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Use of a process analysis tool for diagnostic study on fine particulate matter predictions in the U.S. – Part I: Model evaluation

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ABSTRACT

Regional ozone (O_3) and fine particles ($PM_{2.5}$) modeling for both research–grade and regulation applications is important due to their known impacts on human health, air quality, and climate change. In this study, the fifth–generation Penn State/NCAR Mesoscale Model (MM5) and the U.S. EPA Models–3/Community Multiscale Air Quality (CMAQ) modeling system are applied to simulate the major air pollutants during the 1999 Southern Oxidants Study episode for the period of 12–28 June 1999. As Part I of two companion papers describing CMAQ performance, process analysis, and sensitivity simulations, this paper presents results from an operational evaluation for meteorological and chemical predictions using the available surface, aircraft, and satellite data. Both MM5 and CMAQ show reasonable performance for major meteorological variables (i.e., temperature, relative humidity, wind direction, planetary boundary layer height) with normalized mean biases (NMBs) of 0.4–24.2%, surface concentrations O_3, $PM_{2.5}$, SO_4^{2-}, and NH_4^+ with NMBs of –39% to 24.2%, and vertical profiles of temperature and sulfur dioxide. Relatively poor performance is found in the simulated precipitation (NMBs of –16.3% to 37.4%), the concentrations of NO_3^-, EC, and OC (NMBs of –77.8% to –22%) and total O_3 column mass. The evaluation identifies several research areas that are needed to improve model performance for nitrate, organic carbon, and black carbon at surface, vertical profiles of relative humidity, carbon monoxide, and nitrogen oxides, and tropospheric O_3 column abundance.

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1. Introduction

Particulate matter (PM) with aerodynamic diameter less than or equal to 2.5 µm ($PM_{2.5}$) is known to have impacts on human health, visibility, and climate change. The U.S. Environmental Protection Agency (EPA) establishes the National Ambient Air Quality Standards (NAAQSs) for ozone (O_3) and $PM_{2.5}$ for regulations. The complicated physical and chemical processes associated with $PM_{2.5}$ formation and transport pose challenges in accurately representing $PM_{2.5}$ in three–dimensional (3D) air quality models (Seinfeld, 2004; Seigneur, 2005; Zhang, 2008). A number of 3D models have been developed to simulate O_3 and $PM_{2.5}$ on urban and regional scales (e.g., Binkowski and Roselle, 2003; Zhang et al., 2004a). The EPA's Models–3/Community Multiscale Air Quality (CMAQ) modeling system is one such model (Binkowski and Roselle, 2003). 3D model simulations using CMAQ have been conducted extensively over the continental U.S. (CONUS) or its sub–regions (e.g., Zhang et al., 2004b; Yu et al., 2005; Eder and Yu, 2006; Zhang et al., 2006a; Zhang et al., 2006b; Yu et al., 2007; Roy et al., 2007; Wu et al., 2008). Most of these applications use the Carbon–Bond mechanism IV (CB–IV) (Eder and Yu, 2006; Zhang et al., 2006a; Zhang et al., 2006b; Queen et al., 2008a; Queen et al., 2008b; Wu et al., 2008), fewer use the Statewide Air Pollution Research Center Mechanism (SAPRC99) (e.g., Yu et al., 2005; Luecken et al., 2008). Model evaluation in these studies largely focuses on the temporal and spatial evaluation at/near surface using surface observational networks. Few studies (e.g., Yu et al., 2007; Roy et al., 2007; Yu et al., 2008; Zhang et al., 2009) use the aloft and remotely–sensed observations to evaluate simulated vertical profiles of meteorological variables and air pollutant concentrations in the planetary boundary layer (PBL). Even fewer are on the process analysis (PA) using embedded tool in CMAQ. In this study, CMAQ version 4.4 is applied to the 1999 Southern Oxidants Study (SOS99) (http://www.ncsu.edu/sos) episode for the period of June 12–28. The process analysis (PA) tool available for CB–IV in CMAQ v. 4.4 is extended to SAPRC99. Our objectives are to conduct a comprehensive model evaluation over continental U.S. (CONUS), identify the model biases in simulating $PM_{2.5}$, and apply the PA tool to guide the design of sensitivity simulations to reduce the model biases. To our best knowledge, this is the first of this kind study to use the PA tool to guide the design of sensitivity studies. The results are presented in two parts. Part I describes model configurations and an operational evaluation for O_3 and $PM_{2.5}$ and its species [i.e., sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), organic carbon (OC), and elemental carbon (EC)] using observations from surface networks, aircraft, and satellites. Part II describes results from process analyses and sensitivity simulations.

2. Model Configurations and Evaluation Methodologies

CMAQ simulations are conducted over CONUS at a 32–km horizontal grid spacing with 178 × 124 horizontal grid cells. There are 21 layers vertically from surface (first layer top is ~35 m) to the tropopause (~16 km). In this study, all the meteorological and chemical inputs are provided by the U.S. EPA and the model configurations are the same as those of Yu et al. (2004; 2005). The meteorological fields are simulated with the Pennsylvania State University/National Center for Atmospheric Research Mesoscale Modeling System Generation 5 (MM5) (Grell et al., 1994) version

3.4, with the Four Dimensional Data Assimilation. The emissions are based on the EPA's 1999 National Emission Inventory version 3 (NEI v.3). These emissions are processed with the Sparse Matrix Operator Kernel Emissions system (SMOKE, version 1.4). The initial and boundary conditions are set to be clean tropospheric air conditions. The mechanisms used to solve gas– and aerosol–phase chemistry are SAPRC99 (Carter, 2000) and AERO3, respectively. CMAQ simulates all major atmospheric processes. These include emissions, transport of gaseous and aerosol species, aerosol processes (e.g., thermodynamic equilibrium, nucleation, condensation, and coagulation), dry and wet depositions, and cloud processing of gaseous and aerosol species. The first two days are considered as a spin–up period to minimize the influence of the initial conditions.

Meteorological variables and associated observational databases and references used in the model evaluation are summarized in Table S1 in the Supporting Material (SM). For MM5, an operational evaluation that tests the principal output variables from the model is performed. Major meteorological variables such as 2 m temperature and relative humidity (T2 and RH2), 10 m wind speed (WS10), wind direction (WD10), PBL height (PBLH), and precipitation (Precip) are evaluated in terms of spatial distribution, temporal variation, and performance statistics. Performance statistics include correlation coefficient (R), root mean square error (RMSE), normalized mean bias (NMB), and normalized mean error (NME). For CMAQ, three types of evaluation are performed: operational evaluation that calculates the statistics of observed and simulated concentrations of gaseous and PM species, diagnostic evaluation that analyzes dominant atmospheric processes and their contributions using the PA tool, and mechanistic evaluation (also referred to as sensitivity study) that examines the responses of the output variables to changes in the inputs (e.g., emissions) and parameters for model treatments (e.g., dry deposition velocities, chemical reaction rates).

3. Model Evaluation

3.1. Meteorological predictions

The MM5 simulations of T2 and RH2, WS10, and its U/V components (U10/V10), WD10, PBLH, and PREC are compared with observations from six datasets, including the Southeastern Aerosol Research and Characterization (SEARCH), the Clean Air Status and Trends Network (CASTNET), SOS99, the North American Research Strategy for Tropospheric Ozone 1999 SOS Nashville Study (NARSTO SOS99NASH), the National Atmospheric Deposition Program (NADP), and the Automated Surface Observing System (ASOS). These datasets are summarized in the Supporting Material. Note that there is no data overlapping of sites at different networks. The statistics are calculated based on the time scale of the observations (e.g., hourly, weekly average, or weekly total). Given the different characteristics of network sites and methods used for measurements, the statistics for each measured variable at different networks are calculated separately.

