SIMULATING ATMOSPHERIC FATE OF AMMONIA IN SOUTHEAST U.S. USING CMAQ WITH A 4-KM RESOLUTION

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1. INTRODUCTION

Ammonia (NH_3) plays an important role in many aspects of our environment including participation in the nutrient and nitrogen cycles, neutralization of acidic compounds, and formation of fine particulate matter ($PM_{2.5}$). Major sources of NH_3 include animal and human wastes, synthetic fertilizers, biomass burning, and fossil fuel combustion (Bouwman, 1997). NH_3 emissions from hog farms account for about 50% of total NH_3 emissions in North Carolina (NC) (Aneja et al., 2001). 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 (Walker, 1998). In this study, the fate of NH_3 is simulated with the U.S. EPA Community Multiscale Air Quality (CMAQ) modeling system (Binkowski and Roselle, 2003) in an area in the southeast U.S. Two one-month simulations, one in summer (August) and one in winter (December), are being performed for the year 2002 with a horizontal grid resolution of 4 km. A sensitivity simulation is also performed for August 2002 to assess the impact of NH_3 emissions, particularly those from agriculture-livestock sources in NC, on ambient air quality. In this paper, we present the results for August 2002.

2. AIR QUALITY MODEL CONFIGURATION

Figure 1 shows the modeling domain. It covers nearly the entire state of North Carolina, and a portion of several adjacent states including South Carolina, Georgia, Tennessee, West Virginia, and Virginia. The model input files for initial and boundary conditions and meteorology are developed based on the MM5/CMAQ model simulation results on a 12-km resolution grid and are developed by the Visibility Improvement State and Tribal Association of the Southeast's (VISTAS) 2002 modeling program (http://www.vista-sesarm.org.asp).

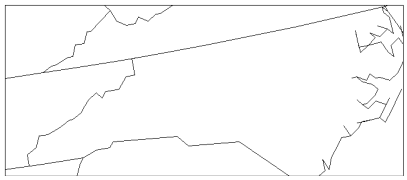

Figure 1. The modeling domain with a 4-km horizontal resolution.

The simulations with a 4-km grid resolution are performed using components of the US-EPA's Modeling system, including the PSU/NCAR Meteorological Model (MM5) version 3.7, the Carolina Environmental Program's (CEP) Sparse Matrix Operator Kernel Emissions (SMOKE) Modeling System version 2.1, and CMAQ version 4.4. The emission inventories for gaseous and PM species for VISTAS's states are based on the revised 2002 emissions developed by VISTAS emission inventory contractors and reviewed by VISTAS stakeholders. For non-VISTAS states, the most updated 2002 emission inventories are obtained from other Regional Planning Organizations (RPO) and the 2002 EPA National Emission Inventory (NEI) Version 1 (available from ftp.epa.gov on March 20, 2004). The configurations and model physics for MM5 and CMAQ in this study are consistent with the 2002 base year VISTAS Phase II modeling study on 12 km resolution grid and are described in the

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modeling protocol for the VISTAS Phase II regional haze modeling (Morris and Koo, 2004).

3. PRELIMINARY RESULTS

3.1 Baseline Simulation

The baseline simulation has been performed for August 2002. The model performance needs to be assessed using available observational data before a detailed analysis on the fate of NH_3 can be analyzed. As the first step of the work, the model predictions are evaluated in terms of temporal and spatial variations of predicted and observed values and the overall statistical performance. The measurements data sets used in the evaluation include those from the North Carolina Department of Environment and Natural Resources (NCDENR), and national networks including the Clean Air Status Trends Network (CASTNet), Interagency Monitoring of Protected Visual Environments (IMPROVE), the EPA Speciation Trends Network (STN), and the EPA Air Quality System (AQS).

Domain-wide statistics provide an overall measure of how well the model has performed. The statistics are calculated separately for each network, because of their distinct characteristics (e.g., temporal resolution and frequency) and the potential measurement bias from the different measurement approaches.

Table1. Summary of data monitoring networks.

