a common feed) that are important for O_3 formation include ethanol, its oxidation product acetaldehyde, and larger alcohols plus alkenes such as 2-butene, 2-methyl 1-propene, etc. A complete list of the detailed VOC species is presented by Howard et al.[10] Nevertheless, the estimates in these previous studies did not take into account

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meteorology (which drives the O_3 chemical formation and transport) and the estimates did not consider the spatial and temporal variability in the precursors' emissions (i.e., the spatial and temporal distributions of the NO_x/VOC ratio which determines the O_3 control regime), leaving high uncertainties in the contribution from the animal feed sources to regional O_3 formation.

Several previous studies have revealed that O_3 formation in the SJV is a mix of local emissions, intra- and interbasin transport.[11−13] Dabdub et al.[11] found that O_3 in the SJV has a significant dependence on the precursors transported from the upwind boundaries. Pun et al.[12] concluded that transport of O_3 and precursors from the San Francisco Bay Area and Sacramento Valley mainly affect the northern part of the SJV, and the within-valley processes (local emissions, chemical reactions, mixing and transport within the SJV) are responsible for regional and urban-scale distributions of O_3 in the downwind areas of Fresno and Bakersfield. Jin et al.[13] determined that O_3 formation is sensitive to VOC in the San Francisco Bay Area, Sacramento, and around the metropolitan areas in the SJV. O_3 formation is sensitive to NO_x in the rural Sierra foothills. A regional analysis is therefore required to evaluate the contribution to regional O_3 formation from animal feed in the SJV.

In the present study, the contribution from livestock feed emissions to the O_3 formation in the SJV is assessed with 8 km spatial resolution using a regional air quality model that represents all major atmospheric processes including emissions, transport, chemical reaction, deposition, etc. The importance of animal feed emissions to O_3 formation is compared to O_3 production from automobile sources during multiple episodes with high O_3 concentrations. Finally, the changes in O_3 source contributions are quantified under the planned emission control programs that have/will be implemented between the years 2000 through 2020.

■ MODEL DESCRIPTION

The UCD/CIT air quality model employed in this study is an Eulerian source-oriented chemical transport model based on the CIT photochemical airshed model.[14,15] The UCD/CIT model includes a complete description of atmospheric transport, deposition, chemical reaction, and gas-particle transfer. Previous studies[16−21] have described the formulation of the UCD/CIT air quality model and its application to estimate airborne particulate matter concentrations. The photochemical mechanism used by the UCD/CIT model was updated in the present study to reflect the latest information from smog-chamber experiments. Both the SAPRC-99[22] and SAPRC-07[23,24] photochemical mechanisms were incorporated into the model framework so that either could be used. The online UV radiative extinction calculations used during periods of high airborne particulate matter concentrations[25] were replaced with the photolysis rate calculations extracted from the Community Multiscale Air Quality (CMAQ) model. The CMAQ photolysis rate preprocessor JPROC[26,27] was modified to generate off-line photolysis rates for the modified SAPRC-99 and SAPRC-07 mechanisms at specific altitudes, latitudes, and solar declination angles. The photolysis rates were then interpolated to model grid cells at specified time-steps and adjusted for the presence of cloud cover.

■ MODEL APPLICATION

Calculations were performed for several O_3 episodes with an emphasis on the Central California Ozone Study (CCOS)[28] episode in the Central Valley of California over the period July 24 to August 2, 2000 (including a 3-day spin-up period). Meteorology during this period was characterized by a strong high pressure ridge that developed over the Four Corners, Wyoming area on July 27 and slowly moved westward from July 30 to August 2. Surface temperatures reached 44 °C during the day, with stagnant wind conditions conducive to O_3 formation and accumulation in the SJV. Hourly meteorological fields were simulated using the Weather Research and Forecasting (WRF) model version 3.1[29,30] for the months of July and August, 2000 over the entire state of California with 4 km horizontal resolution. Four-dimensional data assimilation (FDDA) was utilized in these simulations to anchor the model estimates to observed meteorological patterns. Regional meteorological models such as WRF tend to overestimate the surface winds in the SJV region during periods of low wind speed.[31,32] The FDDA technique improves the meteorological simulations needed for air quality modeling in the SJV region,[17] but FDDA does not completely correct the bias during the low wind-speed events that produce the highest pollution episodes. A recent study[33] indicated that increasing the surface friction velocity (u*) by 50% improves the WRF wind simulations during stagnation events in regions with complex terrain. Preliminary tests confirmed the benefits of increasing u* in the present study and this technique was adopted for all model simulations. Temperature and wind speed estimates produced by WRF were evaluated against observations using the mean fractional bias (MFB) and the root-mean-square error (RMSE) (see Table S1 of the Supporting Information (SI)). Ground-level temperature (MFB = −1.2%; RMSE = 3.6 °C) and wind (MFB = −8.4%; RMSE = 1.4 m/s) were both slightly underestimated in the SJV. WRF performance in other California regions was similar, with a slightly lower MFB for temperature but higher MFB and RMSE for wind.

The emissions model used in the current study was identical to the emissions model described in previous applications of the UCD/CIT model[16] but the input files were updated to accommodate the new photochemical mechanisms and livestock feed emissions data. Base-case hourly emission inputs were estimated using the raw inventory data provided by CARB. Livestock feed VOC emissions were estimated using the method described by Howard et al.[10] with a spatial pattern identical to livestock ammonia emissions. Emissions from animal feed transportation were not directly studied. Motor vehicles (both on-road and off-road) were the major NO_x sources in the SJV during the year 2000 simulations, accounting for 76% of total NO_x emissions on the weekdays and 69% on weekends (SI Table S2). NO_x emissions on weekends were 26% lower than on weekdays due to reductions in diesel truck traffic. Area sources accounted for the majority of the VOC emissions with livestock feed sources contributing 90 tons day^{-1} of VOC (15% of total emissions). No NO_x emissions were attributed to livestock feed sources in the current study. Preliminary measurements indicate that animal feed decomposition may release reactive nitrogen, but quantitative emissions estimates are not available at this time. Weekday and weekend emissions in the SJV are summarized for different types of anthropogenic sources in Table S2 of the SI.

