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Modeling atmospheric transport and fate of ammonia in North Carolina—Part I: Evaluation of meteorological and chemical predictions

Shiang-Yuh Wu[a,1], Srinath Krishnan[b], Yang Zhang[b,*], Viney Aneja[b]

[a]*Department of Environmental Quality, Richmond, VA, USA*
[b]*North Carolina State University, Raleigh, NC, USA*

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Abstract

The atmospheric transport and fate of ammonia (NH_3) depend on both meteorological and chemical conditions once it is emitted into the atmosphere. The largest source contributing to NH_3 emission is the agricultural production, in particular animal operation, in North Carolina (NC). In this study, three-dimensional numerical meteorological and air quality models are applied to study the transport and fate of NH_3 in the atmosphere in an area in southeast US centered over NC. One summer and one winter month simulations with a 4-km horizontal grid were conducted to simulate the meteorological and chemical environments for the transport and transformation of the reduced nitrogen, NH_x ($= NH_3 + NH_4^+$) and to examine its seasonal variations and interactions with other chemical species (e.g., ozone and fine particular matter, $PM_{2.5}$). The model performance for simulated meteorology and air quality was evaluated against observations in terms of spatial distributions, temporal variations, and statistical trends.

MM5/CMAQ gave an overall good performance for meteorological variables and O_3 mixing ratios and a reasonably good performance for $PM_{2.5}$. The simulations show that 10–40% of total NH_3 was converted to NH_4^+ at/near source and 40–100% downwind in August, and the conversion rates were 20–50% at/near source and 50–98% downwind in December. While the 3-D atmospheric models demonstrate some skills in capturing synoptic meteorological patterns, diurnal variations of concentrations of oxidants and $PM_{2.5}$, and regional transport and transformation of NH_x, reproducing meteorological and chemical features at a local scale and the magnitudes of hourly concentrations of oxidants and $PM_{2.5}$ remain challenging due to uncertainties in model inputs and treatments.

Keywords: Ammonia; Transport and fate; North Carolina; Model evaluation; CMAQ; MM5

1. Introduction

Ammonia (NH_3) plays an important role in many aspects of our environment including participation in the nutrient and nitrogen cycles, the neutralization of acids, and the formation of particulate matter with an aerodynamic diameter less than or

*Corresponding author. Tel.: +1 919 515 9688; fax: +1 919 515 7802.
E-mail address: yang_zhang@ncsu.edu (Y. Zhang).
[1]Now at Clark County Department of Air Quality and Environmental Management, NV, USA.

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equal to 2.5 or 10 μm ($PM_{2.5}$ or PM_{10}). Major sources of NH_3 include animal and human wastes, synthetic fertilizers, biomass burning, and fossil fuel combustion (Bouwman et al., 1997). Agriculture-livestock (AL) is the largest source of NH_3 in southeast US, particulalry in North Carolina (NC), which ranks the second in terms of pig production by state nationwide. The swine in NC are estimated to emit 68,540 tons of NH_3 per year, providing the largest contributor among all domesticated animals in NC (Aneja et al., 1998). Most hog farms are located in the coastal plain region of NC or the southeast corner covering Bladen, Duplin, Greene, Lenoir, Sampson, and Wayne counties (Walker et al., 2000). In this study, the transport and fate of NH_3 are simulated using a three-dimensional (3-D) transport and chemistry modeling system that consists of the 5th Generation Penn State/NCAR Mesoscale Model (MM5) version 3.7 with four-dimensional data assimilation (FDDA) and the US EPA Models-3 Community Multiscale Air Quality (CMAQ) modeling system version 4.4 in an area centering NC that has the largest NH_3 emissions among all states in the southeast US. Two one-month simulations, one in summer (August) and one in winter (December) were conducted at a horizontal grid spacing of 4-km for the year 2002 to study the atmospheric transport and fate of NH_3, and to quantify the contributions of major processes to the mixing ratios of NH_x (total reduced nitrogen, $= NH_3 + NH_4^+$) and other related air pollutants (e.g., ozone (O_3), $PM_{2.5}$, and $PM_{2.5}$ composition). While December was the coldest month in 2002, emissions of major pollutants was the highest in August. Sensitivity simulations were also performed to assess the impact of NH_3 emissions on the formation of $PM_{2.5}$, particularly those from AL-NH_3 sources in NC, on ambient air quality. Our results are presented in two parts. Part I describes the model configurations, evaluation protocols and databases used, and the operational evaluation for meteorological and chemical predictions. Part II (Wu et al., 2007) describes the sensitivity simulations under various emission scenarios.

2. Description of models and simulation domain

2.1. Modeling domain and characteristics

The 3-D model simulations were conducted at a 4-km horizontal grid spacing over a domain that covers nearly the entire state of NC, and a portion of several adjacent states including South Carolina (SC), Georgia (GA), Tennessee (TN), West Virginia (WV), and Virginia (VA). The model input files for initial and boundary conditions (ICs and BCs) and meteorology at a 4-km horizontal grid spacing were developed based on the MM5/CMAQ model simulation results at a 12-km horizontal grid spacing obtained from the Visibility Improvement State and Tribal Association of the Southeast's (VISTAS) 2002 modeling program (http://www.vista-sesarm.org.asp). Fig. 1 shows the VISTAS's 12-km domain and the nested 4-km domain along with observational sites selected for meteorological and chemical performance evaluation. The 4-km domain contains 198×84 grid cells. The vertical resolution includes 19 layers from surface to the tropopause (~15 km) with ~38 m for the first layer height. Six meteorological sites were selected around four cities (i.e., Asheville, Raleigh, Kinston, and Charlotte) in NC to illustrate the performance of MM5 at a local scale. KAVL is ~26.5 km southwest

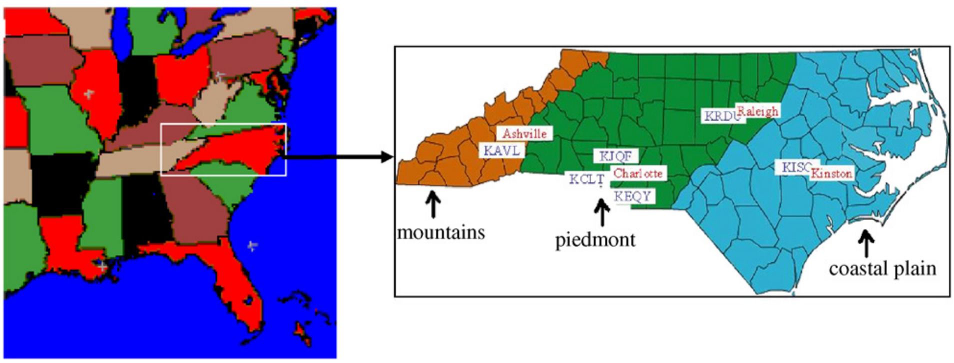

Fig. 1. The VISTAS's 12-km simulation domain and the nested 4-km domain (left) and the selected co-located sites for model performance evaluation of meteorological variables (blue) and chemical species (red) in three physiographic divisions in North Carolina.

of Asheville (in the Mountains area); KRDU is ~18.8 km west of Raleigh (in the northern portion of the Piedmont); KISO is ~11.1 km northwest of Kinston (in the Coastal Plain), and three other surrounding sites, KCLT, KEQY, and KJQF (~15.1, ~28.6, and ~16.9 km) are close to Charlotte (the southern portion of the Piedmont).

As shown in Fig. 1, NC consists of the three physiographic regions from east to west: the Coastal Plain, the Piedmont, and the Mountains with elevations ranging from sea level to 6686 feet, a summit of Mount Mitchell, which is the highest peak in the eastern US. The resultant complex topography combined with synoptic weather patterns often largely affect the formation of ammonium sulfate ($(NH_4)_2SO_4$) and ammonium nitrate (NH_4NO_3) spatially and temporally. In most summer, weather in NC is dominated by the "Bermuda High" pressure system, which gives calm, virtually cloudless condition. Due to the rugged topography and cooler climate in the Mountain areas, the agricultural production is much smaller than in the Coastal Plain and the Piedmont. The Piedmont is the center of population for the state, and the automobile traffic in and between the cities, along with other sources are the major sources of NO_x emissions. For SO_2 emissions, almost 95% come from 14 major coal-fired power plants and other small point sources throughout the state (based on the estimation of VISTAS's 2002 emission inventory). Both SO_2 and NO_x can be oxidized to convert to sulfuric acid and nitric acid, respectively, to neutralize NH_3. Fig. 2 shows the spatial distribution of daily total emissions of SO_2, NO_x, and NH_3 on August 2 and December 8, which are representative of daily total emissions in the domain. The daily total emissions of SO_2, NO_x, and NH_3 for the entire domain in August are higher than those in December by ~20%, ~10%, and ~42%, respectively. Sources of NO_x emissions areas are located mostly in the central NC, and those for SO_2 are located throughout the domain.

