Responses of future air quality to emission controls over North Carolina, Part I: Model evaluation for current-year simulations

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ABSTRACT

The prediction of future air quality and its responses to emission control strategies at national and state levels requires a reliable model that can replicate atmospheric observations. In this work, the Mesoscale Model (MM5) and the Community Multiscale Air Quality Modeling (CMAQ) system are applied at a 4-km horizontal grid resolution for four one-month periods, i.e., January, June, July, and August in 2002 to evaluate model performance and compare with that at 12-km. The evaluation shows skills of MM5/CMAQ that are overall consistent with current model performance. The large cold bias in temperature at 1.5 m is likely due to too cold soil initial temperatures and inappropriate snow treatments. The large overprediction in precipitation in July is due likely to too frequent afternoon convective rainfall and/or an overestimation in the rainfall intensity. The normalized mean biases and errors are −1.6% to 9.1% and 15.3–18.5% in January and −18.7% to −5.7% and 13.9–20.6% in July for max 1-h and 8-h O_3 mixing ratios, respectively, and those for 24-h average $PM_{2.5}$ concentrations are 8.3–25.9% and 27.6–38.5% in January and −57.8% to −45.4% and 46.1–59.3% in July. The large underprediction in $PM_{2.5}$ in summer is attributed mainly to overpredicted precipitation, inaccurate emissions, incomplete treatments for secondary organic aerosols, and model difficulties in resolving complex meteorology and geography. While O_3 prediction shows relatively less sensitivity to horizontal grid resolutions, $PM_{2.5}$ and its secondary components, visibility indices, and dry and wet deposition show a moderate to high sensitivity. These results have important implications for the regulatory applications of MM5/CMAQ for future air quality attainment.

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1. Introduction

The U.S. Environment Protection Agency (EPA) has recently promulgated more stringent National Ambient Air Quality Standards (NAAQS) to protect humans and the environment. For example, the NAAQS of the 8-h ozone (O_3) has been changed from 0.08 ppm in 1997 to 0.075 ppm in 2008 and that of the 24-h average particulate matter with an aerodynamic diameter less than or equal to 2.5 μm ($PM_{2.5}$) has been changed from 65 μg m^{-3} in 1997 to 35 μg m^{-3} in 2006. The Southeastern U.S. is predicted to experience significant and potentially highly costly climate change impacts (IPCC, 2007; US CCSP, 2008), posing great challenges in maintaining and improving air quality for future years with continuous population growth and economic development. Because of its unique meteorology featured by hot and humid summers with strong solar insulation and poor vertical mixing and emission characteristics with high biogenic emissions, this area has been selected for several special intensive field studies for regional photochemistry and $PM_{2.5}$ formation (e.g., Hansen et al., 2003) and modeling studies (Odman et al., 2002; Zhang et al., 2004, 2006a,b; Morris et al., 2005; Arunachalam et al., 2006; Queen and Zhang, 2008a,b; Wu et al., 2008a,b). Most of these modeling studies focus on past air pollution episodes. Fewer simulated future air quality and its responses to changes in climate or pollutant emissions or both (e.g., Odman et al., 2002; Arunachalam et al., 2006). To demonstrate reasonable progress towards regional haze visibility improvement goals, a cooperative group throughout the southeast has been formed among 10 states in the southeastern U.S. and various local and tribal agencies, namely, the Visibility Improvement State and Tribal Association of the Southeast (VISTAS) (http://www.vista-sesarm.org.asp). For the purpose of demonstrating the attainment of the O_3 and $PM_{2.5}$ NAAQS, these states also formed the Association for Southeastern Integrated Planning (ASIP). The projected emissions for 2009 and 2018 have been

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developed based on several control rules (Morris et al., 2007). Model simulations of 2002, 2009, and 2018 have been performed by VISTAS/ASIP contractors at a horizontal grid resolution of 36-km over the contiguous U.S. and a nested 12-km grid over the southeastern U.S. The latest VISTAS/ASIP simulations were conducted using the Fifth Generation National Center for Atmospheric Research/Pennsylvania State University (NCAR/PSU) Mesoscale Model (MM5) version 3.6.1+ (Grell et al., 1994) and the U.S. EPA Community Multiscale Air Quality (CMAQ) modeling system version 4.5.1 (Binkowski and Roselle, 2003) with a modified secondary organic aerosol (SOA) module by ENVIRON, Inc. (referred to as CMAQ v4.5.1 SOAmods hereafter) (Morris et al., 2007). The 12-km CMAQ results from VISTAS/ASIP simulations have been used in the State Implementation Plans (SIPs) by VISTAS/ASIP states to demonstrate the attainment of the 8-h max O_3 and annual $PM_{2.5}$ standards. However, the U.S. EPA has suggested that SIP modeling, particularly over areas with high gaseous precursor emissions and primary PM sources, may benefit from increased grid resolution from 12-km to 4-km (U.S. EPA, 2007). While the North Carolina (NC) Division of Air Quality Early Action Compact modeling work has shown limited benefit in O_3 attainment to moving to higher resolution modeling in NC (Arunachalam et al., 2006), recent studies have reported some sensitivity of precipitation, $PM_{2.5}$, and wet deposition predictions to horizontal grid resolution (Wu et al., 2008b; Queen and Zhang, 2008b). This work presents MM5/CMAQ results at a 4-km horizontal grid spacing over NC. Our objectives are to evaluate the model performance for current-year (i.e., 2002), simulate the responses of air quality to projected emission reductions in future years (i.e., 2009 and 2018), and examine the model sensitivity to horizontal grid resolutions under current and future emission scenarios. The results will provide valuable scientific information for the SIPs. Part I describes a comprehensive model evaluation at both 12- and 4-km grid resolutions for 2002 and the sensitivity of the model predictions to horizontal grid resolutions. Part II (Zhang et al., in press) describes the responses of air quality to emission controls in 2009 and 2018, their sensitivity to grid resolution, the attainment test, and the potential policy implications.

2. Model simulation design and evaluation methodology

The 4-km MM5/CMAQ simulations are conducted for January, June, July, and August in 2002, 2009, and 2018. The simulations for the three summer months would provide a robust dataset for additional attainment test equivalent analyses presented in the Part II paper. The evaluation in Part I will focus only on January and July. The evaluation results in July are used to represent the summer-month simulation; those from June and August are not shown because of their similarity to the results in July. The vertical structure includes 34 layers for MM5 and 19 layers for CMAQ extending from surface to the tropopause with ~38 m for the first layer height. The MM5 v3.7 with four-dimensional data assimilation is used to generate meteorology for CMAQ. The major physics options used in MM5 at 4-km are consistent with those used in the VISTAS/ASIP 36- and 12-km simulations (Olerud and Sims, 2004). CMAQ v4.5.1 SOAmods uses the Carbon Bond IV (CB-IV) gas-phase mechanism, the modified Regional Acid Deposition Model aqueous chemistry, and the modified CMAQ AERO4 aerosol module that treats major aerosol processes including homogeneous nucleation, condensation, coagulation, inorganic aerosol thermodynamics, and SOA formation. Compared with the default SOA module in CMAQ v4.5.1, CMAQ v4.5.1 SOAmods treats additional SOA formation from sesquiterpenes and isoprene and accounts for the polymerization of SOA and has been shown to have a much better model performance in reproducing organic PM in the summer (Morris et al.,

2006). The meteorological and chemical initial and boundary conditions for 4-km MM5/CMAQ simulations are generated based on the 12-km VISTAS/ASIP simulations. The 2002 meteorological fields are also used for 2009 and 2018 CMAQ simulations.

The 4-km emissions are processed using the Sparse Matrix Operator Kernel Emissions (SMOKE) modeling system v2.1 and are based on county-level emission inventories with 7 emission categories including area, biogenic, mobile, Electric Generating Units (EGUs), non-EGUs, fire emissions, and non-road emissions. Two types of emission inventories, actual and typical, were developed by the VISTAS/ASIP contractors for 2002 simulations (Barnard and Sabo, 2008). The 2002 actual emission inventories represent the best estimate of the actual emissions for 2002 and are used for CMAQ model performance evaluation against the 2002 measurements. The 2002 typical emission inventories represent the five-year (2000−2004) period and are used for the determination of the air quality and regional haze reasonable progress in future years since 2002. The 2002 typical emissions projected to 2009 and 2018 are used for future year simulations. The main differences between 2002 actual and typical emission inventories are described in the supplementary data.

The variables evaluated for 2002 simulations with actual emissions (also referred to as baseline simulations) include temperature at 1.5 m above the ground (T1.5), relative humidity at 1.5 m (RH1.5), wind speed at 10 m (WSP10), wind direction at 10 m (WDR10), hourly precipitation, mixing ratios of maximum 1-h and 8-h O_3, mass concentrations of $PM_{2.5}$ and $PM_{2.5}$ components (i.e., ammonium (NH_4^+), nitrate (NO_3^-), sulfate (SO_4^{2-}), elemental carbon (EC), organic matter (OM)), the dry deposition of gases and secondary PM species (i.e., $SO_{2, dry}$, nitric acid ($HNO_{3, dry}$), ammonia ($NH_{3, dry}$), visibility indices, and $SO_{4, dry}^{2-}$, $NH_{4, dry}^+$, and $NO_{3, dry}^-$), and the wet deposition of secondary PM species (i.e., $SO_{4, wet}^{2-}$, $NH_{4, wet}^+$, and $NO_{3, wet}^-$). The observational datasets used for model evaluation include the National Acid Deposition Program (NADP), the Interagency Monitoring of Protected Visual Environments (IMPROVE), the Clean Air Status and Trend Network (CASTNET), the Speciation Trends Network (STN), Aerometric Information Retrieval System-Air Quality System (AIRS-AQS), North Carolina Department of Environment and Natural Resources (NCDENR), and the State Climate Office of North Carolina (SCO). Figures S-1 to S-4 in the supplementary data show the locations of all observational sites in the modeling domain. Tables S-1 to S-4 provide the full names and coordinates of these sites. Figure S-5 shows the three physiographic regions including the coastal plain, Piedmont, and mountains in NC. The dry deposition fluxes estimated by the Multi-Layer Model (MLM) based on meteorological and chemical measurements from CASTNET are also used to compare with simulated dry deposition. Simulations are evaluated in terms of spatial distribution, temporal variations, and domain-wide statistics following the evaluation protocol of Zhang et al. (2006a). The 2002 four-month simulations with typical emissions are compared with the baseline simulations to assess their representativeness as a basis for future-year emission control scenarios. The responses of future air quality to emission reductions in 2009 and 2018 are examined in terms of spatial variations, domain-wide changes, and sensitivity to grid resolution.