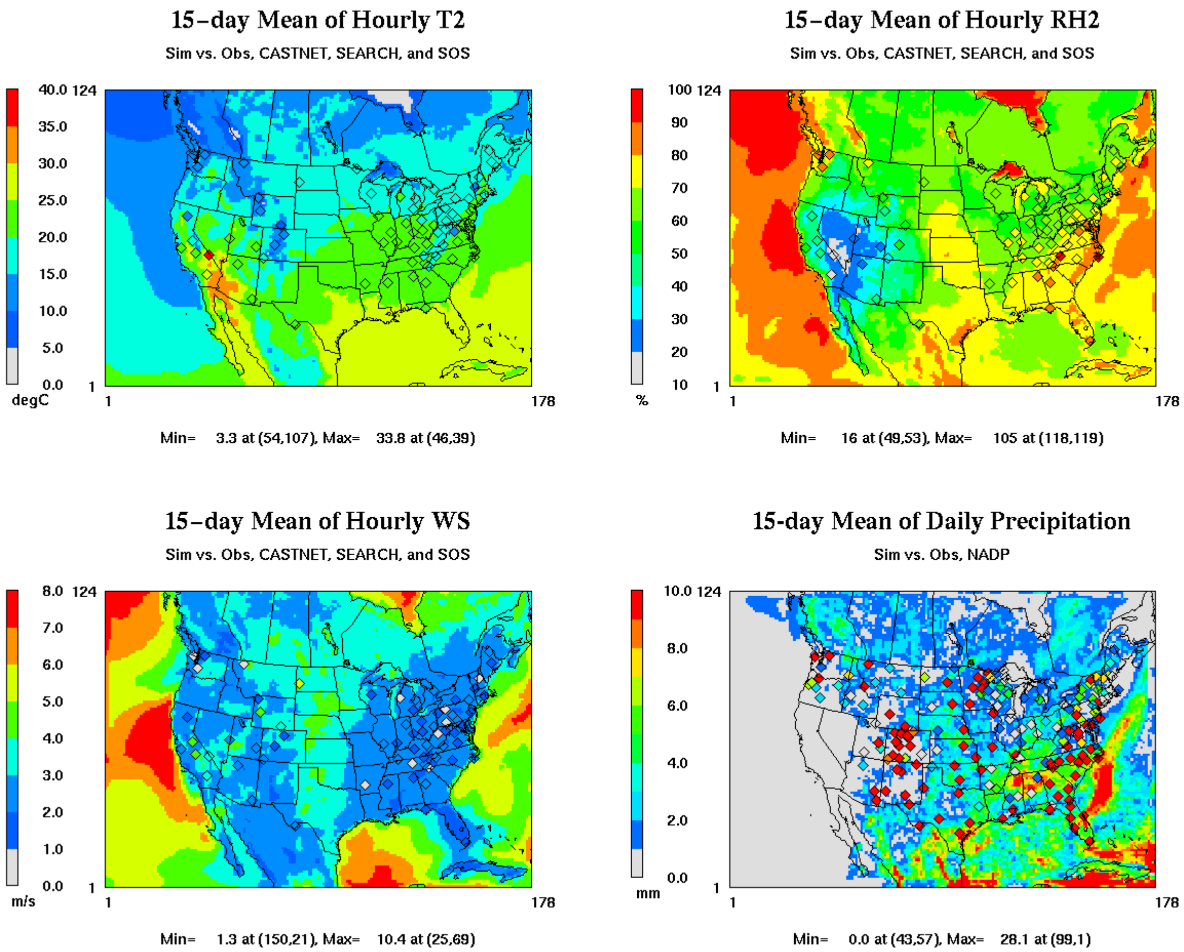

Figure 1. *Spatial distributions of 15–day mean simulated (by MM5) and observed 2–m temperature (T2), 2–m humidity (RH2), 10–m wind speed (WS10), and precipitation from all networks. The diamond denotes observations and the background denotes the model results. A consistent color in the diamond and background indicates a relatively good agreement between the model predictions and observations. Different colors between the two indicate either underpredictions or overpredictions.*

Figure 1 shows simulated 15 day mean hourly T2, RH2, and WS10, and daily PREC overlaid with observations. The simulated spatial patterns of T2, RH2, and WS10 by MM5 are overall consistent with observations, with the best agreement in T2. Compared with observations, MM5 predicts much lower RH2 in the southeastern U.S., Pacific Northwest, and the northeastern U.S., and higher WS10 over most of the domain, particularly in the western U.S. The model predictions of T2 and RH2 in the mid–western states (e.g., ND, SD, NE, KS, OK, and TX) cannot be evaluated because of a lack of observational data in this region. Daily PREC is underpredicted at most NADP sites.

This is not surprising as the Kain–Fritcsh 2 (KF2) cumulus parameterization was developed for mesoscale and large scale applications; it cannot well resolve the convection features observed at a local scale (< 10 km) (Kain, 2004). KF2 has some limitations in representing different types of precipitation and the diurnal cycle of the precipitation (Anderson et al., 2007). For example, it tends to overpredict convective precipitation (as it is the case for ASOS observed precipitation in this work, see Table 1) but underpredict precipitation from more slowly evolving mesoscale processes. In addition, the grid resolution of 32–km is too coarse to resolve local scale processes such as precipitation and cloud formation. Figure 2 and Figure S1 (see the SM) compare the temporal variations of simulated and observed T2, RH2, and wind vector at five eastern sites that represent different terrains and meteorological/chemical conditions. These sites include coastal [Blackwater National Wildlife Refuge (BWR), MD], mountain [Great Smoky Mountain (GRS), TN], urban aloft [James K. Polk Building in downtown Nashville (POLK), TN, ~110 m above the ground], urban surface [Jefferson Street (JST), Atlanta, GA, where only observed wind speed and direction are available], and rural surface [Yorkville (YRK), GA] sites (see sites locations in Figure S2). As shown in Figure 2 and Figure S1 (see the SM), MM5 is able to reproduce the day–to–day variations of those variables at most sites (e.g., T2 at BWR, POLK, YRK), although large underpredictions of RH2 during some hours occur at the coastal and rural sites. MM5 simulates slightly stronger north wind at the coastal, rural, and urban sites, and south wind at the mountain site (see the SM, Figure S1).

Table 1. *Performance statistics of MM5 meteorological predictions during June 14-28, 1999*

	T2	RH2	WS10	U10	V10	WD10	PBLH	PREC	
								NADP	ASOS
MeanObs	19.15	66.6	2.0	-0.30	0.27	157.8	1 079.3	17.9	0.16
MeanMod	19.23	62.2	2.5	-0.32	0.27	151.9	1 165.3	15.0	0.22
Number	25 020	25 299	24 522	7 503	7 503	7 519	92	181	5 244
R	0.9	0.8	0.5	0.7	0.8	0.5	0.8	0.7	0.1
RMSE	3.0	15.9	1.5	1.1	1.3	94.4	502.9	17.3	1.2
NMB, %	0.4	-6.7	24.2	5.8	-1.7	-3.7	8.0	-16.3	37.4
NME, %	11.4	18.5	59.5	266.1	353.0	33.3	33.6	59.4	201.5

Note: T2: 2 m temperature, °C; RH2: 2 m relative humidity, %; WS: 10 m wind speed, m s^{-1}; U10: 10 m U component of WS, m s^{-1}; V10: 10 m V component of WS, m s^{-1}; WD: 10 m wind direction, degree; PBLH: planetary boundary layer height, m; PREC: precipitation, it is evaluated against two datasets: weekly total precipitation at the NADP sites, mm and hourly precipitation at the ASOS sites, mm; R: correlation coefficient; RMSE: root mean square error; NMB: normalized mean bias; NME: normalized mean error.

The simulated wind speeds are comparable with observations at the urban surface site (i.e., JST). They are slightly greater than those observed aloft (i.e., POLK). Figure 3 compares simulated and observed temporal variations of PBLHs at the four sites: i.e., Dickson (DICK), Cornelia Fort Air Park (CFA), Cumberland (CUMB), and Gallatin (GALL), from the SOS99NASH study in Tennessee (see site locations in Figure S2 in the SM). MM5 captures well the early development of PBL and the time for peak PBLH at all sites. Moderate underpredictions of PBLH occur at DICK and GALL on June 19, and at DICK, CFA, and CUMB on June 25. Such underpredictions may be related to limitations of the PBL scheme and the land–surface scheme used for the simulation, as shown in Misenis and Zhang (2010).

Table 1 summarizes the performance statistics. Overall, simulated T2, WS10, U10, and PBLH have NMBs of 0.4%, 24.2%, 5.8%, and 8.0%, respectively. Simulated RH2, V10, and WD10 have NMBs of –6.7%, –1.7%, and –3.7%, respectively. MM5 overpredicts hourly PREC at 13 ASOS sites by 37.4% in the eastern U.S. It underpredicts weekly PREC at the NADP sites by 16.3%. The overpredictions over the ASOS sites are most likely caused by the overpredictions in the summer convective precipitation by the KF2 cumulus parameterization. KF2 cannot capture well the local scale precipitation pattern at the ASOS sites. This deficiency has less impact on precipitation predictions over the NADP sites that spread out the continental U.S. For comparison, turning off KF2 in a MM5 simulation at 4 km over North Carolina underpredicts precipitations at the ASOS sites by 36% (Queen and Zhang, 2008a). A careful interpretation for NMBs for wind predictions in terms of WS10/WD10 and their U10/V10 components is needed. The former is not applicable for the vector WD10. The latter averages negative and positive U10 and V10, thus underestimating the model bias in WS10 predictions (Zhang et al., 2006a). The RMSE values are high for PBLH and WD10, indicating model difficulties in simulating both. The correlation coefficients for T2, RH2, V10, and PBLH are equal to or greater than 0.80. The correlation coefficients for WS10/WD10 and hourly PREC are 0.50 and 0.10, respectively.

