SIMULATING OZONE AND PM WITH CMAQ IN SOUTHEAST U.S.: APPLICATION, EVALUATION, AND PROCESS ANALYSIS

Ping Liu, Evelyn Frazier, Danny Hamilton, Yang Zhang*
North Carolina State University, Raleigh, NC, USA

Shaocai Yu$, Prakash V. Bhave+, Steve Howard+, and Ken L. Schere+
Atmospheric Sciences Modeling Division, Air Resources Laboratory,
National Oceanic and Atmospheric Administration
+On assignment to National Exposure Research Laboratory,
U.S. Environmental Protection Agency, Research Triangle Park, NC, USA
$On assignment from Science and Technology Corporation,
10 Basil Sawyer Drive, Hampton, VA 23666-1393

1. INTRODUCTION

Ozone (O_3) and fine particulate matter ($PM_{2.5}$) are two major concerns in the U.S. These two pollutants are linked to serious health impacts including chronic bronchitis, asthma, and premature deaths, and other effects including reduced visibility (caused by PM), crop damage, and greater vulnerability to disease in some tree species (caused by ozone). The U.S. EPA Models-3/Community Multiscale Air Quality (CMAQ) modeling system is applied widely to simulate the formation and fate of air pollutants (Byun and Ching, 1999; Binkowski and Roselle, 2003; Byun and Schere, 2005).

In this work, CMAQ version 4.4 is applied to simulate O_3 and PM concentrations during the 1999 Southern Oxidants Study (SOS) episode from June 12-28. The domain covers the contiguous U.S. with a 32 km horizontal grid resolution (178×124 grid cells). The meteorological inputs for the CMAQ model are simulated with the Pennsylvania State University (PSU) / National Center for Atmospheric Research (NCAR) Mesoscale Modeling System Generation 5 (MM5) version 3.4, with the Four Dimensional Data Assimilation (FDDA). The emissions are based on the EPA's 1999 National Emission Inventory (NEI) version 1, which is processed with the Sparse Matrix Operator Kernel Emissions system (SMOKE, version 1.4) for 32-km grids. The first two days are used as a spin-up period to minimize the influence of the initial conditions.

The MM5 model predictions of temperature, relative humidity (RH), wind speed, wind direction, and planetary boundary layer (PBL) height, and the CMAQ model predictions of O_3, $PM_{2.5}$, and PM chemical composition, are compared with the observations from several routine monitoring networks and special field studies. The causes of inaccurate predictions are analyzed through sensitivity studies and process analysis that includes the Integrated Process Rate analysis (IPR) and the Integrated Reaction Rate analysis (IRR).

2. EVALUATION OF SIMULATED METEOROLOGICAL VARIABLES

Meteorological inputs are critical for simulating chemical species with CMAQ. In this work, MM5 meteorological predictions are compared with the Clean Air Status and Trends Network (CASTNet), the Southeastern Aerosol Research and Characterization Study (SEARCH), and SOS measurements. The normalized mean bias factor (NMBF) and the normalized mean error factor (NMEF) recommended by Yu et al. (2003) are calculated for performance statistics. Figure 1 shows the temporal variation of temperature, RH, wind speed, and wind direction at Yorkville, GA and PBL height at Dickson, TN. The predicted temperatures match well with the peak observed values on most days, although the model tends to overpredict nighttime temperatures for most days in this rural site. MM5 tends to underpredict RH and gives the largest discrepancies in wind speed predictions. The predictions of wind direction are close to the observations, except for significant deviations at 0 a.m. on June 16 and at 1 a.m. on June 22. The PBL height measurements are only available during daytime, and MM5 tends to overpredict PBL height on most days.

