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Modeling atmospheric transport and fate of ammonia in North Carolina—Part II: Effect of ammonia emissions on fine particulate matter formation

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Abstract

Accurate estimates of ammonia (NH_3) emissions are needed for reliable predictions of fine particulate matter ($PM_{2.5}$) by air quality models (AQMs), but the current estimates contain large uncertainties in the temporal and spatial distributions of NH_3 emissions. In this study, the US EPA Community Multiscale Air Quality (CMAQ) modeling system is applied to study the contributions of the agriculture–livestock NH_3 (AL-NH_3) emissions to the concentration of $PM_{2.5}$ and the uncertainties in the total amount and the temporal variations of NH_3 emissions and their impact on the formation of $PM_{2.5}$ for August and December 2002.

The sensitivity simulation results show that AL-NH_3 emissions contribute significantly to the concentration of $PM_{2.5}$, NH_4^+, and NO_3^-; their contributions to the concentrations of SO_4^{2-} are relatively small. The impact of NH_3 emissions on $PM_{2.5}$ formation shows strong spatial and seasonal variations associated with the meteorological conditions and the ambient chemical conditions. Increases in NH_3 emissions in August 2002 resulted in $>10\%$ increases in the concentrations of NH_4^+ and NO_3^-; reductions in NH_3 emissions in December 2002 resulted in $>20\%$ decreases in their concentrations. The large changes in species concentrations occur downwind of the high NH_3 emissions where the ambient environment is NH_3-poor or neutral. The adjustments in NH_3 emissions improve appreciably the model predictions of NH_4^+ and NO_3^- both in August and December, but resulted in negligible improvements in $PM_{2.5}$ in August and a small improvement in December, indicating that other factors (e.g., inaccuracies in meteorological predictions, emissions of other primary species, aerosol treatments) might be responsible for model biases in $PM_{2.5}$.

Keywords: Ammonia emissions; Agriculture; Livestock; $PM_{2.5}$; CMAQ; Sensitivity study

1. Introduction

Ammonia (NH_3) is an important pollutant that plays a key role in several air pollution problems. It can create odors and have negative impacts on animal and human health. When deposited to ecosystems, NH_3 may cause over-enrichment of

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nitrogen, decrease in biological diversity, damage to sensitive vegetations, and acidification of soils (Fangmeier et al., 1994; Van der Eerden et al., 1998). As the most abundant gas-phase alkaline species in the atmosphere, NH_3 can neutralize sulfuric acid and nitric acid to form fine particulate matter with an aerodynamic diameter $\leqslant 2.5\,\mu m$ ($PM_{2.5}$), which is closely linked to health and climatic effects. In addition, NH_3 likely plays an increased role in $PM_{2.5}$ formation as the emissions of sulfur oxides and nitrogen oxides are reduced and a more stringent 24-h average $PM_{2.5}$ standard of $35\,\mu g\,m^{-3}$ is promulgated by the United States (US) Environmental Protection Agency (EPA) (Zhang et al., 2007).

Sulfate (SO_4^{2-}) and nitrate (NO_3^-) aerosols are two major inorganic components of $PM_{2.5}$ in the eastern US (EPA, 1996). A recent study shows that for the eastern US, a reduction in sulfate dioxide (SO_2) may not be as effective as it is often assumed in reducing PM mass, as a reduction in SO_4^{2-} concentrations results in more free NH_3 available for reaction with nitric acid (HNO_3) to produce ammonium nitrate (NH_4NO_3) particles (West et al., 1999). The accuracy of NH_3 emissions can have a large effect on air quality model (AQM) predictions of aerosol SO_4^{2-}, NO_3^-, and ammonium (NH_4^+) concentrations (Mathur and Dennis, 2003). However, large uncertainties exist in NH_3 emission inventories in both total annual emissions and the monthly, daily, and diurnal variations, since NH_3 emissions are largely from non-point sources such as livestock operations and fertilized fields, all those sources are difficult to be directly measured (Pinder et al., 2006). Current seasonally varied NH_3 emission inventories have been developed using several advanced methods including inverse methods (e.g., Gilliland et al., 2003), process-base models (e.g., Pinder et al., 2004a, b), and hybrid approaches (e.g., Skjøth et al., 2004).

Major emission sources of NH_3 include animal and human wastes, synthetic fertilizers, biomass burning, and soil biogenic emissions (Bouwman et al., 1997) . North Carolina (NC) is one of the largest agricultural product states in the US, ranking the 2nd in hogs, 2nd in turkeys, and 5th in broilers. NH_3 emissions from hog farms account for more than 80% of total NH_3 emissions in NC (Wu et al., 2007). Most hog farms are located in the coastal plain region of the state or the southeast corner covering Bladen, Duplin, Greene, Lenoir, Sampson, and Wayne counties.

In this study, the atmospheric transport and fate of NH_3 are studied using a three-dimensional (3-D) transport and chemistry model. Part I of our studies (Wu et al., 2007) describes the model configurations, evaluation protocols and databases used, and the operational evaluation for meteorological and chemical predictions. In Part II, we describe the sensitivity simulations under various emission scenarios. Our objectives are to quantify the contribution of NH_3 emissions to the formation of $PM_{2.5}$ and its composition and assess the uncertainties in the total amount and temporal variations of NH_3 emissions and their impact on $PM_{2.5}$ predictions.

2. NH_3 emission inventories and sensitivity simulation design

2.1. Baseline NH_3 emission inventories

The baseline simulations at a 4-km grid spacing are conducted for August and December 2002 using the 5th Generation Penn State/NCAR Mesoscale Model (MM5) version 3.7, the Carolina Environmental Program's (CEP) sparse matrix operation emission (SMOKE) modeling system version 2.1, and the US EPA Models-3 Community multiscale air quality (CMAQ) modeling system version 4.4. Detailed configurations can be found in Wu et al. (2007). The baseline 4-km emissions are generated based on the NH_3 emission inventory developed under the Visibility Improvement State and Tribal Association of the Southeast (VISTAS) program (http://www.vista-sesarm.org.asp) (referred to as NH_3-VISTAS hereafter). The Carnegie Mellon University (CMU) NH_3 model version 3.6 is used to calculate NH_3 emissions in NH_3-VISTAS that have been improved from previous emission estimates based on the EPA 1999 National Emission Inventories version 2 with activity and growth data of CMU NH_3 model version 3.1 (Abraczinskas, 2005). NH_3-VISTAS uses the United State Department of Agriculture (USDA) 2002 census county-level livestock amounts and process-level distribution for dairy cattle, beef cattle, swine, goats, poultry, and turkeys for livestock activity levels, and the 2002 fertilizer application activity data of the Association of American Plant Food Control Officials. Other NH_3 sources (e.g., waste treatments, motor vehicles, etc.) are described in CMU model by Strader et al. (2005). NH_3-VISTAS includes all NH_3 sources except the domestic animal emissions

(Mike Abraczinskas, personal communication, NC Division of Air Quality, 2006).

The agriculture–livestock NH_3 emissions (referred to as AL-NH_3 hereafter) provide the largest source among all sources considered. The greatest AL-NH_3 emissions occur over the region around Kenansville, where most hog facilities are located. The total contribution from this area is ~60% of the total NH_3 emissions in NC. The top three contributors are Duplin County (15.5%), Greene County (14.3%), and Sampson County (14%). Large AL-NH_3 emissions also occur at the area around Charlotte and in the northwest corner of NC; the contributions to the total NH_3 emissions in NC from these areas are ~8.3% (e.g., Union, Anson, Richmond, and Stanly Counties) and 8.2% (e.g., Wikes, Alexander and Yadkin counties), respectively.