3.2. Chemical species

The CMAQ model predictions of O_3 are compared with the observations from the Aerometric Information Retrieval System – Air Quality Subsystem (AIRS–AQS), CASTNET, and SEARCH, and those of $PM_{2.5}$ and PM species are compared with the observations from the Interagency Monitoring of Protected Visual Environments (IMPROVE), the Speciation Trends Network (STN), and SEARCH. The major precursors of O_3 and $PM_{2.5}$ are also examined along with O_3 and $PM_{2.5}$ at several SEARCH sites where hourly data are available. The AIRS–AQS and STN sites are mainly located in the urban/suburban areas. The CASTNET and IMPROVE sites are mainly located in the rural and remote areas. SEARCH contains four urban sites and four rural/suburban sites. Figure 4 shows the spatial distributions of 15 day mean of simulated and observed daily maximum 8–hr average O_3 and 24–hr average $PM_{2.5}$ for urban/suburban and rural/remote locations. CMAQ overpredicts the maximum 8–hr average O_3 at most sites in the eastern U.S. and several sites in the state of Washington, and underpredicts the 24–hr average $PM_{2.5}$ at rural sites in the southeastern U.S. The CMAQ–predicted $PM_{2.5}$ concentrations agree better with observations at rural sites than at urban sites in the western U.S., particularly in California. The large discrepancies between simulations and observations indicate possible underestimation in the emissions of primary $PM_{2.5}$ species such as OC and EC and the impact of the assumed clean boundary conditions in urban areas, which is consistent with other studies (e.g., Zhang et al., 2006b; Ying et al., 2008).

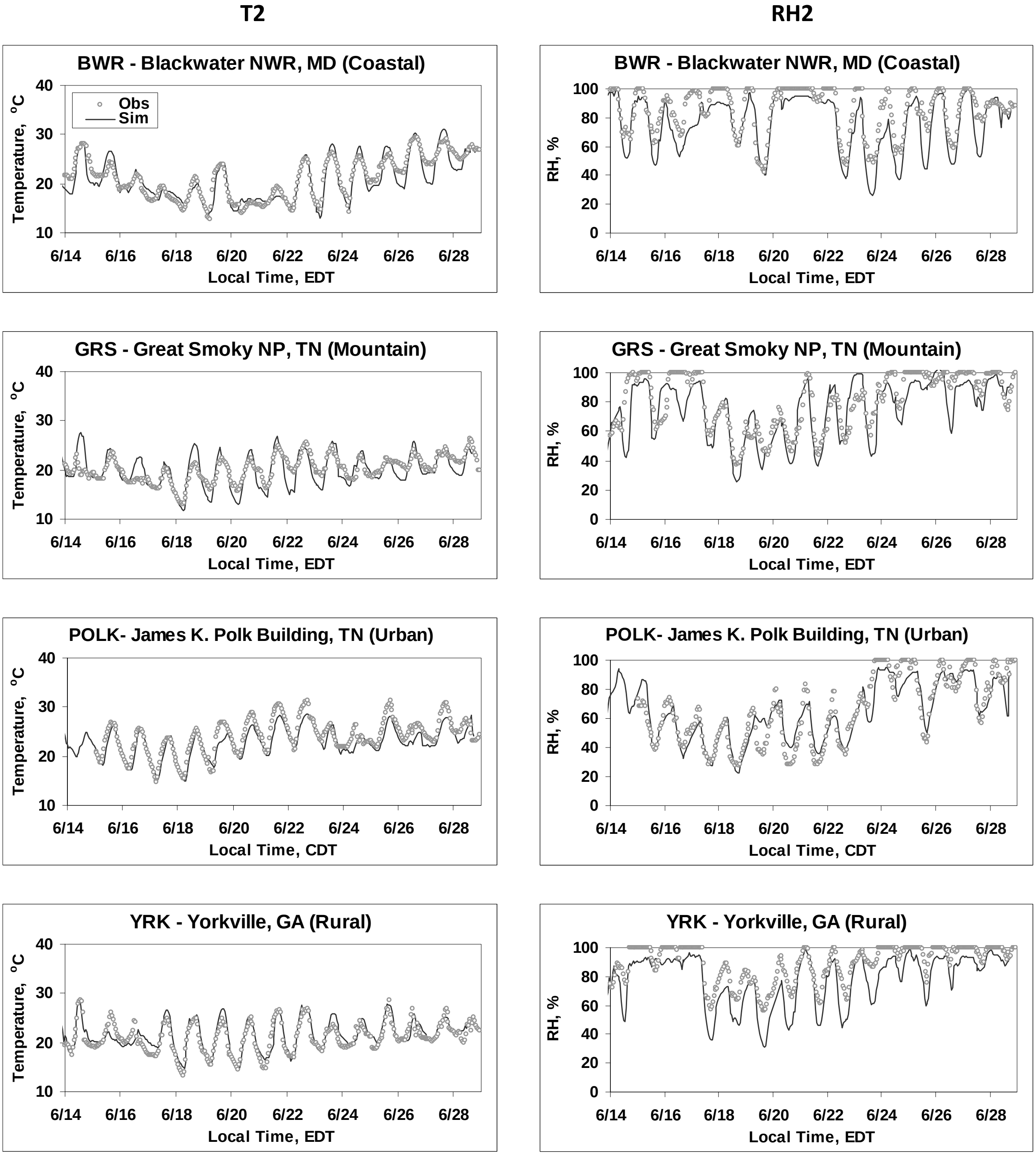

Figure 2. *Temporal variations of simulated (by MM5) and observed 2 m temperature (T2) and 2 m relative humidity (RH2) at coastal, mountain, urban (aloft), and rural sites during June 14-28, 1999.*

Figure 5 shows the temporal variations of O_3 and its precursors, nitric oxide (NO), nitrogen dioxide (NO_2), and carbon monoxide (CO) at an urban (i.e., JST, GA) and a rural site (i.e., YRK, GA). CO is evaluated as a continental tracer for assessing simulated meteorological parameters and the impact of meteorological processes on air pollutant, given its relatively slow reaction rate. Simulated day–to–day patterns of NO and NO_2 are similar to observations, especially at the rural site. CO is overpredicted at JST but underpredicted at YRK during most of time except June 22–23. This may indicate possible underestimation and overestimation in vertical mixing at JST and YRK, respectively. CMAQ well predicts the diurnal variation trends of O_3. The magnitude of nighttime O_3 mixing ratios, however, is higher than observations on some days at the rural site. The magnitude of daytime peak O_3 is also higher than observations on June 21–23 at both sites. The nighttime overprediction of O_3 mixing ratios is due in part to the overestimation in the nighttime vertical mixing. Such an overprediction leads to underpredictions in NO mixing ratios and insufficient titration of O_3 by NO (Zhang et al., 2006b) and the model difficulties in simulating nocturnal PBL (Eder and Yu, 2006). The daytime peak O_3 overpredictions may be associated with underestimation in the daytime vertical mixing during June 21–23.

Figure 6 shows the temporal variations of simulated and observed $PM_{2.5}$, SO_4^{2-}, NO_3^-, total nitrate (i.e., $TNO_3 = HNO_3 + NO_3^-$), and their precursors, sulfur dioxide (SO_2) and nitric acid (HNO_3), at the two sites. Compared with the observations, the temporal variations of simulated HNO_3 are captured relatively better than those of SO_2, except for the significant overpredictions of HNO_3 at YRK on June 22. Major overpredictions of $PM_{2.5}$ occur during June 19–23 at both sites, coinciding with overpredictions of SO_2 and SO_4^{2-} at both sites. Overpredictions of HNO_3 also occur but simulated NO_3^- concentrations are low (< 2 $\mu g\ m^{-3}$) during the same time period at YRK. HNO_3 dominates TNO_3 under the summer conditions at JST and YRK, with averages of 85.4% and 93.8%, respectively. These results indicate that at both sites under warmer weather conditions, little NO_3^- can be formed. This is because of its volatility and the fact that higher temperatures shift the equilibrium of $HNO_3/NH_3/NH_4NO_3$ system, favoring the formation of HNO_3.

