IMPACT OF REDUCED NITROGEN ON AIR QUALITY: FINE SCALE SIMULATION, EVALUATION, AND SENSITIVITY STUDY

Kristen M. Olsen and Yang Zhang*
Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC

John Walker
Division of Air Pollution Prevention and Control, National Risk Management Research Laboratory, US Environmental Protection Agency, Research Triangle Park, NC

Wayne Robarge
Department of Soil Science, North Carolina State University, Raleigh, NC

1. INTRODUCTION

Agricultural air quality is of concern in the southeastern United States (U.S.), particularly in North Carolina (NC), due to a large number of animal feeding operations that emit ammonia (NH_3). NH_3 plays an important role in numerous aspects of environmental issues including contributing to odors near the source, modulating soil nutrient and nitrogen cycles, neutralizing acids in air, and forming fine particulate matter ($PM_{2.5}$) which further affects human health, visibility, and climate.

In this study, two air quality models, the U.S. EPA Community Multiscale Air Quality (CMAQ) modeling system version 4.51 (Byun and Schere, 2006) with a revised secondary organic aerosol (SOA) module by ENVIRON (i.e., CMAQSOAmods v4.51, referred to as CMAQ hereafter) and the ENVIRON Comprehensive Air Quality Model with extensions (CAMx) version 4.42 (ENVIRON, 2006), are applied to an area in the southeastern U.S. to simulate the fate of NH_3 and its impact on air quality. The objective of this study is to evaluate and compare the performance of two air quality models at various grid resolutions in simulating the fate and transport of reduced nitrogen ($NH_x = NH_3 + NH_4^+$).

Model simulations are conducted at a 4-km horizontal grid resolution over NC, South Carolina, and portions of Georgia, Tennessee, Kentucky, and Virginia and at a 1.33-km horizontal grid resolution over eastern NC for two months (January and July) in 2002. Model results are evaluated using available observations through overall performance statistics, spatial distributions, and temporal variations. The conversion rate of NH_3 to ammonium (NH_4^+) and the total budget, lifetime, and seasonality of NH_x are being quantified. The preliminary results from model simulations at a 4-km horizontal grid resolution are presented below.

2. MODEL SETUP

The meteorological fields provided to the Sparse Matrix Operator Kernel Emissions (SMOKE) modeling system, CMAQ, and CAMx are derived from the Penn State University (PSU)/National Center for Atmospheric Research (NCAR) 5th generation Mesoscale Model (MM5) version 3.7 (Grell et al., 1995) with Four Dimensional Data Assimilation (FDDA). The initial and boundary conditions used for simulations at a 4-km horizontal grid resolution are derived from the Visibility Improvement State and Tribal Association of the Southeast (VISTAS) 12-km resolution simulation results. Emission inventories, provided by VISTAS (updated in July 2007), are processed using SMOKE version 2.1 for both modeling domains. The model configurations and physics for MM5 and CMAQ are consistent with VISTAS Phase II modeling study completed at 36- and 12-km grid resolutions

**Corresponding author:* Yang Zhang, Department of Marine, Earth, and Atmospheric Sciences, Campus Box 8208, NCSU, Raleigh, NC 27695; email: yang_zhang@ncsu.edu

(see http://www.vistas-sesarm.org/documents/FinalDocs.asp). When available, similar physical schemes and chemical mechanisms (e.g., the Carbon Bond-IV (CB-IV) gas phase mechanism and the Regional Acid Deposition Model (RADM) aqueous-phase mechanism) are used in both CMAQ and CAMx to reduce potential sources of discrepancies and allow for a fair model inter-comparison. One of the main differences between CMAQ and CAMx is the representation of PM size distribution. CMAQ uses a modal approach (i.e., three log-normally distributed modes: nuclei, accumulation, coarse), whereas CAMx uses a sectional approach (e.g., 2 or more bins as specified by the user). For the CAMx baseline simulation, 2 bins (coarse and fine) are used.

3. PRELIMINARY RESULTS

3.1 Meteorological Evaluation

Two one-month (January and July, 2002) simulations have been completed at the 4-km horizontal grid resolution. Prior to completing the model evaluation for chemical species, the performance of MM5 is evaluated using available observations. The datasets used in the meteorological evaluation include observations from the North Carolina Department of Environment and Natural Resources (NCDENR), the NC Climate Retrieval and Observations Network of the Southeast (NC CRONOS) Database, national networks (i.e., the Clean Air Status and Trends Network (CASTNET), the National Acid Deposition Program (NADP), and the Speciation Trends Network (STN)) and special studies (i.e., the Southeastern Aerosol Research and Characterization (SEARCH)).