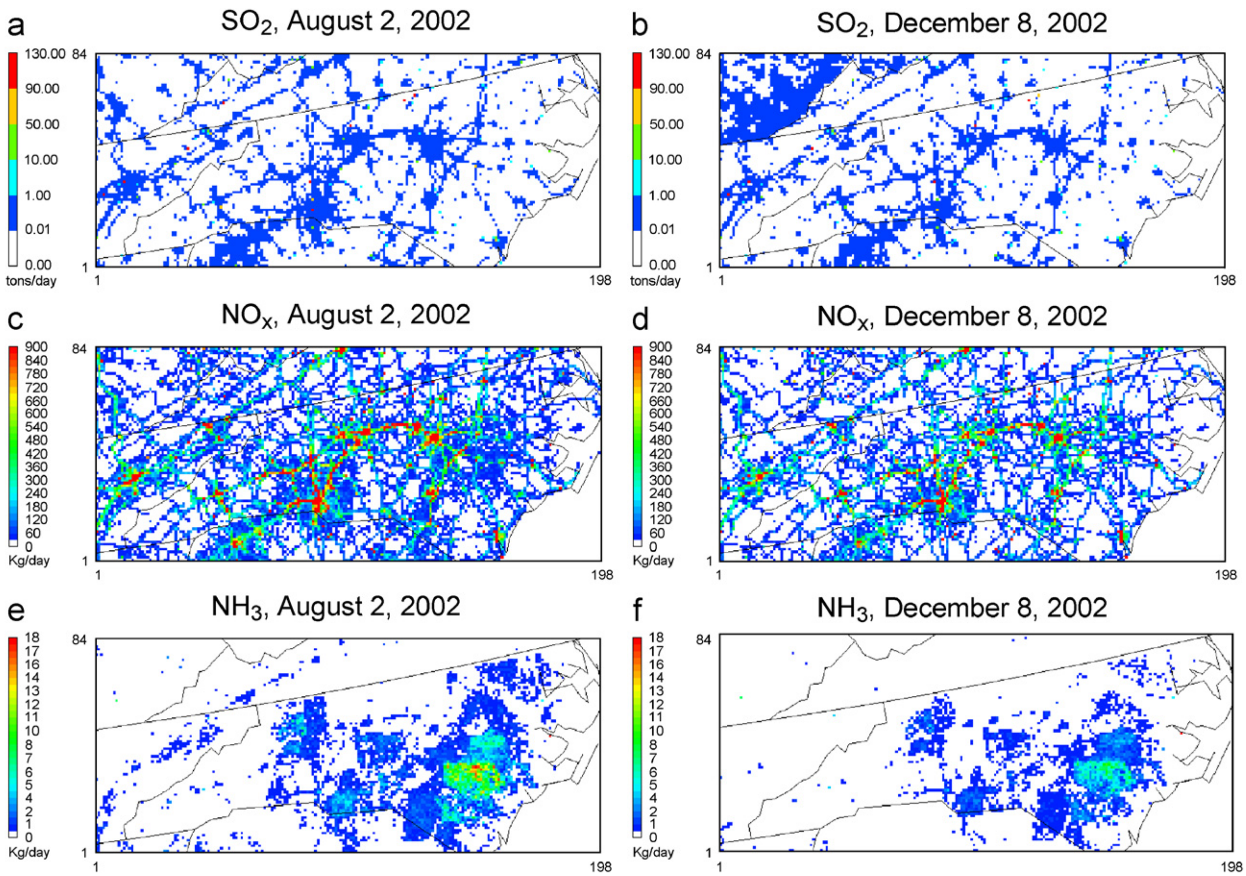

Fig. 2. The daily total emissions of SO_2 (a) and (b), NO_x (c) and (d), and NH_3 (e) and (f) for the 4-km simulation (generated using raw emission inventories from VISTAS).

The AL-NH_3 emission sources are mostly located in the eastern NC. The AL-NH_3 emissions account for about 91% (482.9 ton day^{-1}) in August and 81% (253.4 ton day^{-1}) in December of total NH_3 emissions. They account for ~40% of total nitrogen emissions in NC, making eastern NC an NH_3-rich environment.

2.2. Model configurations and inputs

The models used include the non-hydrostatic MM5 version 3.7 (Grell et al., 1994), the Carolina Environmental Program's (CEP) Sparse Matrix Operator Kernel Emissions (SMOKE) Modeling System version 2.1 (Houyoux et al., 2002), and CMAQ version 4.4 (Byun and Schere, 2006). The configurations and model physics for MM5 and CMAQ in this study are consistent with the 2002 base year VISTAS Phase II modeling study at a 12-km horizontal grid spacing. Table A1 in Appendix A summarizes the options that are selected for MM5 and CMAQ. The initial and boundary conditions for 4-km MM5 and CMAQ simulations are extracted from VISTAS 12-km MM5 and CMAQ simulations. For VISTAS 12-km/36-km MM5 simulations, the ICs and BCs are specified from the mesoscale ETA Data Assimilation System (EDAS) analyses with 40-km resolution and the surface, ship, and upper air observations that are available from National Center for Atmospheric Research (NCAR). For VISTAS 12-km/36-km CMAQ simulations, the simulations were conducted for four 3-month periods, each with a 15-day spin-up to minimize the influence of ICs and the 3-hourly day-specific GEOS-CHEM (a global 3-D model of atmospheric composition driven by assimilated meteorological observations from the Goddard Earth Observing System) output was used for BCs of the 36-km domain. BCs for the 12-km domain were obtained from the CMAQ 36-km simulation. A more detailed description on model configurations can be found in the modeling protocol for the VISTAS Phase II regional haze modeling (Morris and Koo, 2004).

The emission inventories for gaseous and PM species for VISTAS's states are based on the revised VISTAS 2002 emissions. For non-VISTAS states, the most updated 2002 emission inventories are obtained from other Regional Planning Organizations (RPO) and the 2002 EPA National Emission Inventory (NEI) Version 1 (available from ftp.epa.gov on 20 March 2004). In this work, SMOKE v. 2.1 is used to process those county-level emissions to obtain gridded emissions for the 4-km simulations.

3. Performance evaluation

3.1. Evaluation protocol

While the gaseous oxidation of NH_3 is slow and not included in CMAQ, its conversion to NH_4^+ is directly affected by available gaseous HNO_3 (which is affected by precursors (e.g., NO_x, N_2O_5), radicals (e.g., OH, HO_2), and oxidants (e.g., O_3)) and by the chemical regime of a modeling domain (e.g., sulfate-rich or poor). The results from a box model that couples gas-phase chemistry with aerosol thermodynamic and dynamic treatments have shown that these effects may be more pronounced under sulfate-poor and ammonium-rich environments such as eastern NC. The model predictions are therefore evaluated using available measurements of O_3, $PM_{2.5}$ including NH_4^+, NO_3^-, SO_4^{2-}, black carbon (BC), organic carbon (OC), and ratios of NH_4^+/NH_x. The evaluation is conducted in terms of spatial distributions, temporal variations, and statistics based on protocols developed by EPA (2001), Emery and Tai (2001), and Zhang et al. (2006a, b). The statistics include the mean bias (MB), the mean absolute gross error (MAGE), the root mean squared error (RMSE), the normalized mean bias (NMB), and the normalized mean gross error (NMGE). MM5 simulation results are compared with observations from University Corporation for Atmospheric Research's (UCAR) ds472.0 (TDL) archive (http://dss.ucar.edu/datasets/ds472.0) hourly observations of wind speed/wind direction, temperature, humidity and weekly observations of precipitations from the National Acid Deposition Program (NADP). CMAQ simulation results are compared with the routine monitoring networks including the NADP, the Clean Air Status Trends Network (CASTNet) (mostly rural sites), Interagency Monitoring of Protected Visual Environments (IMPROVE) (national parks), the Speciation Trends Network (STN) (urban), the Air Quality System (AQS) (cities and towns), as well as observational data available from the monitoring sites of North Carolina Department of Natural Resources (NCDENR). Those data sets are summarized in Table A2 in Appendix A.

The model evaluation in this work is more comprehensive than those of Mathur et al. (2005) and Arunachalam et al. (2006), which used the Multiscale Air Quality Simulation Platform (MAQSIP) over southeastern US for summer episodes only and evaluate only chemical predictions (e.g., O_3 and inorganic $PM_{2.5}$). Neither studied the impact of grid resolutions on $PM_{2.5}$ predictions.

3.2. Meteorological predictions

3.2.1. Spatial and temporal variations

Figs. 3(a)–(f) show the spatial distributions of observed and simulated monthly-mean surface wind vector, temperature, and water vapor mixing ratio, respectively. The observed wind and temperature are at 10 and 2 m from TDL data, respectively. The simulated temperature and water vapor mixing ratios are at 2 m, but the simulated wind is at midpoint (~19 m) of first layer of CMAQ. There is usually a large current, the Gulf Stream, of warm water with approximate 34.4 °C just off the coast throughout the year. It brings warmer than expected temperatures to coastal areas. The observed mean temperatures vary more than 10 °C from the lower coast to the mountain areas for both months. The model gives mean temperatures that are in a close agreement with the observed values in summer, but underpredicts those in winter at a number of sites in Piedmont. The observed water vapor mixing ratios in both months are the highest in the Coastal Plain, they decrease as the topography changes to the Piedmont and the Mountains, then increase again in the Great Smoky mountain areas in eastern TN and in the southeastern corner of KY. The spatial variation is generally reproduced for both months by MM5, but underpredictions occur at some sites throughout the domain in August and overpredictions occur at some sites in the Coastal Plain and the Piedmont. In general, the summer weather is