*Corresponding author: Yang Zhang, Department Of Marine, Earth and Atmospheric Sciences, Campus Box 8208, NCSU, Raleigh, NC 27695; e-mail: yang_zhang@ncsu.edu

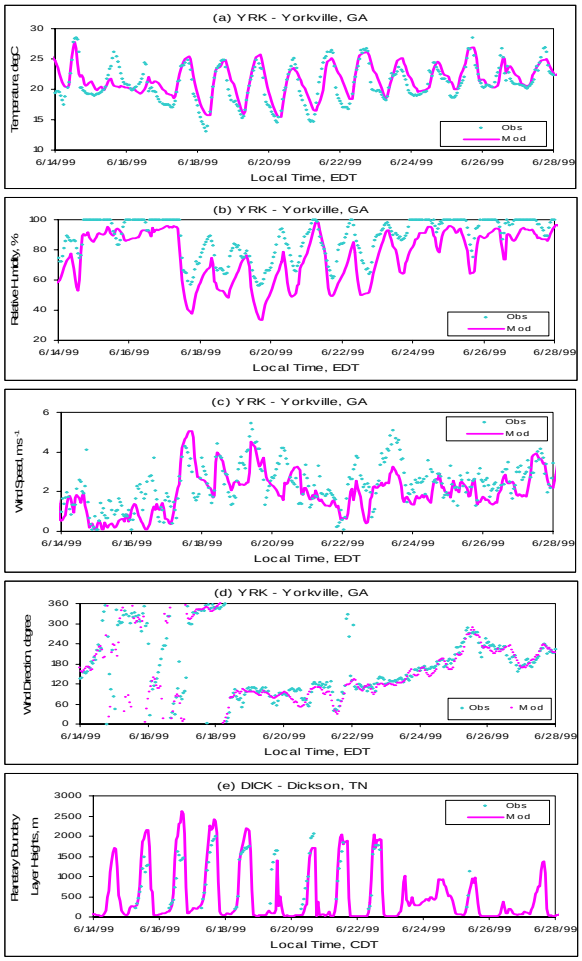


Figure 1. Temporal distributions of (a) temperature, (b) RH, (c) wind speed, and (d) wind direction at Yorkville (YRK), GA and (e) PBL height at Dickson (DICK), TN during 14-28 June, 1999.

Overall, the MM5 model overpredicts temperature, wind speed and PBL height by a factor of 1.02, 1.23, and 1.08, respectively; underpredicts RH by a factor of 1.11, and deviates slightly from the measurements of wind direction, as shown in Table 1. The correlation coefficients are greater than 0.8 for temperature, RH, and PBL height, while that for wind speed is 0.54, indicating a weaker correlation between simulated and observed wind speed, as compared to other meteorological variables considered here.

Table 1. Performance statistics for temperature, RH, wind speed, wind direction, and PBL height.

	TEMP	RH	WSD	WDR	PBL
MeanObs	22.01	77.65	1.87	156.81	1079.30
MeanMod	22.36	69.89	2.29	151.36	1165.27
Number	6781	6865	7513	6809	92
Corr	0.86	0.80	0.54	0.48	0.81
NMBF	0.02	-0.11	0.23	-0.04	0.08
NMEF	0.07	0.17	0.50	0.35	0.34

3. EVALUATION OF SIMULATED OZONE AND $PM_{2.5}$

The O_3 observational datasets are obtained from the Aerometric Information Retrieval System (AIRS)-Air Quality System (AQS), CASTNet, and SEARCH; the $PM_{2.5}$ observational datasets are obtained from the Interagency Monitoring of Protected Visual Environments (IMPROVE) and SEARCH. Figure 2 shows the temporal distribution of O_3 mixing ratios and $PM_{2.5}$ concentrations at Yorkville, GA.

