Photochemical Model Performance for PM2.5 Sulfate, Nitrate, Ammonium, and pre-cursor species SO2, HNO3, and NH3 at Background Monitor Locations in the Central and Eastern United States

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1. INTRODUCTION

The United States Environmental Protection Agency (EPA) has classified many counties in the eastern United States as non-attainment for the annual PM2.5 National Ambient Air Quality Standard (NAAQS). Additionally, EPA passed the Regional Haze rule to improve visibility in Class I areas by 2060. Visibility degradation results from elevated ambient concentrations of PM2.5. Two of the largest chemical components of PM2.5 in the eastern United States include secondarily formed ammonium sulfate and ammonium nitrate. States with PM2.5 non-attainment counties or with sources contributing to visibility impairment at Class I areas must submit an emissions control strategy in a State Implementation Plan (SIP) to the EPA. The SIPs will focus on reducing emissions of sulfur dioxides (SO_X) and nitrogen oxides (NO_X), which form PM2.5 sulfate and nitrate through physical processes and important chemical reactions including ammonia neutralization.

Emission control strategies are modeled with 3-dimensional Eulerian photochemical transport models. A comprehensive performance evaluation of the PM2.5 species and their pre-cursors is necessary to determine if the model will appropriately predict PM2.5 after adjustments to primary emissions species. This type of evaluation has been impossible due to the lack of long-term co-located measurements of PM2.5 sulfate, nitrate, and ammonium ions and key pre-cursor species including sulfur dioxide (SO_2), nitric acid (HNO_3), and ammonia (NH_3).

A monitor network was established in late 2003 and operated through 2004 using predominantly rural locations (9 rural and 1 urban) in the central and eastern United States (Figure 1).

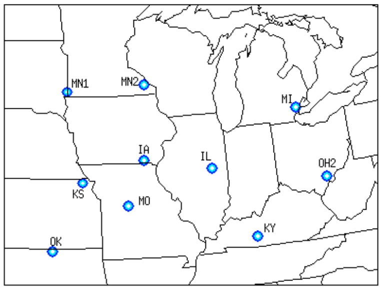

Figure 1. Ammonia network monitor locations

This network simultaneously measures PM2.5 sulfate ion, nitrate ion, ammonium ion, and chemical pre-cursor species sulfur dioxide, nitric acid, and ammonia. These samples were taken on a once in 6 day interval and have a 24-hr averaging time. This monitor network provides a unique opportunity to assess how well the modeling system predicts the spatial and temporal variability of important pre-cursor species and PM2.5 sulfate, nitrate, ammonium ions. Model and observation estimates of the degree of sulfate neutralization (DON) and the excess ammonia indicator term provide additional information about how well the model and observations agree in terms of PM2.5 nitrate and sulfate formation regimes. The excess ammonia term is an indicator about whether PM2.5 nitrate ion formation is limited by the availability of ammonia or nitric acid. The degree of sulfate neutralization (DON) gives an indication about whether PM2.5 sulfate ion is fully or partially neutralized with ammonium.

2. METHODS

The Comprehensive Air Quality Model with Extensions (CAMx) version 4.30 is a 3-dimenstional Eulerian photochemical transport model that uses state of the science routines to model particulate matter formation and removal processes over a large modeling domain (Nobel et al. 2002; Chen et al. 2003; Morris, Mansell, Tai, 2004). The model is applied with ISORROPIA inorganic chemistry, SOAP organic chemistry, regional acid deposition model (RADM) aqueous phase chemistry, and an updated carbon-bond IV (CB4) gas phase chemistry module (ENVIRON, 2005; Nenes et al, 1998; Carter, 1996). Inputs to CAMx include initial and boundary concentrations, meteorological variables, pollutant emissions, and landuse information.

Boundary conditions represent pollution inflow into the model from the lateral edges of the grid and initial conditions provide an estimation of pollution that already exists. The annual model simulation has two weeks of spin-up to minimize initial condition influence. The initial and boundary conditions are based on monthly averaged species output from an annual (calendar year 2002) application of the GEOS-CHEM global chemical transport model (Jacob et al, 2005; Bey et al, 2001).

Emissions data is processed using the EMS-2003 emissions model (Wilkinson et al, 1994). Anthropogenic emission estimates are made for a weekday, Saturday, and Sunday for each month. The biogenic emissions are day-specific. Volatile organic compounds are speciated to the CB4 chemical speciation profile (Carter, 1996). Ammonia emissions are based on the Carnegie Mellon University ammonia model (July 2004 version) using 2002 census of agriculture data (Strader et al. 2005; Pinder et al., 2004; Goebes et al., 2003).