Initial and boundary conditions were interpolated from the measured gas and particulate matter species concentrations during the study period. Point measurements of pollutant concentrations were interpolated to continuous fields using a modified weighted average procedure described by Goodin.[34]

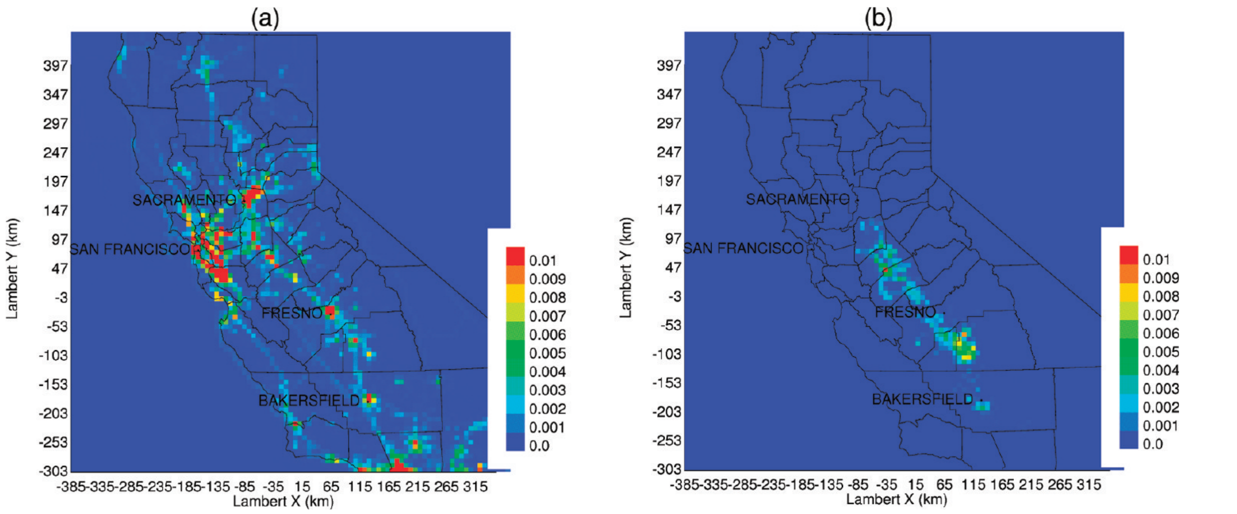

Figure 1. Spatial distribution of VOC emission from motor vehicle sources (a) and livestock feed sources (b). Livestock feed VOC emissions were estimated only in the SJV air basin. Units are (ppm·m·min^{-1}).

Boundary conditions at the western edge of the computational domain were based on measured background concentrations transported to California.[35,36] Details of concentrations of model species on the western boundary were presented in a previous study.[16]

Figure S1 in the SI shows the modeling domains used to simulate O_3 formation in the SJV. The rectangular WRF domain covered the entire state of California with a horizontal resolution of 4 km. The air quality domain followed the California state border on the east and mirrored a line ~100km west of the California coast using a horizontal resolution of 8 km and 10 vertical layers up to height of 5 km. The thickness of each vertical layer was 35, 105, 140, 330, 390, 500, 500, 1000, 1000, and 1000 m. Measurements made at 187 sites were used in the statistical calculations.

Figure 1 shows the spatial patterns of VOC emissions from motor vehicles and livestock feed sources during the year 2000. High emissions from mobile sources were located around urban centers and transportation corridors, whereas livestock feed emissions occurred primarily around dairy farms. Information from the U.S. Department of Agriculture indicates that the majority of livestock feed consumed in California is produced, stored, and used in the SJV.[10] Livestock feed emissions outside the SJV were not estimated in the current study.

The trends in the source contributions to O_3 production in the SJV were analyzed by repeating the year-2000 base-case analysis for the years 2005, 2010, 2015, and 2020. The meteorology in each year was held constant at the base-case values but the emissions were scaled to reflect the effects of emissions control programs over time. Table 1 lists the scaling factors used in the study. The scaling factors for mobile, area and point sources were calculated based on CARB's 2009 almanac emission projection data.[37] Livestock feed emissions were scaled upward in future years based on population projections[38] under the assumption that demand for dairy products per unit of population would remain constant in the future.

RESULTS

Model Evaluation. Two base-case simulations were preformed in which livestock feed VOC emissions were added to the emissions inventory. One base-case was simulated with the SAPRC-99 mechanism and the other was simulated with the SAPRC-07 mechanism. The O_3 results were compared to the measured data to evaluate the model performance. Figure 2 shows the measured and simulated O_3 concentrations using the SAPRC-07 mechanism at Sacramento, Stockton, Modesto, Fresno, Visalia, and Bakersfield for the CCOS episode (July 27 to August 2, 2000). Model estimates at the exact location of monitors and the best fit values (closest to observed values within 15 km of the observation sites[39]) are included in the figure. The difference between the estimated concentrations at the exact location of monitors and the best fit concentrations conveys information about the spatial gradient of O_3 concentrations. The air quality model successfully represents the time variation of daytime O_3 formation at all six sites except Bakersfield. Estimated maximum daytime O_3 concentrations at Sacramento and Stockton are in excellent agreement with measured values, with normalized bias of 2% and 7%, respectively. Daytime maximum O_3 concentrations are underestimated at Modesto, Fresno, and Visalia sites by an average value of 17%. Maximum daytime O_3 concentrations are significantly underestimated at Bakersfield, with sharp spatial gradients observed around this site. Previous modeling studies found that the emissions around Bakersfield are not well-represented in the inventory,[20] leading to problems simulating fine particulate matter concentrations in this area.[40] Model estimates for O_3 concentrations around Bakersfield are likely not accurate in the current study, but estimates for the remainder of the domain agree well with observations. Nighttime O_3 concentrations are consistently overestimated at most of the sites by up to 35 ppb. These trends are similar to other modeling