Farming practices and climate conditions (e.g., temperature and wind speed) influence the NH_3 emission rates. It is not feasible to measure NH_3 emissions throughout the entire processes of the practice under all climate conditions. Current technologies usually use uniform emission factors to represent some categories practices (e.g., one factor for cattle) under a typical climate condition (e.g., a temperature of ~20 °C and a wind speed of $5\,m\,s^{-1}$). Consequently, there are large uncertainties in the estimation of NH_3 emissions in both the total emission amount and the temporal variations. Uncertainties in spatial variations also exist when applying such uniform factors throughout the domain and considering the spatial factors only based on the spatial distributions of the activity level (e.g., amount of cattles in each county and fertilized areas in each county). Other causes, such as missing some NH_3 sources or processes, also bring uncertainties to the estimation of NH_3 emissions.

Our Part I of paper (Wu et al., 2007) shows an underprediction for $PM_{2.5}$, NH_4^+, NO_3^-, and SO_4^{2-} in August but an overprediction for all species except SO_4^{2-} at all observational sites in December for baseline simulations. In addition to meteorology and some model physics (e.g., gas/particle mass transfer), the uncertainties in emissions of NH_3 and other species may contribute to the model biases. Since NH_4^+ and NO_3^- are overpredicted in August and underpredicted in December, one likely reason is that NH_3-VISTAS is overestimated in August and underestimated in December. Abraczinskas (2005) has shown that uncertainties in NH_3 emissions can significantly affect model performance in nitrate prediction in NC. In the following parts, NH_3-VISTAS are compared with another NH_3 inventory and NH_3-VISTAS is then adjusted for CMAQ sensitivity simulations.

2.2. *NH_3 emissions used in the sensitivity simulations*

As discussed previously, farming practices and climatic conditions lead to seasonal variations in hourly emission rates. EPA (2002) indicates that animal emission factors are not well characterized and recommends a process-based modeling approach to estimate emissions from concentrated feeding operations. To improve the accuracy of the estimation of NH_3 emissions, Pinder et al. (2004a, b) estimated livestock emissions based on the temporally resolved dairy cattle inventory for which dairy cattle emissions are calculated by combining a process-based model (i.e., the Farm Emission Model (Pinder et al., 2004a)) with a national database of farming practices and climatic conditions. Other livestock types are simulated by applying a temporal profile derived with surrogate dairy farm types to the annual-average emission factor from the CMU NH_3 Emission Inventory (Pinder et al., 2006). By applying a 3-D chemical transport model, Pinder et al. (2006) concluded that the process-based inventory (referred to as NH_3-CMU hereafter) with spatial and temporal variation improves the model prediction in both summer and winter.

Three sets of sensitivity simulations are conducted to investigate the impact of NH_3 emissions on $PM_{2.5}$ formation and associated uncertainties. In the first sensitivity simulation, the AL-NH_3 emissions are turned off to estimate their contributions to the concentrations of $PM_{2.5}$ and its composition. In the second and third sets of sensitivity simulations, two methods are used to adjust the baseline NH_3 emissions to study the impact of the total amounts and temporal variations of NH_3 emissions on the formation of $PM_{2.5}$ and its composition. The emission adjustments are based on NH_3-CMU. Compared with the VISTAS inventory, NH_3-CMU inventory gives higher rates in August but lower rates in December. Table 1 summarizes the total domainwide emissions in NH_3-VISTAS and NH_3-CMU. Compared with the total amounts in the CMU inventory, NH_3-VISTAS underestimates NH_3 emissions by 22.7% in August but overestimates by 47.8% in December.

Table 1
NH_3 emission inventories used in the baseline and sensitivity simulations

Inventory/simulation	Total domainwide emissions (tons d^{-1})		Ratio to base total emissions		Diurnal variation
	August	December	August	December	
NH_3-VISTAS/ baseline	568	334	1	1	VISTAS
NH_3-CMU/ Sen_uniform	735	226	1.29	0.68	VISTAS
NH_3-CMU/Sen_diurnal	735	226	1.29	0.68	CMU

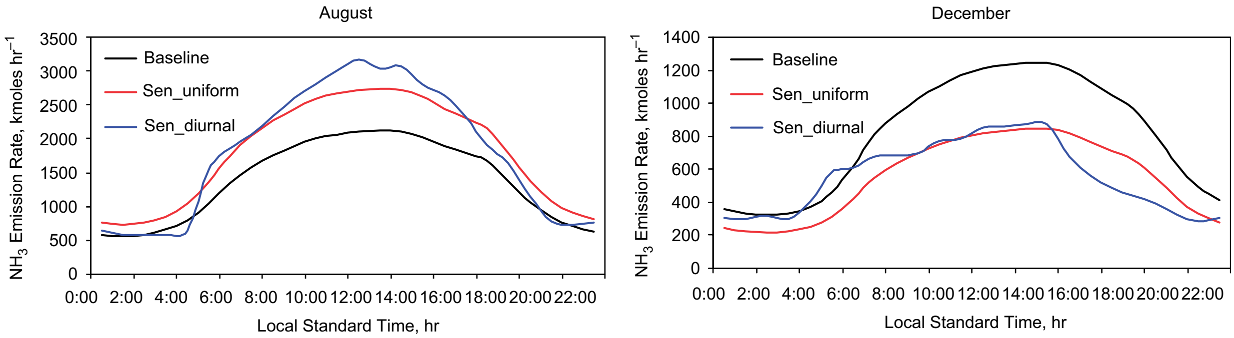

Fig. 1. NH_3 emission profiles used in the baseline and sensitivity simulations.

Using the CMU inventory as a benchmark, two methods have been applied to adjust NH_3-VISTAS emissions used in the baseline simulations. The first method is to use the total CMU NH_3 emissions but still keep the same diurnal variability as the baseline simulations (referred to as Sen_uniform hereafter), namely, multiplying the baseline VISTAS total NH_3 emissions by a domainwide uniform factor of 1.29 for August and by 0.68 for December to match the total NH_3 emissions in NH_3-CMU. Different emission adjustment factors for August and December reflect seasonal variation in NH_3 emissions. The second method is to use the total NH_3 emissions and the diurnal variability in NH_3-CMU (referred to as Sen_diurnal hereafter), namely, replacing the hourly NH_3 emission rates in the baseline simulations by those in NH_3-CMU. Fig. 1 shows the hourly emission rates of NH_3 on 2 August and 19 December (those on other days are similar) used in all simulations. The difference between Sen_uniform and Sen_diurnal lies in the diurnal variability profiles used, namely, Sen_diurnal gives higher daytime emission rates and lower nighttime emission rates than those of Sen_uniform in August, and has emission rates that are higher between 1 and 10 a.m., lower between 4 and 11 p.m., and similar between 10 a.m. and 4 p.m. in December.