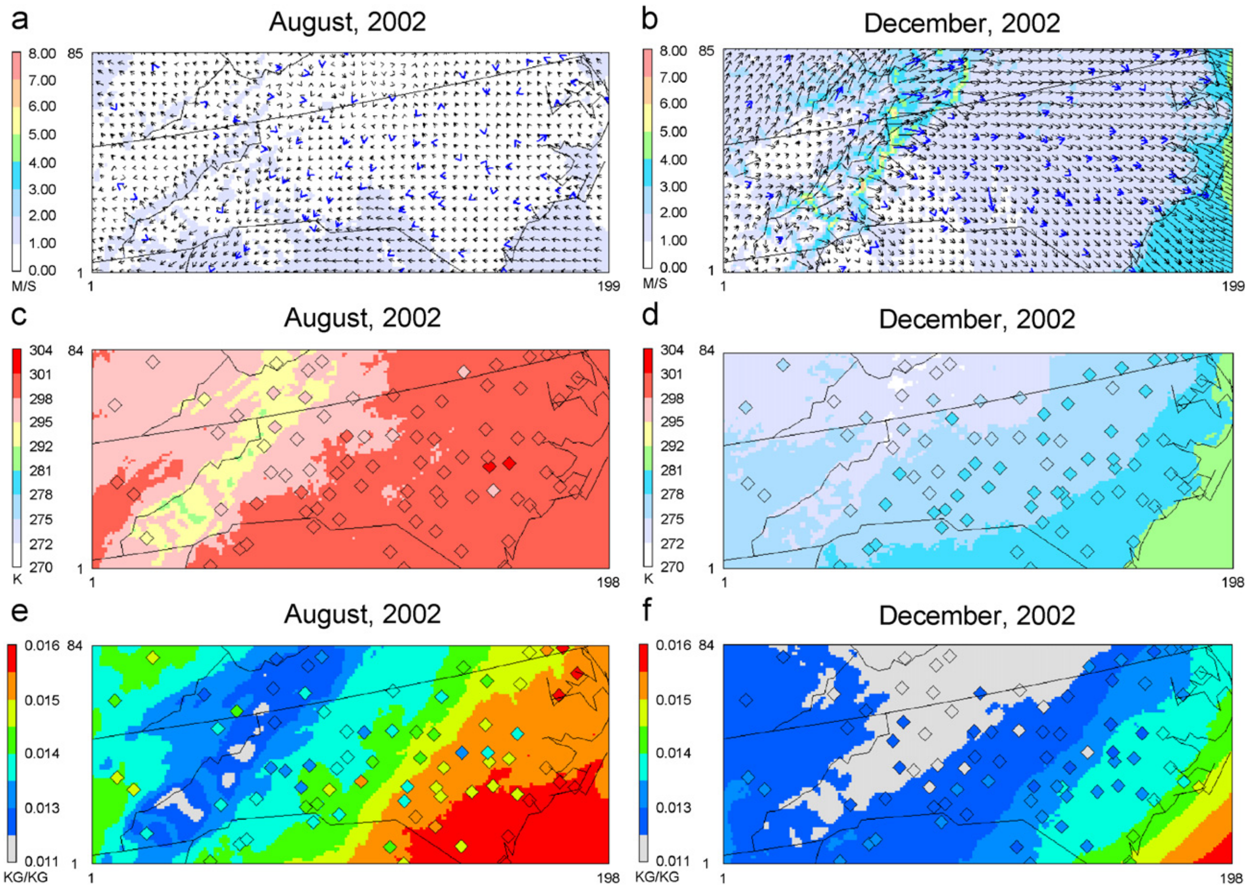

Fig. 3. Observed and simulated monthly-mean surface wind vectors at 10 and 19 m, respectively (a) and (b), monthly-mean surface temperatures at 2-m (c) and (d), and water vapor mixing ratios at 2-m (e) and (f). The diamonds indicate observed values.

characterized by relatively low mean wind speed (WSP) ($<3.32\,m\,s^{-1}$) and diverse mean wind direction (WDR). During winter, westerlies are the prevailing winds with relatively high wind speeds ($1.25–5.22\,m\,s^{-1}$), particularly in Mountains. The simulated mean winds in summer predict the low mean wind speed with easterly mean WDR. In winter, the simulated winds have generally captured the flow pattern and magnitudes of observed winds.

Fig. 4 shows the time series of hourly observed (TDL data) and predicted temperature (T), specific humidity (SH), WSD, and WDR at those selected locations for both months. At sites near Asheville, Raleigh, and Charlotte, MM5 reproduces well the peak daily T and diurnal variation but overpredicts the minimal T at night in August. Although the model generally captures the daily variation in December, it underpredicts peak daily T on some days and overpredicts minimal T on most days. At the site near Kinston, larger underpredictions occur for peak daily T in both months compared with other sites. For SH, MM5 generally captures well the diurnal variations, but tends to underpredict its magnitudes at all sites in both months. For WSD and WDR, while MM5 generally reproduces the overall daily variation trends and scales, significant deviations occur on some days at some sites (e.g., 2–10 August for WSD and at 14–15 August for WDR at Kinston).

3.2.2. Performance statistics

The MM5 model performance is evaluated following the meteorological statistical benchmarks reported by Emery and Tai (2001). Statistical measures for benchmarks include RSME, gross error, bias, and Index of Agreement (IOA). The purpose of these benchmarks is not to give a passing or failing grade to any particular meteorological model application, but rather to understand how poor or good the results are relative to the universe of other model applications.

A preliminary performance evaluation of MM5 simulation with a 12-km horizontal grid spacing has been conducted by BAMS (Olerud and Sims, 2004). The 12-km grid simulation generally captures synoptic features and replicates the state variables such as WSP, WDR, and T. The 4-km MM5 simulation represents the basic flow pattern near the surface during both months. The statistics are calculated as daily mean values using hourly T, SH, and surface WSP and WDR from TDL archive and as weekly mean values using weekly precipitation from NADP network for the 4- and 12-km meteorological predictions. The results are shown along with the benchmarks in Table 1. For 4-km MM5 performance, the averages of daily bias of WSP and gross error of WDR are higher than the benchmarks for August. For December, the averages of daily bias of WSP, the absolute values of daily bias and gross error of T are higher than the benchmarks. The weekly total precipitations are overpredicted with better agreement at 4-km grid spacing in August but slightly underpredicted with better agreement at 12-km grid spacing in December. Overall, the model performs slightly better in December than August for most meteorological variables.

In analyzing results in more details, the entire domain is further divided into coastal, rural, completely urban, and other areas based on the rural–urban continuum codes established by the Economic Research Service, the United States Department of Agriculture (USDA) (having USDA codes 8–9, 1–2, and 3–7, respectively). The statistics for hourly meteorological variables are then computed for the entire domain and those specific areas, as shown in Table A3 in Appendix A. While the domain-wide statistics give an overall performance, the area-specific statistics provide insights into each area. For 4-km results, MM5 performs well in terms of domain-wide statistics with NMBs less than 9%. The highest NMB occurs at the coastal areas for T, both costal and rural areas for SH, and rural areas for WSP and WDR. A possible reason for the difference between the overall and area-specific sites is the averaging of the parameters over the complete domain, whereas in the area-specific domain, factors such as land-surface, topography, and proximity to the sea make a significant difference. This can be clearly shown in certain parameters and regions, e.g., WSP in coastal and rural areas. While the overall domain-wide WSP for the 4-km simulation is overpredicted by 8.8%, it is overpredicted by 14% for coastal areas and 24% for rural areas.

3.3. Chemical predictions

3.3.1. Spatial and temporal variations

Figs. 5 and 6 show the spatial distributions of the observed and simulated monthly-mean maximum 1-h O_3 mixing ratios and 24-h average $PM_{2.5}$ concentrations along with NMBs. Since there is no O_3 observations available from AQS network in winter months, the observed O_3 values used in

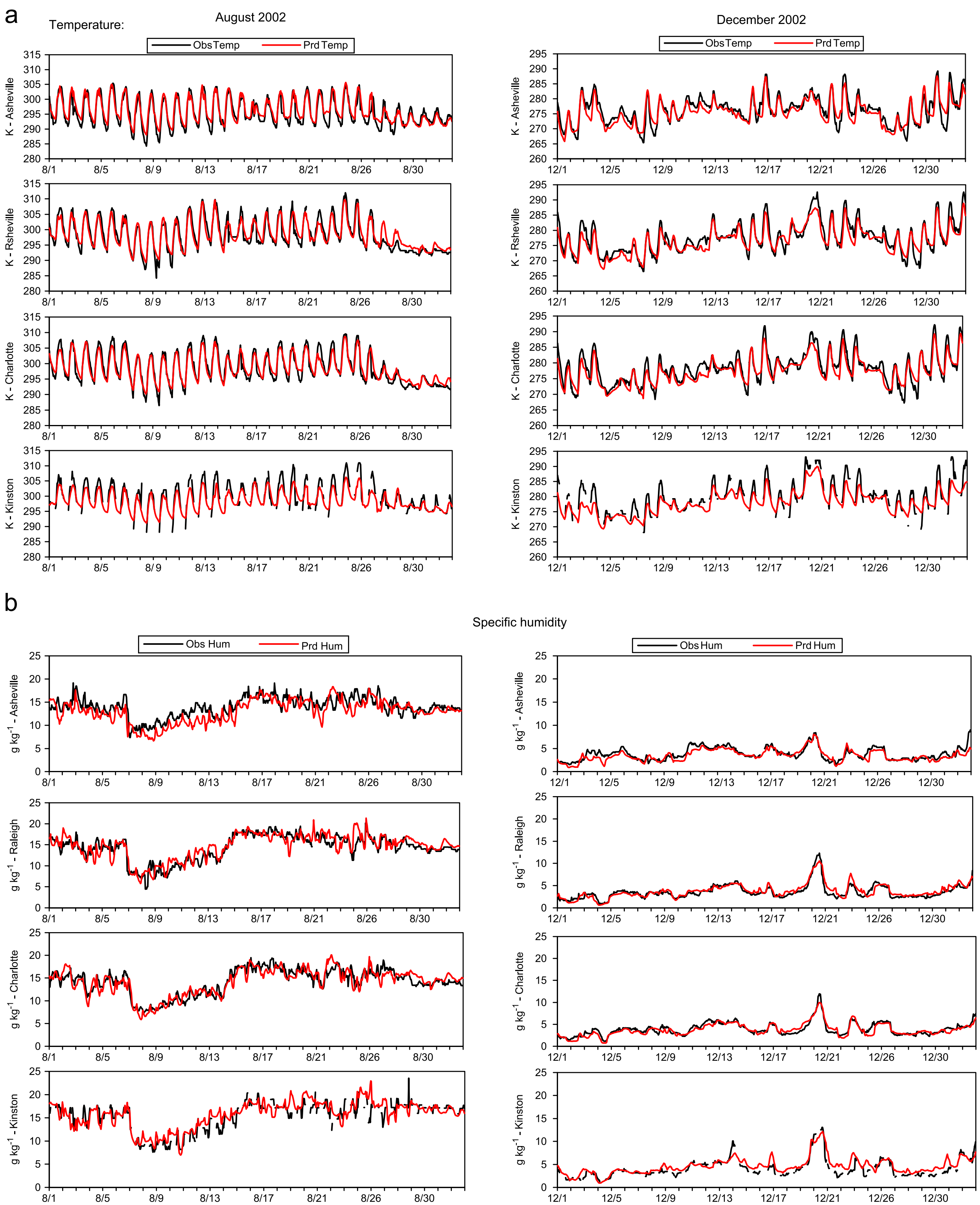

Fig. 4. The time series of hourly observed and predicted surface (a) temperature, (b) specific humidity, (c) wind speed, and (d) wind direction at locations near Asheville, Raleigh, Charlotte, and Kinston in August and December 2002.