Table 1. Emissions Scaling Factors for Different Anthropogenic NO_x and VOC Sources in 2005, 2010, 2015, and 2020 relative to 2000 Base Year Emissions. Livestock Feed Usage Is Assumed to Be Proportion to Milk Consumption and Population

	NO_x			VOC			
year	point	area	mobile	point	area	mobile	silage = population
2005	0.72	0.97	0.95	0.89	1.00	0.79	1.13
2010	0.69	0.94	0.82	0.91	1.03	0.63	1.27
2015	0.64	0.92	0.59	0.92	1.10	0.51	1.43
2020	0.65	0.90	0.43	0.94	1.17	0.44	1.60

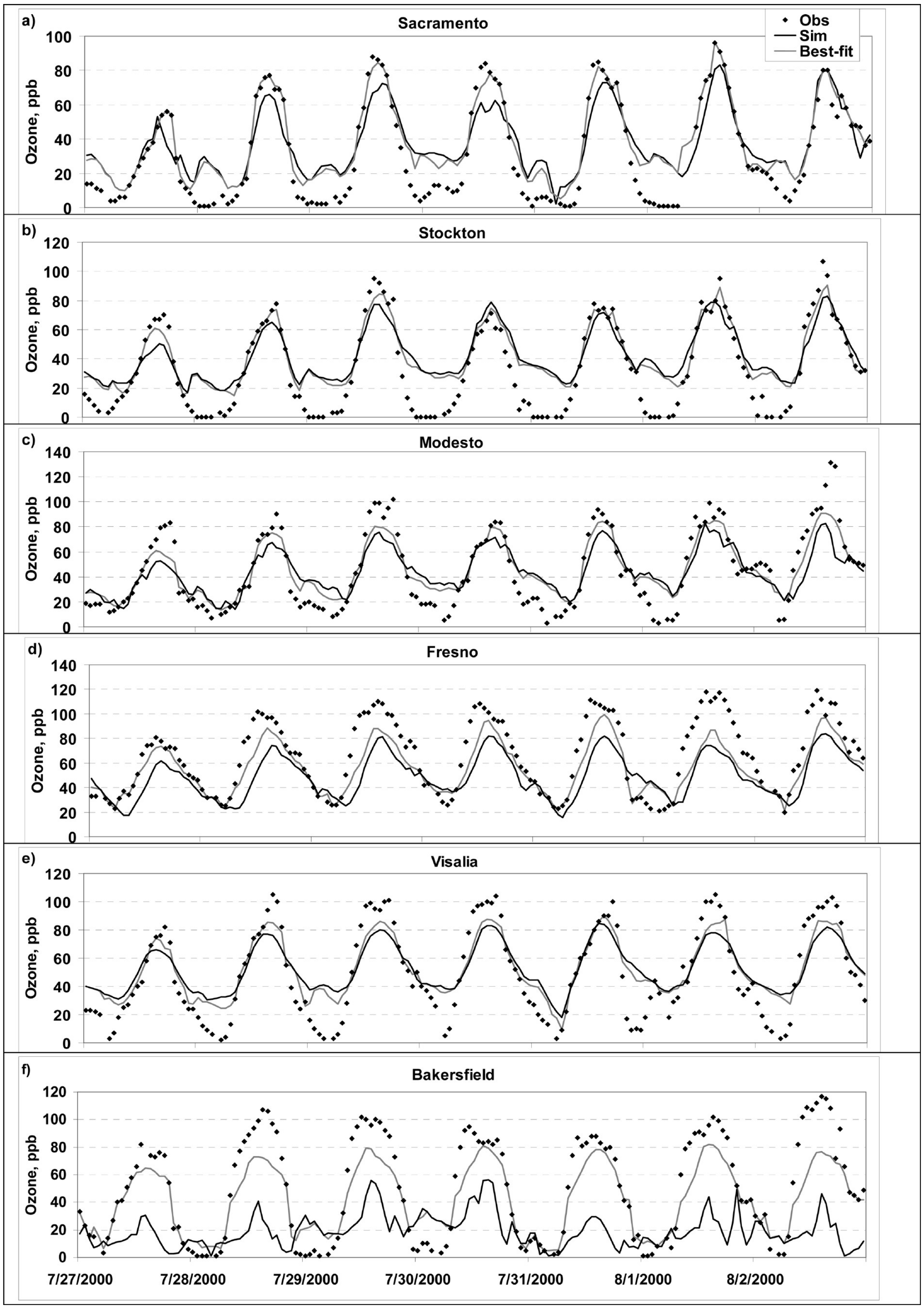

Figure 2. Time series of measured O_3 concentrations (dots), simulated O_3 concentrations in the exact grid cell with a monitor (dark lines), and "best-fit" simulated O_3 concentrations within 15 km of a monitor (gray lines) at Sacramento (a), Stockton (b), Modesto (c), Fresno (d), Visalia (e), and Bakersfield (f) sites during July 27 to August 2, 2000.

studies.[41,42] The observed reduction of O_3 concentrations at night may be caused by titration with fresh NO_x emissions missing from the modeling inventory and/or from enhanced vertical mixing that is not represented by model calculations.

Bias, normalized bias, gross error, and normalized gross error were calculated for 1-h and 8-h peak O_3 concentrations in the two base-case simulations (Table 2). Observations below 60 ppb were excluded from this analysis based on model guidance from US EPA.[39] Best fit estimates for O_3 concentrations were used in all statistical calculations. All metrics are within the EPA model performance guidelines (normalized bias within ±15% and normalized gross error within ±30%,[39]), with the exception that normalized bias of 1-h peak O_3 in the SJV was −15.6% when using the SAPRC-07 mechanism. Statistics were also calculated with a cutoff concentration of 40 ppb as a sensitivity test. The bias in the SJV region for 1-h peak O_3 does not change when a

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Table 2. Model Evaluation Metrics in the Entire Modeling Domain and the SJV Air Basin[a]

		1 h peak ozone		8 h peak ozone	
		SJV	domain	SJV	domain
SAPRC-07	bias (ppb)	−15.3	−12.7	−12.6	−10.8
	normalized bias	−15.6%	−14.5%	−14.4%	−13.5%
	gross error (ppb)	15.6	13.6	12.8	11.5
	normalized gross error	16.0%	15.6%	14.7%	14.4%
SAPRC-99	bias (ppb)	−0.2	−3.6	−0.5	−2.7
	normalized bias	−0.2%	−4.1%	−0.5%	−3.3%
	gross error (ppb)	6.2	11.5	5.7	9.6
	normalized gross error	6.3%	13.1%	6.6%	12.0%

[a]Cutoff = 60 ppb.