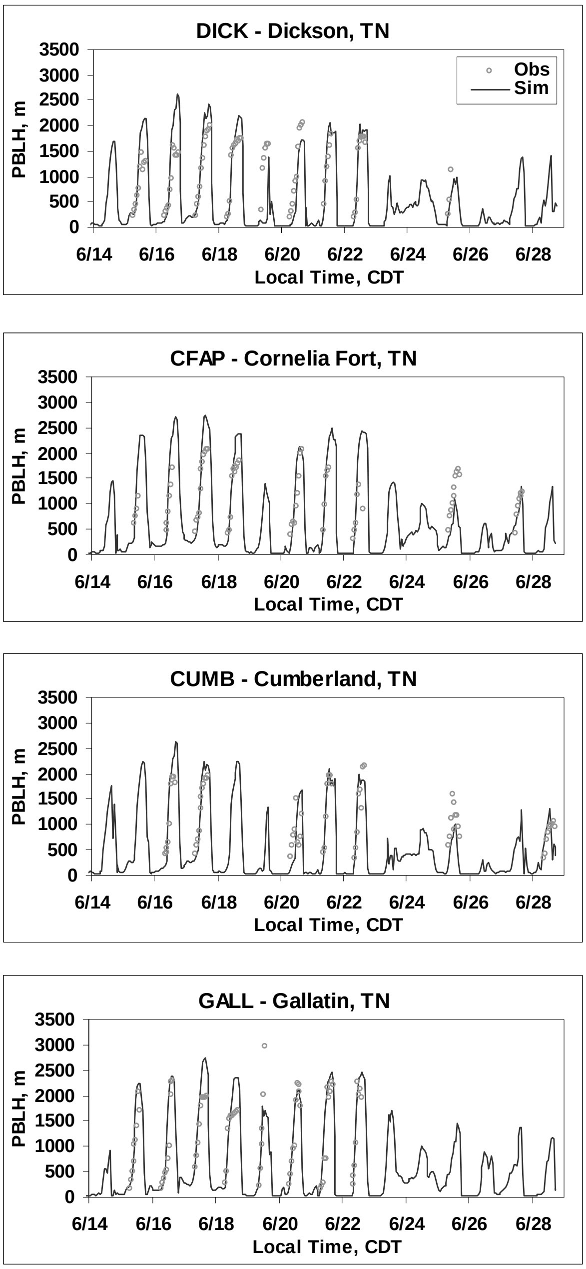

Figure 3. *Simulated (by MM5) and observed temporal variations of PBL height (PBLH) at the four sites available in NARSTO SOS99NASH study in Tennessee during June 14-28, 1999.*

Tables 2(a) and 2(b) summarize the performance statistics for gaseous pollutants and $PM_{2.5}$. Compared with the AIRS–AQS and SEARCH sites where NMBs are greater than 10%, the model performance of daily max 1–hr and 8–hr O_3 is better for CASTNET that mainly contains rural sites, with the overprediction of 4.9% and 8.5%, respectively. At the SEARCH sites, CO, SO_2, NO_2, and HNO_3 are overpredicted by 1.9%, 40.0%, 22.7%, and 26.9%, respectively; NO is underpredicted by 35.4%. Since O_3 chemistry is NO_x–limited over large areas of continental U.S. in summer (Zhang et al., 2009), the overpredictions in NO_2 may help explain some of the overpredicitons in the O_3 mixing ratios. CMAQ underpredicts $PM_{2.5}$ by 25.5%, 10.2%, and 39.0%, respectively, at the IMPROVE, SEARCH, and STN sites. At the IMPROVE and SEARCH sites, such underpredictions are mainly due to the underpredictions of NO_3^-, OC, and EC. CMAQ overpredicts SO_4^{2-} by 17.8%, 20.1%, and 18.3% at the CASTNET, IMPROVE, and SEARCH sites, respectively, likely caused by overestimation in SO_2 emissions (indicated by the NMB of 40% in the SO_2 mixing ratios) and the underprediction in the precipitation at the NADP sites. NH_4^+ is overpredicted at the CASTNET and IMPROVE sites, but underpredicted at the SEARCH sites. The overpredictions of NH_4^+ at the CASTNET and IMPROVE sites are associated with overpredictions in SO_4^{2-} through neutralization of cation and anion. The underpredictions of NH_4^+ at the SEARCH sites are caused by underestimation of NH_3 emissions (Zhang et al., 2006b; Zhang et al., 2006c). NO_3^- has the largest biases among all the PM species evaluated with the largest negative NMB of –77.8% at the SEARCH sites. EC and OC are all underpredicted by 34.4% and 24.9% at the IMPROVE sites and by 54.9% and 58.6% at the SEARCH sites, respectively. The discrepancies between simulated and observed $PM_{2.5}$ and its composition are likely due to uncertainties in emissions, meteorology, model treatments in atmospheric processes, and model configurations used. For example, CMAQ has difficulty in simulating NO_3^- accurately due to volatility issues associated with NO_3^- and uncertainties associated with SO_4^{2-} and total ammonium simulations (Yu et al., 2005). One of the main reasons for the large negative biases for NO_3^- is due to the overestimation of SO_4^{2-} at all sites. The overestimated SO_4^{2-} consumes too much NH_3 and leaves less NH_3 to react with HNO_3. As analyzed in the Part II paper (Liu et al., 2010), the underestimation of NH_3 emissions may also help to explain some of the underpredictions in NH_4^+ over the SEARCH sites. The use of a 32–km horizontal grid resolution cannot resolve the local emission strengths and distributions that are needed to accurately predict point–wise observations at urban/suburban sites over source areas. On the other hand, the observations of volatile species such as NO_3^- and NH_4^+ contain large uncertainties (Zhang et al., 2010). The heterogeneous reaction of N_2O_5 that generates HNO_3 is important for NO_3^- formation and the reaction probability (γ) for this reaction varies with T, RH, and particle composition (e.g., Brown et al., 2006). However, γ is just a simple parameterization treated in CMAQ version 4.4 based on the findings by Riemer et al. (2003). In this simple parameterization, γ is calculated as a function of the sulfate fraction in the total mass of sulfate and nitrate and the lower and upper limit values of γ (0.002 and 0.02, respectively). A more advanced parameterization has been developed based on above factors. This parameterization explicitly considers the phase state (e.g., the γ value on aqueous particles exceed that on solid particles), which reproduces the laboratory data and the major enhancement of γ (Davis et al., 2008). For this SOS episode, however, the impact of this updated parameterization is small. This is because summer temperatures do not favor the formation of NO_3^- and the resulting NO_3^- only contributes to a small portion of $PM_{2.5}$. Detailed analyses concerning the uncertainties for OC and EC can be found elsewhere (e.g., Yu et al., 2004).

Wet deposition is an important removal process that dictates gaseous and aqueous–phase concentrations. In this episode, wet deposition occurs largely over the eastern U.S. and is associated with the spatial distribution of precipitations. The biases of wet deposition predictions are associated with the uncertainties in the predicted precipitation. This is because the convective precipitation is dominant and has more effects on wet deposition predictions during summer than winter (Davis and Swall, 2006). The explicit microphysics schemes in MM5 can also affect the wet deposition predictions in CMAQ (Queen and Zhang, 2008b). As shown in Table 2(c), the wet deposition flux of NO_3^- is underpredicted by 39.9%. Those of SO_4^{2-} and NH_4^+ are slightly overpredicted by 13.3% and 5.3%, respectively, probably due to the overprediction of precipitation at the ASOS sites where SO_4^{2-} concentrations (thus NH_4^+ concentrations) are higher.