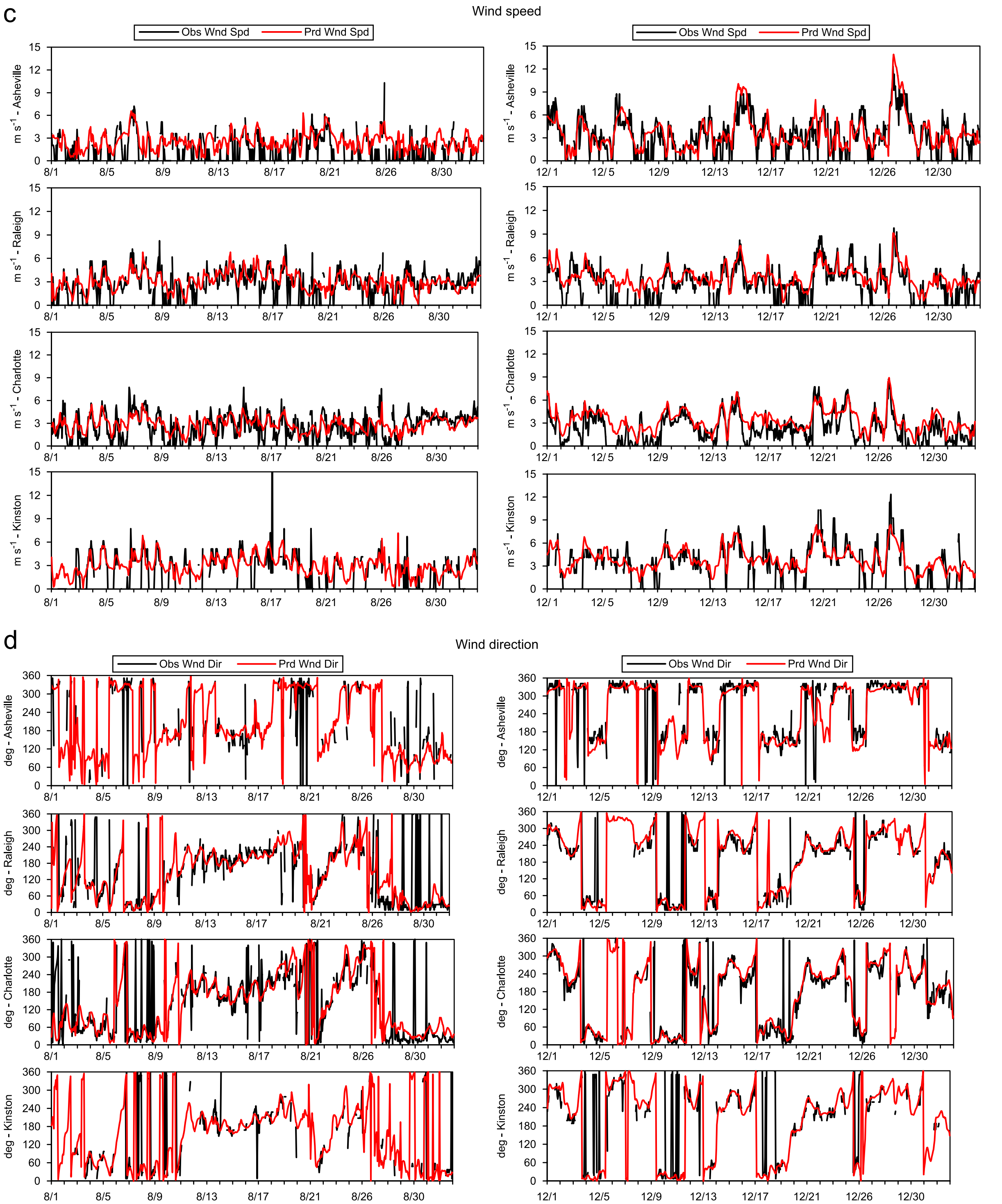

Fig. 4. (*Continued*)

December are from CASTNet network only (i.e., fewer sites in Figs. 5(b) and (d)). For August, the simulated maximum 1-h O_3 mixing ratios are generally lower than the observations by ~10 ppb in the Costal Plain and the Piedmont regions but by ~20 ppb in the Mountains. The model performs

Table 1
The statistical performance for daily mean meteorological predictions[a]

		August		December		Benchmarks
		12 km	4 km	12 km	4 km	
Temperature	Mean observation (°C)	25.4	25.4	5.0	5.0	
	Mean prediction (°C)	25.7	25.2	4.1	3.9	
	Bias (°C)	0.4	−0.1	−0.9	−1.1	$\leqslant \pm 0.5$
	Gross error (°C)	1.6	1.6	1.9	2.2	$\leqslant 2$
	IOA	0.9	0.9	0.9	0.9	$\geqslant 0.8$
Humidity	Mean observation ($g\,kg^{-1}$)	14.5	14.5	3.9	3.9	
	Mean prediction ($g\,kg^{-1}$)	14.0	14.4	3. 8	4.0	
	Bias ($g\,kg^{-1}$)	−0.6	−0.2	−0.1	0.1	$\leqslant \pm 1$
	Gross error ($g\,kg^{-1}$)	1.7	1.6	0.6	0.6	$\leqslant 2$
	IOA	0.7	0.7	0.8	0.8	$\geqslant 0.6$
Wind Speed	Mean observation ($m\,s^{-1}$)	2.0	2.0	2.8	2.8	
	Mean prediction ($m\,s^{-1}$)	2.9	3.0	3. 6	3.7	
	Bias ($m\,s^{-1}$)	0.9	0.9	0.8	0.9	$\leqslant \pm 0.5$
	RMSE ($m\,s^{-1}$)	1.8	1.8	2.0	2.0	$\leqslant 2$
	IOA	0.6	0.6	0.7	0.7	$\geqslant 0.6$
Wind Direction	Mean observation (deg)	125.7	125.7	204.7	204.7	
	Mean prediction (deg)	138.5	139.4	200.5	200.1	
	Bias (deg)	2.5	2.1	6.8	6.5	$\leqslant \pm 10$
	Gross error (deg)	33.9	32.6	24.5	23.4	$\leqslant 30$
Precipitation	Mean observation (mm)	18.0	18.0	29.6	29.6	
	Mean prediction (mm)	28.3	25.4	28.4	22.8	
	Bias (mm)	10.3	7.4	−1.2	−6.7	
	Gross error (mm)	23.7	24.4	9.7	11.5	

[a]The MM5 12-km model simulation results are taken from VISTAS and post-processed in this work.

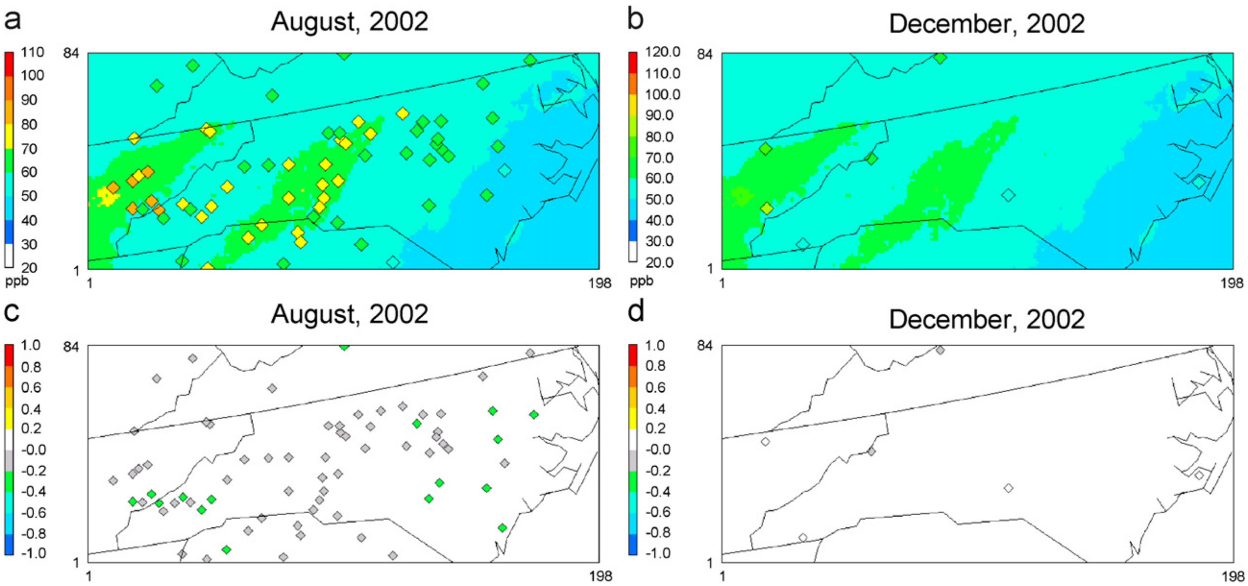

Fig. 5. The overlay of simulated and observed spatial distributions of monthly mean 1-h maximum O_3 mixing ratios (a) and (b) along with NMBs (c) and (d). The observational datasets are taken from AQS and CASTNet in August and December, and from CASTNet only for December.