3. Results and discussions

3.1. AL-NH_3 contributions

To study the contribution of NH_3 emissions from AL-NH_3 to $PM_{2.5}$ and its composition, a sensitivity simulation is conducted by turning off AL-NH_3 emissions. Fig. 2 shows the monthly average contributions of AL-NH_3 emissions to $PM_{2.5}$, NH_4^+, NO_3^-, and SO_4^{2-} in term of absolute and percent changes in August. The plots are obtained by subtracting the sensitivity simulation results from the baseline simulation results. The highest contributions to $PM_{2.5}$, NH_4^+, and NO_3^- are found to be in the areas around Kenansville, Charlotte, and Alexander County. For example, AL-NH_3 emissions contribute to more than 10% of $PM_{2.5}$, with the highest value of 20.8% over Kenansville (up to 2.1 $\mu g\,m^{-3}$). Their contributions to NH_4^+ and NO_3^- are even larger, with 20–50% (up to 1.4 $\mu g\,m^{-3}$) for NH_4^+ in most areas, and more than 50% (up to 1 $\mu g\,m^{-3}$) of NO_3^- in a large area surrounding Kenansville, Charlotte, and Alexander County. AL-NH_3 emissions can slightly increase SO_4^{2-} (e.g., by up to 4.9%, or 0.2 $\mu g\,m^{-3}$ over Kenansville) for the following reason. HNO_3 in the gas-phase reacts with additional NH_3 to form

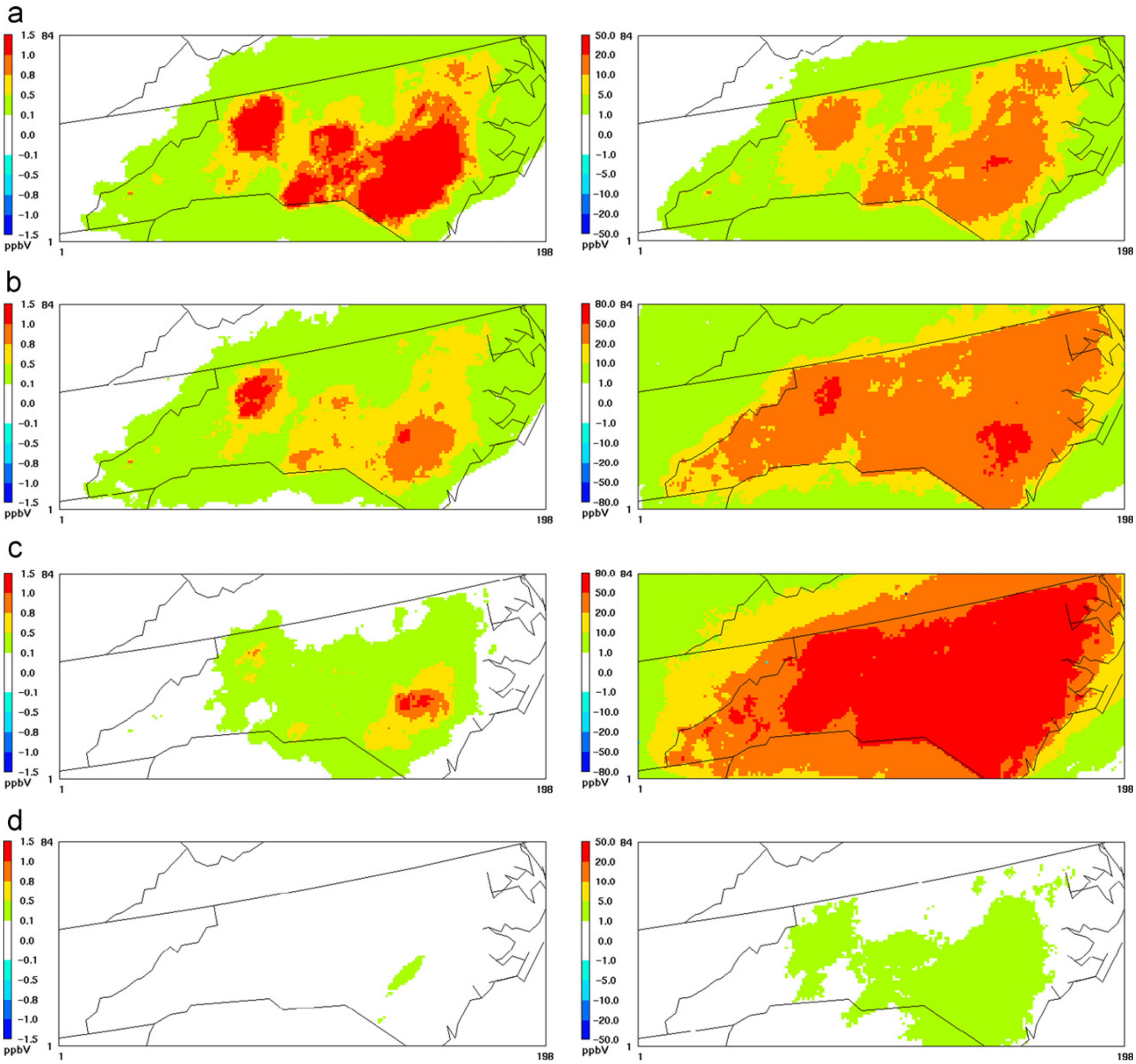

Fig. 2. The monthly mean contributions of AL-NH_3 emissions to (a) $PM_{2.5}$, (b) NH_4^+, (c) NO_3^-, and (d) SO_4^{2-} in term of absolute (left) and percent (right) changes in August 2002.

NH_4NO_3(s) when large AL-NH_3 emissions are included in the baseline simulation, resulting in a higher OH mixing ratio (which will otherwise react with HNO_3). The higher OH in turn oxidizes more SO_2 to form more H_2SO_4, which is neutralized by available NH_3 to form more SO_4^{2-}. Those results demonstrate the local and the regional impacts of AL-NH_3 emissions in $PM_{2.5}$ formation and control in NC.

The magnitudes and spatial distributions of those impacts vary from day to day, depending on both meteorological and chemical conditions that affect the transport and fate of $PM_{2.5}$ and its precursors. Fig. 3 shows the contributions of the AL-NH_3 emissions to $PM_{2.5}$, SO_4^{2-}, NO_3^-, and NH_4^+ on 2 and 31 August, respectively. As shown in Fig. 3, the contribution patterns of the AL-NH_3 emissions to $PM_{2.5}$, NH_4^+, NO_3^-, and SO_4^{2-} are quite different on 2 and 31 August. On 2 August, the highest contribution of the AL-NH_3 emissions to $PM_{2.5}$ concentration is 10.1 $\mu g\,m^{-3}$ (25.5%) occurring over the northwestern NC. Those to the concentrations