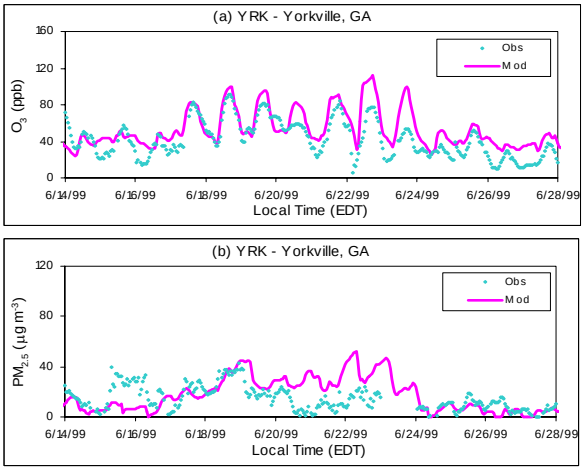


Figure 2. Temporal distributions of (a) O_3 mixing ratios and (b) $PM_{2.5}$ concentrations at Yorkville (YRK), GA during 14-28 June, 1999.

As shown in Table 2, the model overpredicts maximum 1-hr and 8-hr average O_3 mixing ratios by a factor of 1.14 and 1.19 for AIRS-AQS, 1.05 and 1.08 for CASTNet, and 1.17 and 1.25 for SEARCH, respectively. The performance is better for CASTNet network which mainly contains rural sites, indicating the CMAQ model can predict rural ground level O_3 more accurately than urban O_3 during this episode.

Table 2. Performance statistics for O_3 mixing ratios for AIRS-AQS, CASTNet, and SEARCH networks.

	AIRS-AQS		CASTNet		SEARCH	
	max. $1hO_3$	max. $8hO_3$	max. $1hO_3$	max. $8hO_3$	max. $1hO_3$	max. $8hO_3$
MeanObs	59.32	52.21	60.26	54.95	52.95	46.61
MeanMod	67.42	62.18	63.21	59.59	61.98	58.28
Number	14659	14619	988	982	84	82
Corr	0.72	0.75	0.79	0.79	0.74	0.79
NMBF	0.14	0.19	0.05	0.08	0.17	0.25
NMEF	0.22	0.25	0.16	0.17	0.26	0.30

As shown in Table 3, the model underpredicts $PM_{2.5}$ by a factor of 1.34 and 1.03, respectively, at IMPROVE and SEARCH sites. For $PM_{2.5}$ composition, the model overpredicts SO_4^{2-} and

underpredicts NO_3^-, organic carbon (OC), and black carbon (BC) for both networks (Table 3). CMAQ overpredicts NH_4^+ at IMPROVE sites, but underpredicts it at SEARCH sites. NO_3^- predictions have the smallest NMBF value (i.e., the largest bias in terms of magnitude) at SEARCH sites (by a factor of 4.04), indicating a significant underprediction. The performance of NO_3^- and NH_4^+ predictions at IMPROVE sites is better than that at SEARCH sites, indicating that CMAQ can simulate NO_3^- and NH_4^+ more accurately in rural/remote areas since most of the IMPROVE sites are in the national parks and wilderness areas. The discrepancies between predictions and observations of PM composition are likely due to uncertainties in emissions and model treatments in physical and chemical atmospheric processes (e.g., the floor value used in vertical diffusivities, K_{zz}). The CMAQ model has historically had a difficult time simulating concentrations of NO_3^- accurately due to volatility issues associated with NO_3^-, and their exacerbation because of uncertainties associated with SO_4^{2-} and total ammonium simulations (Yu et al., 2005). Detailed analyses about the uncertainties for OC and EC can be found elsewhere (Bhave et al., 2004; Yu et al., 2004).

Table 3. Performance statistics for $PM_{2.5}$ concentrations for IMPROVE and SEARCH networks.