Meteorological input data for the photochemical modeling runs are processed using the National Center for Atmospheric Research (NCAR) 5th generation Mesoscale Model (MM5) version 3.6.1 (Dudhia, 1993; Grell et al, 1994). Important meteorological model parameterizations and physics options include mixed phase (Reisner1) microphysics, Kain-Fritsch 2 cumulus scheme, Rapid Radiative Transfer Model, Pleim-Chang planetary boundary layer (PBL), and the Pleim-Xiu land surface module. These parameters and options are selected as an optimal configuration for the central United States based on multiple MM5 simulations using a variety of physics and configuration options (Johnson, 2003).

All models are applied with a Lambert projection centered at (-97, 40) and true latitudes at 33 and 45. The photochemical modeling domain consists of 97 cells in the X direction and 90 cells in the Y direction covering the central and eastern United States with square 36 km grid cells (Figure 2). CAMx4 is applied with the vertical atmosphere resolved with 16 layers up to approximately 15 km above ground level.

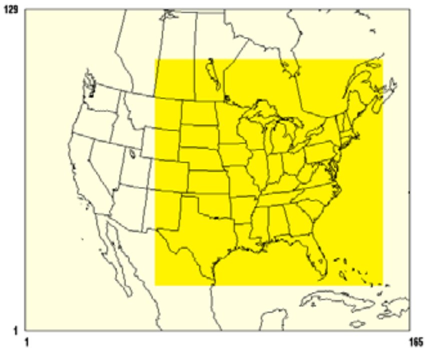

Figure 2. CAMx4 36 km modeling domain (dark yellow box) and MM5 36 km domain (light yellow box).

Performance metrics used to describe model performance include mean bias, gross error, fractional bias, and fractional error (Table 1) (Boylan et al, 2006). Performance metrics include all non-negative data points unless data censoring is specifically notated. The bias and error metrics are used to describe performance in terms of the measured concentration units ($\mu g/m^3$) and the fractional metrics describe performance as a percent.

Table 1. Model Performance Metrics

Mean Bias	$=\frac{1}{N\times M}\sum_{i=1}^{N}\sum_{j=1}^{M}(P_i^j-O_i^j)$
Gross Error	$=\frac{1}{N\times M}\sum_{i=1}^{N}\sum_{j=1}^{M}\lvert P_i^j-O_i^j\rvert$
Mean Fractional Bias	$=\frac{1}{N\times M}\sum_{i=1}^{N}\sum_{j=1}^{M}\left(2\times\frac{P_i^j-O_i^j}{P_i^j+O_i^j}\right)$
Fractional Gross Error	$=\frac{1}{N\times M}\sum_{i=1}^{N}\sum_{j=1}^{M}\left\lvert 2\times\frac{P_i^j-O_i^j}{P_i^j+O_i^j}\right\rvert$

*P=model prediction; O=observation; N=number of days; M=number of monitors

The best possible model performance is when the bias and error metrics approach 0. The fractional metrics are bounded by 200%, which is considered very poor performance.

An indicator of whether PM2.5 nitrate ion formation is limited by the availability of nitric acid or ammonia is the excess ammonia term (Blanchard et al, 2000). All the terms in the equation below are expressed in units of $\mu mole/m^3$.

$$\text{Excess Ammonia} = NH_3 + NH_4^+ - 2*SO_4^= - NO_3 - HNO_3$$

When the excess ammonia term is less than 0 then PM2.5 nitrate formation would be ammonia limited and when the term is greater than 0 then PM2.5 nitrate formation is nitric acid limited. The degree of sulfate neutralization (DON) is estimated to determine whether sulfate is completely acidic, fully neutralized by ammonia, or in between.

$$DON = \frac{[NH4]/18-[NO3]/62}{[SO4]/96}$$

There are 2 moles of ammonium for every mole of sulfate when sulfate is fully neutralized in the form of ammonium sulfate, giving a DON value of 2. If DON is 1, then sulfate would be ammonium bisulfate and particulate sulfuric acid when DON is 0.

3. RESULTS and DISCUSSION

An examination of the mean bias for all monitor locations and entire modeling period show a regional over-prediction of total sulfate ($SO_2+SO_4^=$), but good relationship between prediction-observation pairs (mean bias=5.05 $\mu g/m^3$ and r^2= .54). This over-prediction is dominated by sulfur dioxide (mean bias=4.00 $\mu g/m^3$). The large bias for only sulfur dioxide suggests PM2.5 sulfate formation in the model is not always limited by sulfur dioxide availability in the eastern and central United States. Total nitrate ($HNO_3+NO_3^-$) is slightly over-predicted by the model (mean bias=1.22 $\mu g/m^3$ and r^2= .28). NH_X ($NH_3+NH_4^+$) has little overall bias (mean bias=0.13 $\mu g/m^3$ and r^2= .13).