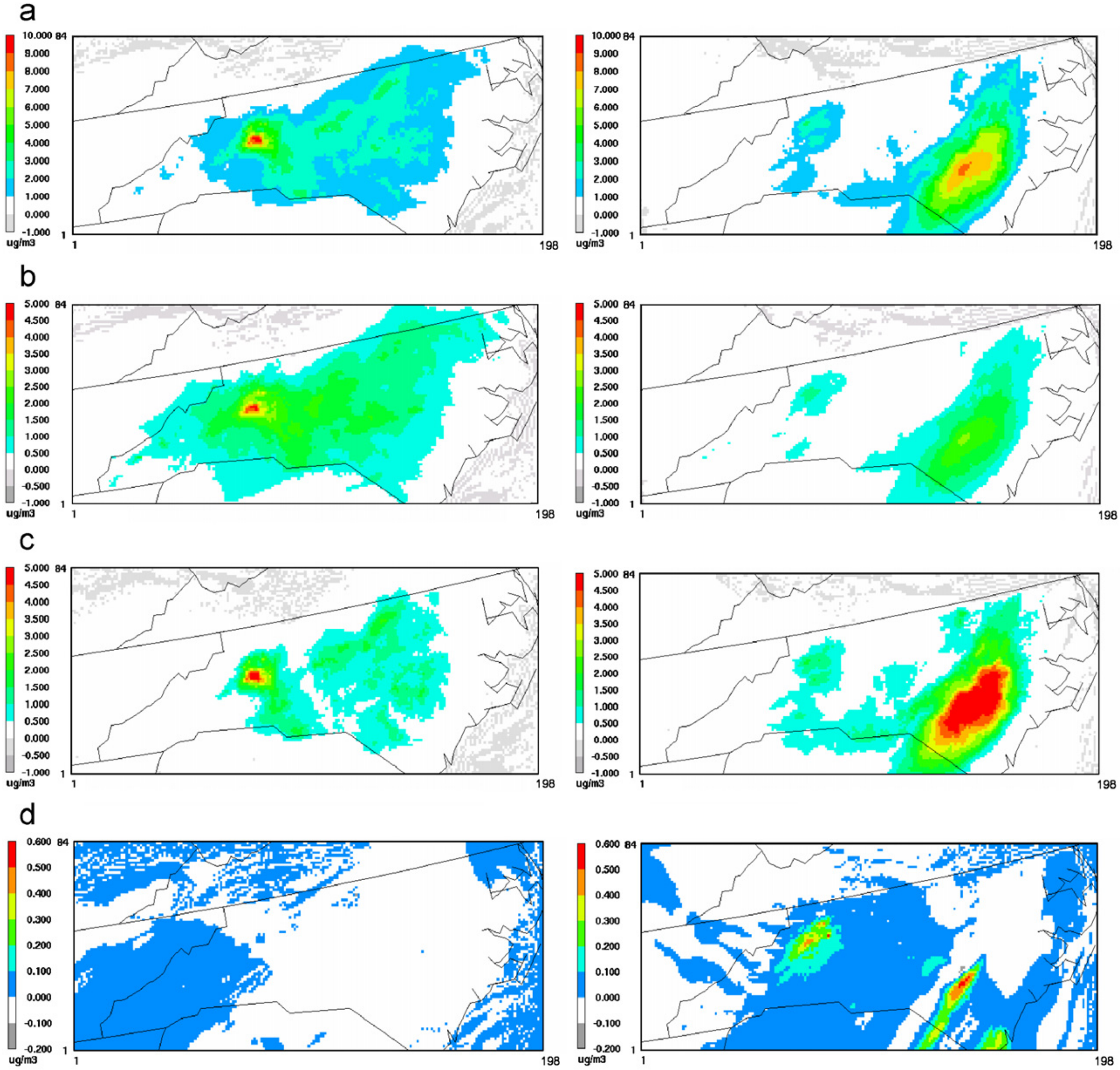

Fig. 3. The contribution of AL-NH_3 emissions to daily average concentrations of (a) $PM_{2.5}$, (b) NH_4^+, (c) NO_3^-, and (d) SO_4^{2-} on 2 August (left) and 31 August (right) 2002.

of NH_4^+, NO_3^-, and SO_4^{2-} are 4.63 $\mu g\,m^{-3}$ (73.7%), 5.68 μgm^{-3} (99.9%), and 0.07 $\mu g\,m^{-3}$ (0.6%), respectively. On 31 August, the highest contribution of the AL-NH_3 emissions to $PM_{2.5}$ is 8.35 $\mu g\,m^{-3}$ (54.2%) occurring over the Kenansville area. Those to the concentrations of NH_4^+, NO_3^-, and SO_4^{2-} are 2.61 $\mu g\,m^{-3}$ (79.9%), 5.58 $\mu g\,m^{-3}$ (96%), and 0.53 $\mu g\,m^{-3}$ (11.9%), respectively.

With similar AL-NH_3 emissions for both days, meteorological conditions have large influence on the spatial distributions of the impact of AL-NH_3 on $PM_{2.5}$ formation. Fig. 4 shows the meteorological field on both days. On 2 August, morning surface winds are relatively calm. In late morning, the prevailing wind direction over NC becomes easterly (~2–6 $m\,s^{-1}$) in response to a high-pressure system centered over VA. On 31 August, the prevailing wind direction in the east of the Blue Ridge mountains in NC is north–northeast (~2–8 $m\,s^{-1}$) in response to a stationary frontal boundary located along the east coast. The distinct meteorology leads to different distributions of

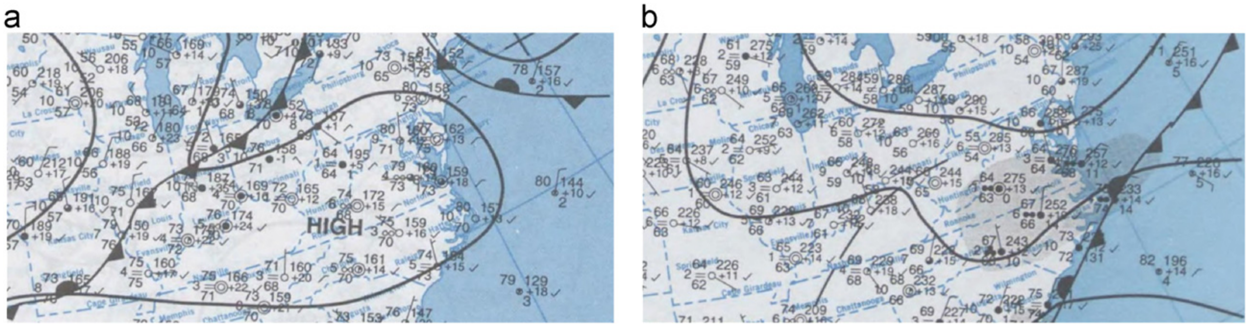

Fig. 4. Surface weather map at 9 a.m. EST on (a) 2 August and (b) 31 August 2002, respectively.