IMPROVE	$PM_{2.5}$	SO_4^{2-}	NO_3^-	NH_4^+	OC	BC
MeanObs	6.73	1.88	0.26	1.51	1.30	0.29
MeanMod	5.02	2.26	0.14	1.87	0.97	0.19
Number	211	201	201	12	195	191
Corr	0.83	0.88	0.36	0.38	0.55	0.77
NMBF	-0.34	0.20	-0.82	0.24	-0.33	-0.53
NMEF	0.50	0.49	1.73	0.36	0.57	0.72
SEARCH	$PM_{2.5}$	SO_4^{2-}	NO_3^-	NH_4^+	OC	BC
MeanObs	13.19	5.06	0.43	2.33	2.65	0.86
MeanMod	12.86	6.25	0.11	1.59	1.74	0.42
Number	112	112	112	112	116	116
Corr	0.67	0.68	0.50	0.55	0.70	0.59
NMBF	-0.03	0.24	-3.04	-0.46	-0.52	-1.05
NMEF	0.43	0.53	3.29	0.68	0.63	1.11

4. PROCESS ANALYSIS OF OZONE AND PM

Process Analysis can be used in CMAQ to obtain the information that provides the insights into how model predictions are obtained. In this work, the integrated process rate analysis (IPR) is applied to identify the relative contributions of individual physical and chemical processes in CMAQ (e.g., emissions, chemical reaction, horizontal advection, vertical transport, dry deposition, etc.). Figures 4 and 5 show the changes in hourly O_3 mixing ratios (ppm hr^{-1}) and $PM_{2.5}$ concentrations (μg m^{-3} hr^{-1}) simulated by CMAQ in the surface layer due to each process at Jefferson Street (JST, urban site) and Yorkville (YRK, rural site), GA. Vertical transport and dry deposition are the two major contributors to the changes in O_3 mixing ratios at both sites. Vertical transport through downward motion brings excessive amount of the high O_3 concentrations at the high altitudes to the ground and contributes mostly to the production of O_3 and dry deposition contributes mostly to the removal of O_3 at both sites. Gas-phase chemistry through the NO titration also contributes significantly to the removal of O_3 at JST site. Emission is the major contributor to the production and vertical transport is the major contributor to the loss of $PM_{2.5}$ at both sites. PM processes also contribute to the production of $PM_{2.5}$, while aqueous processes by wet deposition and horizontal transport contribute to the loss of $PM_{2.5}$.

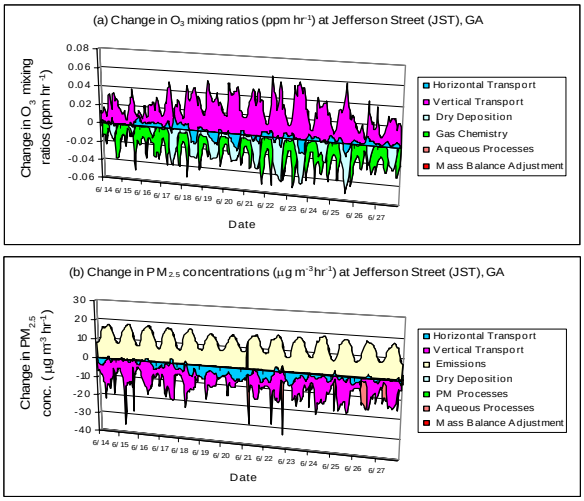
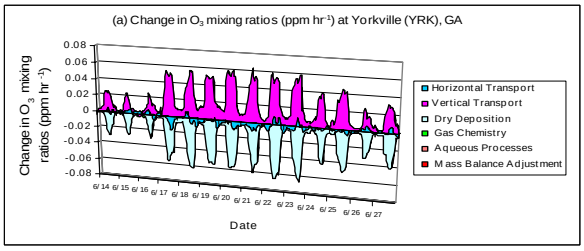


Figure 4. Changes in (a) O_3 mixing ratios (ppm hr^{-1}), and (b) $PM_{2.5}$ concentrations (μg m^{-3} hr^{-1}) simulated by CMAQ in the surface layer due to each process at Jefferson Street (JST), GA, during June 14-28, 1999.