40 ppb cutoff value is used, and the bias for 8-h peak O_3 becomes slightly positive by 0.5 ppb. The 1-h and 8-h peak O_3 concentrations were consistently above 60 ppb at the SJV sites during the base-case episode, making the results insensitive to cutoff values lower than 60 ppb. In contrast, peak O_3 concentrations were often less than 60 ppb outside the SJV. The bias in estimated O_3 concentrations becomes positive by ~3 ppb for both 1-h and 8-h peak O_3 when a 40 ppb cutoff value is used in those regions. This variability is not critical given the current focus on the SJV.

The SAPRC-99 mechanism only slightly underestimates O_3 concentrations during the base-case episode, with a normalized bias of −0.2% and a normalized gross error of 6.3% for 1 h peak O_3, and a normalized bias of −0.5% and a normalized gross error of 6.6% for 8 h peak O_3 in the SJV. A recent study[43] compared the SAPRC-99 and SAPRC-07 mechanisms for the same episode using the CMAQ framework, and revealed that SAPRC-07 produces lower 8 h peak O_3 in the SJV by up to 10 ppb. The model results generated in the current study are consistent with the trends from the CMAQ model evaluation. The SAPRC-07 mechanism reflects the latest smog chamber experiments and these results are used for the analysis in the remainder of the study. It should be noted that the overall CMAQ and UCD/CIT modeling systems may contain compensating errors that were exposed through the use of an updated chemical mechanism. Such errors could include unknown O_3 formation pathways and/or missing emissions sources. The present study investigates the effects of one possible previously unrecognized source: animal feed emissions.

Source Contributions to Ozone in the SJV. Sensitivity simulations were performed to study the O_3 production from the livestock feed sources and the mobile sources in the SJV. Analysis was conducted for 1 h peak O_3 and 8-h peak O_3 in the SJV; the results of 8 h peak O_3 are discussed in the main text and the results of 1-h peak O_3 are described in the Supporting Information.

Figure 3a shows the simulated regional pattern of average 8 h peak O_3 concentrations during the CCOS episode (average of July 27 to August 2, 2000). Peak 8 h O_3 concentrations of ~110 ppb occurred along the foothills of the Sierra Nevada Mountains in El Dorado County (downwind of the Sacramento metropolitan area). A second region of peak 8 h O_3 concentrations (~95 ppb) was simulated in Madera, Fresno, and Tulare Counties (downwind of the Fresno metropolitan region).

In addition to the base-case emissions simulation, three sensitivity simulations were conducted for each year that was studied: (1) VOC emissions withheld from livestock feed; (2) NO_x and VOC emissions withheld from mobile sources; and (3) only VOC emissions withheld from mobile sources. The O_3 contribution from each source was then calculated as ($O_{3\_base\text{-}case}$- $O_{3\_sensitivity\text{-}case}$). Figures 3b−d show the estimated change in peak 8 h O_3 concentrations during the year 2000 associated with livestock feed VOC (3b), mobile source NO_x + VOC (3c), and mobile source VOC only (3d). During the 2000 CCOS simulation period, livestock feed VOC contributed 3−4 ppb of 8 h peak O_3 in Tulare County (where most livestock feeding operations are located) and 1−2 ppb throughout the central and southern parts of the SJV. The VOC emitted from mobile sources contributed 6−10 ppb of 8 h peak O_3 in the SJV. A previous study[10] had estimated that VOC emissions from livestock feed have greater O_3 formation potential than VOC emissions from motor vehicles. This estimate did not account for the proximity of mobile source VOC emissions to NO_x emissions, which increases the efficiency of O_3 production from the mobile source VOC.

The perturbation that simultaneously reduced NO_x and VOC emitted from mobile sources reduced 8 h average O_3 concentrations by ~70 ppb in El Dorado County and 40 ppb in the SJV. The results determined in this study indicate that livestock feed emissions were the second leading VOC source of O_3 formation in the SJV during the year 2000 (behind only mobile source VOC emissions). VOC source contributions to O_3 formation from livestock feed and mobile sources were far behind the mobile source NO_x contributions. It should be noted that mobile sources accounted for over 70% of the total NO_x emissions in the SJV in the year 2000, and so the NO_x perturbation illustrated in Figure (3c) represent an unrealistic level of total emissions control. Furthermore, the base-case O_3 system may exist in either a NO_x-controlled or VOC-controlled region on an O_3 isopleth diagram depending on the exact geographical location.[43,44] Small reductions in NO_x emissions may actually increase O_3 formation at some locations, but reductions in VOC emissions almost never cause O_3 formation to increase at any location.

Two additional CCOS O_3 episodes on June 8−17, 2000 and September 14−23, 2000 were simulated in the present study to examine the contribution of mobile source and livestock feed emissions to regional O_3 formation under different meteorological conditions. The June CCOS episode was characterized by a high pressure ridge centered west of Oakland that slowly progressed toward the southeast; the September CCOS episode was characterized by a high pressure ridge over the West Coast interrupted by a trough that moved downward from the northern Rocky Mountains into Nevada and California. A detailed description of the synoptic meteorological patterns during these episodes is provided by Lurman et al.[45] The simulations for the two additional CCOS episodes confirm that livestock feed emissions are the second largest VOC source of O_3 formation in the SJV during the year 2000 (behind mobile source VOC). VOC source contributions to 8 h peak O_3 concentrations across the SJV varied from 2.8 tons (feed)/ 9.4 tons (mobile) in the June episode, 3.4 tons (feed)/12.0 tons (mobile) in the July−August episode, and 2.2 tons (feed)/ 8.9 tons (mobile) in the September episode. The absolute contributions to O_3 production were a function of the exact meteorological conditions, but the ratio of animal feed VOC/ mobile source VOC contribution to O_3 production was almost constant at 0.25 to 0.29.