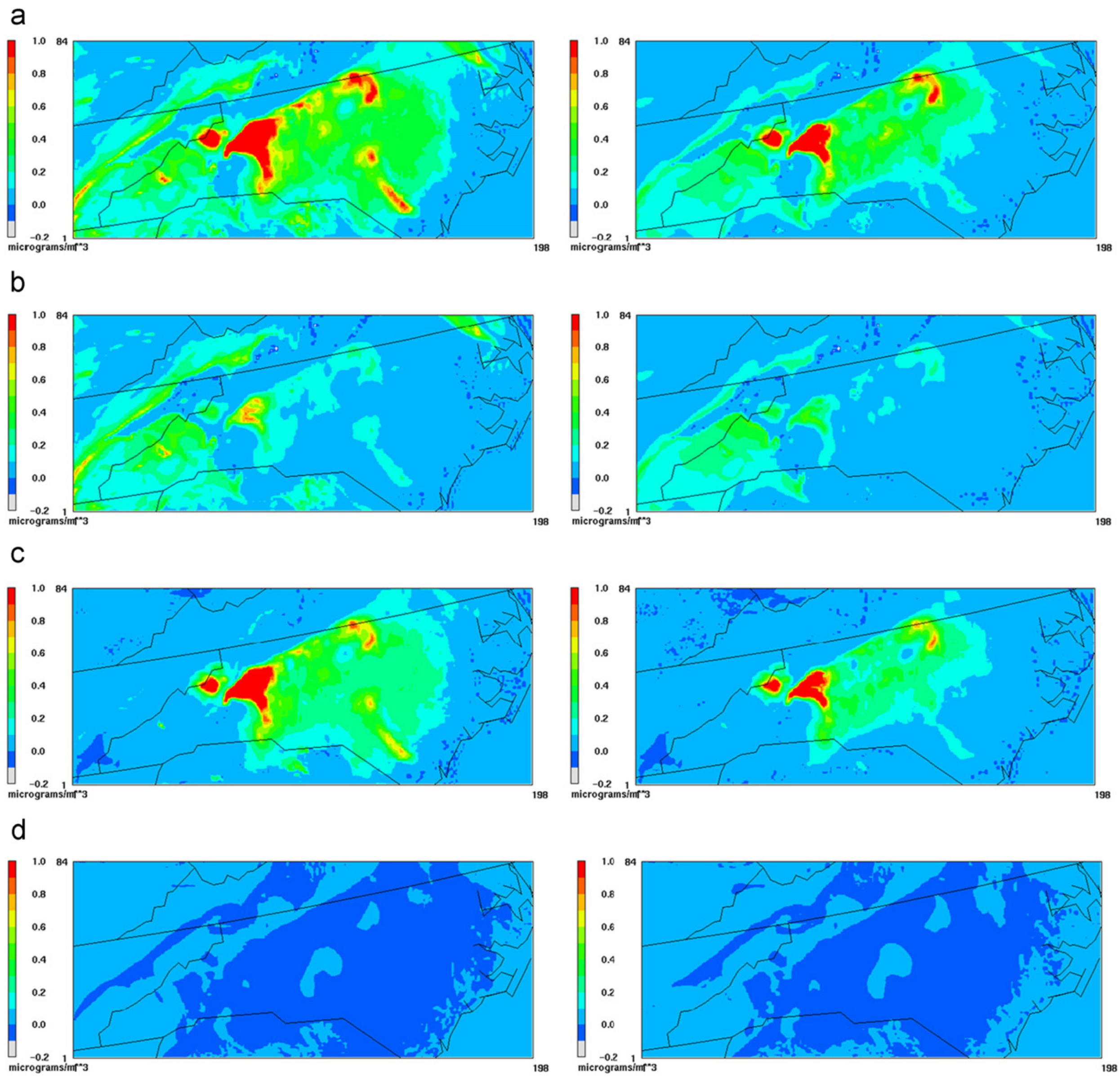

Fig. 5. Changes in concentrations of (a) $PM_{2.5}$, (b) NH_4^+, (c) NO_3^-, and (d) SO_4^{2-} due to different emission adjustments at 1 a.m. EST on 2 August 2002.

$PM_{2.5}$ and its precursors. The airflow on 2 August transported HNO_3 (formed via the reaction of NO_2 with OH) to the western portion of the domain. Although the AL–NH_3 emissions are not the highest around the Wilkes County area, the highest NH_4NO_3 (thus $PM_{2.5}$) formation from the AL-NH_3 sources occurs over Wilkes County area because of the availability of HNO_3. On 31 August, the airflow mainly transported HNO_3 to the area around Kenansville where the most hog facilities are located, resulting in the highest NH_4NO_3 formation in the southeastern NC. Changes in the concentrations of SO_4^{2-} are relatively small compared with those in the concentrations of NH_4^+ and NO_3^- since changes in NH_3 emissions do not cause significant changes in the NH_3 amounts needed to neutralize all SO_4^{2-} as $(NH_4)_2SO_4$ in particulate phase because sulfate formation is limited by available H_2SO_4 in most areas in both months. Turning off the AL-NH_3 emissions also causes a very small increase (mostly $<0.1\,\mu g\,m^{-3}$) in the concentrations of $PM_{2.5}$, NH_4^+, and NO_3^- along the northwestern and eastern boundaries and in the concentrations of SO_4^{2-} over central NC (appeared as negative values in Fig. 5).

3.2. Spatial and temporal trends of effect of NH_3 emission uncertainties

Figs. 5 and 6 show the changes in the concentrations of $PM_{2.5}$, NH_4^+, NO_3^-, and SO_4^{2-} due to changes in the NH_3 emissions using the two adjustment methods at 1 a.m. Eastern Standard Time (EST) on 2 August, and 2 a.m. EST 19 December, 2002, respectively. The results are obtained by subtracting the sensitivity simulation results from the baseline simulation results. Compared with the baseline results, the increases in the concentrations of NH_4^+, NO_3^-, and SO_4^{2-} predicted by Sen_uniform on 2 August are up to 0.859, 2.952, and $0.035\,\mu g\,m^{-3}$, respectively. Those predicted by Sen_diurnal are up to 0.476, 1.646, and $0.058\,\mu g\,m^{-3}$, respectively. The decreases in the concentrations of NH_4^+, NO_3^-, and SO_4^{2-} predicted by Sen_uniform on 19 December are up to 1.323, 4.499, and $0.146\,\mu g\,m^{-3}$, respectively. Those predicted by Sen_diurnal are up to 1.175, 3.989, and $0.146\,\mu g\,m^{-3}$, respectively. Sen_uniform predicts larger changes in the nighttime concentrations of $PM_{2.5}$, NH_4^+, and NO_3^- than Sen_diurnal in both months due to the higher NH_3 emissions at night used in the Sen_uniform simulations (see Fig. 1).

The impact of NH_3 emissions on $PM_{2.5}$ formation shows strong spatial and seasonal variations. The prevailing northeast–east winds transported HNO_3 to the western portion of the domain on 2 August and 19 December. Increases in NH_3 emissions resulted in $>10\%$ increases in the concentrations of NH_4^+ and NO_3^- (0.4 and $0.2\,\mu g\,m^{-3}$, respectively) on 2 August. Reductions in NH_3 emissions resulted in $>20\%$ decreases in the concentrations of NH_4^+ and NO_3^- (0.7 and $1.5\,\mu g\,m^{-3}$, respectively) on 19 December. The large changes in concentrations occurred over Wilkes County, a downwind area of the high NH_3 emissions.

Fig. 7 shows the changes in the concentrations of NH_4^+ and NO_3^- due to changes in the NH_3 emissions in Sen_uniform at 11 a.m. EST 2 August, 2002. The increases in the concentrations of NH_4^+ and NO_3^- predicted by Sen_uniform are up to 0.604 and $0.302\,\mu g\,m^{-3}$, respectively. The changes in the concentrations of NH_4^+ and NO_3^- are larger at night than during daytime because the nighttime meteorological conditions (e.g., lower boundary layer height, lower temperature, and higher RH) are more favorable for NH_4NO_3 formation.