Network	Species		Sampling Period
NCDENR	GAS	O_3, CO, NO_2, SO_2	Hourly average
	PM	$PM_{2.5}$, NH_4^+, NO_3^-, SO_4^{2-}, EC, OC	$PM_{2.5}$: 1 in 3 days; 24 hour average other: weekly average
CASTNET	GAS	O_3, SO_2	Hourly average
	PM	NH_4^+, NO_3^-, SO_4^{2-}	Weekly average
AQS	GAS	O_3	Hourly average
IMPROVE	PM	$PM_{2.5}$, NH_4^+, NO_3^-, SO_4^{2-}, EC, OC	1 in 3 days; 24 hour average
STN	PM	$PM_{2.5}$, NH_4^+, NO_3^-, SO_4^{2-}, EC, OC	1 in 3 days; 24 hour average

Table 1 summarizes ambient monitoring networks used in this evaluation. Table 2 summarizes the mean observed and simulated values, and performance statistics in terms of normalized mean bias (NMB) and normalized mean error (NME) for gaseous species, $PM_{2.5}$, and $PM_{2.5}$ composition. The NMB and NME are calculated as follows (Yu et al., 2003):

$$NMB = \frac{\sum_{i=1}^{N}(M_i - O_i)}{\sum_{i=1}^{N} O_i} \cdot 100\%$$

$$NME = \frac{\sum_{i=1}^{N}|M_i - O_i|}{\sum_{i=1}^{N} O_i} \cdot 100\%$$

where M_i and O_i are values of model prediction and observation at a specific time or location *i* in a given time period or a spatial domain or both, N is the number of samples (by time and/or location).

The comparisons against the measurements classified under "NCDENR", consist of specialized sites as well as those of the AQS and STN that are located within the state of NC. The 40 ppb threshold is applied to calculate the statistics for hourly average mixing ratios of O_3. The simulation of O_3 is reasonably good with NMBs and NMEs ranging from -24% to -7% and 27% to 37%, respectively. For CO and NO_2 simulations, the NMBs values are within 40%. For SO_2, the NMBs and NMEs range from -19% to 69% and 82-87%, respectively. Significant overpredictions occur at CASTNet sites (rural) where only a few samples are available.

Table 2. Model performance statistics for the August 2002 simulation.

Species	Network	Mean Obs	Mean Mod	Sample #	NMB %	NME %
O_3 (ppb)	NCDENR	40.28	37.28	31415	-7	37
	CASTNET	61.07	46.50	2896	-24	27
	AQS	63.43	47.90	24565	-24	27
CO(ppb)	NCDENR	511.39	304.57	4882	-40	49
NO_2(ppb)	NCDENR	12.08	16.92	1453	40	70
SO_2 (ppb)	NCDENR	4.05	3.26	3381	-19	87
	CASTNET	2.36	4.00	21	69	82
$PM_{2.5}$ ($\mu g\ m^{-3}$)	NCDENR	16.05	12.42	452	-23	36
	IMPROVE	14.87	8.26	37	-44	47
	STN	17.83	12.23	81	-31	44
NH4 ($\mu g\ m^{-3}$)	NCDENR	1.85	1.72	39	-7	36
	IMPROVE	1.74	1.13	9	-35	43
	STN	1.95	1.47	86	-24	45
	CASTNET	1.74	1.08	21	-38	40
NO3 ($\mu g\ m^{-3}$)	NCDENR	0.49	0.39	39	-21	72
	IMPROVE	0.18	0.08	36	-56	112
	STN	0.48	0.22	86	-54	80
	CASTNET	0.32	0.07	21	-78	85
SO4 ($\mu g\ m^{-3}$)	NCDENR	6.29	5.63	39	-10	27
	IMPROVE	6.02	5.16	37	-14	28
	STN	6.88	5.96	86	-13	39
	CASTNET	6.36	5.09	21	-20	30
EC ($\mu g\ m^{-3}$)	NCDENR	0.35	0.81	39	130	146
	IMPROVE	0.32	0.16	30	-50	53
OC ($\mu g\ m^{-3}$)	NCDENR	6.07	2.37	39	-61	62
	IMPROVE	2.07	0.84	30	-60	60

The performance of SO_4^{2-} is the best among all PM species. The NMBs are relatively small, ranging from -10% (NCDENR) to -20% (CASTNet). The NMEs are also relatively small as well, with the range from 27% (NCDENR) to 39%