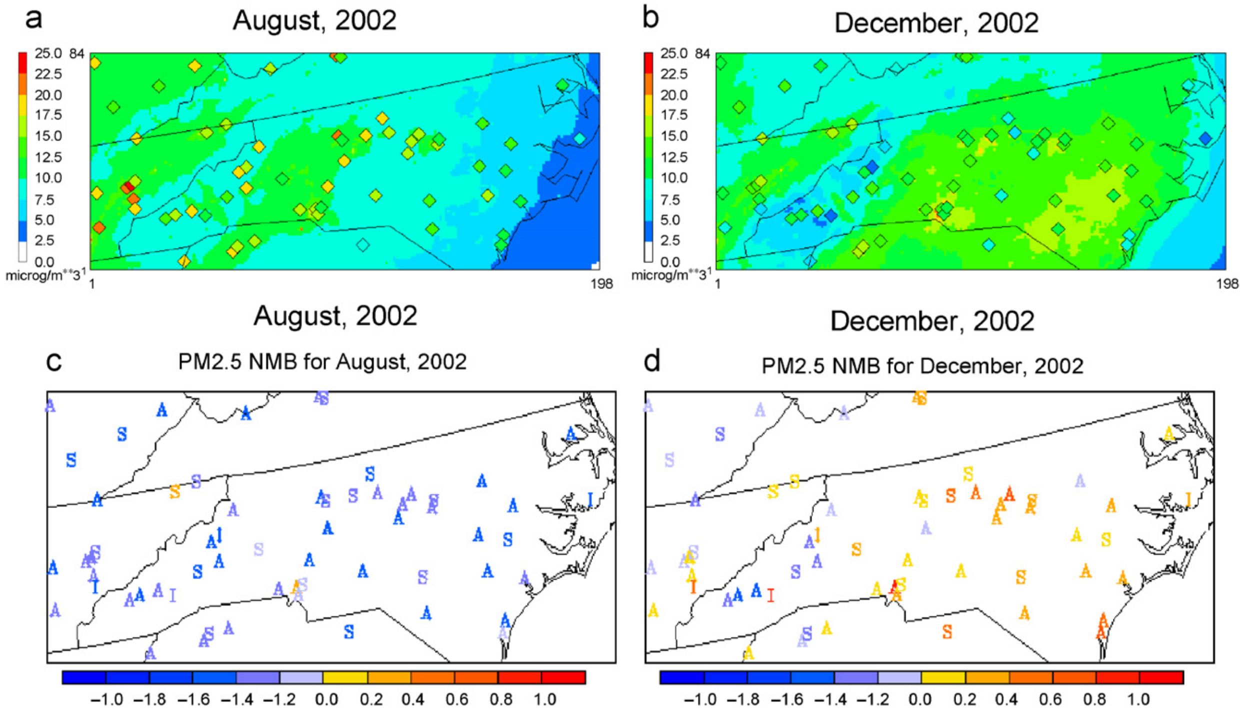

Fig. 6. The overlay of simulated and observed spatial distributions of monthly mean 24-h average $PM_{2.5}$ concentrations (a) and (b) along with NMBs (c) and (d). The observational datasets are taken from AQS, STN, and IMPROVE networks for both months.

better in December. The spatial distribution of NMBs for O_3 shows NMBs of 20–30% at a number of sites at south end of the Mountains and in the Coastal Plain region in August and an overall good agreement at all CASTNet sites in winter. The spatial distribution of observed 24-h averaged $PM_{2.5}$ concentrations is similar to that of observed maximum 1-h O_3 mixing ratios in August, with lower values in the Coastal Plain and higher values in the Mountains. While the 24-h averaged $PM_{2.5}$ concentrations in August are underpredicted with NMBs up to -60%, those in December are significantly overpredicted (up to 100%), particularly over the Piedmont and Coastal Plain. $PM_{2.5}$ concentrations are dominated by sulfate in August due to strong photochemical oxidation of SO_2 to form H_2SO_4 that subsequently condenses on the surface of particles under summer conditions and by nitrate, OM, and sulfate in December due to the fact that low temperatures favor the formation of nitrate and secondary organic aerosol (SOA) and that the primary OM emissions are higher in December than in August.

Fig. 7 shows simulated spatial distribution of monthly-mean percent contributions (%) of NH_4^+ to total NH_x. In August, 10–40% of total NH_3 are converted to NH_4^+ at/near source and 40–100% downwind. In December, the conversion percentages are 20–50% at/near source and 50–98% downwind. Robarge et al. (2002) measured the concentrations of NH_3 and NH_4^+ at an agricultural site located in Sampson county in NC during the period of October 1998–September 1999 and found that NH_4^+ accounts for ~18% and ~27% of NH_x in summer and winter. The simulated NH_4^+/NH_x and seasonal trends agree qualitatively with the limited measurements.

Figs. 8 and 9 show the time series of observed and predicted daily maximum O_3 mixing ratios and 24-h average $PM_{2.5}$ concentrations, respectively, at Asheville, Raleigh, Charlotte, and Kinston. The time series of daily maximum O_3 mixing ratios are only made for August 2002 since no data from AQS is available for winter months. While CMAQ reproduces the general daily variation trends for daily maximum O_3, it tends to underpredict their magnitudes, particularly during the period of 2–13 August. For 24-h average $PM_{2.5}$ concentrations, the model shows some skills in capturing daily variations at some sites such as Asheville in December and Raleigh and Charlotte in both months, but underpredictions occur during most time periods at

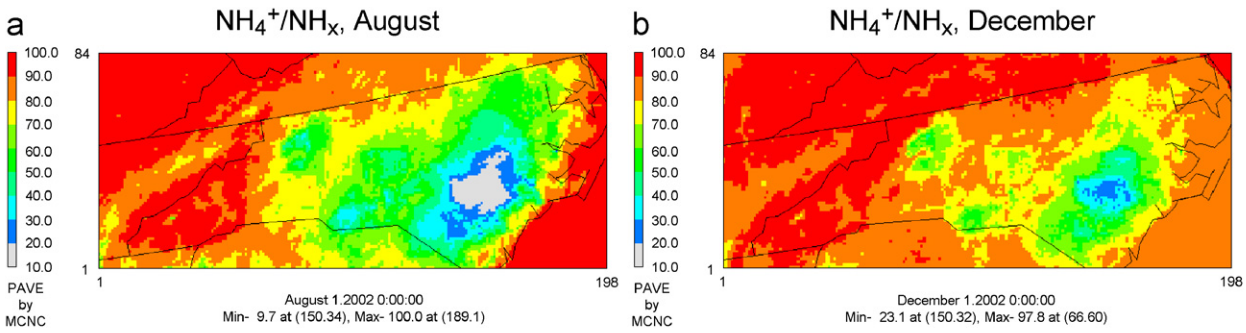

Fig. 7. Simulated monthly-mean ratios (%) of NH_4^+/NH_x ($=NH_3+NH_4^+$).

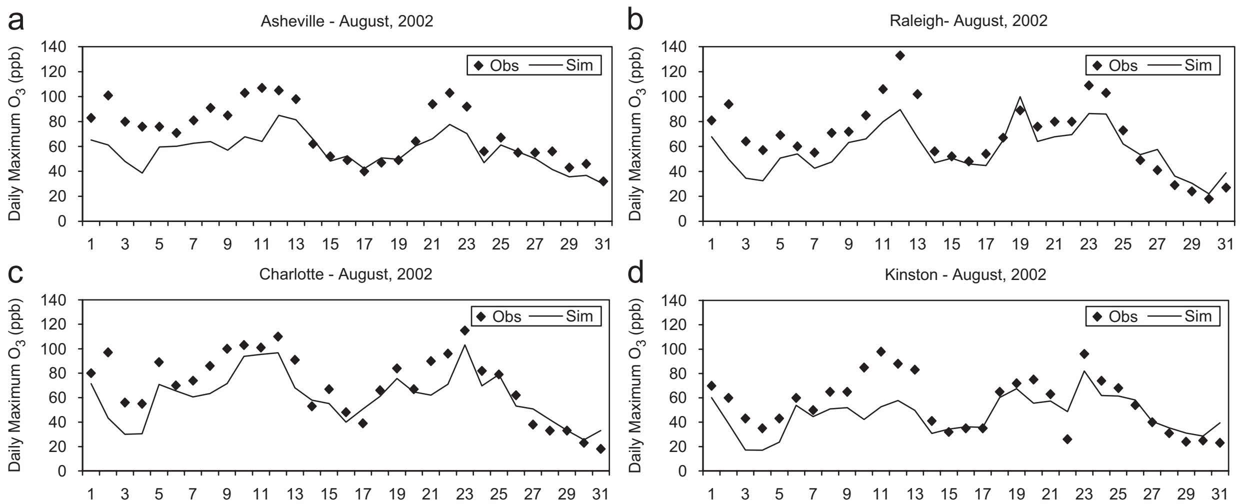

Fig. 8. The time series of observed and simulated daily maximum O_3 at Asheville (a), Raleigh (b), Charlotte (c), and Kinston (d) in August 2002.