3. Evaluation of 2002 simulations with actual emissions

3.1. Meteorological evaluation

Table 1 shows performance statistics for simulated meteorological variables. The observed vs. simulated overlay plots are given in Figures S-6 and S-7. The MM5 simulations at 4- and 12-km show similar temperature gradients from the mountain to the coastal areas in both months. Large cold biases in T1.5 exist in January.

Table 1
Meteorological performance statistics.[a,b,c]

		CASTNET Data#	NMB	NME	MNB	MNE	SCO Data#	NMB	NME	MNB	MNE	NADP Data#	NMB	NME	MNB	MNE
January																
T1.5	4-km	3519	−2.8	7.0	−2.7	6.9	22,817	−22.3	32.9	−19.9	58.2	–	–	–	–	–
	12-km	3519	−2.8	7.2	−2.8	7.2	22,773	−13.1	25.0	−12.7	50.7	–	–	–	–	–
RH1.5	4-km	4633	3.4	17.8	8.1	21.4	29,087	12.2	21.7	20.3	28.3	–	–	–	–	–
	12-km	4633	3.1	16.6	6.9	19.7	29,087	13.0	21.3	18.5	26.3	–	–	–	–	–
WSP10	4-km	5051	50.3	68.4	243.4	255.8	19,203	7.0	34.0	23.1	43.5	–	–	–	–	–
	12-km	5051	36.4	58.8	204.7	219.9	19,187	5.5	33.2	21.0	41.6	–	–	–	–	–
WDR10	4-km	4884	6.9	39.0	330.6	357.6	19,203	0.1	20.9	47.5	47.7	–	–	–	–	–
	12-km	4884	11.4	37.2	356.0	378.0	19,186	1.4	20.2	59.2	59.4	–	–	–	–	–
Precip	4-km	–	–	–	–	–	–	–	–	–	–	50	−28.5	41.8	−0.8	59.6
	12-km	–	–	–	–	–	–	–	–	–	–	50	−7.6	31.1	28.8	59.9
July																
T1.5	4-km	5170	5.2	7.7	5.8	8.1	29,303	−0.6	6.0	−0.5	6.0	–	–	–	–	–
	12-km	5170	5.3	7.6	5.9	8.1	29,326	0.6	6.4	1.4	6.7	–	–	–	–	–
RH1.5	4-km	4626	−9.0	14.7	−10.0	21.8	28,550	−3.4	14.6	−1.1	16.4	–	–	–	–	–
	12-km	4626	−7.0	13.6	1.2	21.3	28,550	−0.2	14.7	1.7	17.1	–	–	–	–	–
WSP10	4-km	4884	69.7	85.5	217.5	229.5	17,302	5.6	36.7	16.1	42.4	–	–	–	–	–
	12-km	4884	57.8	75.8	200.1	214.0	17,333	2.8	34.6	13.1	39.8	–	–	–	–	–
WDR10	4-km	4875	2.8	49.1	390.2	424.2	17,302	−5.3	31.6	56.6	56.9	–	–	–	–	–
	12-km	4875	2.8	48.4	372.0	406.0	17,333	−2.9	30.2	75.1	75.4	–	–	–	–	–
Precip	4-km	–	–	–	–	–	–	–	–	–	–	51	69.9	147.4	931.3	998.1
	12-km	–	–	–	–	–	–	–	–	–	–	51	74.8	118.8	1002.6	1037.1

[a] NMB − normalized mean bias, %, NME − normalized mean error, %, MNB − mean normalized bias, %, MNE − mean normalized error, %. The performance statistics are calculated for all meteorological variables except for Precip based on hourly observations and model simulations. For Precip, it is based on daily total values.

[b] A cutoff value of 3 knots (1.54 m s^{-1}) was used to remove any data pairs with calm conditions (i.e., observed WSP10 < 3 knots) since the instruments have a minimum speed threshold of 3 knots.

[c] "−" indicates no observational data are available for model evaluation.

Compared to the 12-km simulation, the 4-km simulation gives lower T1.5 values particularly in the western coastal plain area in January, resulting in a much larger cold bias (mean biases (MBs) of −2.0 °C vs. −1.18 °C, the normalized mean bias (NMB) of −22.3% vs. −13.1% at the SCO sites) that dominates its winter performance, although it gives slightly better agreement at the CASTNET sites (MBs of −0.79 °C vs. −0.8 °C or NMB of −10.4% vs. −10.6%). The cold biases in January occur mostly during daytime (see Figure S-8), which may be attributed to several possible reasons including too cold soil temperatures, too moist soil initial conditions, too many daytime clouds, and poor treatments of snow related processes (Olerud and Sims, 2004). In particular, the inadequate treatments for snow effects in MM5 could contribute to the large cold biases, due to the occurrence of 12−14 inches of snow occurred over NC during 2−4 January 2002. The 4-km simulation gives slightly lower T1.5 values in the Piedmont area in July. The MBs for July T1.5 are 1.2 °C and 0.16 °C (or NMBs of 5.3% and 0.6%) at 12-km and 1.17 °C and −0.18 °C (or NMBs of 5.2% vs. −0.7%) at 4-km at the CASTNET and SCO sites, respectively. The warm biases at the CASTNET sites occur during both day and night in July (Figure S-8). For RH1.5 in January, MM5 at 12- and 4-km performs similarly in terms of MBs, NMBs or normalized mean errors (NMEs), mean normalized bias and errors (MNBs and MNEs). Its spatial distributions, however, are quite different in two regions: the Piedmont area along the eastern bound of the Blue Ridge Mountains and the coastal plain area where the 4-km simulation gives higher RHs than the 12-km simulation. Compared with the 12-km simulation in July, the 4-km simulation gives higher RHs in the western Piedmont area but lower values in the mountain areas and the southeastern corner of NC, resulting in a slightly worse agreement with observations in terms of domain-wide statistics. WSP10 values are positively biased at both resolutions in both months, particularly at night (Figure S-8). Compared with 12-km simulation in January, the 4-km simulation gives a similar spatial distribution with higher WSP10 values along the Blue Ridge Mountains and coastal plain areas, resulting in larger overpredictions (e.g., MBs of 1.23 vs. 0.89 m s^{-1} or NMBs of 50.3% vs.

36.4%, NMEs of 68.4% vs. 58.8% at the CASTNET sites). A similar trend is found almost throughout the domain in July during which the 4-km simulation also gives worse agreement, particularly at the CASTNET sites (MBs of 1.11 vs. 0.92 m s^{-1} or NMBs of 69.7% vs. 57.8% or NMEs of 85.5% vs. 75.8%). For WDR10, the 4-km simulations give much better agreement in January but slightly worse in July. The MBs are 14.0° vs. 22.8° (or NMBs of 7.1% vs. 11.6%) at the CASTNET sites and 0.33° vs. 2.95° (or NMBs of 0.1% vs. 1.4%) at the SCO sites in January and 6.2° vs. 6.0° (or NMBs of 3.4% vs. 3.3%) at the CASTNET sites and −9.7° vs. −5.4° (or NMBs of −5.3% vs. −2.9%) at the SCO sites in July. For daily precipitation, the 4-km simulations give lower values than the 12-km simulations in the mountain and coastal plain areas in both months. Compared with observations, the 4-km simulations give larger underpredictions (with MBs of −10.11 mm vs. −2.68 mm or NMBs of −28.5% vs. −7.6%) in January but slightly less overpredictions (with MBs of 21.97 mm vs. 23.51 mm or NMBs of 68.2% vs. 72.9% in July). The positive bias in July precipitation is the highest among all months in 2002 based on the 12-km VISTAS/ASIP simulations, due likely to too frequent afternoon convective rainfall and/or an overestimation in the intensity of the rainfall (Olerud and Sims, 2004). Note that MNB and MNE for WSP10, WDR10, and Precip are much larger than NMB and NME because of occurrence of very small-observed values at some sites during some hours. As shown in Figure S-3, the model performs generally well in reproducing the temporal variations of major meteorological variables except a few periods (e.g., 2−4 January when a heavy snow occurred) during which the simulated T1.5 at 4-km deviates largely from observations due likely to a slower snow melting rate simulated by the MM5/PX-LSM. More detailed analysis is provided in the supplementary data.