(STN). The performances of $PM_{2.5}$ and NH_4^+ are not as good as that of SO_4^{2-}. The NMBs are negative, ranging from -7 to -38% for NH_4^+ and -23 to -44% for $PM_{2.5}$. The NMEs are less than 50%. The performances of NO_3^- and OC are similar and fairly poor. The NMBs are negative and most of them have an absolute value greater than 50%, indicating significant underpredictions. The NMEs are also greater than 50%. The NMBs for EC vary significantly for different networks, ranging from -50% (IMPROVE) to 130% (NCDENR). The NMEs for EC range from 53% to 146%.

Large biases (> 50%) occur for nitrate at Great Smoky Mountains (GRSM), and several sites in NC including Swanquarter (SWAN), Hickory, and Fayetteville; large biases for EC occur at several sites in NC including Linville Gorge (LIGO), Charlotte, Winston-Salem, Kinston, Raleigh, and Fayetteville and for OC at GRSM, and several sites in NC including Shining Rock (SHRO), SWAN, Asheville, Hickory, Kinston, and Fayetteville.

3.2 Sensitivity Simulation

Ammonia plays an important role in PM formation. It is one of the precursors to ammonium nitrate and ammonium sulfate. A sensitivity simulation is conducted by turning off the NH_3 emissions from the Agriculture-Livestock source category (referred to as AL-NH_3 emissions hereafter) to estimate the contributions of NH_3 emissions from the Agriculture-Livestock source category to the formation of PM. Figure 2 shows the distribution of the daily contribution of this source category to the NH_3 emission on August 12, 2002. For other days in August, the distribution of the daily contribution of AL-NH_3 is very similar to August 12, 2002.

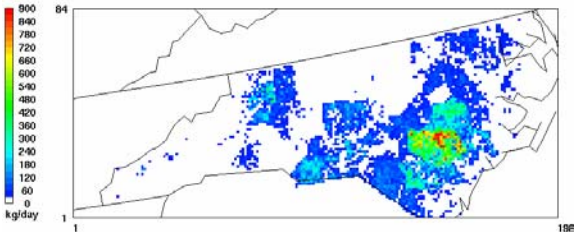

Figure 2. The spatial distribution of the AL-NH_3 emissions on August 12, 2002.

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 North Carolina. 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 the area in the northwest corner of NC; the contributions to the total NH_3 emissions in NC from these areas is approximately 8.3% (e.g., Union, Anson, Richmond, Stanly Counties, etc.) and 8.2% (e.g., Wikes, Alexander, Yadkin Counties, etc.), respectively.

Figures 3 and 4 show the contributions of the AL-NH_3 emissions to $PM_{2.5}$, sulfate (SO_4^{2-}), nitrate (NO_3^-), and ammonium (NH_4^+) on August 2 and 31, respectively. The plots are obtained by subtracting the sensitivity simulation results from those obtained in the baseline simulation**.** On August 2, the highest contributions of the AL-NH_3 emissions to $PM_{2.5}$ (10.1 $\mu g\ m^{-3}$, corresponding to a percent contribution of 25.5%) occur over the northwestern NC. The highest contributions of the AL-NH_3 emissions to the concentrations of NH_4^+, NO_3^-, and SO_4^{2-} are 4.63 $\mu g\ m^{-3}$ (73.7%), 5.68 $\mu g\ m^{-3}$ (99.9%), and 0.07 $\mu g\ m^{-3}$ (0.6%), respectively. On August 31, the highest contributions of the AL-NH_3 emissions to $PM_{2.5}$ (8.35 $\mu g\ m^{-3}$, i.e., 54.2%) occur over the Kenansville area. The highest contributions of the AL-NH_3 emissions 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. The contribution pattern of the AL-NH_3 emissions to $PM_{2.5}$, NH_4^+, NO_3^-, and SO_4^{2-} is very different on August 2 and 31. With similar AL-NH_3 emissions for both days, the possible reasons for this difference could include different meteorology and the availability of other PM precursors such as HNO_3 and H_2SO_4 to react with NH_3. More analyses on those likely causes are being conducted. Turning off the AL-NH_3 emissions also cause a very small increase (mostly < 0.1 $\mu g\ m^{-3}$) in the concentrations of $PM_{2.5}$, NH_4^+, NO_3^- along the northwestern and eastern boundaries and in the concentrations of SO_4^{2-} over central NC (appeared as negative values in Figures 3 and 4). This is likely due to the changed spatial distribution of NH_3 emissions and the subsequent changes in the concentrations of NH_3, NH_4^+, and related species, the initial conditions used for all days except day 1, as well as the chemical balance between $PM_{2.5}$ species and their gas precursors (e.g., the partitioning between NH_3 and NH_4^+, and between HNO_3 and NO_3^-).