Temporal analysis allows for the evaluation of the diurnal variations of model predictions. As an example, Figure 1 shows the temporal variation in Jul. 2002 for temperature at 2-m (T2), relative humidity at 2-m (RH2), wind speed at 10-m (WSP10), and wind direction at 10-m (WDR10) at Kinston, NC, a site in Lenoir County, which is one of the six NC counties with the highest swine population densities (Walker et al., 2000). MM5 generally captures the diurnal variation of T2 and RH2, however, it fails to accurately capture their max and min values. The wind speed at this site is largely overpredicted, while the wind direction is well represented.

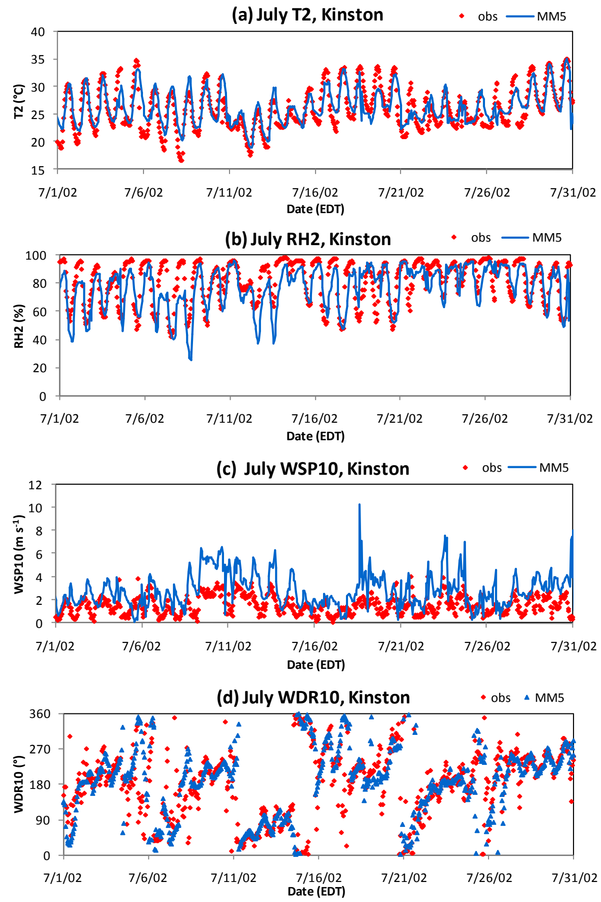

Figure 1. Hourly (a) temperature at 2-m (T2), (b) relative humidity at 2-m (RH2), (c) wind speed at 10-m (WSP10), and (d) wind direction at 10-m (WDR10) at Kinston in eastern NC.

Domain-wide statistics are valuable in assessing the overall model performance and are calculated for each network separately because of their varying characteristics in terms of sampling frequency and resolution, monitoring approaches, and type of area (e.g., urban vs. rural). Table 1 provides the statistics for Jan. and Jul. for T2, RH2, WSP10, WDR10, and precipitation (Prec). The normalized mean biases (NMBs) of T2 and RH2 are generally between ±10%, with the exceptions of Jan. T2 at the CASTNET and SEARCH sites, and Jan. RH2 at the SEARCH sites. WSP10 is overpredicted in both months, with a better performance in Jan. The mean

WDR10 simulated by MM5 is within 12° of the mean observed wind. Precipitation is largely overpredicted in Jul., which will have a large impact on the wet deposition of chemical species. There is a slight underprediction in precipitation in Jan. Discrepancies between the model simulations and observations may be a result of inaccurate model treatments for meteorological predictions and/or uncertainties in observations. Additionally, the evaluation is completed by comparing the 4-km grid average values with point-wise observations within the grid cell, which may partially contribute to the discrepancies.

Table 1. MM5 performance statistics for Jan. (top) and Jul. (bottom, italic) 2002.