3.2. Chemical evaluation

3.2.1. O$_3$ mixing ratios

Fig. 1 shows an overlay of observed and simulated monthly-mean max 1-h and 8-h O$_3$ mixing ratios from the January and July
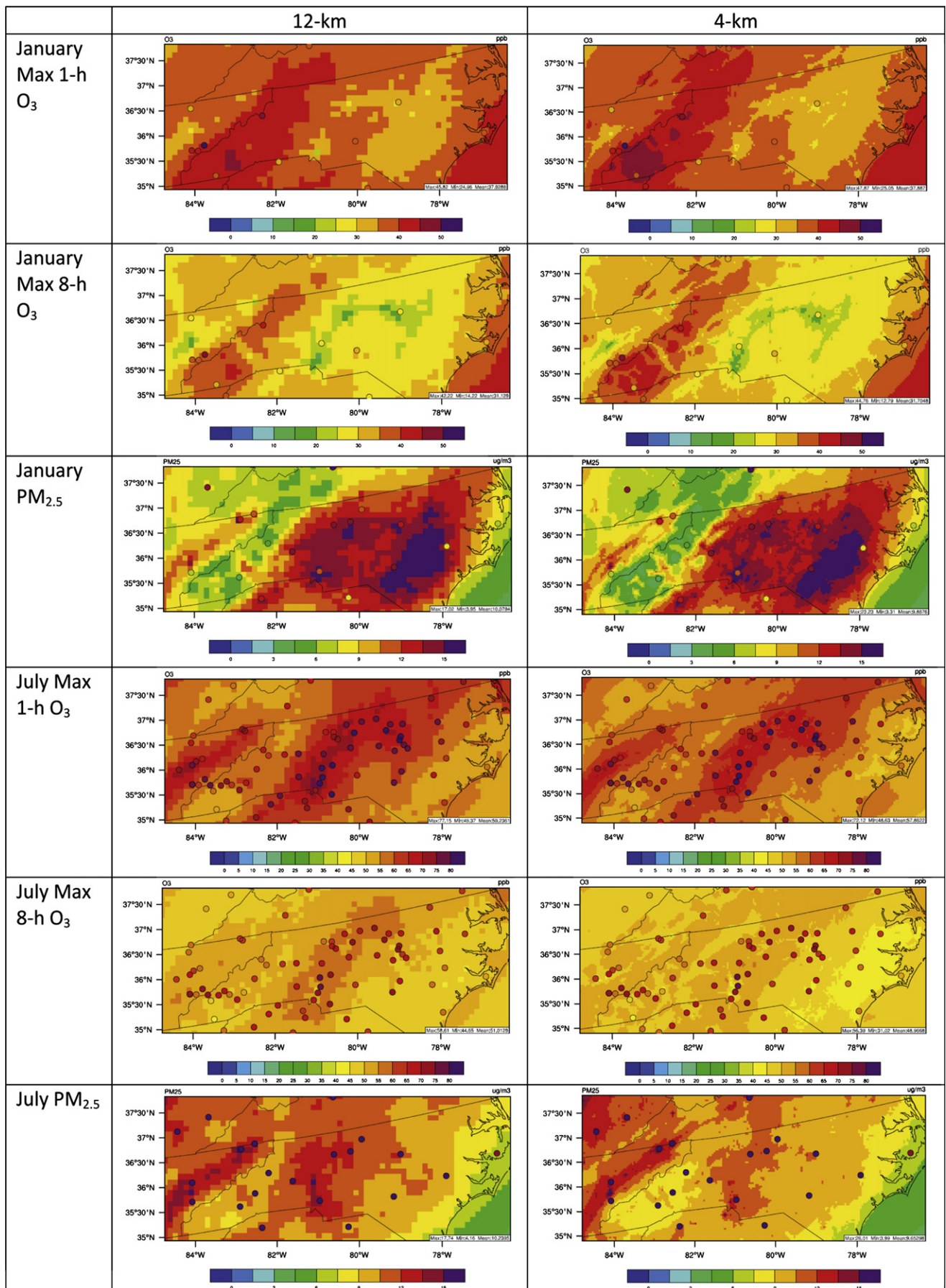
Fig. 1. Simulated vs. observed (diamond symbols) monthly-mean max 1-h and max 8-h O₃ mixing ratios in January and July 2002.

2002 baseline simulations. Table 2 shows the performance statistics. The highest max 1-h and 8-h O_3 mixing ratios simulated at 12- and 4-km occur along the Appalachian Mountains in January (40–45 ppb). While the overall spatial distributions at 4- and 12-km are similar in January, the 4-km simulation gives 1–5 ppb (by 2–10%) higher values in the mountain and its west and larger areas with 1–3 ppb (by 1–12%) lower O_3 in the coastal plain and Piedmont areas. The 4-km simulation captures the high O_3 values over the Knoxville area, which are underpredicted at 12-km. Its statistical performance is slightly better for max 1-h O_3 but slightly worse for max 8-h O_3 than that at 12-km. The NMBs for maximum 1-h O_3 mixing ratios at 4- and 12-km are 1.2% and −1.6% at the CASTNET sites and 2.1% and 2.2% at the AIRS-AQS sites; those for max 8-h O_3 mixing ratios are 9.1% and 6.2% at the CASTNET sites and 4.6% and 3.2% at the AIRS-AQS sites, respectively. Different from the simulated results in January, the simulated max 1-h O_3 mixing ratios at 4- and 12-km in July are higher over the Piedmont area of NC and the western part of mountains in TN than those in the remaining areas. The highest 1-h O_3 mixing ratio of ∼70 ppb occurs in several big cities such as Raleigh, Greensboro, Winston-Salem, High Point, and Charlotte. Compared with observations, underpredictions occur for max 1-h and 8-h O_3 throughout the domain, with larger areas having higher O_3 values above 64 ppb from the 12-km simulation. Compared with results at 12-km, the 4-km simulation in July predicts up to 1–5 ppb (4–10%) throughout the entire domain except in the mountain areas in NC and VA. The NMBs, NMEs, MNBs, and MNEs at the AIRS-AQS and CASTNET sites are within expected ranges for max 1-h and 8-h O_3, with a slightly better performance at 12-km. Although the 4-km simulation gives generally higher O_3 than the 12-km simulation in January and the absolute differences between simulated O_3 mixing ratios at the two grid resolutions are larger (1–5 ppb vs. 1–3 ppb), the relatively small model sensitivity to horizontal grid resolutions for max 1- and 8-h O_3 mixing ratios in January and July 2002 is overall consistent with that of Wu et al. (2008a) and Arunachalam et al. (2006) who reported generally lower O_3 mixing ratios at 4-km in both summer and winter months.

Fig. 2 shows temporal variation of simulated O_3 at 4-km and 12-km at four sites in NC. Observations in July are also plotted for comparison (note that no observations are available in January). Bryson City represents mountain areas; Castle Hayne is a coastal site; Raleigh, located in the central NC, represents urban areas; Garinger, which is in Charlotte and the central NC, also represents urban areas. At Bryson city where NO_x and VOC sources are small, the January 4-km simulation gives similar temporal variations but with slightly higher values on some days than at 12-km. Appreciable differences between the 4- and 12-km simulations are found at other sites, with the largest differences at Raleigh. Compared

with the 12-km simulation, the 4-km simulation gives much higher daytime NO_x during some days at Garinger and most days at Raleigh having large sources of NO_x, which leads to lower O_3 during both daytime and nighttime because of the VOC-limited O_3 photochemistry and stronger NO titration at nighttime in January. In addition, hourly O_3 mixing ratios are much lower at Garinger and Raleigh at 4-km than those at 12-km mainly because simulated T1.5 values are much lower at 4-km than at 12-km during January 8–12 (see Figure S-8). Compared with other sites, the interplay between meteorology and chemistry is different at Castle Hayne, because of a lack of large NO_x and VOC sources, and the effect of sea-breeze near the coast and its sensitivity to grid resolution, leading to lower O_3 mixing ratios than urban sites and a different pattern of O_3 temporal variations at 4- and 12-km (e.g., hourly O_3 during some hours at 4-km are higher than those at 12-km, due likely to a lower daytime mixing height simulated at 4-km than that at 12-km). Compared with observations, CMAQ with both grid resolutions performs relatively well in terms of diurnal O_3 variations and the O_3 magnitudes at Raleigh and Garinger in July. The observed O_3 temporal variations and daytime values at Bryson city and Castle Hayne are captured but the nighttime O_3 values at both sites are significantly overpredicted. This is likely caused by a relatively poor representation of the nocturnal PBL and insufficient titration by NO at night at both sites. While the 12-km simulation reproduces daytime values better at both sites, the 4-km simulation reproduces nighttime values better at Garinger and Raleigh.

3.2.2. $PM_{2.5}$ concentrations

As also shown in Fig. 2, the simulated highest 24-h average $PM_{2.5}$ concentrations (12–25 μg m^{-3}) at both 12- and 4-km in January occur in central and eastern NC where the NH_3 concentrations are high due to high NH_3 emissions from animal feeding operations, making this area sulfate-poor (Wu et al., 2008b). Under such conditions, NH_3 concentrations are neutralized by both sulfuric acid (H_2SO_4) and nitric acid (HNO_3), leading to high NH_4^+ and NO_3^- in the area, particularly in winter when the photochemical production of H_2SO_4 is the lowest and the low temperatures favor the NO_3^- formation. For the same reasons, NH_4^+, NO_3^-, and OM dominate $PM_{2.5}$ in winter (Wu et al., 2008a). Simulated $PM_{2.5}$ and its major components (i.e., NO_3^-, SO_4^{2-}, NH_4^+, EC, and OM) (see Figure S-9) at 4-km have overall similar distributions to those at 12-km in January, although lower (e.g., by 10–30% for $PM_{2.5}$ and NH_4^+, more than 30% for NO_3^-, more than 10% for EC, and 10–40% for OM) concentrations at 4-km are found for all species expect for SO_4^{2-} (higher by 5%) in the mountain areas. The NMBs and NMEs of $PM_{2.5}$ in January at 4- and 12-km are in the range of 4.8–25.9% and 27.6–38.5%, respectively. The model performance for $PM_{2.5}$ in winter is better than that in summer, consistent with Wu et al.