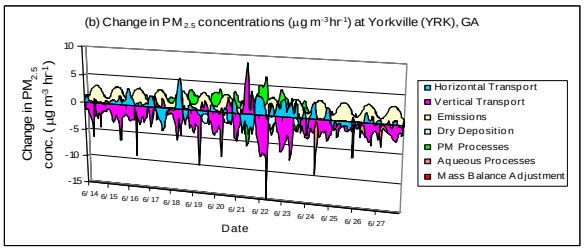
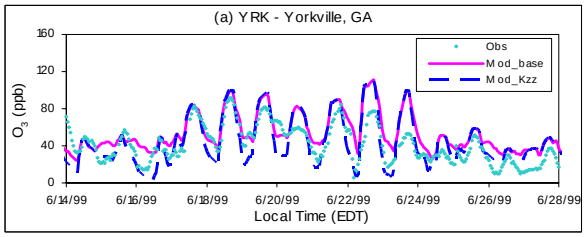


Figure 5. Changes in (a) O_3 mixing ratios (ppm hr^{-1}) and (b) $PM_{2.5}$ concentrations (µg m^{-3} hr^{-1}) simulated by CMAQ in the surface layer due to each process at Yorkville (YRK), GA, during June 14-28, 1999.

5. SENSITIVITY STUDY

The results from the process analysis indicate that vertical transport can affect largely the predictions of chemical species, such as O_3 and $PM_{2.5}$. K theory is applied for vertical and horizontal diffusion in CMAQ version 4.4. The default floor value of K_{zz} is set to be 1 m^2 sec^{-1} in CMAQ version 4.4. This value may be too high (Zhang et al., 2004). In this work, a sensitivity run is conducted using 0.1 m^2 sec^{-1} as a floor value of K_{zz}. Figure 6 shows the temporal distribution of O_3 mixing ratios and $PM_{2.5}$ concentrations at Yorkville, GA, from the base and the sensitivity simulations. With a minimum K_{zz} value (0.1 m^2 sec^{-1}) the simulated nighttime O_3 mixing ratios are reduced by an average of 3.0 ppb during June 14-28 and a maximum of 33.4 ppb at 7 a.m. on June 16 while the simulated $PM_{2.5}$ concentrations are increased at this site, especially during nighttime from June 19 to 23. Compared to the base case, the simulation with a minimum K_{zz} value of 0.1 m^2 sec^{-1} improves the model performance for $PM_{2.5}$ at IMPROVE rural sites (NMBF value changes from -0.34 to -0.14). However, the change makes the model performance for $PM_{2.5}$ at SEARCH sites slightly worse (NMBF value changes from -0.03 to 0.20). This suggests that a K_{zz} value of 1 m^2 sec^{-1} is reasonable for the urban areas.



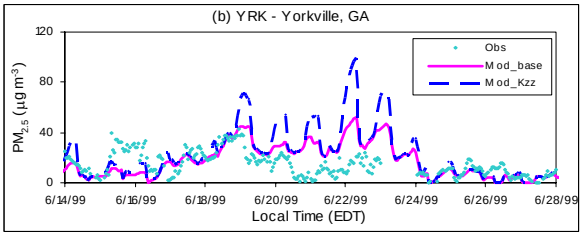


Figure 6. Temporal distributions of (a) O_3 mixing ratios and (b) $PM_{2.5}$ concentrations at Yorkville (YRK), GA during 14-28 June, 1999.

6. SUMMARY

Our preliminary evaluation has shown that, for the summer June 12-28 SOS 1999 episode MM5 can simulate temperature and wind direction relatively well especially for rural sites, but give larger deviations from measurements for RH, wind speed, and PBL height. The CMAQ model tends to overpredict maximum 1-hr and 8-hr O_3 by a factor of 1.14 and 1.19 at the AIRS-AQS sites, 1.05 and 1.08 at the CASTNet sites, and 1.17 and 1.25 at the SEARCH sites. The model has better skill of simulating maximum 1-hr and 8-hr O_3 in the rural areas. The model underpredicts $PM_{2.5}$ by a factor of 1.34 and 1.03, respectively, at the IMPROVE and SEARCH sites. NO_3^- predictions have the largest negative NMBF, indicating significant underpredictions. Moderate-to-large underpredictions also occur for BC and OC.