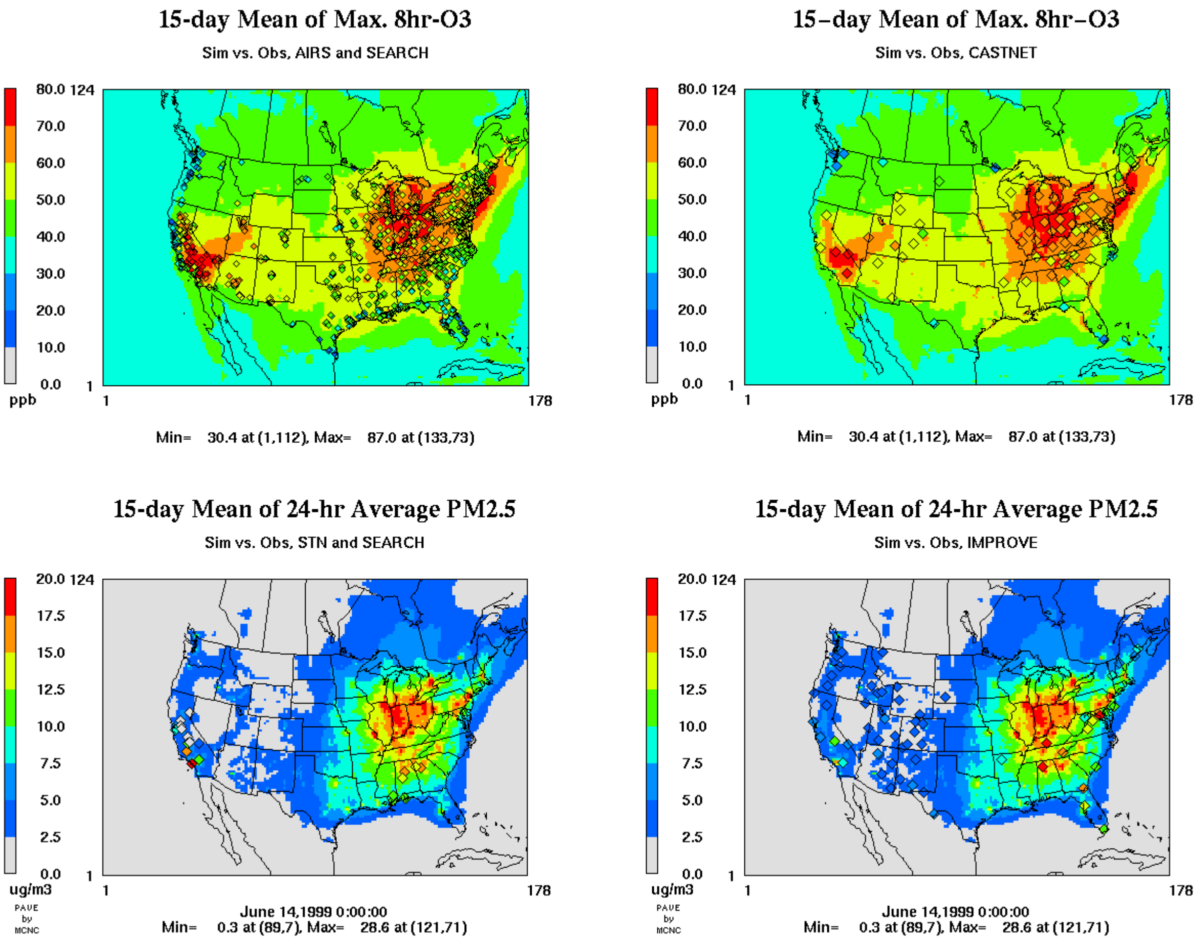

Figure 4. *Spatial distributions of 15–day mean simulated (by CMAQ) and observed maximum 8–hr average O_3 (ppb) at urban (i.e., the AIRS–AQS and SEARCH sites) and rural locations (i.e., the CASTNET sites), and 24–hr average $PM_{2.5}$ ($\mu g\ m^{-3}$) at urban (i.e., the STN and SEARCH sites) and rural locations (i.e., the IMPROVE sites) during June 14–28, 1999. The diamonds denote observations.*

Table 2. *Performance statistics of CMAQ chemical predictions during June 14-28, 1999* **(a)** *maximum 1-hr and 8-hr average O_3 and 1-hr average other gases (ppb),* **(b)** 24-hr average $PM_{2.5}$ and its components ($\mu g\ m^{-3}$), **(c)** wet deposition fluxes of $PM_{2.5}$ components ($mg\ L^{-1}$)

(a)	AIRS-AQS		CASTNET		SEARCH						
	max. $1hO_3$	max. $8hO_3$	max. $1hO_3$	max. $8hO_3$	max. $1hO_3$	max. $8hO_3$	CO	NO	SO_2	NO_2	HNO_3
MeanObs	59.3	52.2	60.3	55.0	53.0	46.6	190.7	2.8	1.5	9.7	1.0
MeanMod	67.4	62.2	63.2	59.6	62.0	58.3	194.4	1.8	2.2	11.9	1.3
Number	14 659	14 619	988	982	84	82	1314	753	1 345	683	998
R	0.7	0.8	0.8	0.8	0.7	0.8	0.6	0.5	0.3	0.8	0.5
NMB, %	13.7	19.1	4.9	8.5	17.0	25.0	1.9	-35.4	40.0	22.7	26.9
NME, %	21.6	24.5	15.6	17.0	25.7	30.1	50.4	79.3	107.1	51.5	75.1

(b)	CASTNET			IMPROVE						SEARCH						STN
	SO_4^{2-}	NH_4^+	NO_3^-	$PM_{2.5}$	SO_4^{2-}	NH_4^+	NO_3^-	OC^a	EC	$PM_{2.5}$	SO_4^{2-}	NH_4^+	NO_3^-	OC	EC	$PM_{2.5}$
MeanObs	3.9	1.3	0.5	6.7	1.9	1.5	0.3	1.3	0.3	13.4	4.8	1.9	0.4	3.8	0.9	11.9
MeanMod	4.6	1.4	0.4	5.0	2.3	1.9	0.1	1.0	0.2	12.0	5.7	1.5	0.1	1.6	0.4	7.2
Number	75	75	75	211	201	12	201	195	191	124	134	110	134	132	115	25
R	0.9	0.9	0.3	0.8	0.9	0.4	0.4	0.6	0.8	0.6	0.6	0.7	0.5	0.3	0.6	0.5
NMB, %	17.8	8.1	-22.2	-25.5	20.1	24.2	-45.1	-24.9	-34.4	-10.2	18.3	-20.6	-77.8	-58.6	-54.9	-39.0
NME, %	31.3	28.8	85.9	37.2	49.0	36.5	94.7	42.9	47.3	50.2	57.7	42.7	82.5	60.2	56.2	39.0

(c)	SO_4^{2-}	NH_4^+	NO_3^-
MeanObs	1.7	0.4	1.7
MeanMod	1.9	0.4	1.0
Number	132	132	132
R	0.4	0.2	0.4
NMB, %	13.3	5.3	-39.9
NME, %	75.8	81.3	69.1

[a] *OC is a surrogate for all primary organic compounds in CMAQ.*

Note: No cutoff values are applied; R: correlation coefficient; NMB: normalized mean bias; NME: normalized mean error.

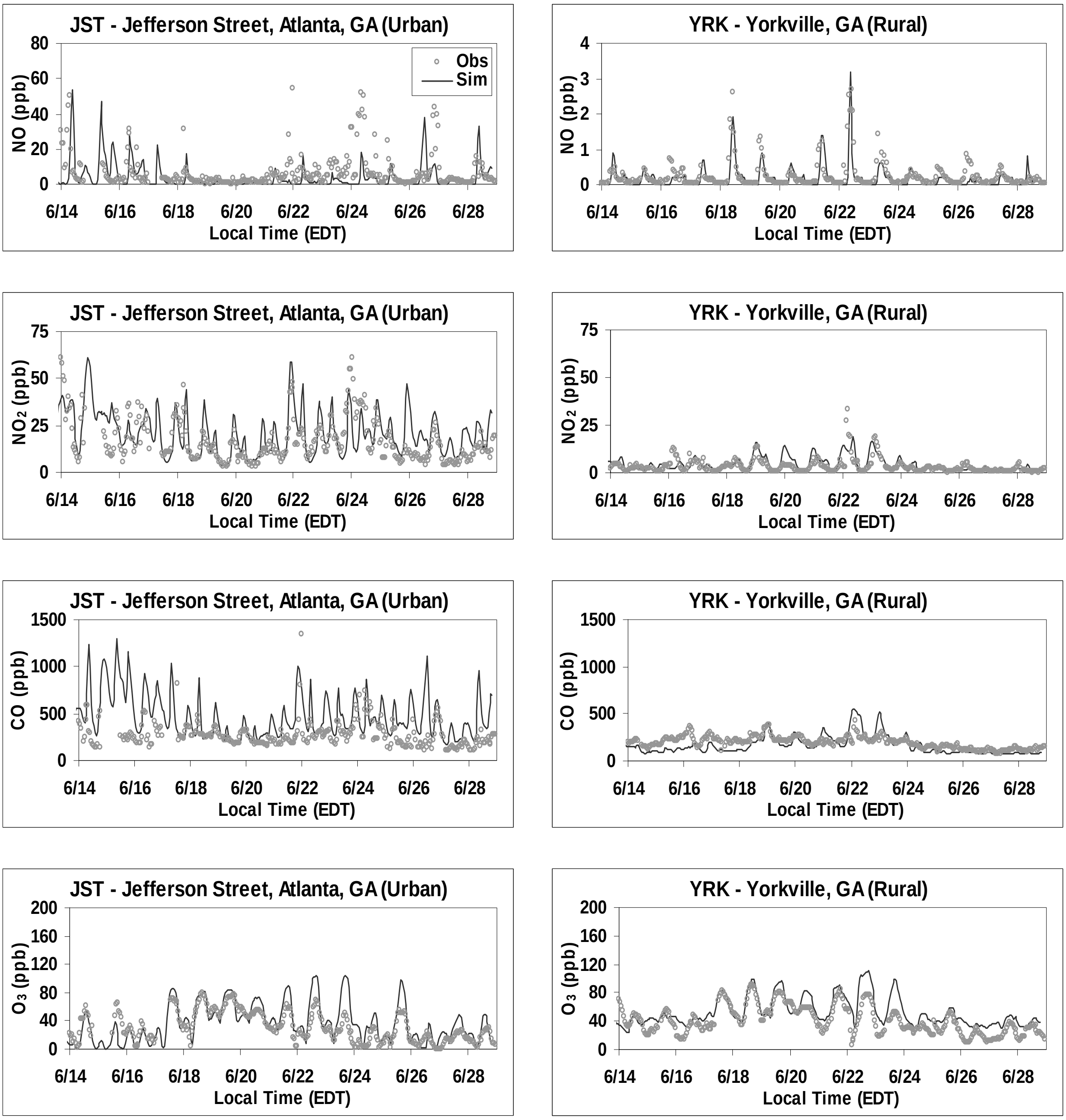

Figure 5. *Simulated (by CMAQ) and observed temporal variations of NO, NO_2, CO, and O_3 at Jefferson Street in Atlanta, GA (JST, urban) and Yorkville, GA (YRK, rural) during June 14-28, 1999.*