	Network	Data #	Mean Obs	Mean Sim	NMB (%)
T2	CAST	5157	7.9	7.0	-11.0
		7410	*23.4*	*24.4*	*4.4*
	STN	60	6.3	6.9	8.9
		134	*26.0*	*25.6*	*-1.7*
	SEARCH	1360	10.0	7.0	-30.2
		1393	*28.5*	*26.0*	*-8.8*
RH2	CAST	6857	70.7	75.1	6.3
		6741	*76.4*	*70.7*	*-7.4*
	SEARCH	1455	69.6	80.2	15.3
		1164	*75.1*	*71.8*	*-8.8*
WSP10	CAST	4877	3.4	4.1	18.7
		3251	*2.5*	*3.2*	*31.0*
	SEARCH	1067	3.3	3.4	3.5
		571	*2.5*	*2.8*	*22.8*
WDR10	CAST	7098	200.5	212.6	6.0
		7140	*183.5*	*184.5*	*0.5*
	SEARCH	1455	210.3	210.6	0.1
		1182	*222.8*	*216.4*	*-2.9*
Prec	NADP	72	29.3	26.1	-11.0
		84	*30.1*	*75.7*	*151.3*

Obs – Observation, Sim – Simulation, NMB – Normalized Mean Bias (%), CAST – CASTNET, T2 – Temperature at 2-m (°C), RH2 – Relative Humidity at 2-m (%), WSP10 – Wind Speed at 2-m (m s^{-1}), WDR10 – Wind Direction at 10-m (°), Prec – Precipitation (mm)

3.2 Air Quality Evaluation

Similar evaluation is completed for several chemical species. Additional networks used for chemical evaluation include the Interagency Monitoring of Protected Visual Environments (IMPROVE) and the Aerometric Information Retrieval System – Air Quality Subsystem (AIRS-AQS). Figure 2 shows 24-hour average $PM_{2.5}$ concentrations observed at the surface and simulated in the surface layer of the model (0-36 m) at Kinston, NC in Jul. and Jan. $PM_{2.5}$ is overpredicted in Jan. and underpredicted in Jul. by both models with CAMx generally simulating higher concentrations than CMAQ.

The bias in $PM_{2.5}$ is also seen in the domain-wide statistics. In Jan., all the major components of $PM_{2.5}$ are overpredicted, leading to an overprediction in $PM_{2.5}$. The NMBs for $PM_{2.5}$ range from 13.9% by CMAQ at the IMPROVE sites to 32.8% by CAMx at the STN sites. In Jul., the opposite occurs; $PM_{2.5}$ and its major components are generally underpredicted, with NMBs of $PM_{2.5}$ ranging from -57.8% by CMAQ at the IMPROVE sites to -32.0% by CAMx at the STN sites. One of the major factors likely affecting simulated $PM_{2.5}$ concentrations is the model representation of vertical mixing. CAMx typically has a weaker vertical mixing than CMAQ (Zhang et al., 2004), resulting in higher levels of gases and $PM_{2.5}$. For example, carbon monoxide (CO), a moderately-long lived gas, is overpredicted by both models in both months but more so in Jan. (86.4% and 69.8% in Jan., as compared to 20.6% and 18.9% in Jul. by CAMx and CMAQ, respectively). This indicates that the vertical mixing simulated by both models in Jan. may be

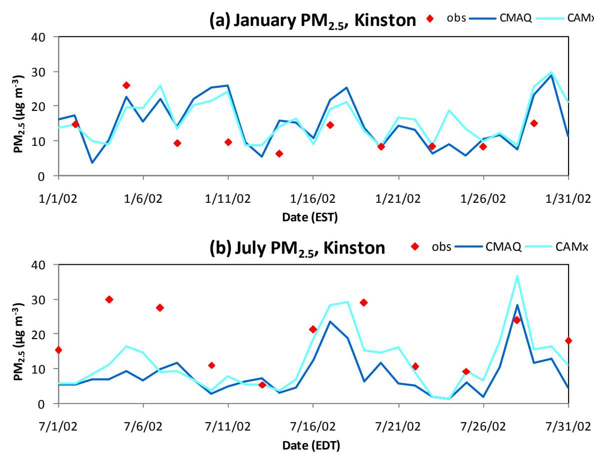

Figure 2. Time series of 24-hour average $PM_{2.5}$ in (a) Jan. and (b) Jul. The observations are available every 3 days.