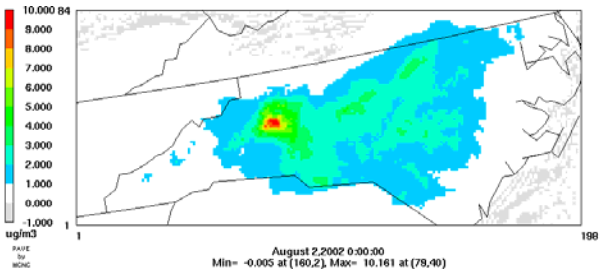

Figure 3a. The contribution of AL-NH_3 emissions to daily average $PM_{2.5}$ concentrations on August 2, 2002.

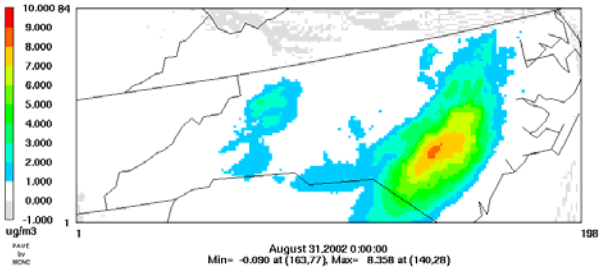

Figure 4a. The contribution of AL-NH_3 emissions to daily average $PM_{2.5}$ concentrations on August 31, 2002.

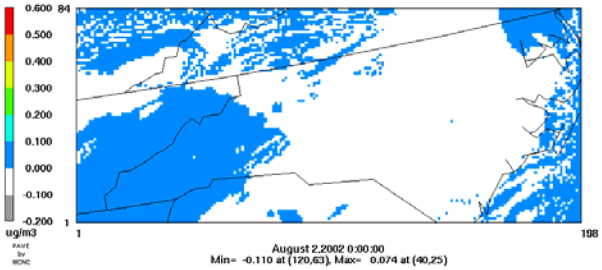

Figure 3b. The contribution of AL-NH_3 emissions to daily average SO_4^{2-} concentrations on August 2, 2002.

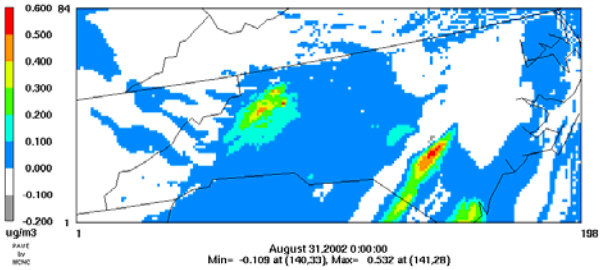

Figure 4b. The contribution of AL-NH_3 emissions to daily average SO_4^{2-} concentrations on August 31, 2002.

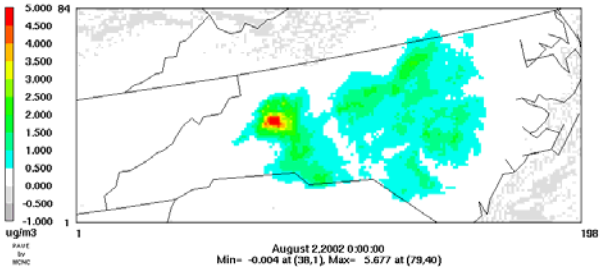

Figure 3c. The contribution of AL-NH_3 emissions to daily average NO_3^- concentrations on August 2, 2002.