In addition to meteorological conditions, the PM formation depends on the ambient chemical conditions. The gas ratio (GR) (Ansari and Pandis, 1998; Takahama et al., 2004) is used to describe different chemical regimes in terms of the amount of free NH_3:

$$GR = \frac{[TA] - 2[TS]}{[TN]}, \tag{1}$$

where $[TA] = [NH_3] + [NH_4^+]$ is the total amount of reduced nitrogen (NH_x), [TS] is the sulfate aerosol concentration, and $[TN] = [NO_3^-] + [HNO_3]$ is the total amount of nitrate. Negative GR values indicate insufficient amounts of NH_3 to neutralize all SO_4^{2-}, which is often called NH_3-poor regime. Moderate GR values (0–1) indicate sufficient amounts of NH_3 to neutralize SO_4^{2-} but not NO_3^-. High GR values (>1) indicate NH_3-rich conditions with sufficient amounts of NH_3 to neutralize both SO_4^{2-} and NO_3^-. However, NH_x may not be fully neutralized by SO_4^{2-} under winter conditions, making the equation of free $NH_3 = [\text{Total } NH_3] - 2 \times [SO_4^{2-}]$ invalid. A more generic equation of free $NH_3 = [NH_3] + [NO_3^-]$ should be used to account for the neutralization by NO_3^- under such conditions (Robert Pinder, personal communication, the US EPA/NOAA, 2006). The corresponding adjusted GR (AdjGR), as an indicator of $PM_{2.5}$

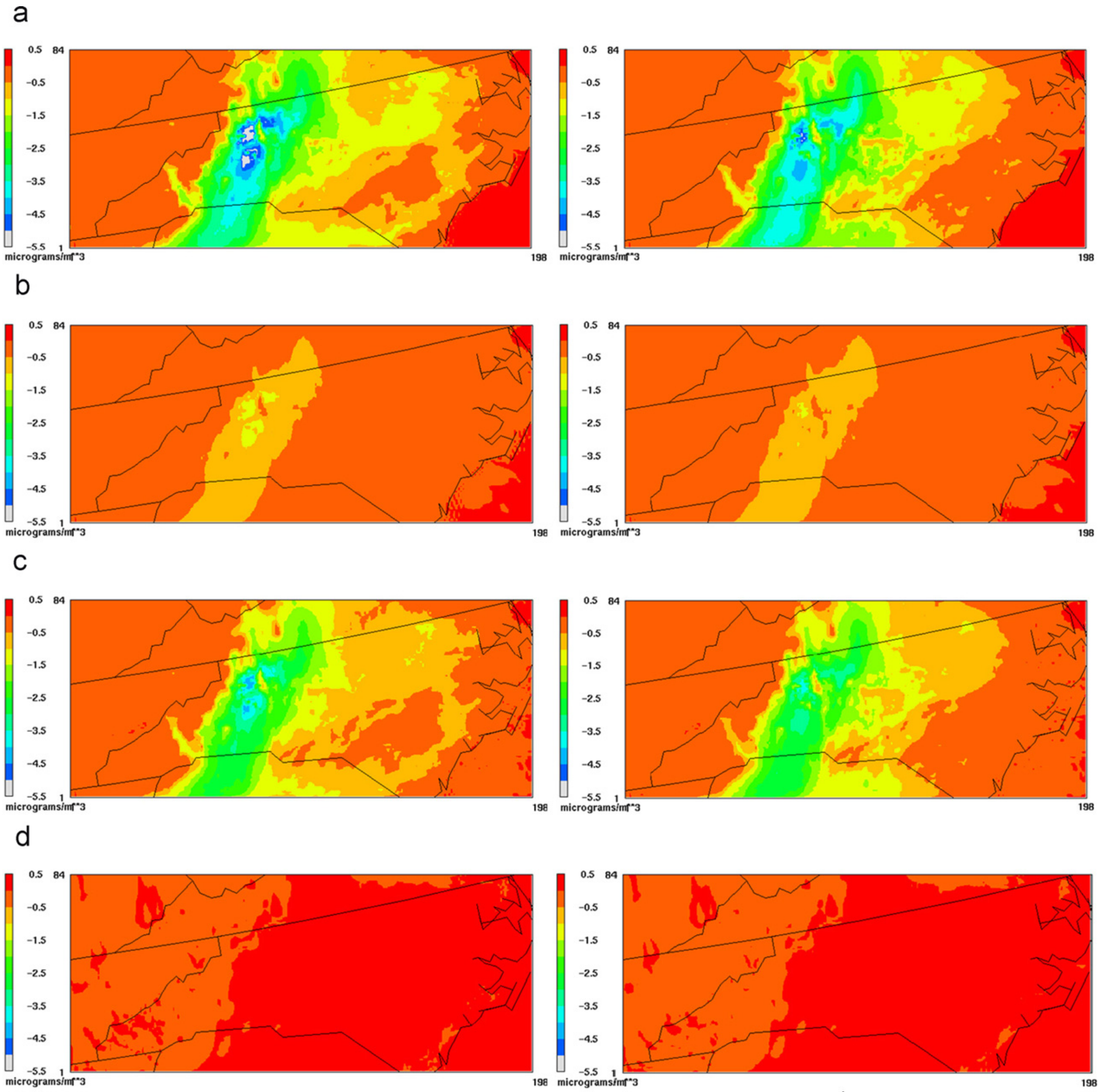

Fig. 6. Changes in concentrations of (a) $PM_{2.5}$, (b) NH_4^+, (c) NO_3^-, and (d) SO_4^{2-} due to different emission adjustments at 2 a.m. EST on 19 December 2002.

sensitivity to NH_3 emission changes can then be calculated as follows:

$$\mathrm{AdjGR} = \frac{[NO_3^-] + [NH_3]}{\mathrm{TN}}. \qquad (2)$$

Fig. 8 compares the spatial distributions of GR and AdjGR on 2 August and 19 December. The comparison shows that the NH_3-rich areas (with GR and AdjGR >1, meaning sufficient free NH_3 to neutralize nitrate) are very similar in August. Most of the eastern domain is in NH_3-rich environment on 2 August. In this area, the increased amount of NH_3 as a result of higher emissions in the two sensitivity simulations will not result in a significant conversion to particulate NH_4^+, as there are large amounts of free NH_3 after neutralizing SO_4^{2-} and NO_3^-. The high increase in the concentrations of NH_4^+ on 2 August does not occur in the eastern

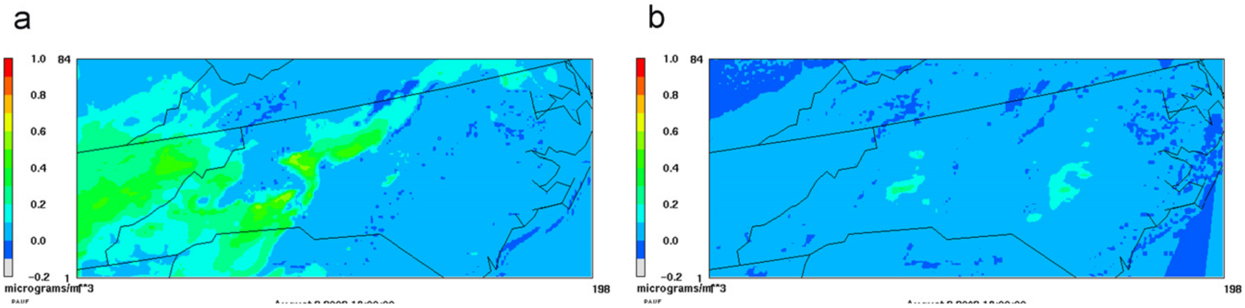

Fig. 7. Changes in the concentrations of (a) NH_4^+ and (b) NO_3^- due to emission adjustments in Sen_uniform at 11 a.m. EST 2 August 2002.