much weaker than the actual vertical mixing, resulting in the overprediction of $PM_{2.5}$. Despite weaker vertical mixing simulated in Jul., $PM_{2.5}$ is underpredicted, indicating other factors, such as underestimated emissions, overpredicted removal through precipitation, or inaccurate treatments for other processes within the models, may have a larger impact than vertical mixing on $PM_{2.5}$ concentrations. Additionally, during the first week of Jul. 2002, some smoke transported from forest fires in Quebec, Canada (see www.ncdc.noaa.gov/oa/climate/extremes/2002/july/extremes0702.html) may have contributed to higher $PM_{2.5}$ observed in eastern NC, which the model was not able to reproduce, due to uncertainties in the forest fire emission inventories used in the simulation.

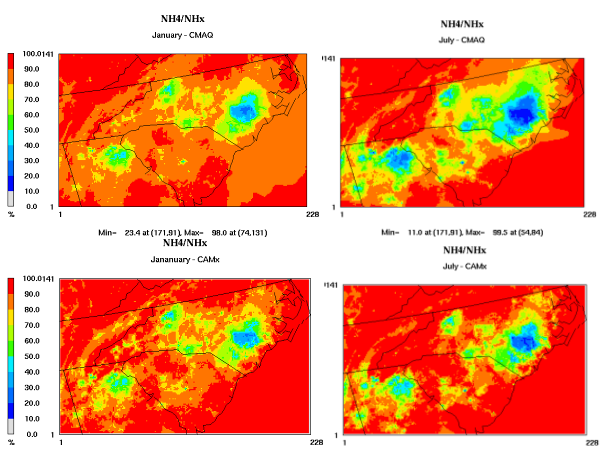

Figure 3. Monthly mean ratios of NH_4^+/NH_x (%) simulated by CMAQ (top) and CAMx (bottom) for Jan. (left) and Jul. (right), 2002.

The fate and transport of NH_x are assessed through the ratio of NH_4^+/NH_x (%), which indicates the percentage of NH_3 that has been converted to NH_4^+. Figure 3 shows the monthly average spatial distribution of this ratio in the surface layer for Jan. and Jul. as simulated by both CMAQ and CAMx. Both models give similar conversion rates and their spatial distributions in Jan. CAMx gives a higher conversion rate of NH_3 to NH_4^+ near the source in Jul. One possible explanation for the similarities between the models in Jan. but differences in Jul. is the difference in simulated aqueous-phase concentrations of hydrogen peroxide (H_2O_2) in both months. H_2O_2 is one of the major species responsible for the conversion of sulfur dioxide (SO_2) to sulfate (SO_4^{2-}) through aqueous-phase oxidation. NH_4^+ is more likely to enter particles that contain SO_4^{2-} or nitrate (NO_3^-) in order to neutralize the aerosol. In Jan., both models simulate similar gas-phase concentrations of H_2O_2 (and thus similar aqueous-phase concentrations of H_2O_2), resulting in similar concentrations of SO_4^{2-} and NH_4^+. In Jul., however, CAMx simulates up to 60% more H_2O_2 in the gas-phase than CMAQ, which would result in more aqueous-phase H_2O_2, and thus more SO_4^{2-} and NH_4^+ through the aqueous-phase oxidation reactions. CMAQ, on the other hand, removes more H_2O_2, SO_4^{2-}, and NH_4^+ through wet deposition. Compared with CMAQ, the higher H_2O_2, SO_4^{2-}, and NH_4^+ concentrations simulated by CAMx can be attributed to several factors, such as weaker vertical mixing, less removal through wet deposition, and different aerosol size representation and microphysics treatments. Wu et al. (2008) found similar results for the fate and transport of NH_x over NC in August and December 2002 using CMAQ. They reported a conversion rate of 10-40% in August and 20-50% in December at/near the source. There are limited observations of NH_3 and NH_4^+ available for comparison, however, Robarge et al. (2002) measured concentrations from October 1998 to September 1999 in Sampson County, NC and found that NH_4^+ accounts for ~18% and ~27% of NH_x in summer and winter, respectively, which are also comparable to the results found in this study.