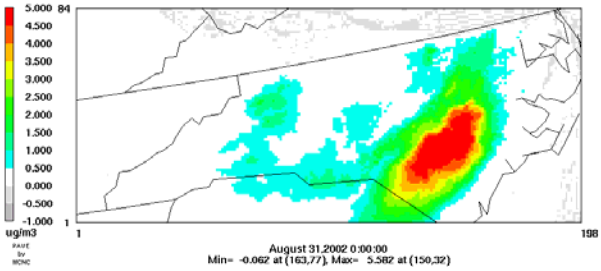

Figure 4c. The contribution of AL-NH_3 emissions to daily average NO_3^- concentrations on August 31, 2002.

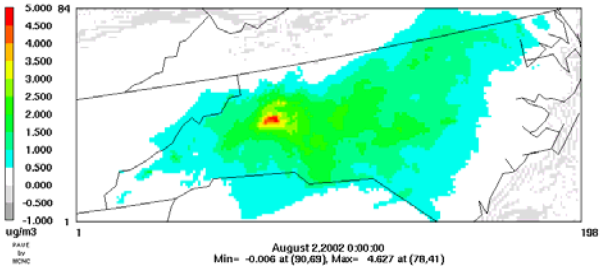

Figure 3d. The contribution of AL-NH_3 emissions to daily average NH_4^+ concentrations on August 2, 2002.

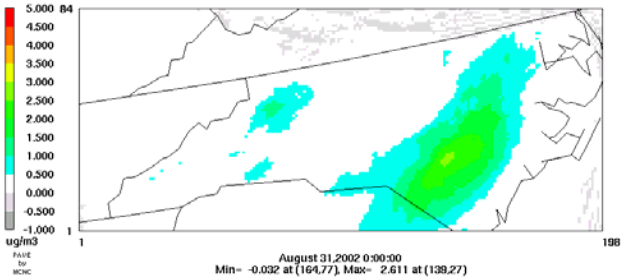

Figure 4d. The contribution of AL-NH_3 emissions to daily average NH_4^+ concentrations on August 31, 2002.

4. SUMMARY

CMAQ v4.4 has been applied to simulate the fate of NH_3 in NC. As the first step of this work, the model evaluation has been conducted using available observational datasets. Our preliminary results show that the model performance of O_3 is reasonably good, with NMBs within 24%. The performance is worse for CO and NO_2, with NMBs within 40%. For SO_2, the NMBs and NMEs range from -19% to 69% and 82-87%, respectively. Significant overpredictions for SO_2 occur at CASTNet sites (rural), which is partially due to the fact that very few samples are available. The model performance for $PM_{2.5}$, SO_4^{2-}, and NH_4^+ is consistent with what is expected from current PM models (Seigneur, 2001), with values of NMB < 50%. Large biases (> 50%) occur for nitrate at IMPROVE, STN and CASTNet sites, for EC at NCDENR and IMPROVE, and for OC at NCDENR, and IMPROVE. The likely causes for the under- and over-predictions are being analyzed. In addition to overall statistics, the spatial plots for monthly mean concentrations of O_3 and PM, and the time series plots at individual sites are being processed to provide a comprehensive model performance evaluation.

Our sensitivity simulation results show that the AL-NH_3 emissions contribute to the formation of $PM_{2.5}$ predominately. The percent contributions of AL-NH_3 emissions to the total concentrations of $PM_{2.5}$, sulfate (SO_4^{2-}), nitrate (NO_3^-), and ammonium (NH_4^+) range from 0.6% to 99.9% **(**i.e., 0.07 to 10.1 $\mu g\ m^{-3}$) on August 2, and 11.9% to 96% (i.e., 0.53 to 8.35 $\mu g\ m^{-3}$) on August 31. Turning off the AL-NH_3 emissions also causes small negative changes in the concentrations of $PM_{2.5}$ and its constituents, however, those changes are negligible. The spatial distributions of the contributions of the AL-NH_3 emissions to $PM_{2.5}$ and its composition differ significantly from day to day. More detailed analyses of meteorology, PM precursors, and their interactions are being conducted for the base and sensitivity simulations. In addition, CMAQ simulations with process analysis will also be conducted to fully understand the role of AL-NH_3 emissions in affecting the formation of PM and the fate of NH_3 in southeast U.S.

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