The results calculated for the year 2000 are subject to change as the emissions in California evolve in response to control

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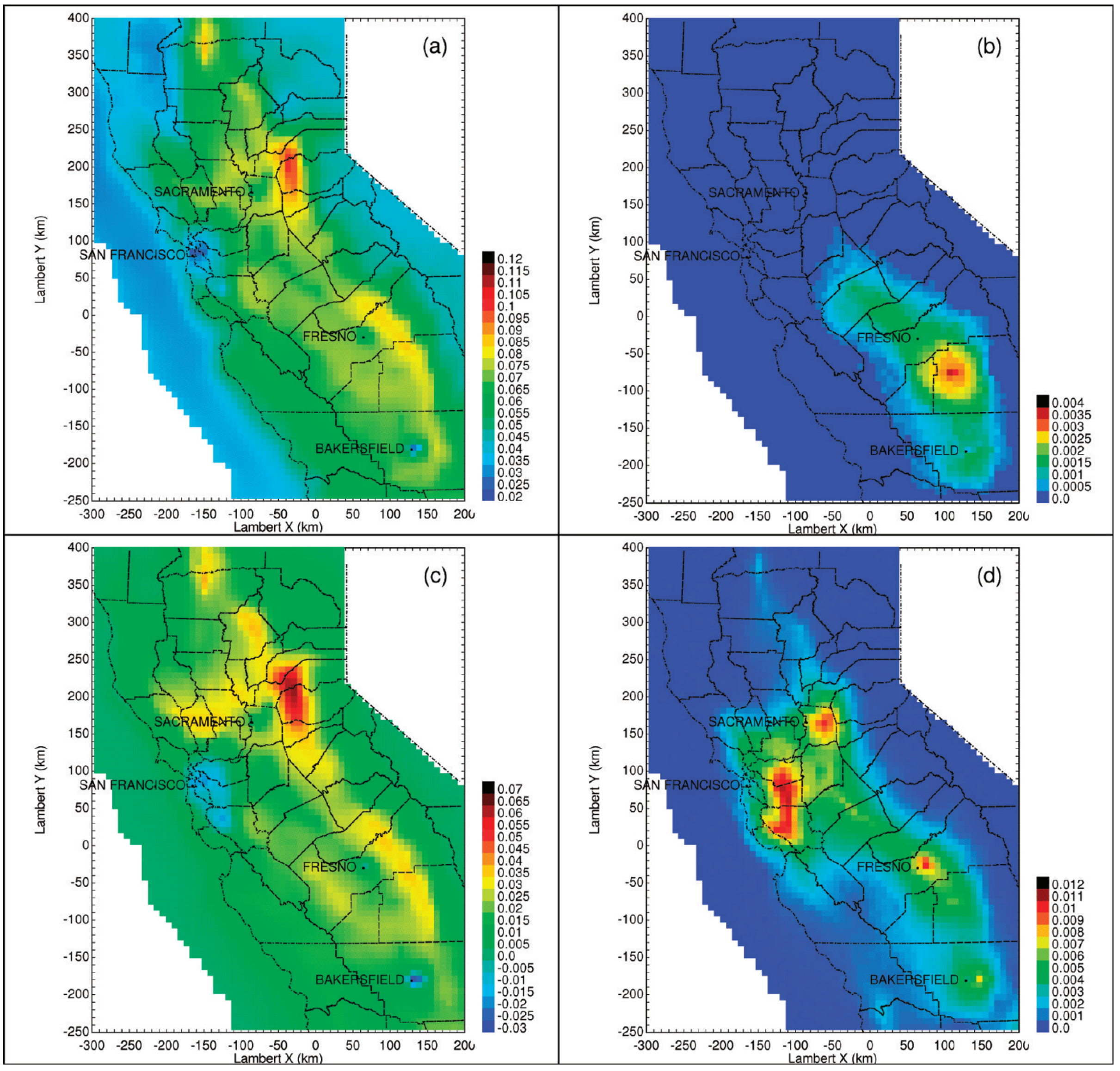

Figure 3. Simulated spatial distribution of episode-average 8 h peak O_3 (a) and contributions from livestock feed and mobile sources: (b) livestock feed VOC, (c) mobile NO_x plus VOC, and (d) mobile VOC only.

programs and changing population. Figure 4 shows the predicted 8-h average O_3 production from livestock feed VOC in the years 2005, 2010, 2015, and 2020. The spatial patterns in all the years are similar to the 2000 CCOS result (Figure 3b), with greatest impact from animal feed VOC emissions on O_3 production found in Tulare County. The maximum predicted O_3 contribution from livestock feed increases in 2005 and 2010 by 0.5 ppb; it then decreases by 1 ppb in 2015, and by 1.5 ppb in 2020, due to the predicted decreases in regional NO_x emissions, which lowered O_3 production efficiency for all VOC sources.

Figure 5 compares the accumulated mass of 8-h average O_3 summed across the entire SJV from mobile source VOC and livestock feed VOC in the year 2000, 2005, 2010, 2015, and 2020. In the 2000 CCOS episode, mobile VOC contributed ~12 tons of ground level 8 h peak O_3 in the SJV region, whereas livestock feed VOC contributed ~3.5 tons. The O_3 mass attributed to mobile source VOC decreased in later years in response to emissions control plans. In 2020, mobile source VOC emissions are predicted to produce ~3 tons of 8 h average ground level O_3. The predicted O_3 production from livestock feed VOC emissions stayed constant or increases slightly in 2005 and 2010 as the animal feed VOC emissions increased, but then decrease in 2015 and 2020. In 2020, livestock feed VOC emissions are estimated to contribute ~2.5 tons of ground level 8 h peak O_3, which is approximately equivalent to O_3 production from mobile source VOC under the meteorological conditions studied.