all four sites in August and overpredictions occur at Charlotte and Kinston in December. Observations show a significant buildup in O_3 and $PM_{2.5}$ at nearly all four sites during 11–13 August. While CMAQ correctly reproduces the buildup, it underestimates the highest concentrations for both O_3 and $PM_{2.5}$ at all sites on 12 August. During this time period, the center of a high-pressure system at 850 mb was observed over the states of NC/GA and a strong low level inversion was caped at ~770 mb on 12 August. In addition, an analysis of surface weather maps from NOAA/NWS shows that there was a development of an Appalachian lee trough (APLT) on 12 August and it continued into 13 August at surface (http://www.hpc.ncep.noaa.gov/html/sfc_archive.shtml). APLT is typically accompanied by anticyclonic flow which brings westerly winds across the Appalachian mountain chain and by the formation of a column of hot air in the air descending (Seaman and Michelson, 2000). Previous studies (e.g., Pagnotti, 1987; Seaman and Michelson, 2000) have shown a strong correction between APLT and high O_3 episodes. While MM5 was able to reproduce some meteorological variables such as T, SH, WSD, and WDR and some features of high-pressure system and APLT, it is likely that the scale of those mesoscale features and other meteorological variables such as mixing depths are not well captured, which contributes partially to the underpredictions in O_3 and $PM_{2.5}$. For example, there was a strong contrast in simulated mixing depths across the APLT, in the range of 900–2199 m in the west of the trough, and 400–1000 m in the east of trough, due to the fact that the air mass in the east has been modified by relatively clean marine flows. The differences in the simulated and actually observed mixing heights across the APLT could contribute to the model biases in O_3 and $PM_{2.5}$

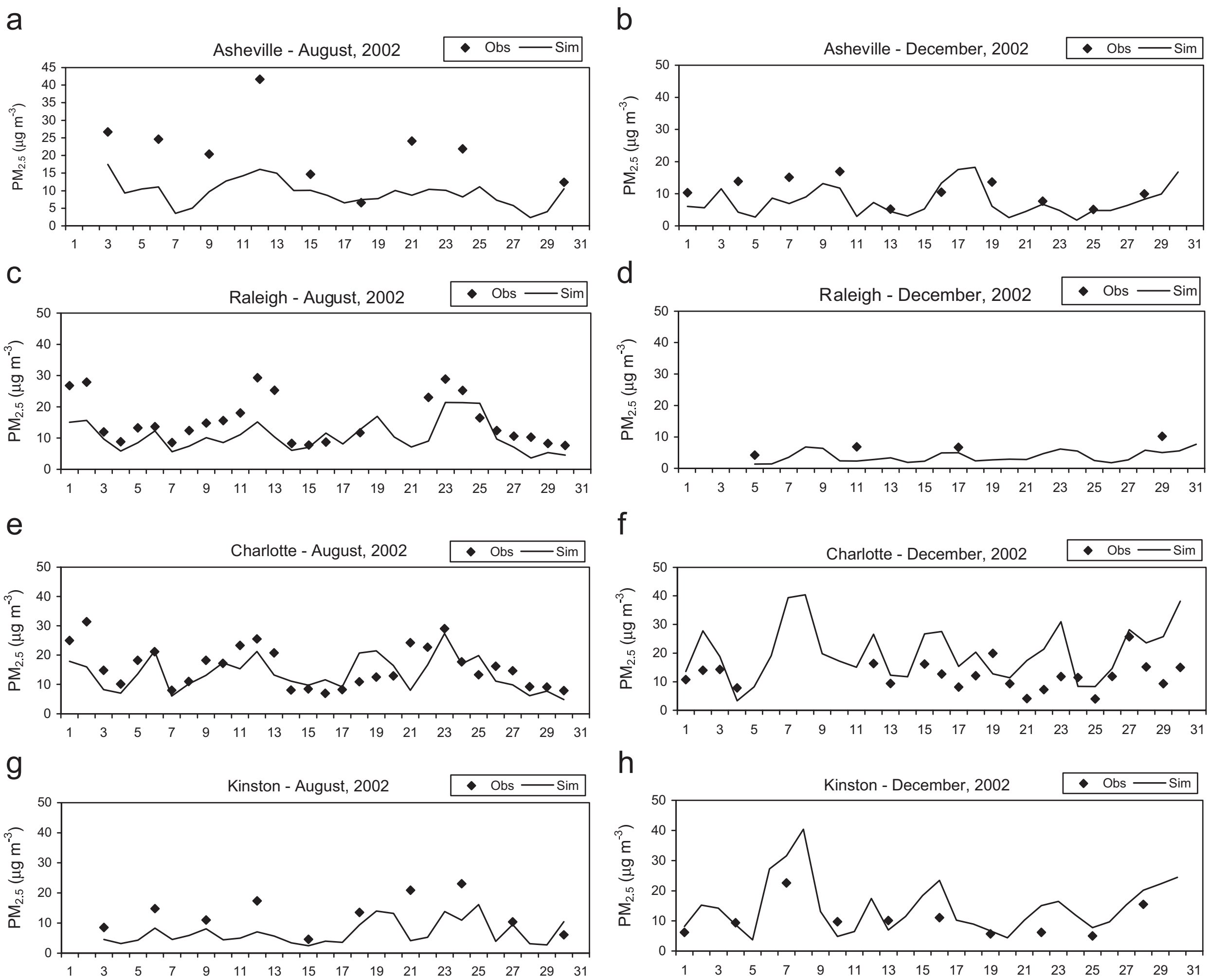

Fig. 9. The time series of observed and simulated 24-h average $PM_{2.5}$ at Asheville (a) and (b), Raleigh (c) and (d), Charlotte (e) and (f), and Kinston (g) and (h) in August and December 2002.

predictions on both sides of trough. While MM5 may overpredict mixing heights in both sides, it is likely that MM5 overpredicts mixing heights more in the west of APLT than in the east of APLT, resulting in larger underpredictions in O_3 and $PM_{2.5}$ at Asheville (west of APLT) than those at Charlotte (east of APLT but close to APLT) and Raleigh and Kinston (east of APLT). Another possible factor may be due to an underestimate in emissions of their precursors.

Observed hourly $PM_{2.5}$ concentrations are available at 8 sites in NC in August, which are plotted against simulated values in Fig. 10. The model captures the temporal variations at Winston-Salem, Garinger, and Charlotte. Significant underpredictions occur at other sites (e.g., Fayetteville, Greensboro, and Bryson City). The large discrepancies between observations and predictions indicate that the model fails to capture local-scale emission and meteorological characteristics.

3.3.2. Performance statistics

Model performance is evaluated for O_3 and $PM_{2.5}$ to assess its overall ability in simulating major criteria air pollutants. Evaluation of $PM_{2.5}$ includes its mass concentrations and composition such as NH_4^+. While CASTNet, IMPROVE, and STN provide observed NH_4^+ concentrations for model evaluation, no measurements data are available to evaluate simulated mixing ratios of NH_3.

Tables 2 and 3 summarize the overall statistical performance of CMAQ for the daily max 1-h and