Table 2
Performance statistics of max 1-h and 8-h mixing ratios of O_3.[a]

		AIRS-AQS					CASTNET				
		Data#	NMB	NME	MNB	MNE	Data#	NMB	NME	MNB	MNE
January											
Max 1-h O_3	4-km	175	2.1	17.7	8.5	23.1	210	1.2	15.3	2.7	16.7
	12-km	175	2.2	17.8	8.1	23.0	210	−1.6	17.3	0.1	18.8
Max 8-h O_3	4-km	175	4.6	18.5	10.2	23.0	210	9.1	17.6	17.0	25.1
	12-km	175	3.2	18.3	8.4	22.5	210	6.2	18.2	13.5	25.1
July											
Max 1-h O_3	4-km	2120	−13.5	16.9	−11.2	16.1	216	−18.7	20.6	−16.5	19.2
	12-km	2120	−10.6	15.1	−8.2	14.6	216	−17.6	20.3	−15.2	19.0
Max 8-h O_3	4-km	2120	−10.6	15.7	−7.7	15.4	216	−9.8	17.2	−5.6	17.4
	12-km	2120	−5.7	13.9	−2.6	14.2	216	−8.2	17.3	3.8	18.0

[a] NMB −normalized mean bias, %, NME − normalized mean error, %, MNB − mean normalized bias, %, MNE − mean normalized error, %.
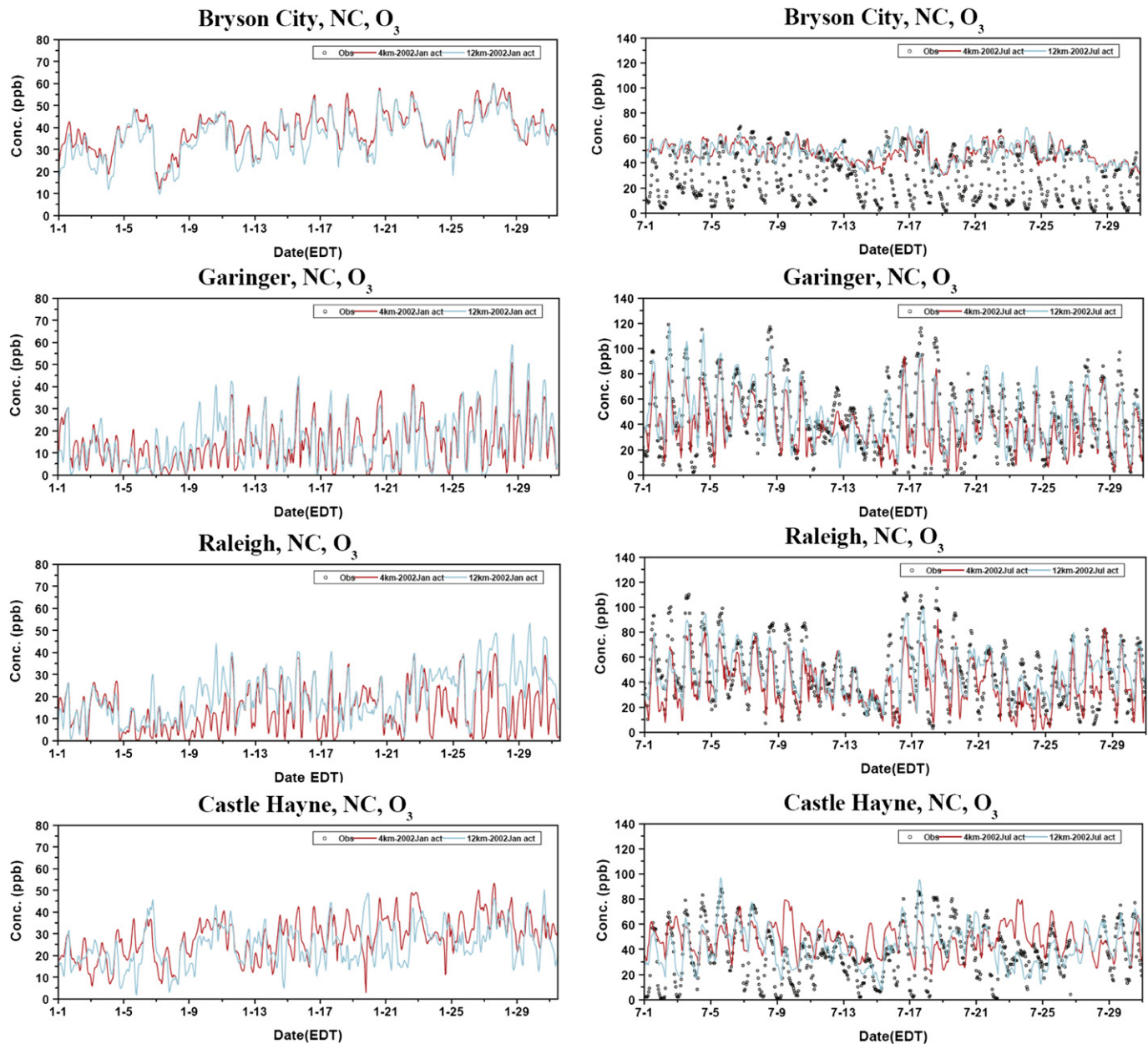
Fig. 2. Temporal variations of O_3 at 4 sites in NC in January and July 2002.

(2008a) and Morris et al. (2005). Among PM components, the largest biases and errors occur for NO_3^- (e.g., up to 117.7% for NMB, 143.8% for NME, 154.3% for MNB, and 178.6 for MNE at 4-km). Larger NMBs occur for $PM_{2.5}$ species at the AIRS-AQS and STN sites than the CASTNET and IMPROVE sites, indicating a possibility of underestimation in emissions of primary $PM_{2.5}$ and precursors of secondary $PM_{2.5}$ in the urban areas.

Simulated distributions of $PM_{2.5}$ and its composition at 12- and 4-km in July are very different from those in January (Fig. 1 and Figure S-10). The highest 24-h average $PM_{2.5}$ level occurs in the west side of the Appalachian Mountains in KY and TN in July ($13-25\ \mu g\ m^{-3}$) and higher $PM_{2.5}$ concentrations also occur over the central NC. Coastal plain and the mountain areas in the southwest corner of NC have relatively lower $PM_{2.5}$ throughout the domain. Both SO_4^{2-} and $PM_{2.5}$ show the highest concentrations in the western domain and the lowest in the coastal area, because of the abundance of SO_2 in the western domain. For the same reason

stated previously, both NH_4^+ and NO_3^- have the high concentrations in the eastern and southeast corner of NC, which are somewhat different from the spatial distributions of $PM_{2.5}$ and SO_4^{2-}. In addition, high NH_4^+ also occurs in the central and northwest NC and the west side of Appalachian Mountains. While relatively high NH_3 emissions are neutralized by H_2SO_4 to form ammonium sulfate $((NH_4)_2SO_4)$ locally in the west part of the mountain areas, the high NH_4^+ for the central and northwest NC is mostly resulted from the long range transport of NH_4^+ from the eastern NC (Queen and Zhang, 2008a; Wu et al., 2008a). Compared with January, larger differences exist in the spatial distributions of $PM_{2.5}$ and SO_4^{2-} simulated at 12- and 4-km. Simulated $PM_{2.5}$ concentrations at 12-km in July are higher in most NC than at 4-km, especially in the Piedmont area (by >10%). The 12-km simulation performs slightly better than 4-km in July. Opposite results are found in the west side of mountain areas in KY where the 4-km simulation gives higher $PM_{2.5}$ concentrations than 12-km that are in better agreement with

Table 3
Performance statistics of 24-h average concentrations of $PM_{2.5}$ and its components.[a,b,c]