DISCUSSION

The current study identifies animal feed VOC emissions as the second leading VOC contributor to O_3 production in the SJV. Uncertainties associated with the emission estimation could affect the conclusions of this study. The livestock feed VOC emissions were projected based on population growth in California, but new techniques may be able to increase dairy milk production while holding animal feed emissions constant. The main conclusion that VOC emissions from mobile sources will produce less O_3 in the future, making livestock feed VOC emissions more important, should not change. The analysis in

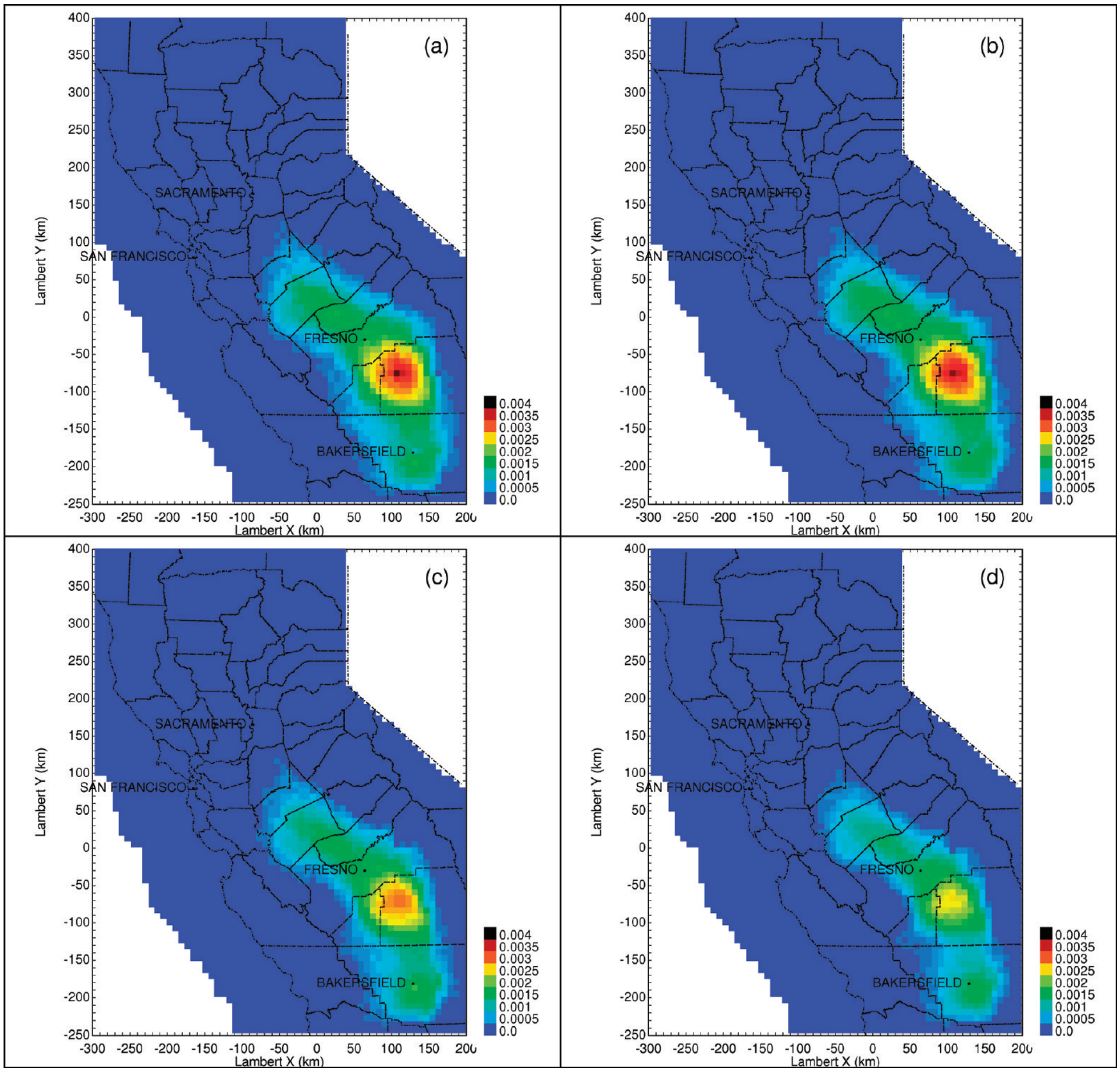

Figure 4. Simulated spatial distribution of contributions to 8 h peak O_3 from livestock feed VOC emissions in 2005(a), 2010(b), 2015(c), and 2020(d).

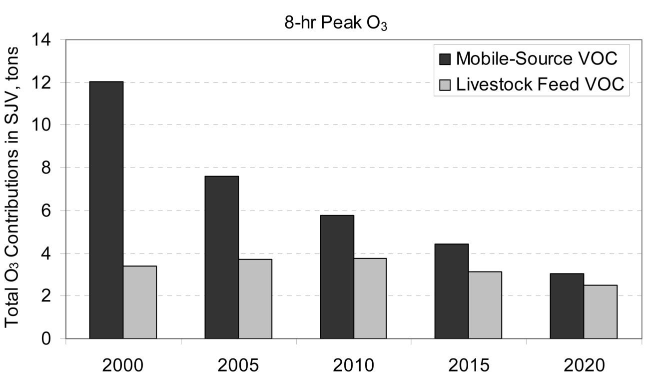

Figure 5. Total contributions to 8 h peak O_3 in the SJV from mobile VOC and livestock feed VOC in 2000, 2005, 2010, 2015, and 2020.