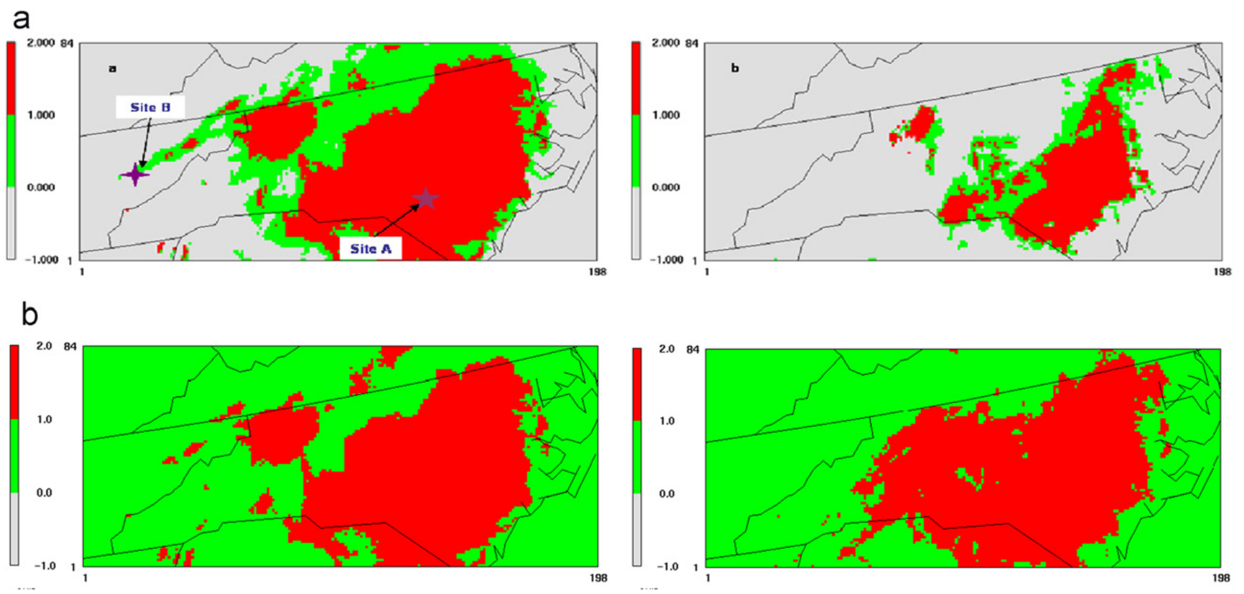

Fig. 8. The spatial distributions of (a) GR and (b) AdjGR on 2 August and 19 December 2002.

portions of the domain, where there are large NH_3 emissions and in an NH_3-rich environment as shown in Figs. 5 and 7. However, in December the NH_3-rich area defined by GR is much smaller than that defined by AdjGR, confirming that in December NH_x may not be fully neutralized by SO_4^{2-} and that nitrate provides additional anions to neutralize NH_3. This helps explain why absolute changes in sulfate in December are slightly larger than those in August as a result of perturbed NH_3 emissions, as shown in Figs. 5d and 6d. In addition, the areas with $GR<0$ defined by GR become areas with $0<AdjGR<1$ defined by AdjGR in both months, indicating that the NH_3-poor (i.e., sulfate-rich) regime defined by GR does not exist with the corrected free NH_3 calculation.

Two sites, STN 370510009 (site A) and STN 470931020 (site B) are chosen to further analyze the impact of NH_3 emission on PM formation in different GR regions. The locations of sites A and B are shown in Fig. 8(a). Site A is in the Cumberland, NC, near the hog farms, and consequently, with a high GR value of 3.3. Site B is in Bristol, TN, with a low GR value of 1.1. Fig. 9 shows the observed and simulated NH_4^+ and NO_3^- concentrations and their percent changes at the two sites. The percent change is defined as (Sen_uniform−Baseline) × 100%/Baseline or (Sen_diurnal−Baseline) × 100%/Baseline. Larger percent changes in NH_4^+ and NO_3^- concentrations occur at site B than at site A, indicating that the PM formation is more sensitive to NH_3 emission in the NH_3-poor or NH_3-neutral regions. The changes in Sen_uniform are overall larger than those in Sen_diurnal due to the larger changes of emissions at night. The discrepancies can be attributed to other uncertainties in meteorology and the inaccuracies in some model

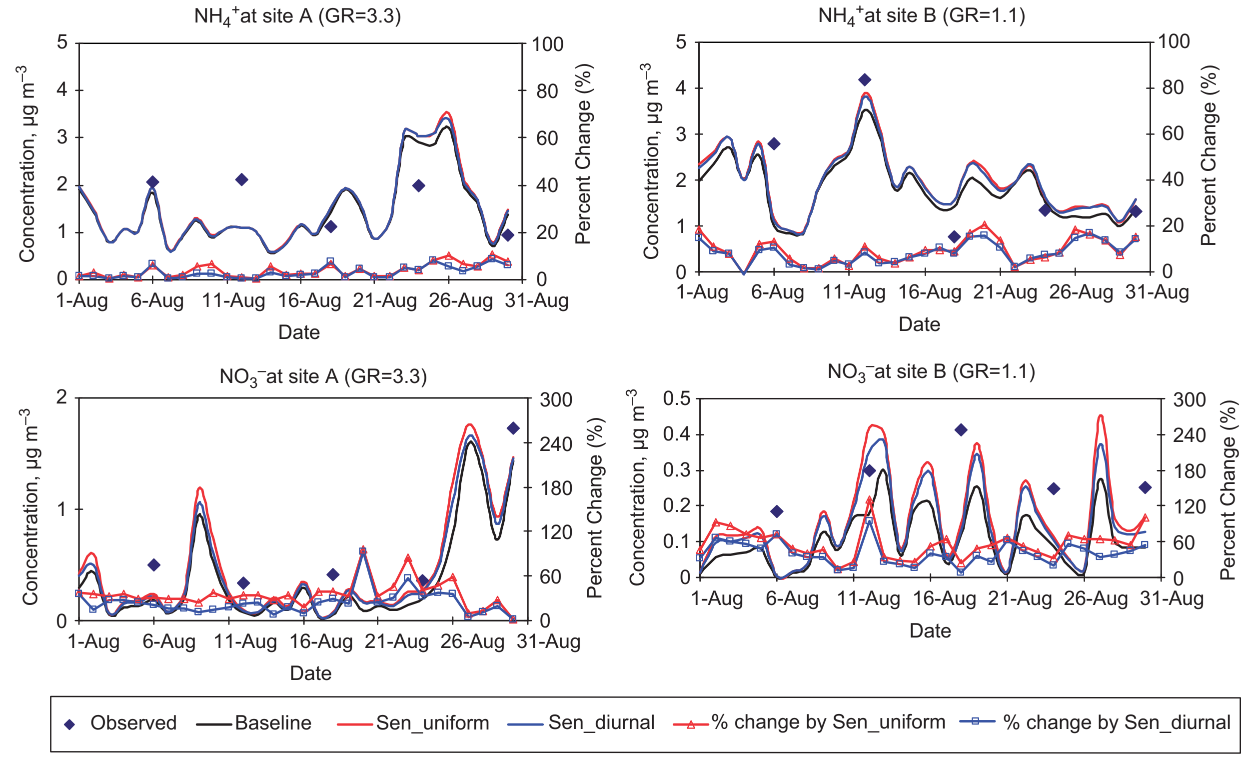

Fig. 9. Observed and simulated concentrations of NH_4^+ and NO_3^- (left Y-axis) and their percent changes (right Y-axis) at sites A and B.

treatments (e.g., gas/particle partitioning) (Zhang et al., 2006a).

3.3. Statistical assessment of the effect of NH_3 emission uncertainties

Domainwide statistics provide an overall measure of model performance. Tables 2 and 3 summarize the mean observed and simulated values, and performance statistics in terms of normalized mean bias (NMB) and normalized mean error (NME) for $PM_{2.5}$ and its composition using the formulae in Zhang et al. (2006b) and Yu et al. (2006). To evaluate model predictions, several available databases are used including the Speciation Trends Network (STN), the Clean Air Status and Trends Network (CASTNet), EPA Air Quality System (AQS), the Interagency Monitoring of Protected Visual Environments (IMPROVE), and the North Carolina Department of Environment and Natural Resources (NCDENR).