4. SUMMARY

Two air quality modeling systems, MM5/CMAQ and MM5/CAMx, are used in this study to simulate the meteorology and air quality for July and January 2002 over a portion of the southeastern U.S. The model results are compared to available observations to evaluate the model performance. The performance of MM5 at a 4-km horizontal grid resolution is generally acceptable with the best performance for temperature and relative humidity at 2-m. However, improvements are needed in simulating the maximum and minimum 2-m temperature and relative humidity, as well as precipitation and the diurnal variations of wind speed at 10-m. Compared to CMAQ, CAMx gives weaker vertical mixing, resulting in higher levels of gases (e.g., CO) and primary PM (e.g., black carbon). Both models seem to simulate much weaker vertical mixing than what was actually occurring, leading to the overprediction in $PM_{2.5}$ by both models in January. The undeprediction in $PM_{2.5}$ in July is more likely due to other factors, such as underestimated emissions, overpredicted removal through excess precipitation, or model treatments of some other processes.

CAMx simulates a faster conversion of NH_3 to NH_4^+ near the source in July, resulting in higher NH_4^+ predictions as compared to CMAQ. The conversion near and away from the source is similar between the two models in Jan.

Additional sensitivity simulations are being completed with both models in which the NH_3 emissions from agricultural livestock (AL-NH_3) will be reduced by 50% to evaluate the impact of potential regulatory controls. Simulations are also being conducted at a finer horizontal grid resolution of 1.33-km. The sensitivity of the models to various horizontal grid resolutions (i.e., 1.33-, 4-, and 12-km) will be evaluated. The impacts of NH_3 on air quality and the implications of AL-NH_3 emission control for air quality management at state and regional scales will be elucidated.

5. ACKNOWLEDGEMENTS

This project is supported by National Research Initiative Competitive Grant no. 2008-35112-18758 from the USDA Cooperative State Research, Education, and Extension Service Air Quality Program. Thanks are due to Pat Brewer, Mike Abraczinskas, George Bridgers, Bebhinn Do, Chris Misenis, Hoko Kimball, and Wayne Cornelius NCDENR, for providing 12-km VISTAS CMAQ inputs, outputs, and observational data for NC; Don Olerud, Baron Advanced Meteorological Systems, for providing 12-km MM5 outputs; Dennis McNally and Cyndi Loomis, Alpinephysics, Inc., for providing the source code of the CMAQSOAmods v4.51 and updated VISTAS emission inventories; Ryan Boyles, NC State Climate Office, for providing NC CRONOS observational data; Alice Gilliland, Steve Howard, and Shao-Cai Yu, the U.S. EPA, for providing observational data and FORTRAN scripts used for statistical calculations; and Shiang-Yuh Wu, Clark County Department of Air Quality and Environmental Management, NV, for providing guidance in setting up some model inputs.

6. REFERENCES

Byun, D. W., and K. L. Schere, 2006: Review of the governing equations, computational algorithms and other components of the Models-3 Community Multiscale Air Quality (CMAQ) Modeling System. *Applied Mechanics Reviews*, **59**, 51-77.

ENVIRON, 2006. User's Guide – Comprehensive Air Quality Model with extensions, Version 4.40. ENVIRON International Corporation, Novato, California. <http://www.camx.com/>.

Grell, G. A., J. Dudhia, and D. R. Stauffer, 1995: A description of the Fifth-Generation Penn State/NCAR Mesoscale Model (MM5). NCAR Technical Report, NCAR/TN-398+STR, 122pp.

Robarge, W. P., J. T. Walker, R. B. McCulloch, and G. Murray, 2002: Atmospheric concentrations of ammonia and ammonium at an agricultural site in the southeast United States. *Atmospheric Environment*, **36**, 1661-1674.

Walker, J. T., V. P. Aneja, and D. A. Dickey, 2000: Atmospheric transport and wet deposition of ammonium in North Carolina. *Atmospheric Environment,* **34**, 3407-3418.

Wu, S.-Y., S. Krishnan, Y. Zhang, and V. Aneja, 2008: Modeling atmospheric transport and fate of ammonia in North Carolina – Part I: Evaluation of meteorological and chemical predictions. *Atmospheric Environment*, **42**, 3419-3436.

Zhang, Y., B. Pun, S.-Y. Wu, K. Vijayaraghavan, and C. Seigneur, 2004: Application and Evaluation of Two Air Quality Models for Particulate Matter for a Southeastern U.S. Episode. *Journal of the Air & Waste Management Association*, **54**, 1478-1493.