		AIRS-AQS					STN					CASTNET					IMPROVE				
		Data#	NMB	NME	MNB	MNE	Data#	NMB	NME	MNB	MNE	Data#	NMB	NME	MNB	MNE	Data#	NMB	NME	MNB	MNE
January																					
$PM_{2.5}$	4-km	750	8.6	34.9	14.6	38.2	51	15.6	38.5	23.4	43.4	–	–	–	–	–	35	17.1	27.6	27.2	39.2
	12-km	750	4.8	32.3	9.1	34.3	51	8.3	33.3	14.8	36.6	–	–	–	–	–	35	25.9	32.0	41.8	48.0
NH_4^+	4-km	48	36.6	59.9	67.3	82.5	54	61.0	84.5	95.0	109.4	27	−0.5	26.8	−0.2	26.5	–	–	–	–	–
	12-km	48	30.5	53.4	56.5	71.7	54	55.2	77.8	82.4	96.7	27	6.0	25.2	7.9	24.7	–	–	–	–	–
SO_4^{2-}	4-km	48	−24.9	35.9	−16.9	33.3	54	−19.0	39.6	−7.1	38.9	27	−15.7	24.0	−11.1	22.0	35	6.1	27.8	17.5	35.1
	12-km	48	−34.0	39.2	−26.7	33.3	54	−25.8	39.9	−14.3	36.0	27	−19.2	25.1	−14.6	23.2	35	7.1	34.6	18.2	38.0
NO_3^-	4-km	48	76.9	106.6	91.7	125.9	54	117.7	143.8	154.3	178.6	27	16.2	64.7	59.3	91.8	35	65.2	119.1	70.5	144.5
	12-km	48	74.6	101.8	88.5	121.7	54	112.8	137.6	141.9	169.3	27	33.4	70.7	110.5	132.5	35	53.8	91.5	52.5	115.9
EC	4-km	–	–	–	–	–	54	−15.8	39.0	3.9	37.1	–	–	–	–	–	35	−1.2	34.2	10.1	43.7
	12-km	–	–	–	–	–	54	−16.0	40.8	4.6	39.2	–	–	–	–	–	35	17.5	43.0	33.7	57.8
OM	4-km	–	–	–	–	–	54	−41.1	47.4	−31.5	42.9	–	–	–	–	–	35	−4.2	30.1	18.8	49.2
	12-km	–	–	–	–	–	54	−42.5	46.0	−33.2	40.5	–	–	–	–	–	35	10.0	35.3	41.9	41.9
July																					
$PM_{2.5}$	4-km	756	−48.3	49.2	−43.9	46.3	84	−49.1	50.9	−44.1	47.6	–	–	–	–	–	35	−57.8	59.3	−50.6	56.4
	12-km	756	−45.4	46.1	−41.3	43.5	84	−46.9	47.0	−46.9	47.0	–	–	–	–	–	35	−51.2	52.8	−45.1	51.1
NH_4^+	4-km	78	−45.6	47.8	−34.9	40.2	88	−44.4	48.4	−34.1	42.7	28	−53.4	53.4	−49.7	49.7	9	−51.3	55.1	−34.7	48.1
	12-km	78	−42.6	44.5	−33.8	38.2	88	−43.4	45.8	−43.4	45.8	28	−52.6	52.8	−48.4	49.4	9	−48.4	49.6	−36.2	40.5
SO_4^{2-}	4-km	78	−33.0	39.3	−27.5	36.8	88	−31.0	38.9	−26.9	38.5	28	−27.1	28.0	−25.5	26.8	36	−36.9	41.8	−28.2	38.4
	12-km	78	−22.0	29.9	−18.4	28.7	88	−19.7	31.3	−17.1	31.3	28	−17.6	19.8	−14.6	17.9	36	−22.2	32.2	−13.7	32.2
NO_3^-	4-km	78	−84.4	84.4	−82.6	82.6	88	−89.3	89.3	−89.2	89.2	28	−69.4	88.5	−37.2	86.3	36	−72.3	102.4	−80.8	100.0
	12-km	78	−88.1	88.1	−87.0	87.0	88	−91.2	91.2	−90.3	90.3	28	−78.6	83.2	−53.5	70.3	36	−80.4	100.2	−97.2	99.8
EC	4-km	–	–	–	–	–	87	32.7	81.3	108.7	144.3	–	–	–	–	–	33	−39.4	62.5	32.6	124.2
	12-km	–	–	–	–	–	87	20.4	81.1	92.1	136.8	–	–	–	–	–	33	−37.5	60.0	33.4	119.8
OM	4-km	–	–	–	–	–	87	−68.1	70.2	−60.5	70.4	–	–	–	–	–	33	−64.1	69.4	−57.2	70.7
	12-km	–	–	–	–	–	87	−70.9	71.5	−66.5	70.2	–	–	–	–	–	33	−64.9	69.3	−59.8	70.3

[a] NMB − normalized mean bias, %, NME − normalized mean error, %, MNB − mean normalized bias, %, MNE − mean normalized error, %.
[b] AIRS-AQS includes some data from STN at some sites. For completeness, observed data from both STN and AIRS-AQS are included.
[c] "−" Indicates no observational data are available for model evaluation.

observed high PM$_{2.5}$ concentrations in this area. As a dominant component of PM$_{2.5}$ in July, simulated SO$_4^{2-}$ concentrations at 12-km are 10–20% higher than those at 4-km over most NC and ∼10% lower than those at 4-km in KY, which is similar to PM$_{2.5}$. For NH$_4^+$, the 12-km simulation shows higher concentrations throughout most NC and SC but lower values in the west side of mountains in KY and TN. The 4-km simulation gives higher NO$_3^-$ over the central NC and in the west side of Appalachian Mountains in TN but lower values in other mountain areas. Compared with observations (see Table 3), the 4-km simulations give slightly worse performance in PM$_{2.5}$, SO$_4^{2-}$, NH$_4^+$, and EC at all sites, but slightly better performance in NO$_3^-$ and OM at all sites than that at 12-km. These results are generally better or consistent with other modeling studies. For example, Morris et al. (2005) used the an older version of 2002 emissions from VISTAS/ASIP at 12-km and underpredicted NO$_3^-$ in summer by more than 100% and about 100% for OC in the southeastern U.S. OC concentrations are significantly underpredicted despite the use of an improved treatment of SOA in the simulations conducted in this work, indicating the importance of additional precursors and pathways for SOA formation. PM$_{2.5}$ and its secondary components exhibit an overall higher sensitivity to horizontal grid resolutions, particularly in the Piedmont and mountain areas.

Fig. 3 shows simulated vs. observed hourly PM$_{2.5}$ concentrations at 4- and 12-km at the 4 sites in NC. Simulated PM$_{2.5}$ concentrations are the highest either at Garinger or Raleigh and the lowest at Bryson City in both months. The observed diurnal variations in January at Raleigh and Garinger are overall well reproduced, although overpredictions occur on most days, due in part to the larger cold bias in January, particularly during 8–11 January at 4-km. The simulated hourly PM$_{2.5}$ concentrations in July are underpredicted at all 4 sites, especially at the mountain site, Bryson City, with elevation of 534 m. Raleigh and Garinger have slightly better agreement with observations in terms of temporal variations and magnitudes. At Castle Hayne, CMAQ reproduces the same magnitude of PM$_{2.5}$ on several days but underpredicts it during the rest of the days in July. Several reasons may cause the dominant underpredictions in PM$_{2.5}$ in July including large overpredictions (by 72.9%) in precipitation, inaccuracies in emissions of primary PM$_{2.5}$ such as EC and primary OM and gaseous precursors of secondary PM$_{2.5}$ such as VOCs, NO$_x$, and NH$_3$ as reported in several studies (e.g., Wu et al., 2008b; Liu et al., submitted for publication), small overpredictions in T1.5 and underpredictions in RH1.5, as well as difficulties in resolving complex meteorology and geography over the domain (e.g., the effects of small-scale sea breezes; the mix of costal, Piedmont, and mountain areas). For example, dozens of forest fires in Quebec occurred during the first week of July 2002 destroyed more than 250,000 acres of forest and generated large amounts of smoke that were transported to many areas in the eastern U.S. While such fire emissions may have contributed to higher PM$_{2.5}$ observed in NC (e.g., Bryson city, Castle Hayne, and Raleigh), they may not be accurately represented in the forest fire emissions in the VISTAS/ASIP inventories. Significant underpredictions for PM$_{2.5}$ at Bryson City and Castle Hayne indicate that CMAQ performs relatively poor over the mountain and coastal areas. The vertical mixing usually has a significant impact on PM$_{2.5}$, but this is unlikely a factor for PM$_{2.5}$ underpredictions for July 2002, because CMAQ tends to have a weaker vertical mixing than the actual observations over the southeastern U.S. In addition to large overpredictions in precipitation, the underestimation in emissions over the source regions may be another important factor causing underestimated PM$_{2.5}$ over the mountain and coastal areas through horizontal and vertical transport and/or sea/land-breeze processes. On the other hand, uncertainties may also exist in the measurement methods used for PM$_{2.5}$ and components. For example,

the federal reference method (FRM) is used to obtain 24-h average PM$_{2.5}$ concentrations at the STN and IMPROVE sites, and the Tapered Element Oscillating Microbalance (TEOM) method is used by NCDENR for hourly PM$_{2.5}$ concentrations. The differences between PM$_{2.5}$ observations (in particular, semi-volatile nitrate or OC) measured by the two methods can be quite large and may vary from site to site (Allen et al., 1997).

3.2.3. Visibility and extinction coefficient

CMAQ calculates two PM visibility indices, haziness in terms of deciview (DCV) and extinction coefficient (EXT), based on two methods: an approximation to Mie theory and a mass reconstruction technique, referred to as DCV_Mie and EXT_Mie, and DCV_Recon and EXT_Recon, respectively. Similar to PM$_{2.5}$ shown in Fig. 1, visibility indices are very sensitive to horizontal grid resolutions (Fig. 4 and Table 4). Compared with the 12-km simulation, the 4-km simulation gives 4–16% and 12–50% higher DCV and EXT, respectively, over most of the domain except for some mountain and Piedmont areas in January and 4–20% and 12–40% lower DCV and EXT, respectively, over most of the domain except for the mountain areas in KY and some coastal areas in July. The model performs worse at 4-km for EXT_Recon and but slightly better DCV_Recon in January and slightly worse for EXT_Recon and DCV_Recon in July than at 12-km. The spatial distributions of simulated EXT_Mie and DCV_Mie are overall similar to those of EXT_Recon and DCV_Recon at 4- and 12-km for both months. Compared with predictions at 12-km, higher PM$_{2.5}$ concentrations at 4-km at sites with observed visibility indices in January lead to higher EXT, and thus greater overpredictions.