3.3. Vertical profiles and column ozone

In addition to surface–based observations, the observations from the NARSTO SOS99NASH, the U.S. Department of Energy G–1 aircraft, are used to qualitatively evaluate simulated vertical profiles. The aircraft measurements were conducted mostly at 500 to 1 000 m altitudes, within the PBL in Nashville, Tennessee during mid–afternoon (i.e., 1:00 to 2:00 pm, local time) on June 22, 1999. The vertical profiles of observed and simulated O_3, NO, NO_2, CO, SO_2, T, and RH, as well as the flight track are shown in Figure 7. The simulated data are extracted according to the latitude, longitude, height, and time of the aircraft data. Multiple observational points during the flight track are thus compared with simulated results if they are located in the same 32–km grid cell. A warm and humid atmospheric condition was observed during this period for the altitudes of 200–800 m, with Ts of 21 to 32 °C and RHs of 40% to 66%. T decreases while RH increases with the increased altitude. The simulated T profiles agree well with the aircraft observations. The simulated RH profiles are consistent with observations in terms of variation trend with height but RH values are lower by ~8%. The model fails to capture the profiles of O_3 and its precursors, NO, NO_2, and CO in terms of magnitudes and their variation trends with height. This is due in part to uncertainties in emissions and boundary conditions in the PBL. Note that O_3 vertical profile follows closely the vertical profiles of its precursor gases (NO and NO_2). In contrast, simulated SO_2 profile agrees well with observations. None of these profiles, however, capture the observed peaks between 700–800 m. This is due most likely to the fact that such peaks were observed within a plume that contained high concentrations of those species during the aircraft measurements (Kleinman et al., 2002). These high concentrations were not reproduced in the model simulation. In addition, the model also fails to reproduce observed vertical gradients for several species.

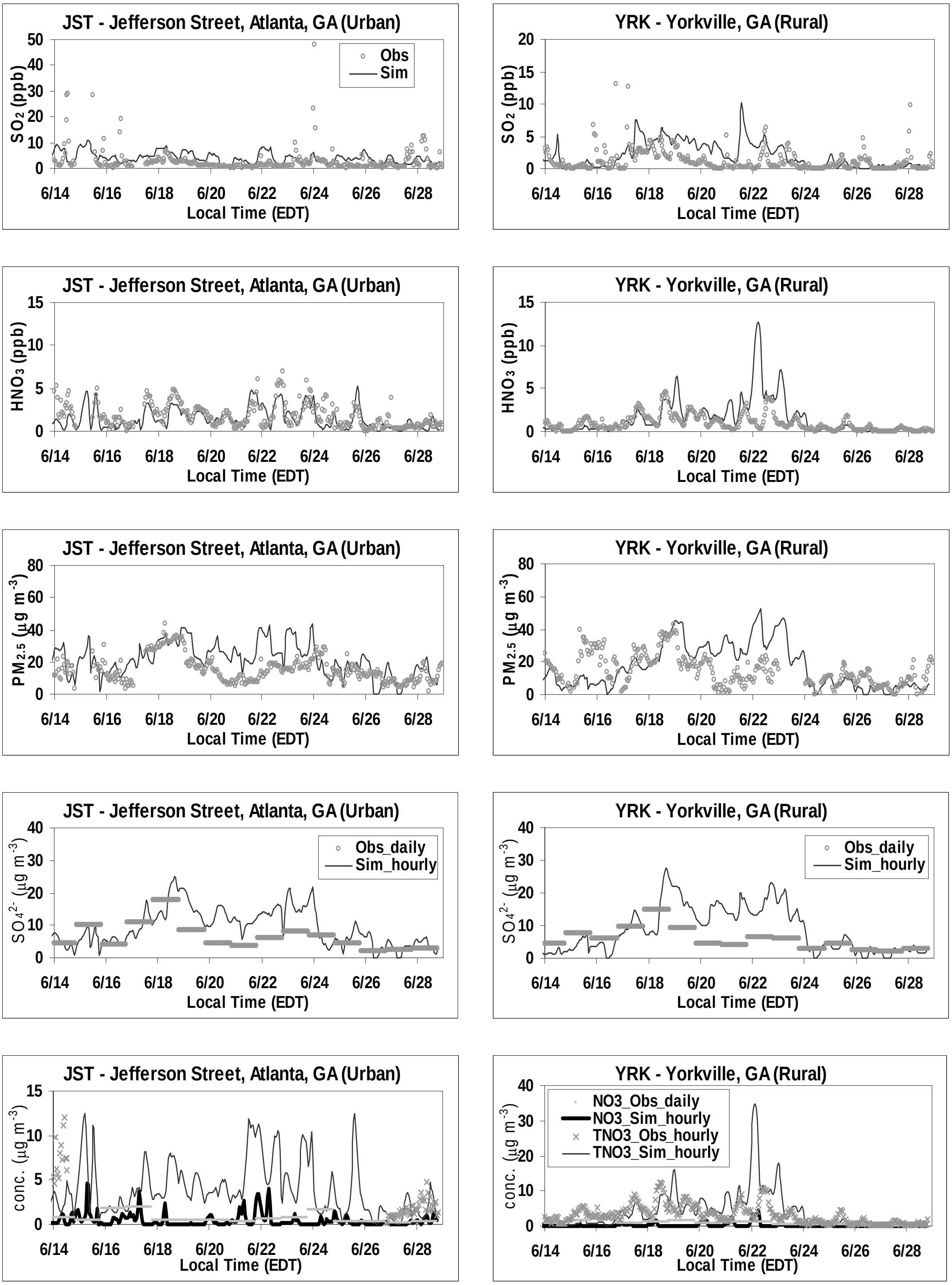

Figure 6. *Simulated (by CMAQ) and observed temporal variations of hourly SO_2, HNO_3, $PM_{2.5}$, 24-hr average SO_4^{2-} and NO_3^-, and hourly total nitrate (TNO_3 that is sum of NO_3^- and HNO_3 in $\mu g\ m^{-3}$) at Jefferson Street in Atlanta, GA (JST, urban) and Yorkville, GA (YRK, rural) during June 14-28, 1999. Measured TNO3 at JST is only available on June 14, 27, and 28.*