the present study was conducted by zeroing out particular emissions sectors and then comparing the results to the base case. This linear approach does not calculate the response of O_3 formation to relatively small changes in emissions from individual sectors. Techniques such as adjoints or the direct decoupled method can be used to efficiently calculate these local gradients. As a further limitation, the conclusions of the current study may be influenced by missing sources in the emissions inventory (from agriculture, industry, residential, etc). The under-prediction of O_3 in the southern portion of the SJV suggests some unknown source or chemical reaction pathway that is missing in the base-case calculations. The VOC emissions from animal feed appear to explain part of the unknown O_3 production in the SJV, but they do not completely close the gap between measurements and model predictions

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Meteorology evaluation statistics (Table S1), SJV emissions summary (Table S2), model domain (Figure S1), spatial distribution of 1 h peak O_3 and contributions from livestock feed and mobile sources (Figure S2), spatial distribution of O_3 productions to 1 h peak O_3 from livestock feed VOC emissions in the years of 2005, 2010, 2015, and 2020 (Figure S3), total O_3 productions to 1 h peak O_3 in the SJV from mobile VOC and livestock feed VOC in 2000, 2005, 2010, 2015, and 2020 (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Classifications of 8-h Ozone Nonattainment Areas. The Green Book Nonattainment Areas for Criteria Pollutants. US Environmental Protection Agency, April 2011. http://www.epa.gov/air/oaqps/greenbk/index.html.

(2) Ferreria, S. R., *Air Quality Forecasting and Trends.* Presented at CSUF Air Quality Management Certificate Program, Oct. 2006.

(3) California Agricultural Statistical Review. California Department of Food and Agriculture: Sacramento, CA, 2009.

(4) San Joaquin Valley Air Pollution Control District, 8-h Ozone plan. 2007 http://www.valleyair.org/Air_Quality_Plans/AQ_Final_Adopted_Ozone2007.htm (accessed July, 2011).

(5) Shaw, S. L.; Mitloehner, F. M.; Jackson, W.; Depeters, E. J.; Fadel, J. G.; Robinson, P. H.; Holzinger, R.; Goldstein, A. H. Volatile organic compound emissions from dairy cows and their waste as measured by proton-transfer-reaction mass spectrometry. *Environ. Sci. Technol.* **2007**, *41* (4), 1310−1316.

(6) Howard, C. J.; Yang, W.; Green, P. G.; Mitloehner, F.; Malkina, I. L.; Flocchini, R. G.; Kleeman, M. J. Direct measurements of the ozone formation potential from dairy cattle emissions using a transportable smog chamber. *Atmos. Environ.* **2008**, *42* (21), 5267−5277.

(7) Howard, C. J.; Kumar, A.; Mitloehner, F.; Stackhouse, K.; Green, P. G.; Flocchini, R. G.; Kleeman, M. J. Direct measurements of the ozone formation potential from livestock and poultry waste emissions. *Environ. Sci. Technol.* **2010**, *44* (7), 2292−2298.

(8) Alanis, P.; Sorenson, M.; Beene, M.; Krauter, C.; Shamp, B.; Hasson, A. S. Measurement of non-enteric emission fluxes of volatile fatty acids from a California dairy by solid phase micro-extraction with gas chromatography/mass spectrometry. *Atmos. Environ.* **2008**, *42* (26), 6417−6424.

(9) Malkina, I. L.; Kumar, A.; Green, P. G.; Mitloehner, F. M. Identification and quantitation of volatile organic compounds emitted from dairy silages and other feedstuffs. *J. Environ. Qual.* **2011**, *40* (1), 28−36.

(10) Howard, C. J.; Kumar, A.; Malkina, I.; Mitloehner, F.; Green, P. G.; Flocchini, R. G.; Kleeman, M. J. Reactive organic gas emissions from livestock feed contribute significantly to ozone production in central California. *Environ. Sci. Technol.* **2010**, *44* (7), 2309−2314.

(11) Dabdub, D.; DeHaan, L. L.; Seinfeld, J. H. Analysis of ozone in the San Joaquin Valley of California. *Atmos. Environ.* **1999**, *33* (16), 2501−2514.

(12) Pun, B. K.; Louis, J. F.; Pai, P.; Seigneur, C.; Altshuler, S.; Franco, G. Ozone formation in California's San Joaquin Valley: A critical assessment of modeling and data needs. *J. Air Waste Manage. Assoc.* **2000**, *50* (6), 961−971.

(13) Jin, L.; Tonse, S.; Cohan, D. S.; Mao, X. L.; Harley, R. A.; Brown, N. J. Sensitivity analysis of ozone formation and transport for a central california air pollution episode. *Environ. Sci. Technol.* **2008**, *42* (10), 3683−3689.

(14) Mcrae, G. J.; Goodin, W. R.; Seinfeld, J. H. Development of a 2nd-generation mathematical-model for urban air-pollution 0.1. Model formulation. *Atmos. Environ.* **1982**, *16* (4), 679−696.

(15) Harley, R. A.; Russell, A. G.; Cass, G. R. Mathematical-modeling of the concentrations of volatile organic compounds—Model performance using a lumped chemical mechanism. *Environ. Sci. Technol.* **1993**, *27* (8), 1638−1649.

(16) Mahmud, A.; Hixson, M.; Hu, J.; Zhao, Z.; Chen, S. H.; Kleeman, M. J. Climate impact on airborne particulate matter concentrations in California using seven year analysis periods. *Atmos. Chem. Phys.* **2010**, *10* (22), 11097−11114.

(17) Hu, J. L.; Ying, Q.; Chen, J. J.; Mahmud, A.; Zhao, Z.; Chen, S. H.; Kleeman, M. J. Particulate air quality model predictions using prognostic vs. diagnostic meteorology in central California. *Atmos. Environ.* **2010**, *44* (2), 215−226.

(18) Ying, Q.; Lu, J.; Allen, P.; Livingstone, P.; Kaduwela, A.; Kleeman, M. Modeling air quality during the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS) using the UCD/CIT source-oriented air quality model—Part I. Base case model results. *Atmos. Environ.* **2008**, *42* (39), 8954−8966.

(19) Mysliwiec, M. J.; Kleeman, M. J. Source apportionment of secondary airborne particulate matter in a polluted atmospbere. *Environ. Sci. Technol.* **2002**, *36* (24), 5376−5384.