3.2.4. Dry and wet deposition

Dry deposition fluxes are proportional to the ambient concentrations and dry deposition velocities (V_d) of species. V_d is a strong function of aerodynamic, quasi-laminar, and surface resistances (where surface resistance consists of cuticle, stomatal, and water surface resistances) that depend highly on the surface characteristics (e.g., surface types, moisture, and roughness), PBL processes (e.g., heat, momentum, and turbulent transport, molecular or Brownian diffusion), and PBL meteorological variables (e.g., wind speed, temperature, radiation, and atmospheric stability). Simulations at different grid resolutions cause differences in simulated concentration, surface characteristics, and meteorology which in turn affect predictions of V_d and dry deposition fluxes. As expected, simulated monthly-mean hourly dry deposition fluxes are sensitive to grid resolution, particularly in the mountain and coastal areas in January, with much higher values at 4-km for NH$_4^+$, SO$_4^{2-}$, and NO$_3^-$ (Fig. 5). The higher sensitivity in January is because of dominancy of the impact of surface characteristics and meteorological predictions over that of concentrations under winter conditions. By contrast, photochemistry dominates in July, leading to an overall similarity in the simulated spatial distributions of dry deposition amounts at 12- and 4-km, with higher NH$_{4, dry}^+$ and NO$_{3, dry}^-$ at 4-km but higher SO$_{4, dry}^{2-}$ at 12-km.

Measurement data for V_d and dry deposition fluxes are sparse, due mainly to several complicating factors including their dependence on characteristics of various surfaces (e.g., the leaf stomata of the vegetation cover, soils, water, and snow and ice sheets) and various atmospheric processes (e.g., chemical reactions, radiation, turbulence, and precipitation), bidirectional (instead of uni-directional) nature of the fluxes for some species such as NH$_3$, NO$_x$, and H$_2$S, as well as uncertainties associated with and assumptions underlying existing measurement methods. The only observations available for NH$_3$ in NC were 2.41 and 0.19 cm s^{-1} for V_d during day and night, respectively, and 7.2 × 10^{-4} kg ha^{-1} day^{-1} for NH$_{3, dry}$ in winter and 3.94 and 0.76 cm s^{-1} for V_d during day and night,
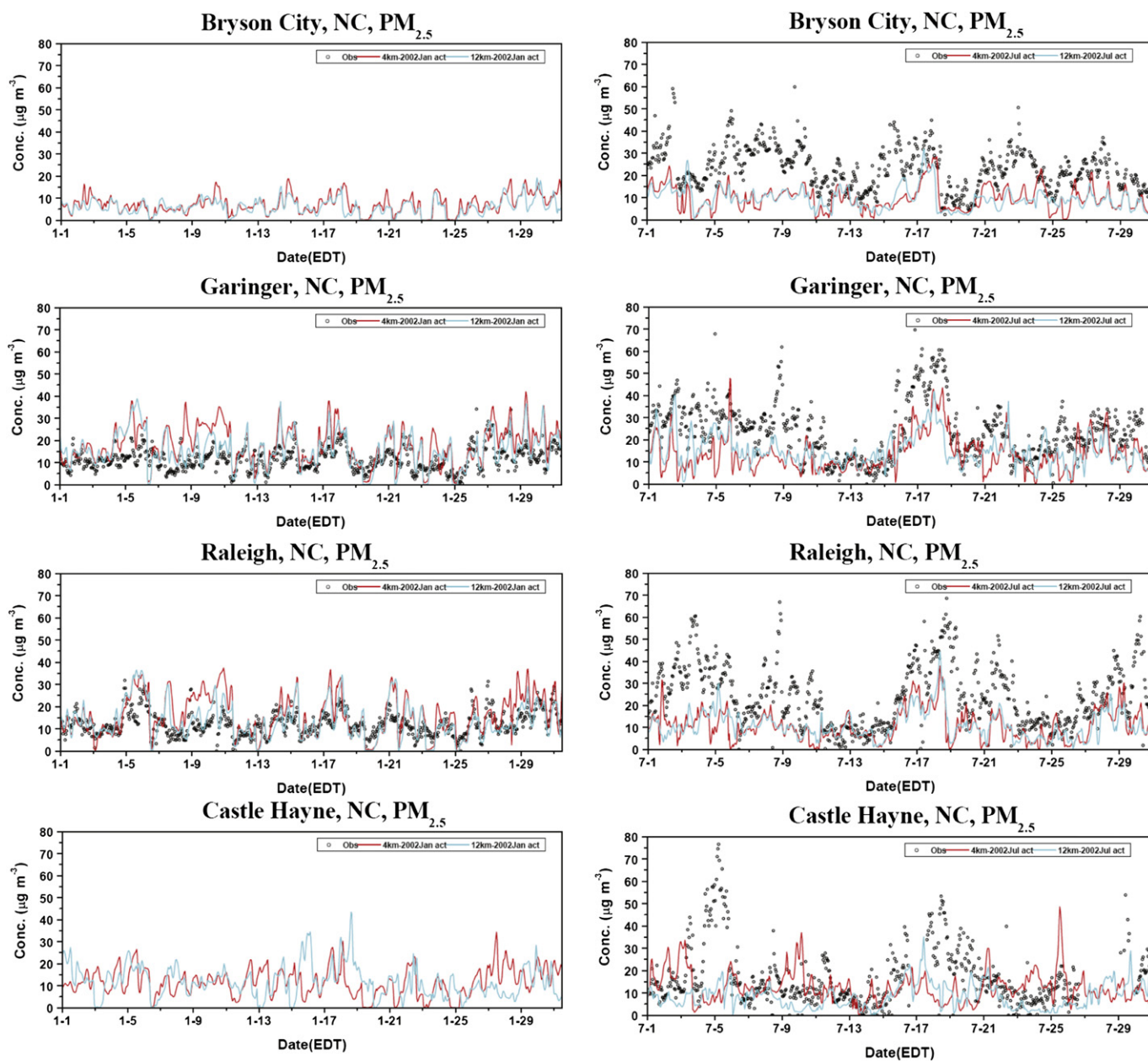
Fig. 3. Simulated vs. observed PM$_{2.5}$ temporal variations at 4 sites in NC in January and July 2002 from the 4-km simulations. No observations are available at Bryson City and Castle Hayne in January.

respectively, and 9.7×10^{-3} kg ha^{-1} day^{-1} for NH$_{3, \, dry}$ in summer at Raleigh in Phillips et al. (2004). For comparison, simulated V_d for NH$_3$ are 1.84 and 1.22 cm s^{-1} during daytime and 1.0 and 0.6 cm s^{-1} at night in January, and 2.18 and 2.09 cm s^{-1} during daytime and 1.40 and 1.06 cm s^{-1} at night in July for 4- and 12-km, respectively. Simulated NH$_{3, \, dry}$ are 3.4×10^{-4} and 2.6×10^{-4} kg ha^{-1} day^{-1} in January and 1.18×10^{-3} and 8.5×10^{-4} kg ha^{-1} day^{-1} in July for 4- and 12-km, respectively. In addition to aforementioned uncertainties in simulating V_d and NH$_{3, \, dry}$, the measurements were taken at natural surfaces near animal farms, waste storage, and lagoons with very high NH$_3$ emissions, for which CMAQ at 4-km cannot well reproduce and a finer grid resolution is needed. MLM uses the inferential method of Clarke et al. (1997) to estimate dry deposition fluxes of species based on CASTNET meteorological and chemical measurements. As shown in Figure S-11, large differences

exist between MLM and CMAQ predictions of dry deposition of fluxes of PM components, particularly NO$_3^-$, at two sites: Beaufort (BFT) and Coweeta (COW), NC, due to differences in the V_d of NO$_3^-$ used by both models. More detailed analysis is given in the supplementary data.

Wet deposition predictions are highly sensitive to horizontal grid resolution throughout the domain in both months, with higher values in January and lower values in July at 4-km (Fig. 6 and Table 4). Among the three species, NO$_{3, \, wet}^-$ has the highest sensitivity. Compared with observations, simulations at 4-km perform worse for all wet deposition amounts in January and better for NH$_{4, \, wet}^+$ and NO$_{3, \, wet}^-$ in July than at 12-km. The model performance is overall consistent with Queen and Zhang (2008b) who attributed similar performance to seasonalities in meteorology and different land use and emissions between different grid resolutions.
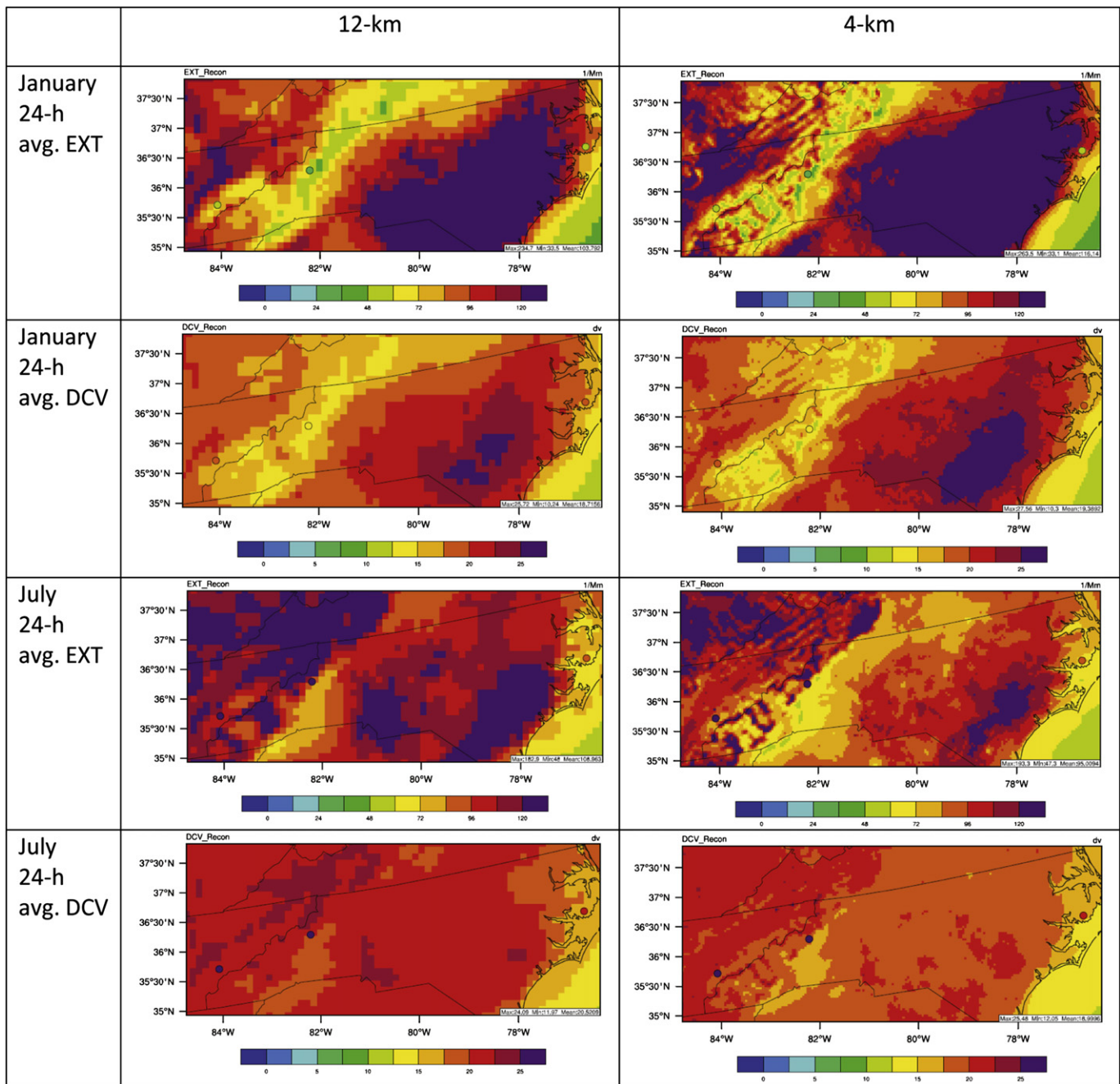
Fig. 4. Simulated vs. observed (diamond symbol) monthly-mean 24-h average extinction coefficient (EXT_Recon) and deciview (DCV_Recon) in January and July 2002.