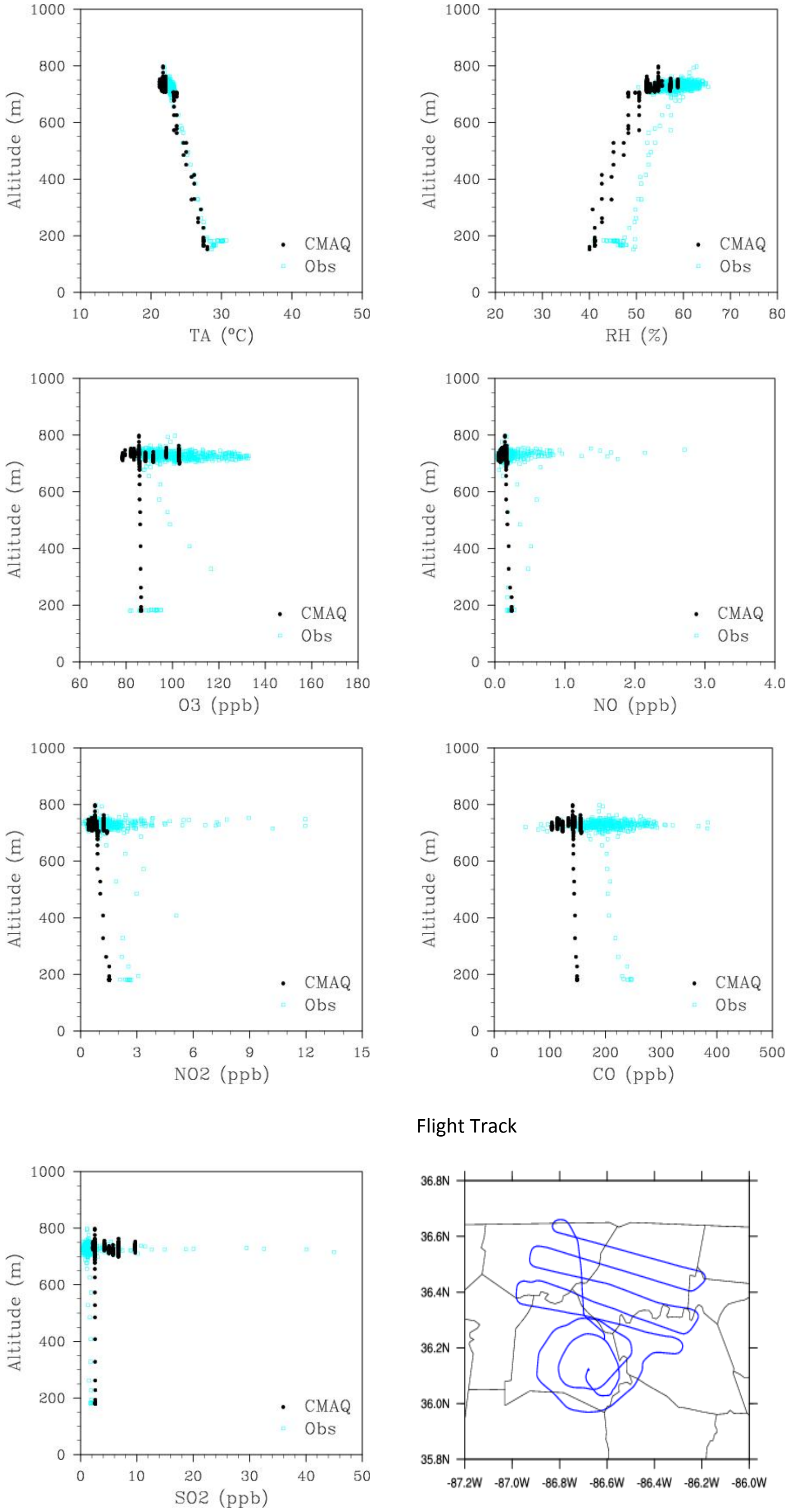

Figure 7. *Simulated (by CMAQ) and observed (by NARSTO SOS99NASH DOE G-1 aircraft) vertical profiles of temperature, RH, O_3, NO, NO_2, CO, and SO_2 and the flight track in Nashville, TN, at 1:00 to 2:00 pm, June 22, 1999. CMAQ includes 6 layers (layers 5 to 10) between 200-800 m above the ground level, with the mid-level heights of about 190 m for layer 5 and 790 m for layer 10.*

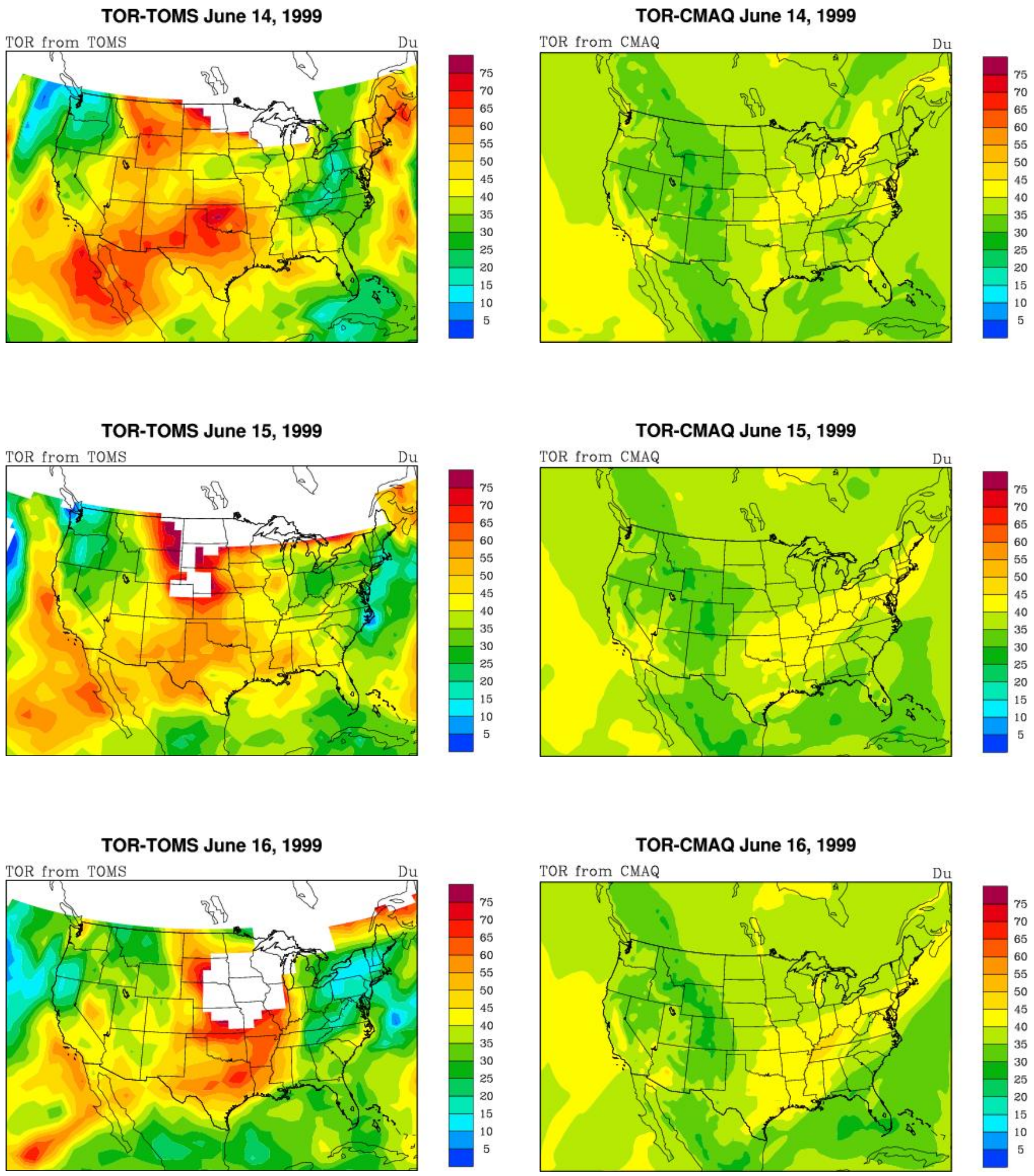

Figure 8. *The tropospheric ozone residual (TOR) from the Total Ozone Mapping Spectrometer (TOMS)/the Solar Backscattered Ultraviolet (SBUV) instruments and CMAQ on June 14-16, 1999.*

The simulated column O_3 abundance is compared with the tropospheric O_3 residual (TOR) calculated from the Total Ozone Mapping Spectrometer (TOMS) and the Solar Backscattered Ultraviolet (SBUV) instruments and by subtracting the stratospheric column O_3 from the total column O_3 (Fishman et al., 2003). Figure 8 shows simulated and TOMS/SBUV–derived TOR in Dobson Units (DU) for three days (June 14–16) when satellite observations were available. CMAQ grossly underpredicts column O_3 mass over most of the domain. Compared to the TOR spatial distribution trend from TOMS/SBUV, CMAQ gives relatively high TOR in California and several states in the eastern U.S. (e.g., MO, AR, IL, IN, OH, KY), although the magnitude of the column O_3 is lower than observations over these states. CMAQ fails to reproduce the relatively high TOR in the central U.S. and the relatively low TOR in the northeast. This is consistent with the underestimation of vertical O_3 profiles as shown in Figure 7. It is attributed to the inappropriate O_3 boundary condition for upper layers used in CMAQ which is kept to be a constant mixing ratio of 70 ppb (Vijayaraghavan et al., 2006). Other possible reasons include the uncertainties in the distribution and variability of the stratospheric column O_3 based on SBUV profile that can affect the accuracy of representing tropospheric O_3 by TOR in daily base (Fishman et al., 2005).

4. Summary

The MM5–CMAQ is applied to the contiguous U.S. during a 17 day episode in June 1999. The model evaluation based on in–situ measurements shows a reasonable performance of MM5 and CMAQ in the surface layer: the NMBs are within 1% for T2, 8% for RH2, WD10, and PBLH, 25% for WS10 and precipitation (at the NADP sites only), 25% for maximum 8–hr average O_3, and 40% for 24–hr average $PM_{2.5}$. Among all PM components evaluated, SO_4^{2-} has the best performance, with an NMB of ~20% at all networks.

NO_3^-, EC, and OC have relatively poor performance at the urban sites, with the worst for NO_3^- (an NMB of –78% at the SEARCH sites). Likely causes for large model biases in NO_3^- include the uncertainties in the partitioning of total nitrate between gas and particle–phases, and other model inputs such as emissions and meteorology. The comparisons with aircraft data show a good model performance in simulating vertical profiles of T and SO_2. The discrepancies in simulated vertical profiles for other species are likely due to the fact that the aircraft observations within a polluted plume are not well represented in CMAQ. The evaluation of simulated total O_3 column mass indicates a need to better characterize the vertical profile of O_3 in regional air quality models.

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Supporting Material Available

Parameters and associated observational databases included in the model evaluation (Table S1); Simulated (by MM5) and observed temporal variations of 10–m wind speed/direction at coastal, mountain, urban (aloft and surface), and rural sites during June 14–28, 1999 (Figure S1); The locations of the observational sites shown in Figures 1, 2, and S1 in this study (Figure S2). This information is available free of charge via the Internet at http://www.atmospolres.com.

References

Anderson, C.J., Arritt, R.W., Kain, J.S., 2007. An alternative mass flux profile in the Kain–Fritsch convective parameterization and its effects in seasonal precipitation. *Journal of Hydrometeorology* 8, 1128-1140.

Binkowski, F.S., Roselle, S.J., 2003. Models-3 community multiscale air quality (CMAQ) model aerosol component - 1. model description. *Journal of Geophysical Research-Atmospheres* 108, art. no. 4183.