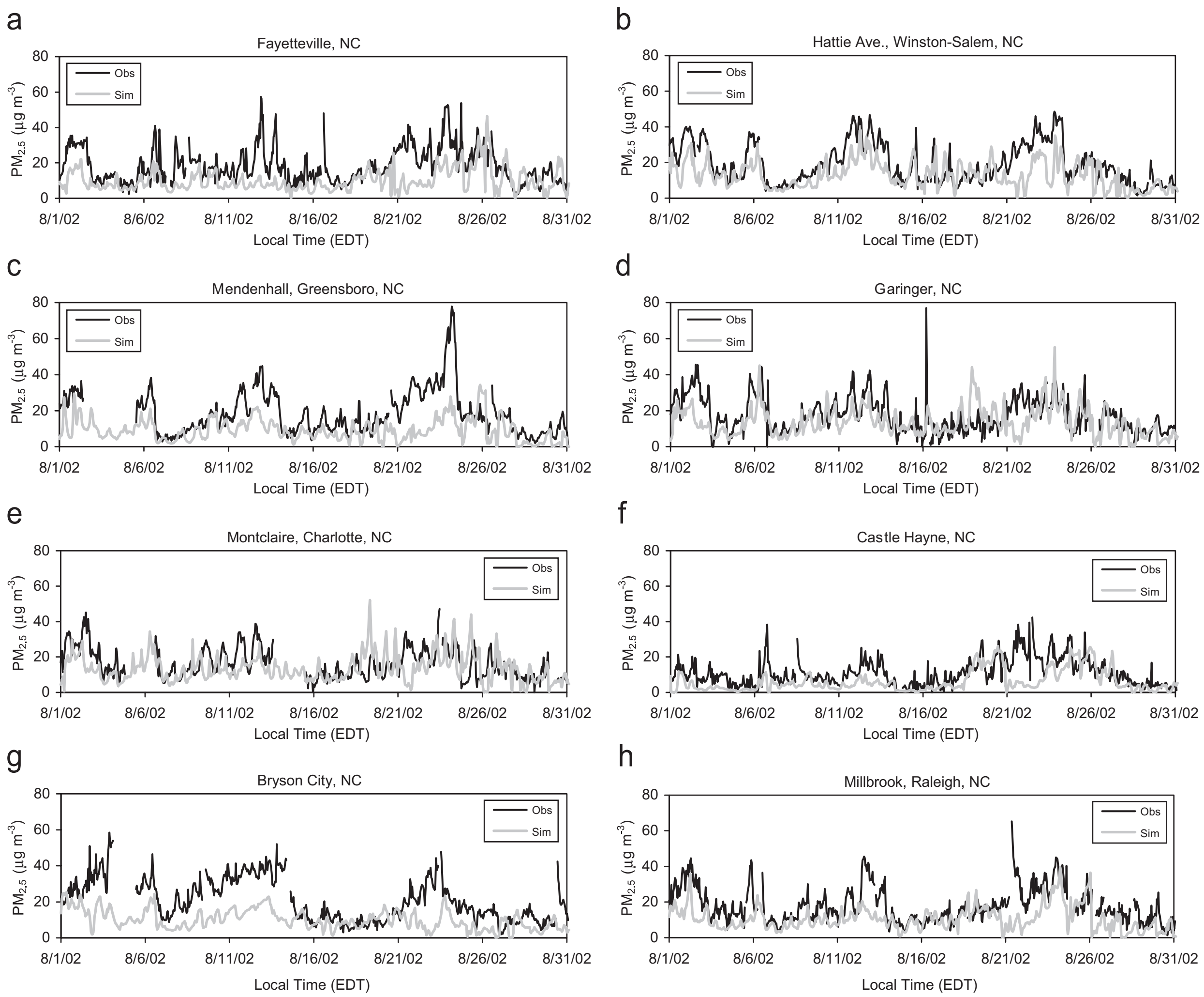

Fig. 10. The time series of observed and simulated hourly $PM_{2.5}$ concentrations at (a) Fayetteville, (b) Hattie Ave., Winston-Salem, (c) Mendenhall, Greensboro, (d) Garinger, (e) Montclaire, Charlotte, (f) Castle Hayne, (g) Bryson City, (h) Millbrook, Raleigh in August 2002.

max 8-h average O_3 mixing ratios and the monthly-mean 24-h average $PM_{2.5}$ from the 36-, 12-, and 4-km simulations. For the 4-km results, the max 1-h and 8-h O_3 mixing ratios are underpredicted with NMBs of −17% in August and overpredicted with NMBs of 4% and 7% in December. The model performs slightly better in December than in August. The CMAQ performance with an underprediction in O_3 in August is just the opposite to that in Eder and Yu (2006) and Zhang et al. (2006b) in summer months, indicating a need to assess CMAQ performance for multiple episodes over multiple domains.

For a good performance of $PM_{2.5}$, EPA recommended the values of MNB and MNGE less than 15% and 30%, respectively (EPA, 2001). The values of NMB/NME are similar to MNB/MNGE in many cases, but provide a more reasonable model evaluation with small measurements in calculation (Zhang et al., 2006a; Yu et al., 2006). For 4-km results, the model consistently underpredicts $PM_{2.5}$ and its composition in August at all networks with NMBs from −64% to −6% and overpredicts $PM_{2.5}$ and its composition in December with the NMBs from 6% to 158% with a few exceptions (e.g., −4% and −21% for SO_4^{-2} at CASTNet and STN; −27% for BC at IMPROVE). Among all PM species for the two months, the model performs the best for SO_4^{-2} with NMBs of −21% to 9%; the worst for NO_3^- with NMBs of −64% to 158%. Current

Table 2
Performance statistics for O_3 mixing ratios for the August and December 2002 simulations[a,b]

	Max 1-h O_3						Max 8-h O_3					
	August			December			August			December		
	4-km	12-km	36-km	4-km	12-km	36-km	4-km	12-km	36-km	4-km	12-km	36-km
Mean Obs. (ppb)	70	70	70	36	36	36	62	62	62	32	32	32
Mean Sim. (ppb)	58	59	61	37	37	37	51	54	56	34	35	33
Total #	2130	2130	2130	180	180	180	2130	2127	2127	180	180	180
NMB (%)	−17	−13	−12	4	4	5	−17	−10	−6	7	12	7
NME (%)	21	21	22	17	22	21	22	22	22	20	27	23

[a]The CMAQ 36- and 12-km model simulation results are taken from VISTAS and post-processed in this work.
[b]Both AQS and CASTNet sites are included in model evaluation for August simulation. AQS data sets are not available in December, thus only CASTNet sites are included in model evaluation for December.

Table 3
Model performance statistics for $PM_{2.5}$ and its composition for the August and December 2002 simulations[a,b]

	Network	Sample #	Mean Obs. ($\mu g\,m^{-3}$)	Mean Sim. ($\mu g\,m^{-3}$)			NMB (%)			NME (%)		
				4-km	12-km	36-km	4-km	12-km	36-km	4-km	12-km	36-km
(a) *August 2002*												
$PM_{2.5}$	AQS	708	17.4	11.8	12.0	10.9	−32.0	−31.0	−37.4	39.0	36.6	39.9
	IMPROVE	33	14.3	7.9	8.5	7.4	−45.2	−40.7	−41.4	46.0	44.9	43.8
	STN	77	19.0	12.9	12.7	11.2	−31.8	−32.9	−40.7	38.5	37.0	43.2
NH_4^+	IMPROVE	9	1.7	1.1	1.2	1.1	−35.2	−33.3	−36.7	43.6	43.2	41.1
	STN	77	1.9	1.6	1.6	1.5	−18.0	−15.6	−21.8	39.1	40.9	42.4
	CASTNET	16	1.7	1.1	1.2	1.2	−34.1	−31.9	−31.3	37.4	36.7	36.5
NO_3^-	IMPROVE	30	0.2	0.1	0.1	0.1	−40.9	−54.6	−50.5	122.0	113.6	111.6
	STN	77	0.5	0.2	0.1	0.1	−50.6	−68.4	−71.8	75.5	75.2	78.6
	CASTNET	16	0.2	0.1	0.1	0.1	−64.2	−64.7	−62.4	73.6	73.1	74.1
SO_4^{2-}	IMPROVE	31	6.2	5.2	6.2	5.6	−16.7	−9.2	−9.0	27.8	34.2	33.6
	STN	77	6.7	6.3	6.9	6.2	−6.2	2.0	−8.0	30.4	29.3	31.9
	CASTNET	16	6.3	5.1	5.5	5.3	−18.7	−11.8	−20.4	29.8	25.3	27.3
BC	IMPROVE	37	0.3	0.2	0.2	0.2	−48.9	−50.7	−44.4	51.9	53.1	50.3
OC	IMPROVE	37	2.7	1.1	1.0	1.3	−58.5	−63.3	−53.3	58.5	63.7	55.3
(b) *December 2002*												
$PM_{2.5}$	AQS	691	11.9	13.9	12.9	12.8	17.1	8.0	7.9	44.2	39.2	39.5
	IMPROVE	30	4.2	6.2	6.5	7.6	46.7	54.4	78.3	68.7	79.7	91.2
	STN	59	13.1	14.3	13.3	13.5	8.8	1.3	2.5	37.0	33.6	32.4
NH_4^+	IMPROVE	27	0.5	0.8	0.8	1.0	53.2	63.5	105.5	81.1	90.7	119.3
	STN	59	1.4	1.8	1.7	1.8	30.8	22.7	30.7	48.2	44.6	47.3
	CASTNET	19	0.9	1.3	1.3	1.4	40.6	42.6	60.3	41.2	44.2	60.6
NO_3^-	IMPROVE	27	0.5	1.1	1.2	1.8	142.9	162.4	275.2	156.2	177.6	288.9
	STN	58	2.2	3.4	3.2	3.6	58.6	49.7	64.4	68.6	69.6	79.9
	CASTNET	19	0.8	2.1	2.3	2.6	158.1	181.0	223.5	158.1	181.0	223.5
SO_4^{2-}	IMPROVE	27	1.5	1.7	1.6	1.8	9.1	2.1	14.5	48.1	49.9	47.2
	STN	58	2.8	2.2	2.0	2.1	−21.0	−28.5	−26.8	34.0	34.9	31.5
	CASTNET	19	2.3	2.2	1.9	2.1	−4.2	−14.4	−8.8	22.3	20.4	22.2
BC	IMPROVE	18	0.3	0.2	0.2	0.2	−26.6	−23.8	−30.5	37.3	40.8	35.0
OC	IMPROVE	18	1.4	1.5	1.5	1.5	5.9	5.9	1.9	39.5	41.9	39.6

[a]The CMAQ 36- and 12-km model simulation results are taken from VISTAS and post-processed in this work.
[b]The statistics are calculated when the observed concentration is $>0.05\,\mu g\,m^{-3}$.

model evaluation for $PM_{2.5}$ has been mostly conducted for summer episodes (e.g., Zhang et al., 2006b) and sometimes largely on an annual basis (e.g., Eder and Yu, 2006). The strong seasonal variation in CMAQ $PM_{2.5}$ performance indicates a need to assess both summer and winter periods at all time scales including hourly, daily, monthly, and annually to provide a complete evaluation of CMAQ overall performance.

The model biases can be attributed to inaccuracies/uncertainties in model inputs such as emissions and meteorology and model physics such as chemistry and PM dynamics. A close comparison of the NH_3 emissions in the VISTAS emission inventories with those in the Carnegie Mellon University (CMU) NH_3 Emission Inventory has shown that the NH_3 emissions in the VISTAS emission inventories may be underestimated by ~23% in August and overestimated by 48% in December (see details in Part II paper, Wu et al., 2007). Those inaccuracies are clearly responsible for the underpredictions in NH_4^+ and NO_3^- in August and overpredictions in December. While those underpredictions cannot help explain underpredictions in $PM_{2.5}$ in August because of their relatively small mass fractions in $PM_{2.5}$, the underpredictions in $PM_{2.5}$ may be caused by underpredictions in emissions of BC and primary OM and the concentrations of SOA. In December, the overpredictions in NH_4^+ and NO_3^- are partially responsible for overpredictions in $PM_{2.5}$.