4. Comparison between 2002 actual and typical simulations

Although the fire and EGUs emissions are different between 2002 actual and typical simulations, the simulated spatial distributions of monthly-mean max 1-h and 8-h O₃, PM₂.₅, PM₂.₅, PM₂.₅ components, visibility indices, and dry and wet deposition amounts are overall similar in both January and July (figures not shown). For example, the differences in monthly-mean concentrations are within 1% for O₃, 4.5% for PM₂.₅, and 6.6% for PM components. The small difference between the typical and actual simulations indicates an overall good representation of typical emissions of the actual emissions for this particular episode. In Part II paper (Zhang et al., in press), the results from the 2002 simulations with typical emissions are used as a basis to project future emissions and the impact of emission control on future air quality.

5. Summary

The January and July 2002 MM5 evaluation shows model skills in reproducing meteorological variables that are consistent with the current meteorological model performance. Compared to the 12-km MM5 simulation, the 4-km simulation shows overall similar spatial distributions for major meteorological variables but differences are evident for RH1.5 and WSP10 in Piedmont and coastal areas in both months and for precipitation in mountain and coastal plain areas in January. The 4-km simulation gives slightly better agreement for T1.5 in January and July at all sites, WDR10 in January at the CASNET sites, RH1.5 in January at the SCO sites, and precipitation in July at the NADP sites, but overall slightly worse performance than 12-km. The model is noticeably cold biased in January, particularly at 4-km, with slightly better agreement at the CASTNET

Table 4
Performance statistics of weekly total wet deposition amounts of PM$_{2.5}$ components and 24-h average visibility indices.[a,b]

		NADP					IMPROVE				
		Data#	NMB	NME	MNB	MNE	Data#	NMB	NME	MNB	MNE
January											
NH$_{4,\ wet}^{+}$	4-km	41	34.1	90.4	144.3	174.7	–	–	–	–	–
	12-km	41	−14.9	66.2	56.1	114.5	–	–	–	–	–
SO$_{4,\ wet}^{2-}$	4-km	41	37.3	55.0	62.6	73.0	–	–	–	–	–
	12-km	41	−17.8	43.8	−1.1	51.1	–	–	–	–	–
NO$_{3,\ wet}^{-}$	4-km	41	89.1	102.3	149.6	157.2	–	–	–	–	–
	12-km	41	16.0	61.5	56.5	94.6	–	–	–	–	–
EXT_Recon	4-km	–	–	–	–	–	28	22.4	48.6	20.2	43.8
	12-km	–	–	–	–	–	28	0.9	26.3	2.7	25.1
DCV_Recon	4-km	–	–	–	–	–	28	−15.0	26.3	−17.6	27.9
	12-km	–	–	–	–	–	28	−19.6	22.3	−21.3	23.6
July											
NH$_{4,\ wet}^{+}$	4-km	41	−20.6	58.4	10.0	73.3	–	–	–	–	–
	12-km	41	−41.2	48.1	−9.0	66.8	–	–	–	–	–
SO$_{4,\ wet}^{2-}$	4-km	48	27.4	76.4	49.9	102.8	–	–	–	–	–
	12-km	48	−19.3	45.1	−4.2	48.5	–	–	–	–	–
NO$_{3,\ wet}^{-}$	4-km	44	−44.4	62.8	−25.8	79.7					
	12-km	44	−69.1	69.9	−61.5	65.2					
EXT_Recon	4-km	–	–	–	–	–	22	−47.4	52.6	−36.5	47.0
	12-km	–	–	–	–	–	22	−46.9	50.2	−37.8	44.2
DCV_Recon	4-km	–	–	–	–	–	22	−34.8	35.4	−33.0	33.8
	12-km	–	–	–	–	–	22	−31.7	31.9	−30.8	31.1

[a] NMB − normalized mean bias, %, NME − normalized mean error, %, MNB − mean normalized bias, %, MNE − mean normalized error, %.

[b] "−" Indicates no observational data are available for model evaluation.

sites but larger cold bias at the SCO sites at 4-km, likely due to too cold soil temperatures and poor treatments of snow related processes. Simulations at both grid resolutions grossly overpredict precipitation in July, with the 4-km simulations give larger underpredictions in January but slightly less overpredictions, due likely to too frequent afternoon convective rainfall and/or an overestimation in the intensity of the rainfall. While synoptic features are generally reproduced, temporal variations of T1.5 at a local scale in central NC on some days are not well reproduced because of inaccuracies in snow cover. Compared to the 12-km simulation, the 4-km simulation gives similar temporal variations but worse performance on a few days for some variables (e.g., T1.5 during 8−12 January at Candor and Raleigh). The temporal variations of WSP10 and WDR10 are biased high, particularly in the mountain areas.

The evaluation of CMAQ results with actual emissions shows a reasonably good performance, with the NMBs/MNBs within ±18.7% and NMEs/MNEs within ±20.6% for max 1-h and 8-h O$_3$ mixing ratios and relatively small sensitivity to grid resolution in both January and July. The 4-km simulation in January captures the high O$_3$ values over the Knoxville area, which are underpredicted at 12-km. Its statistical performance is slightly better for max 1-h O$_3$ but slightly worse for max 8-h O$_3$ than that at 12-km. The July 4-km simulation gives a slightly worse O$_3$ performance than that at 12-km. The model predictions show higher sensitivity to the horizontal grid resolution for O$_3$ mixing ratios over the western domain in January and the central and eastern domain in July. Compared with observations, CMAQ performs relatively well in terms of diurnal variations and magnitudes of O$_3$ at Raleigh and Garinger in July. The observed O$_3$ temporal variations and daytime values are captured but the nighttime O$_3$ values are significantly overpredicted at both mountain and coastal sites. This is likely caused by a relatively poor representation of the nocturnal PBL and insufficient titration by NO at night.

The model performance for PM$_{2.5}$ in winter is better than that in summer. Overpredictions in PM$_{2.5}$ occur in January, with NMBs of 8.6−17.1% and NMEs of 27.6−34.9% at 4-km. Underpredictions occur in July, with NMBs of −57.8% to −48.3% and NMEs of 49.2−59.3% at 4-km. For PM$_{2.5}$ components, CMAQ at 4-km

performs the best for SO$_4^{2-}$ with NMBs of −24.9% to 6.1%, and the worst for NO$_3^-$ with NMBs of 16.2−117.7% in January; significant underpredictions occur for all major PM$_{2.5}$ composition in July. Larger absolute NMBs occur for all PM$_{2.5}$ species at the AIRS-AQS and STN sites than the CASTNET and IMPROVE sites in January, indicating larger uncertainties in emissions of primary PM$_{2.5}$ and precursors of secondary PM$_{2.5}$. Underestimations in emissions of precursors of O$_3$ and secondary PM$_{2.5}$ such as VOCs, NO$_x$, and NH$_3$ and overpredictions in precipitation in summer are likely the main sources of model biases. Larger sensitivity to horizontal grid resolution is found over the entire domain in January and in the western domain in July. Compared to the 12-km simulation, the 4-km simulation gives better performance for SO$_4^{2-}$ in January and for NO$_3^-$ in July at the AIRS-AQS sites, for NH$_4^+$, SO$_4^{2-}$, and NO$_3^-$ in January and for NO$_3^-$ in July at the CASTNET sites, for PM$_{2.5}$, SO$_4^{2-}$, EC, and OM in January and NO$_3^-$ and OM in July at the IMPROVE sites, for OM in January and for NO$_3^-$ and OM in July at the STN sites. The observed diurnal variations in January at Raleigh and Garinger are overall well reproduced, although overpredictions occur on most days, particularly during January 8−11 at 4-km. The simulated hourly PM$_{2.5}$ concentrations in July are underperdicted at all 4 sites. CMAQ has a relatively good agreement at urban and rural sites but significantly underpredicts PM$_{2.5}$ at the mountain and costal sites. Results at 4- and 12-km are overall similar at most sites during most of time, but the 4-km simulation gives better agreement to observations on some days.