Brown, S.S., Ryerson, T.B., Wollny, A.G., Brock, C.A., Peltier, R., Sullivan, A.P., Weber, R.J., Dube, W.P., Trainer, M., Meagher, J.F., Fehsenfeld, F.C., Ravishankara, A.R., 2006. Variability in nocturnal nitrogen oxide processing and its role in regional air quality. *Science* 311, 67-70.

Carter, W.P.L., 2000. Implementation of the SAPRC99 chemical mechanism into the Models-3 Framework, Report to the US Environmental Agency, http://www.engr.ucr.edu/~carter/pubs/s99mod3.pdf.

Davis, J.M., Swall, J.L., 2006. An examination of the CMAQ simulations of the wet deposition of ammonium from a Bayesian perspective. *Atmospheric Environment* 40, 4562-4573.

Davis, J.M., Bhave, P.V., Foley, K.M., 2008. Parameterization of N_2O_5 reaction probabilities on the surface of particles containing ammonium, sulfate, and nitrate. *Atmospheric Chemistry and Physics* 8, 5295-5311.

Eder, B., Yu, S.C., 2006. A performance evaluation of the 2004 release of Models-3 CMAQ. *Atmospheric Environment* 40, 4811-4824.

Fishman, J., Wozniak, A.E., Creilson, J.K., 2003. Global distribution of tropospheric ozone from satellite measurements using the empirically corrected tropospheric ozone residual technique: identification of the regional aspects of air pollution. *Atmospheric Chemistry and Physics* 3, 893-907.

Fishman, J., Creilson, J.K., Wozniak, A.E., Crutzen, P.J., 2005. Interannual variability of stratospheric and tropospheric ozone determined from satellite measurements. *Journal of Geophysical Research-Atmospheres* 110, art. no. D20306.

Grell, G.A., Dudhia, J., Stauffer, D.R., 1994. A description of the fifth-generation Penn State/NCAR Mesoscale Model (MM5), NCAR Technical Note, NCAR/TN-398+STR, National Center for Atmospheric Research, Boulder, CO.

Kain, J.S., 2004. The Kain-Fritsch convective parameterization: an update. *Journal of Applied Meteorology* 43,170-181.

Kleinman, L.I., Daum, P.H., Imre, D., Lee, Y.N., Nunnermacker, L.J., Springston, S.R., Weinstein-Lloyd, J., Rudolph, J., 2002. Ozone production rate and hydrocarbon reactivity in 5 urban areas: a cause of high ozone concentration in Houston. *Geophysical Research Letters* 29, art. no. 1467.

Liu, P., Zhang, Y., Yu, S.C., Schere, K.L., 2010. Use of a process analysis tool for diagnostic study on fine particulate matter predictions in the U.S. Part II: process analyses and sensitivity simulations. *Atmospheric Pollution Research 2*, 61-71.

Luecken, D.J., Phillips, S., Sarwar, G., Jang, C., 2008. Effects of using the CB05 vs. SAPRC99 vs. CB4 chemical mechanism on model predictions: ozone and gas-phase photochemical precursor concentrations. *Atmospheric Environment* 42, 5805-5820.

Misenis, C., Zhang, Y., 2010. An Examination of WRF/Chem: physical parameterizations, nesting options, and grid resolutions. *Atmospheric Research* 97, 315-334.

Queen, A., Zhang, Y., 2008a. Examining the sensitivity of MM5-CMAQ predictions to explicit microphysics schemes and horizontal grid resolutions, part III-the impact of horizontal grid resolution. *Atmospheric Environment* 42, 3869-3881.

Queen, A., Zhang, Y., 2008b. Examining the sensitivity of MM5-CMAQ predictions to explicit microphysics schemes and horizontal grid resolutions, part II - PM concentrations and wet deposition predictions. *Atmospheric Environment* 42, 3856-3868.

Riemer, N., Vogel, H., Vogel, B., Schell, B., Ackermann, I., Kessler, C., Hass, H., 2003. Impact of the heterogeneous hydrolysis of N_2O_5 on chemistry and nitrate aerosol formation in the lower troposphere under photosmog conditions. *Journal of Geophysical Research-Atmospheres* 108, art. no. 4144.

Roy, B., Mathur, R., Gilliland, A.B., Howard, S.C., 2007. A comparison of CMAQ-based aerosol properties with IMPROVE, MODIS, and AERONET data. *Journal of Geophysical Research-Atmospheres* 112, art. no. D14301.

Seigneur, C., 2005. Air pollution: current challenges and future opportunities. *American Institute of Chemical Engineers Journal* 51, 356-364.

Seinfeld, J.H., 2004. Air pollution: a half century of progress. *American Institute of Chemical Engineers Journal* 50, 1096-1108.

Vijayaraghavan, K., Hu, J.-H., Zhang, Y., Liu, X., Chance, K., Snell, H.E., 2006. Evaluation of CMAQ using satellite remote sensing measurements over North America. 5th Annual CMAS Models-3 Users' Conference, Chapel Hill, NC, October 16-18.

Wu, S.Y., Krishnan, S., Zhang, Y., Aneja, V., 2008. Modeling atmospheric transport and fate of ammonia in North Carolina - Part I: evaluation of meteorological and chemical predictions. *Atmospheric Environment* 42, 3419-3436.

Ying, Q., Lu, J., Allen, P., Livingstone, P., Kaduwela, A., Kleeman, M., 2008. 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. *Atmospheric Environment* 42, 8954-8966.

Yu, S., Mathur, R., Schere, K., Kang, D., Pleim, J., Young, J., Tong, D., Pouliot, G., McKeen, S.A., Rao, S.T., 2008. Evaluation of real-time $PM_{2.5}$ forecasts and process analysis for $PM_{2.5}$ formation over the eastern United States using the Eta-CMAQ forecast model during the 2004 ICARTT study. *Journal of Geophysical Research-Atmospheres* 113, art. no. D06204.

Yu, S., Mathur, R., Schere, K., Kang, D., Pleim, J., Otte, T.L., 2007. A detailed evaluation of the Eta-CMAQ forecast model performance for O_3, its related precursors, and meteorological parameters during the 2004

ICARTT study. *Journal of Geophysical Research-Atmospheres* 112, art. no. D12S14.

Yu, S., Dennis, R., Roselle, S., Nenes, A., Walker, J., Eder, B., Schere, K., Swall, J., Robarge, W., 2005. An assessment of the ability of three-dimensional air quality models with current thermodynamic equilibrium models to predict aerosol NO_3^-. *Journal of Geophysical Research-Atmospheres* 110, art. no. D07S13.

Yu, S., Dennis, R.L., Bhave, P.V., Eder, B.K., 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. *Atmospheric Environment* 38, 5257-5268.

Zhang, Y., Liu, P., Liu, X.H., Pun, B., Seigneur, C., Jacobson, M.Z., Wang, W.X., 2010. Fine scale modeling of wintertime aerosol mass, number, and size distributions in central California, *Journal of Geophysical Research-Atmospheres* 115, art. no. D15207.

Zhang, Y., Vijayaraghavan, K., Wen, X.Y., Snell, H.E., Jacobson, M.Z., 2009. Probing into regional O_3 and PM pollution in the United States, part I. a 1-year CMAQ simulation and evaluation using surface and satellite data. *Journal of Geophysical Research-Atmospheres* 114, art. no. D22304.

Zhang, Y., 2008. Online coupled meteorology and chemistry models: history, current status, and outlook. *Atmospheric Chemistry and Physics* 8, 2895-2932.

Zhang, Y., Liu, P., Pun, B., Seigneur, C., 2006a. A comprehensive performance evaluation of MM5-CMAQ for the summer 1999 southern oxidants study episode-part I: evaluation protocols, databases, and meteorological predictions. *Atmospheric Environment* 40, 4825-4838.

Zhang, Y., Liu, P., Queen, A., Misenis, C., Pun, B., Seigneur, C., Wu, S.Y., 2006b. A comprehensive performance evaluation of MM5-CMAQ for the summer 1999 southern oxidants study episode-part II: gas and aerosol predictions. *Atmospheric Environment* 40, 4839-4855.

Zhang, Y., Liu, P., Pun, B., Seigneur, C., 2006c. A comprehensive performance evaluation of MM5-CMAQ for the summer 1999 southern oxidants study episode, part III. diagnostic and mechanistic evaluations. *Atmospheric Environment* 40, 4856-4873.

Zhang, Y., Pun, B., Vijayaraghavan, K., Wu, S.Y., Seigneur, C., Pandis, S.N., Jacobson, M.Z., Nenes, A., Seinfeld, J.H., 2004a. Development and application of the model for aerosol dynamics, reaction, ionization and dissolution (MADRID). *Journal of Geophysical Research-Atmospheres* 109, art. no. D01202.

Zhang, Y., Pun, B., Wu, S.Y., Vijayaraghavan, K., Seigneur, C., 2004b. Application and evaluation of two air quality models for particulate matter for a Southeastern U.S. episode. *Journal of The Air and Waste Management Association* 54, 1478-1493.