The contributions of major atmospheric processes to the formation of O_3 and $PM_{2.5}$ at the JST and YRK sites are quantified using IPR. Vertical transport and dry deposition are the two major processes affecting O_3 mixing ratios. Gas-phase chemistry also contributes to the removal of O_3 at these sites. Emission and vertical transport are the two major processes affecting $PM_{2.5}$ concentrations. However, PM processes, horizontal transport, and aqueous processes also contribute significantly on some days. Based on the IPR results, a sensitivity study is conducted to investigate the changes in the vertical transport of O_3 and $PM_{2.5}$ to the floor value of K_{zz} used in CMAQ. The predicted nighttime O_3 mixing ratios with a K_{zz} value of 0.1 m^2 sec^{-1} are reduced by an average of 3.0 ppb compared with those from the base simulation. Additional process analysis will be conducted for individual PM components to determine the relative contributions of physical and chemical processes to their fate in the atmosphere. IRR is applied to investigate gas-phase chemical transformations that are simulated in the model, and IRR results will be analyzed for O_3 related reactions to investigate important

chemical pathways for the chemical evolution of O_3.

Acknowledgements

This work is performed under the National Science Foundation Award No. Atm-0348819, and the Memorandum of Understanding between the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Commerce's National Oceanic and Atmospheric Administration (NOAA) and under agreement number DW13921548. The authors thank Alice Gilliland, U.S. NOAA/EPA, for providing the Fortran code for extracting data from observational databases and CMAQ and the observational databases from CASTNet, IMPROVE, and AIRS-AQS.

Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

7. REFERENCES

Bhave, P.V., G.A. Pouliot, and M. Zheng (2004), Source apportionment of primary carbonaceous aerosol using the Community Multiscale Air Quality Model, Presented at the 27th NATO/CCMS International Technical Meeting on Air Pollution Modeling and its Application, Banff, Alberta, Canada, October 25-29.

Binkowski, F.S., and S.J. Roselle (2003), Models-3 Community Multiscale Air Quality (CMAQ) Model aerosol component, 1. Model description, *J. Geophys. Res.*108, 4183, doi:10.1029/2001JD001409.

Byun, D.W., and J.K.S. Ching (1999), Science algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System, EPA/600/R-99/030, U.S. Environmental Protection Agency: Research Triangle Park, NC, 3805-3818.

Byun, D.W., and K.L. Schere (2005), Review of the governing equations, computational algorithms, and other components of the Models-3 Community Multiscale Air Quality (CMAQ) Modeling System. *Appl. Mech. Rev.* (in press).

Yu, S., B. Eder, R. Dennis, S.-H. Chu, S. Schwartz (2003), New unbiased symmetric metrics for evaluation of the air quality model, the 2nd Annual CMAS Models-3 User's Conference, Oct 27-29, 2003, Research Triangle Park, NC.

Yu., S., R.L. Dennis, P.V. Bhave, and B.K. Eder (2004), Primary and secondary organic aerosols over the United States: estimates on the basis of observed organic carbon (OC) and elemental carbon (EC), and air quality modeled primary OC/EC ratios, *Atmos. Environ.*, 38, 5257-5268.

Yu, S., R. Dennis, S. Roselle, A. Nenes, J. Walker, B. Eder, K. Schere, J. Swall, and W. Robarge (2005), An assessment of the ability of three-dimensional air quality models with current thermodynamic equilibrium models to predict aerosol NO_3^-, *J. Geophys. Res*., 110 (D07S13), doi:10.1029/2004JD004718.

Zhang, Y., B. Pun, S.-Y. Wu, K. Vijayaraghavan, and C. Seigneur (2004), Application and evaluation of two air quality models for particulate matter for a southeastern U.S. episode, *J. Air & Waste Management*, 54, 1478-1493.