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\textsubscript{3}) emissions are needed for reliable predictions of fine particulate matter (PM\textsubscript{2.5}) by air quality models (AQMs), but the current estimates contain large uncertainties in the temporal and spatial distributions of NH\textsubscript{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\textsubscript{3} (AL-NH\textsubscript{3}) emissions to the concentration of PM\textsubscript{2.5} and the uncertainties in the total amount and the temporal variations of NH\textsubscript{3} emissions and their impact on the formation of PM\textsubscript{2.5} for August and December 2002.

The sensitivity simulation results show that AL-NH\textsubscript{3} emissions contribute significantly to the concentration of PM\textsubscript{2.5}, NH\textsubscript{4}\textsuperscript{+}, and NO\textsubscript{3}\textsuperscript{-}; their contributions to the concentrations of SO\textsubscript{4}\textsuperscript{2-} are relatively small. The impact of NH\textsubscript{3} emissions on PM\textsubscript{2.5} formation shows strong spatial and seasonal variations associated with the meteorological conditions and the ambient chemical conditions. Increases in NH\textsubscript{3} emissions in August 2002 resulted in $>10\%$ increases in the concentrations of NH\textsubscript{4}\textsuperscript{+} and NO\textsubscript{3}\textsuperscript{-}; reductions in NH\textsubscript{3} emissions in December 2002 resulted in $>20\%$ decreases in their concentrations. The large changes in species concentrations occur downwind of the high NH\textsubscript{3} emissions where the ambient environment is NH\textsubscript{3}-poor or neutral. The adjustments in NH\textsubscript{3} emissions improve appreciably the model predictions of NH\textsubscript{4}\textsuperscript{+} and NO\textsubscript{3}\textsuperscript{-} both in August and December, but resulted in negligible improvements in PM\textsubscript{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\textsubscript{2.5}.

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Keywords: Ammonia emissions; Agriculture; Livestock; PM\textsubscript{2.5}; CMAQ; Sensitivity study

1. Introduction

Ammonia (NH\textsubscript{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\textsubscript{3} may cause over-enrichment of
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, NH3 can neutralize sulfuric acid and nitric acid to form fine particulate matter with an aerodynamic diameter $\leq 2.5\, \mu m$ (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$_4$NO$_3$) 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.
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.
Using the CMU inventory as a benchmark, two methods have been applied to adjust NH₃-VISTAS emissions used in the baseline simulations. The first method is to use the total CMU NH₃ emissions but still keep the same diurnal variability as the baseline simulations (referred to as Sen_uniform hereafter), namely, multiplying the baseline VISTAS total NH₃ emissions by a domainwide uniform factor of 1.29 for August and by 0.68 for December to match the total NH₃ emissions in NH₃-CMU. Different emission adjustment factors for August and December reflect seasonal variation in NH₃ emissions. The second method is to use the total NH₃ emissions and the diurnal variability in NH₃-CMU (referred to as Sen_diurnal hereafter), namely, replacing the hourly NH₃ emission rates in the baseline simulations by those in NH₃-CMU. Fig. 1 shows the hourly emission rates of NH₃ 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-NH₃ contributions

To study the contribution of NH₃ emissions from AL-NH₃ to PM₂.₅ and its composition, a sensitivity simulation is conducted by turning off AL-NH₃ emissions. Fig. 2 shows the monthly average contributions of AL-NH₃ emissions to PM₂.₅, NH₄⁺, NO₃⁻, and SO₄²⁻ 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 PM₂.₅, NH₄⁺, and NO₃⁻ are found to be in the areas around Kenansville, Charlotte, and Alexander County. For example, AL-NH₃ emissions can slightly increase SO₄²⁻ (e.g., by up to 4.9%, or 0.2 μg m⁻³ over Kenansville) for the following reason. HNO₃ in the gas-phase reacts with additional NH₃ to form...
NH\textsubscript{4}NO\textsubscript{3}(s) when large AL-NH\textsubscript{3} emissions are included in the baseline simulation, resulting in a higher OH mixing ratio (which will otherwise react with HNO\textsubscript{3}). The higher OH in turn oxidizes more SO\textsubscript{2} to form more H\textsubscript{2}SO\textsubscript{4}, which is neutralized by available NH\textsubscript{3} to form more SO\textsubscript{4}\textsuperscript{2-}. Those results demonstrate the local and the regional impacts of AL-NH\textsubscript{3} emissions in PM\textsubscript{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\textsubscript{2.5} and its precursors. Fig. 3 shows the contributions of the AL-NH\textsubscript{3} emissions to PM\textsubscript{2.5}, SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{3}\textsuperscript{-}, and NH\textsubscript{4}\textsuperscript{+} on 2 and 31 August, respectively. As shown in Fig. 3, the contribution patterns of the AL-NH\textsubscript{3} emissions to PM\textsubscript{2.5}, NH\textsubscript{4}\textsuperscript{+}, NO\textsubscript{3}\textsuperscript{-}, and SO\textsubscript{4}\textsuperscript{2-} are quite different on 2 and 31 August. On 2 August, the highest contribution of the AL-NH\textsubscript{3} emissions to PM\textsubscript{2.5} concentration is 10.1 \(\mu\text{g m}^{-3}\) (25.5\%) occurring over the northwestern NC. Those to the concentrations