Visibility indices and dry and wet deposition are very sensitive to horizontal grid resolution. Compared with results at 12-km, the 4-km simulation gives higher values of EXT and DCV in January but lower values in July, with a worse performance for EXT in both months and for DCV in Jul. For dry deposition, CMAQ gives lower dry deposition amounts than MLM, due mainly to lower V_d of species. Simulated dry deposition amounts show higher sensitivity to horizontal grid resolution in January than July, with higher values at 4-km for all species except for SO$_{4,\ dry}^{2-}$ in July. For wet deposition, SO$_{4,\ wet}^{2-}$ is overpredicted in both January and July, NH$_{4,\ wet}^+$ and NO$_{3,\ wet}^-$ are overpredicted in January but underpredicted in July. The 4-km simulation gives better performance for wet
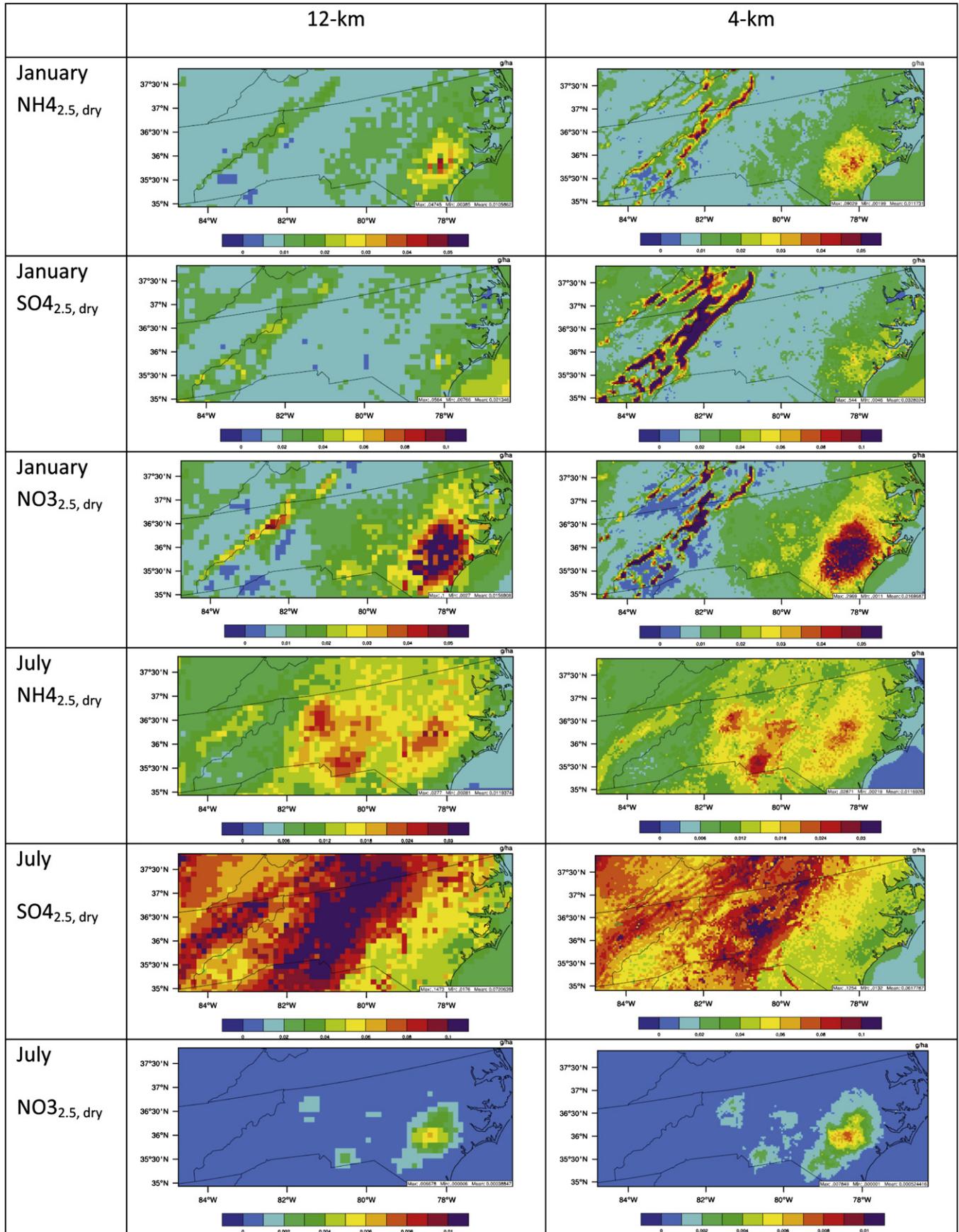
Fig. 5. Simulated monthly-mean hourly dry deposition of $PM_{2.5}$, NH_4^+, SO_4^{2-}, and NO_3^- in January and July 2002.
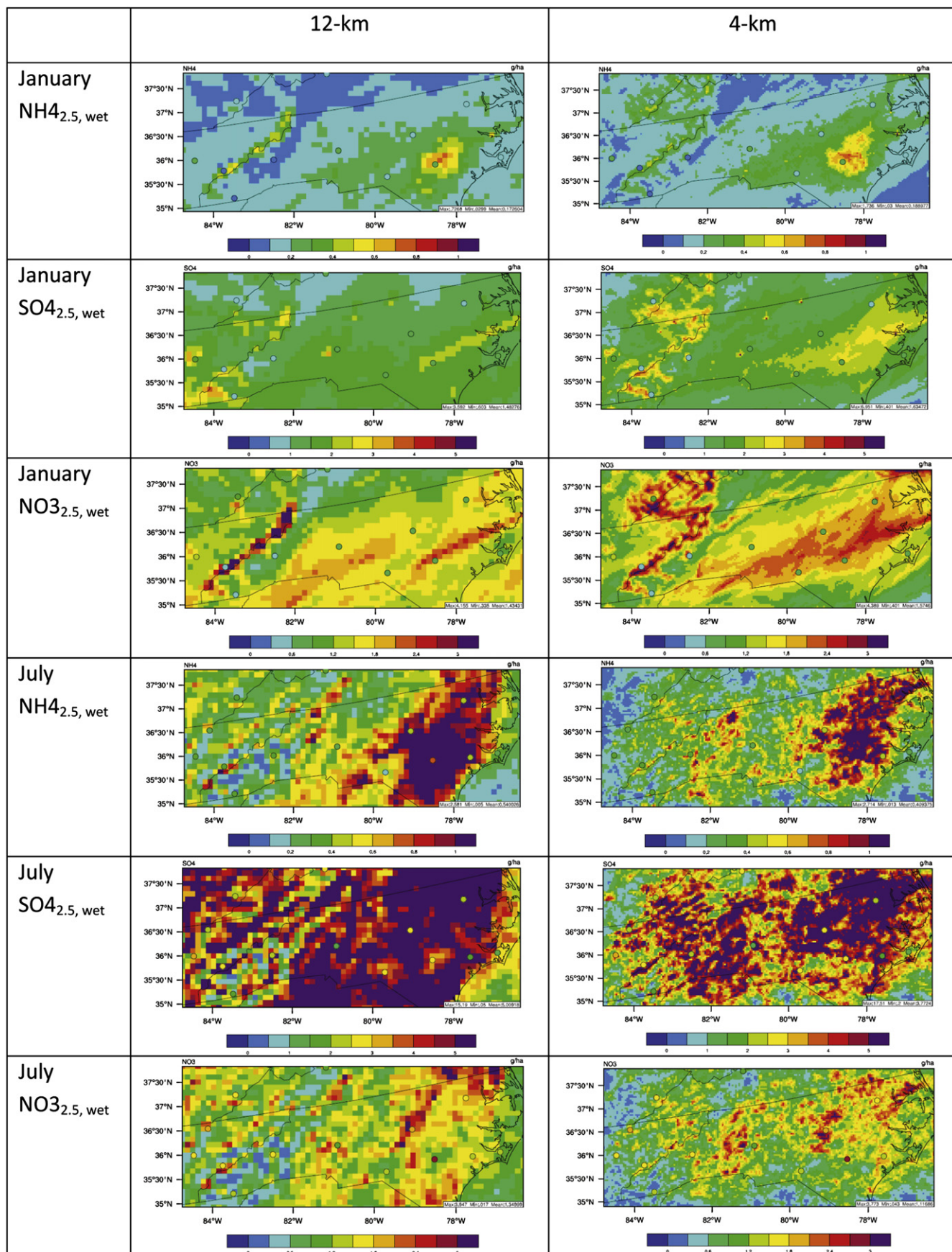
Fig. 6. Simulated vs. observed (diamond symbol) monthly-mean hourly wet deposition of $PM_{2.5}$, NH_4^+, SO_4^{2-}, and NO_3^- in January and July 2002.

deposition of NH_4^+ and NO_3^- but worse performance for wet deposition of SO_4^{2-} in July and for those of all species in January. Compared with the 12-km simulation, the 4-km simulation gives higher wet deposition values in January but lower values in July, with $NO_{3,\ wet}^-$ having the highest sensitivity to gird resolution.

Appendix. Supplementary information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2010.04.002.

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