(20) Held, T.; Ying, Q.; Kaduwela, A.; Kleeman, M. Modeling particulate matter in the San Joaquin Valley with a source-oriented externally mixed three-dimensional photochemical grid model. *Atmos. Environ.* **2004**, *38* (22), 3689−3711.

(21) Kleeman, M. J.; Cass, G. R. A 3D Eulerian source-oriented model for an externally mixed aerosol. *Environ. Sci. Technol.* **2001**, *35* (24), 4834−4848.

(22) Carter, W. P. L. Documentation of the SAPRC-99 chemical mechanism for VOC reactivity assessment; contracts 92-329 and 95-308; California Air Resources Board: Sacramento, CA. 2000.

(23) Carter, W. P. L. *Development of the SAPRC-07 Chemical Mechanism and Updated Ozone Reactivity Scale; Final Report*, Contract No. 03-318; California Air Resources Board: Sacramento, CA. 2010.

(24) Carter, W. P. L. Development of the SAPRC-07 chemical mechanism. *Atmos. Environ.*, **2010**. *44*(40), 5324−5335.

(25) Ying, Q.; Kleeman, M. J. Effects of aerosol UV extinction on the formation of ozone and secondary particulate matter. *Atmos. Environ.* **2003**, *37* (36), 5047−5068.

(26) Byun, D.; Schere, K. L. Review of the governing equations, computational algorithms, and other components of the models-3 Community Multiscale Air Quality (CMAQ) modeling system. *Appl. Mech. Rev.* **2006**, *59* (1−6), 51−77.

(27) Roselle, S. J.; Schere, K. L.; Pleim, J. E.; Hanna, A. F. *Photolysis rates for CMAQ. Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System*, Chapter 14, March 1999.

(28) Fujita, E. M.; Campbell, D. E.; Snorradottir, T. *Central California Ozone Study (CCOS) Data Validation Final Report*, May 2005.

(29) Skamarock, W. C.; Klemp, J. B.; Dudhia, J.; Gill, D. O.; Barker, D. M.; Duda, M. G.; Huang, X.-Y.; Wang, W.; Powers, J. G. *A Description of the Advanced Research WRF Version 3.* NCAR Technical Note NCAR/TN-475+STR, June 2008.

(30) Wang, W.; Bruyere, C.; Duda, M.; Dudhia, J.; Gill, D.; Lin, H.-C.; Michalakes, J.; Rizvi, S.; Zhang, X. *The Advanced Research WRF (ARW) Version 3 Modeling System User's Guide*, January 2010.

(31) Bao, J. W.; Michelson, S. A.; Persson, P. O. G.; Djalalova, I. V.; Wilczak, J. M. Observed and WRF-simulated low-level winds in a high-ozone episode during the Central California Ozone Study. *J. Appl. Meteorol. Climatol.* **2008**, *47* (9), 2372−2394.

(32) Michelson, S. A.; Djalalova, I. V.; Bao, J. W. Evaluation of the summertime low-level winds simulated by MM5 in the Central Valley of California. *J. Appl. Meteorol. Climatology* **2010**, *49* (11), 2230−2245.

(33) Mass, C. F. *personal communication.* University of Washington, Seattle, WA, 2010.

(34) Goodin, W. R.; Mcrae, G. J.; Seinfeld, J. H. Comparison of interpolation methods for sparse data—Application to wind and concentration fields. *J. Appl. Meteorol.* **1979**, *18* (6), 761−771.

(35) Jaffe, D.; Tamura, S.; Harris, J. Seasonal cycle and composition of background fine particles along the west coast of the US. *Atmos. Environ.* **2005**, *39* (2), 297−306.

(36) Liang, J. Y.; et al. Seasonal budgets of reactive nitrogen species and ozone over the United States, and export fluxes to the global atmosphere. *J. Geophys. Res., [Atmos.]* **1998**, *103* (D11), 13435−13450.

(37) California Air Resource Board 2009 Almanac Emission Projection Data. http://www.arb.ca.gov/app/emsinv/emssumcat.php (accessed March 2011).

(38) Population Projections for California and Its Counties 2000–2050. State of California, Department of Finance, July 2007. http://www.dof.ca.gov/html/DEMOGRAP/ReportsPapers/Projections/P1/P1.php (accessed March 2011).

(39) *Guidance on the Use of Models and Other Analyses for Demonstrating Attainment of Air Quality Goals for Ozone, $PM_{2.5}$, and Regional Haze*, EPA-454/B-07-002; U.S. Environmental Protection Agency: RTP, NC, April 2007.

(40) Kleeman, M. J. A preliminary assessment of the sensitivity of air quality in California to global change. *Clim. Change* **2008**, *87*, S273–S292.

(41) Eder, B.; Kang, D. W.; Mathur, R.; Yu, S. C.; Schere, K. An operational evaluation of the Eta-CMAQ air quality forecast model. *Atmos. Environ.* **2006**, *40* (26), 4894–4905.

(42) Jin, L., Brown, N. J., Harley, R. A., Bao, J. W., Michelson, S. A., Wilczak, J. M., Seasonal versus episodic performance evaluation for an Eulerian photochemical air quality model. *J. Geophys. Res., [Atmos.]*, **2010**. *115*.

(43) Cai, C. X.; Kelly, J. T.; Avise, J. C.; Stockwell, W. R.; Kaduwela, A. P. *Photochemical Modeling in California with Two Chemical Mechanisms: Model Intercomparison and Response to Emission Reductions. J. Air Waste Manage. Assoc.* **2011**, *61* (5), 559–572.

(44) Reynolds, S. D.; Blanchard, C. L.; Ziman, S. D. Understanding the effectiveness of precursor reductions in lowering 8-Hr ozone concentrations. *J. Air Waste Manage. Assoc.* **2003**, *53* (2), 195–205.

(45) Lehrman, D., Knuth, B. *Characterization of the CCOS 2000 Measurement Period*, Interim Report, 2001, Contract No. 01–2CCOS.