![Fig. 2. The monthly mean contributions of AL-NH\textsubscript{3} emissions to (a) PM\textsubscript{2.5}, (b) NH\textsubscript{4}\textsuperscript{+}, (c) NO\textsubscript{3}\textsuperscript{-}, and (d) SO\textsubscript{4}\textsuperscript{2-} in term of absolute (left) and percent (right) changes in August 2002.](image-url)
of \( \text{NH}_4^+ \), \( \text{NO}_3^- \), and \( \text{SO}_4^{2-} \) are 4.63 \( \mu \text{g m}^{-3} \) (73.7%), 5.68 \( \mu \text{g m}^{-3} \) (99.9%), and 0.07 \( \mu \text{g m}^{-3} \) (0.6%), respectively. On 31 August, the highest contribution of the AL-NH\(_3\) emissions to PM\(_{2.5}\) is 8.35 \( \mu \text{g m}^{-3} \) (54.2%) occurring over the Kenansville area. Those to the concentrations of \( \text{NH}_4^+ \), \( \text{NO}_3^- \), and \( \text{SO}_4^{2-} \) are 2.61 \( \mu \text{g m}^{-3} \) (79.9%), 5.58 \( \mu \text{g m}^{-3} \) (96%), and 0.53 \( \mu \text{g m}^{-3} \) (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 (\( \sim 2-6 \text{ m s}^{-1} \)) 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 (\( \sim 2-8 \text{ m s}^{-1} \)) in response to a stationary frontal boundary located along the east coast. The distinct meteorology leads to different distributions of

![Fig. 3. The contribution of AL-NH\(_3\) emissions to daily average concentrations of (a) PM\(_{2.5}\), (b) \( \text{NH}_4^+ \), (c) \( \text{NO}_3^- \), and (d) \( \text{SO}_4^{2-} \) on 2 August (left) and 31 August (right) 2002.](image-url)
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$_4$NO$_3$ (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$_4$NO$_3$ 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$_4$)$_2$SO$_4$ in particulate phase because sulfate formation is limited by available H$_2$SO$_4$ in most areas in both months. Turning off the AL–NH$_3$ emissions also causes a very small increase (mostly $<$0.1 mg/m$^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 mg/m$^3$, respectively. Those predicted by Sen_diurnal are up to 0.476, 1.646, and 0.058 mg/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 mg/m$^3$, respectively. Those predicted by Sen_diurnal are up to 1.755, 3.989, and 0.146 mg/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 mg/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 mg/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 mg/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$_4$NO$_3$ 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$_3$:

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

(1)

where [TA] = [NH$_3$]+[NH$_4^+$] is the total amount of reduced nitrogen (NH$_3$), [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$_3$ may not be fully neutralized by SO$_4^{2-}$ under winter conditions, making the equation of free NH$_3$ = [Total NH$_3$]–2 × [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$_{2.5}$
sensitivity to NH\textsubscript{3} emission changes can then be calculated as follows:

\begin{equation}
\text{AdjGR} = \frac{\text{NO}/C_0^3}{\text{NH}_3/C_1^{38}}. \quad (2)
\end{equation}

Fig. 8 compares the spatial distributions of GR and AdjGR on 2 August and 19 December. The comparison shows that the NH\textsubscript{3}-rich areas (with GR and AdjGR > 1, meaning sufficient free NH\textsubscript{3} to neutralize nitrate) are very similar in August. Most of the eastern domain is in NH\textsubscript{3}-rich environment on 2 August. In this area, the increased amount of NH\textsubscript{3} as a result of higher emissions in the two sensitivity simulations will not result in a significant conversion to particulate NH\textsubscript{4}\textsuperscript{+}, as there are large amounts of free NH\textsubscript{3} after neutralizing SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3}-. The high increase in the concentrations of NH\textsubscript{4}\textsuperscript{+} on 2 August does not occur in the eastern
portions of the domain, where there are large NH₃ emissions and in an NH₃-rich environment as shown in Figs. 5 and 7. However, in December the NH₃-rich area defined by GR is much smaller than that defined by AdjGR, confirming that in December NH₃ may not be fully neutralized by SO₄²⁻ and that nitrate provides additional anions to neutralize NH₃. This helps explain why absolute changes in sulfate in December are slightly larger than those in August as a result of perturbed NH₃ 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 NH₃-poor (i.e., sulfate-rich) regime defined by GR does not exist with the corrected free NH₃ calculation.

Two sites, STN 370510009 (site A) and STN 470931020 (site B) are chosen to further analyze the impact of NH₃ 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 NH₄⁺ and NO₃⁻ concentrations and their percent changes at the two sites. The percent change is defined as \( \frac{\text{Sen}_{\text{uniform}} - \text{Baseline}}{\text{Baseline}} \times 100\% \) or \( \frac{\text{Sen}_{\text{diurnal}} - \text{Baseline}}{\text{Baseline}} \times 100\% \). Larger percent changes in NH₄⁺ and NO₃⁻ concentrations occur at site B than at site A, indicating that the PM formation is more sensitive to NH₃ emission in the NH₃-poor or NH₃-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.
3.3. Statistical assessment of the effect of NH3 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$_3^-$/C$_0^-$ both in August and December. For example, in August, the absolute values of NMBs of both Sen_uniform and Sen_diurnal decrease by 0.6–0.9%, and those of NMBs of NH$_4^+$ and NO$_3^-$/C$_0^-$ 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$_3^-$/C$_0^-$ 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$_4$NO$_3$ 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

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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 transfer, 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$_{2.5}$.

Acknowledgements

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References


Environmental Protection Agency (EPA), 2002. Review of emissions factors and methodologies to estimate ammonia emissions from animal waste handling, EPA-600/R-02-017, Washington, D.C.