The sensitivity simulation results show that the adjustments on NH_3 emissions improve the model performance in terms of $PM_{2.5}$, NH_4^+ and NO_3^- both in August and December. For example, in August, the absolute values of NMBs of $PM_{2.5}$ of both Sen_uniform and Sen_diurnal decrease by 0.6–0.9%, and those of NMBs of NH_4^+ and NO_3^- decrease by 4–7% and 11–20%, respectively. In December, the absolute values of NMBs of $PM_{2.5}$ of both sensitivity simulations decrease by 5.8–6.4%, and those of NMBs of NH_4^+ and NO_3^- decrease by 12–15% and 29–45%, respectively. A more pronounced impact on $PM_{2.5}$ is found in December than in August, due to a higher percent contribution of NH_4NO_3 to $PM_{2.5}$ (14.1–15.5% in August, and 30.7–36.6% in December).

4. Conclusions

In this study, the MM5/CMAQ modeling system is applied to conduct sensitivity studies to assess the impact of the AL-NH_3 emissions in NC on ambient $PM_{2.5}$ and study the uncertainties in the total amount and temporal variations of NH_3 emissions. The sensitivity simulation results show that the highest monthly contributions of the AL-NH_3 emissions to the concentrations of $PM_{2.5}$, NH_4^+, and NO_3^- are 20.8%, 55.2%, and 90.6% in August 2002. They may either slightly increase or decrease (−6.4% to 3.3%)

Table 2
Performance statistics for August 2002

	Network	Sample #	Mean obs. ($\mu g\,m^{-3}$)	Mean sim			NMB (%)			NME (%)		
				Baseline	Sen_uniform	Sen_diurnal	Baseline	Sen_uniform	Sen_diurnal	Baseline	Sen_uniform	Sen_diurnal
$PM_{2.5}$	AQS	708	17.4	11.8	12.0	12.0	−32.0	−31.0	−31.1	39.0	38.5	38.6
	IMPROVE	33	14.3	7.9	8.0	7.9	−45.2	−44.5	−44.6	46.0	45.4	45.4
	STN	77	19.0	12.9	13.1	13.1	−31.8	−30.7	−30.9	38.5	37.9	38.0
NH_4^+	IMPROVE	9	1.7	1.1	1.2	1.2	−35.2	−28.6	−28.7	43.6	38.5	39.0
	STN	77	1.9	1.6	1.7	1.7	−18.0	−10.7	−11.8	39.1	38.0	38.4
	CASTNET	16	1.7	1.1	1.2	1.2	−34.1	−29.8	−30.2	37.4	34.2	34.5
NO_3^-	IMPROVE	30	0.2	0.1	0.1	0.1	−40.9	−20.1	−24.4	122.0	140.6	137.0
	STN	77	0.5	0.2	0.3	0.3	−50.6	−39.1	−42.6	75.5	72.9	73.6
	CASTNET	16	0.2	0.1	0.1	0.1	−64.2	−53.9	−58.4	73.6	71.3	72.2
SO_4^{2-}	IMPROVE	31	6.2	5.2	5.2	5.2	−16.7	−16.8	−16.8	27.8	28.0	28.0
	STN	77	6.7	6.3	6.3	6.3	−6.2	−6.0	−6.0	30.4	30.3	30.3
	CASTNET	16	6.3	5.1	5.1	5.1	−18.7	−18.6	−18.6	29.8	29.8	29.8
BC	IMPROVE	37	0.3	0.2	0.2	0.2	−48.9	−48.9	−48.9	51.9	51.9	51.9
OC	IMPROVE	37	2.7	1.1	1.1	1.1	−58.5	−58.6	−58.6	58.5	58.6	58.6

Table 3
Performance statistics for December 2002

	Network	Sample #	Mean obs. ($\mu g\,m^{-3}$)	Mean sim. ($\mu g\,m^{-3}$)			NMB (%)			NME (%)		
				Baseline	Sen_uniform	Sen_diurnal	Baseline	Sen_uniform	Sen_diurnal	baseline	Sen_uniform	Sen_diurnal
$PM_{2.5}$	AQS	691	11.9	13.9	13.2	13.2	17.1	10.8	11.3	44.2	42.3	42.5
	IMPROVE	30	4.2	6.2	6.0	6.0	46.7	40.9	40.9	68.7	65.4	65.6
	STN	59	13.1	14.3	13.4	13.5	8.8	2.4	2.8	37.0	35.1	35.2
NH_4^+	IMPROVE	27	0.5	0.8	0.7	0.7	53.2	41.9	42.1	81.1	73.3	74.0
	STN	59	1.4	1.8	1.6	1.6	30.8	15.6	16.8	48.2	40.5	41.4
	CASTNET	19	0.9	1.3	1.1	1.1	40.6	26.0	26.8	41.2	32.5	32.9
NO_3^-	IMPROVE	27	0.5	1.1	1.0	1.0	142.9	107.9	109.5	156.2	128.0	128.7
	STN	58	2.2	3.4	2.8	2.8	58.6	29.1	31.2	68.6	52.7	53.5
	CASTNET	19	0.8	2.1	1.7	1.7	158.1	112.9	115.0	158.1	113.7	115.0
SO_4^{2-}	IMPROVE	27	1.5	1.7	1.7	1.7	9.1	8.8	8.8	48.1	48.0	48.0
	STN	58	2.8	2.2	2.2	2.2	−21.0	−21.5	−21.4	34.0	34.5	34.4
	CASTNET	19	2.3	2.2	2.2	2.2	−4.2	−4.7	−4.6	22.3	22.5	22.4
BC	IMPROVE	18	0.3	0.2	0.2	0.2	−26.6	−26.6	−26.6	37.3	37.2	37.2
OC	IMPROVE	18	1.4	1.5	1.5	1.5	5.9	5.8	5.8	39.5	39.5	39.5

SO_4^{2-}, depending largely on chemical conditions. The impact of NH_3 emissions on $PM_{2.5}$ formation shows strong spatial and seasonal variations associated with the meteorological and the ambient chemical conditions. Adjustments in NH_3 emissions result in $>10\%$ increases in the concentrations of NH_4^+ and NO_3^- in August and $>20\%$ decreases in their concentrations in December. The large changes in concentrations occur downwind of the high NH_3 emissions under the NH_3-poor to neutral conditions. Statistical results show that the adjustments on NH_3 emissions improve the predicted NH_4^+ and NO_3^- in both months, with NMBs of NH_4^+ and NO_3^- decrease by 4–7%, and 11–20%, respectively, in August and decrease by 12–15%, and 29–45%, respectively in December. However, emission adjustments result in an overall little improvement $PM_{2.5}$ in August and a small improvement in December (reducing NMBs by 5.8–6.7%), indicating other factors such as inaccuracies in meteorological predictions (e.g., mixing heights), the uncertainties in emissions of other species (e.g., SO_2, NO_x, BC, and primary OM, etc.) and the uncertainties in the PM treatment in model (e.g., gas/particle mass tranfer, etc.) may cause model biases in $PM_{2.5}$ predictions. More accurate emission inventory and representations of PM formation processes in the model are needed to enhance the model capability in simulating $PM_{2.5}$.

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