CMAQ with a 4-km grid spacing overpredicts weekly total wet deposition of NH_4^+, NO_3^-, and SO_4^{2-} in December (with NMBs of 24.7%, 34.5% and 6.3%, respectively) and that of NH_4^+ and SO_4^{2-} in August but underpredicts that of NO_3^- in August (with NMBs of 36.8%, 88.1%, and −36.9%, respectively). Wet deposition amount of a species depends on the rate of precipitation and its aqueous-phase concentrations. In August, while overpredictions in precipitation may be responsible for the overpredictions in the wet deposition of NH_4^+ and SO_4^{2-}, the large underpredictions in NO_3^- concentrations (thus its aqueous-phase concentrations) may lead to underpredictions in its wet deposition amount. In December, the overall trend of overpredictions for concentrations of NH_4^+, NO_3^-, and SO_4^{2-} may be responsible for the overpredictions in their wet deposition amounts. A more detailed evaluation of wet deposition can be found in Queen and Zhang (2007a).

4. Sensitivity to grid resolutions

The results using 4-km grid spacing are compared with those with the 12- and 36-km grid spacing in Tables A3, 2 and 3 to study the effects of horizontal grid resolutions on the model performance. The temperatures are well predicted with a similar performance at both 4- and 12-km grid spacings. For SH, the 4-km results are slightly better for all areas than the 12-km results (with NMBs of 0% to −4% vs. −3.6% to −6%, respectively). For WSP, the 4-km results are also generally better than the 12-km results except for other areas. The corresponding NMBs for 4-km vs. 12-km simulations are 14.0% vs. 15%, 23.9% vs. 30.4%, and 3.2% vs. 3.9%, for coastal, rural, and urban areas, respectively. A more detailed topography structure is used in the 4-km simulation. This could be one factor for better predictions with a 4-km grid spacing as smaller scale feature-specific motions such as lee winds are incorporated in the model. Lacking of a complete meteorological data set, however, could affect the statistical evaluation of the 4-km simulation in a negative way. This will affect the analysis nudging scheme as well, where the difference between the observed and the simulated values on a grid is used to calculate the nudging term. The statistics for WDR suggest that the 12-km results are better for all areas than the 4-km results, particularly in rural areas with NMBs of 0.8% vs. −8.1%. This is because the number of days of deviations in opposite directions for the 12-km results is about the same (roughly 10 days each), resulting in a small net bias; whereas a consistent deviation in one direction occurs for most days in the case of the 4-km simulation.

For O_3 simulation, the results using 36-, 12- and 4-km grid spacings are quite similar. The model performs slightly better with the 36- and 12-km spacings in August but the same or slightly worse in December. For $PM_{2.5}$ in August, the 12-km simulation predicts the mean $PM_{2.5}$ concentrations higher than the 4-km simulation by 0.2 $\mu g\,m^{-3}$ at AQS sites and by 0.6 $\mu g\,m^{-3}$ at IMPROVE sites, and lower by 0.2 $\mu g\,m^{-3}$ at STN sites; the 36-km simulation predicts the mean $PM_{2.5}$ concentrations lower than the 4-km simulation by 0.5, 0.9, and 1.7 $\mu g\,m^{-3}$ at IMPROVE, AQS, and STN sites, respectively. Correspondingly, the absolute values of NMBs of the 12-km simulation are higher by 1.0% at AQS sites, 4.5% at IMPROVE sites, and 1.1% at STN sites; and those of the 36-km simulation are higher by 5.4% at AQS sites and 8.9% at STN sites, and lower by 3.8% at IMPROVE sites. In December, the 12-km simulation predicts the mean $PM_{2.5}$ concentrations lower than the 4-km simulation by 1.0 $\mu g\, m^{-3}$ at AQS and STN sites, but higher by 0.3 $\mu g\, m^{-3}$ at IMPROVE sites; the 36-km simulation predicts the mean $PM_{2.5}$ concentrations lower than by 1.1 and 0.8 $\mu g\, m^{-3}$ at AQS and STN sites, respectively, but higher by 1.4 $\mu g\, m^{-3}$ at IMPROVE sites. Correspondingly, the NMBs of the 12-km simulation are lower by 9.1% at AQS sites and by 7.5% at STN sites and but higher by 7.7% at IMPROVE sites; and those of the 36-km simulation are lower by 9.2% at the AQS sites and by 6.3% at the STN sites but higher by 31.6% at IMPROVE sites. Increasing the spatial resolution from 36- to 12- and 4-km generally leads to an improved model performance since a finer spatial resolution is expected to lead to a better representation of topography, emissions, and other atmospheric processes. The 4-km results are generally better for $PM_{2.5}$ at AQS and STN sites, NO_3^- at all sites, SO_4^{2-} at IMPROVE sites in August. They are generally better or similar for $PM_{2.5}$, NH_4^+, NO_3^-, BC, and OM at IMPROVE and CASTNet sites and for SO_4^{2-} at STN and CASTNet sites in December. Overall, the results between 4- and 12-km are not significantly different for $PM_{2.5}$, NH_4^+, BC, and OM in August and BC and OM in December, probably due to the lesser sensitivity of emissions to grid resolution when the grid resolution changes from 12- to 4-km for this scenario. However, relatively more pronounced differences are found in $PM_{2.5}$ in December and SO_4^{2-} and NO_3^- concentrations in both months, indicating higher sensitivity of model simulation to nonlinearity in chemistry and meteorology (e.g., via cloud fractions and precipitation which affect aqueous-phase formation of sulfate) due to different grid resolutions as compared with that of emissions. Arunachalam et al. (2006) quantitatively assessed the influence of grid resolution on air quality model predictions in NC and found similar results, i.e., the 12- and 4-km predictions are not very different, while the differences are larger between 4- (or 12-) and 36-km results.

The model predictions of NH_4^+ and NO_3^- are more sensitive to grid resolutions in December than in August. For example, compared with the 36-km simulation, the 4- and 12-km simulations predict NH_4^+ with NMBs lower by ~50% and 40%, respectively, and NO_3^- with NMBs lower by ~130% and ~110%, respectively, at IMPROVE sites in December. For comparison, the NMBs from the 4- and 12-km simulations are lower by 1.5% and 3.4% than those from the 36-km simulation at IMPROVE sites in August. The model predictions for NH_4^+ and NO_3^- with 12- and 4-km grid spacings are generally better than those with the 36-km grid spacing. SO_4^{2-} prediction is less sensitive to grid resolutions, and the results with finer resolutions (12- or 4-km) are not always better than those with a 36-km resolution. This is likely caused by the sensitivity of SO_4^{2-} to several factors that depend highly and nonlinearly on grid resolutions including cloud fractions, precipitation, SO_2 emissions, and aqueous-phase oxidation of SO_2.

The model predictions of wet deposition amounts of NH_4^+, NO_3^-, and SO_4^{2-} are sensitive to good resolutions in terms of both spatial distribution and statistics (Queen and Zhang, 2007b). A greater sensitivity is found in August than December. The model results with a 4-km grid resolution are not always better than those with 12- or 36-km grid resolutions.

5. Summary

MM5 and CMAQ are applied at a 4-km grid spacing to August and December 2002 over NC to study the transport and fate of NH_x. MM5 at a 4-km grid spacing can generally reproduce the spatial distribution in temperature, water vapor mixing ratios, and winds, with a better performance in both spatial distribution and daily statistics in December. MM5 reproduces well the peak daily temperature and diurnal variation but overpredicts the minimal temperature at night at most sites in August. It generally captures well the diurnal variations of specific humidity, but underpredicts the magnitude at all sites in both months. MM5 generally reproduces the overall daily variation trends and scales for WSD and WDR, but significant deviations occur on some days at some sites, indicating challenges in simulating local-scale meteorological features. For hourly statistics, MM5 performs well in terms of domain-wide statistics with NMBs less than 9%. The highest NMB occurs at the coastal areas for T, both coastal and rural areas for SH, and rural areas for WSP and WDR. Compared with chemical predictions, meteorological predictions are generally less sensitive to grid resolutions. Compared with 12-km simulation, the 4-km simulation gives slightly better performance for specific humidity and wind speed, due in part to more detailed topography structure.

CMAQ at a 4-km grid spacing gives a good performance for the maximum 1- and 8-h average O_3 mixing ratios in terms of spatial distributions, temporal variations, and statistics with NMBs of −17% to 7%. It gives a better performance for December and similar performance at both 12- and 4-km grid spacings. CMAQ performs reasonably well for 24-h averaged $PM_{2.5}$ in terms of a spatial distribution and temporal variations, but significantly underpredicts its concentrations with NMBs up to −60% in August and up to 100% in December, particularly over the Piedmont and Coastal Plain in NC. Among all PM composition, the largest biases occur for NO_3^- with NMBs of −64% to 158%. The model biases for $PM_{2.5}$ and its components are attributed to several factors including inaccuracies in meteorological predictions, uncertainties in emissions (e.g., NH_3 emissions), and model treatments for gas/particle partitioning (e.g., total nitrate and ammonium partitioning). Model predictions with 12- and 4-km resolutions are similar, and generally better than those with the 36-km grid spacing. The predicted NH_4^+ and NO_3^- are more sensitive to grid resolutions in December than in August.

CMAQ demonstrates some skills in simulating the transport and fate of NH_x despite the aforementioned inaccuracies in meteorological and chemical predictions. The simulations show that 10–40% of total NH_3 is converted to NH_4^+ at/near source and 40–100% downwind in August, and 20–50% of total NH_3 is converted to NH_4^+ at/near source and 50–98% downwind in December. The simulated NH_4^+/NH_x and seasonal trends agree qualitatively with the limited measurements. Sensitivity of model simulations to NH_3 emissions will be further examined in Part II paper.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2007.04.031.

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