Since the modeling system will be used to support regulatory applications to reduce PM2.5 ammonium sulfate and ammonium nitrate, performance is examined when these species are highest. Model performance for PM2.5 sulfate ion is best in the summer (fractional bias=36%, r^2=.57) when ambient concentrations are highest. PM2.5 nitrate ion performance has a fractional bias of -19% and 41% in the winter and fall seasons respectively. The prediction-observation pairs are well correlated for winter (r^2=.49) and fall (r^2=.39) seasons. PM2.5 ammonium performance is best during the winter and summer months when concentrations tend to be highest with a fractional bias of 0% and 79% for winter and summer.

Scatter-plots in Figure 3 show the prediction-observation relationship for each of the species.

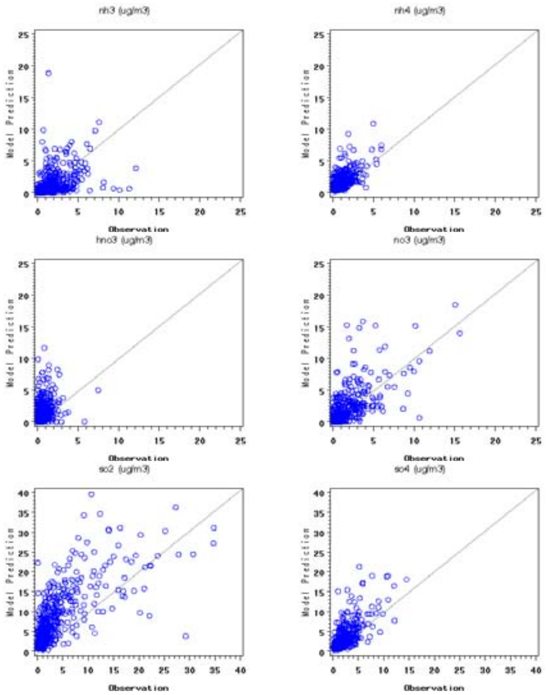

Figure 3. Observations and Model Predictions of NH_3, NH_4^+, HNO_3, NO_3^-, SO_2, and $SO_4^=$ ($\mu g/m^3$)

A visual examination of the scatter-plots shows the photochemical model does well at predicting concentrations of PM2.5 species even though the pre-cursor species are not as consistently well predicted.

The mean bias metric estimated by station over all days is shown in Figure 4. The mean bias for each species is fairly similar from site to site suggesting systematic biases in the modeling process rather than specific local emission inventory deficiencies. The MN2 site is the only site to over-predict ammonia concentrations. MN2 is also unique in that the bias for PM2.5 sulfate ion is higher than the bias for sulfur dioxide. At the other monitor locations the model over-prediction bias for sulfur dioxide is much higher than the bias for PM2.5 sulfate ion.

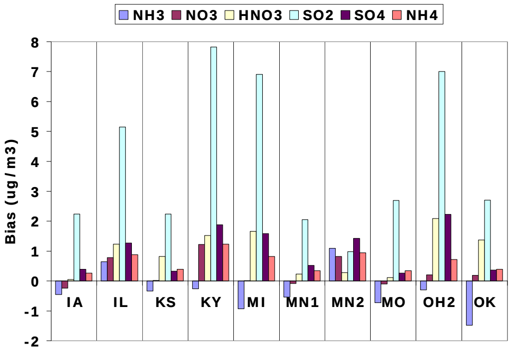

Figure 4. Bias metric by Site

The mean bias metric averaged over all sites by season is shown in Figure 5. Ammonia is under-predicted in the winter and spring months and has little bias in the summer and fall.

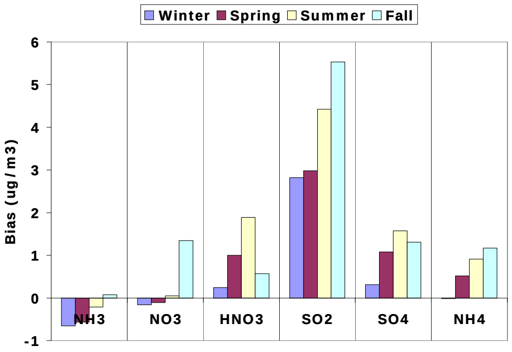

Figure 5. Bias metric by season

PM2.5 nitrate ion is over-predicted in the fall and slightly under-predicted in the winter months. Sulfur dioxide and PM2.5 ammonium ion have their largest over-prediction bias in the fall months. PM2.5 nitrate under-prediction in the winter months is partly symptomatic of PM2.5 sulfate over-predictions. The PM2.5 sulfate ion is keeping ammonia sequestered that would otherwise be free to react with nitric acid and form PM2.5 ammonium nitrate.

Measurements of sulfur dioxide and nitric acid at the ammonia monitor network may be under-estimated. Monthly averaged nitric acid and sulfur dioxide concentrations at 24 Midwest CASTNET monitors, 9 ammonia network monitors, and model predictions at the ammonia network locations are compared in Figure 6.

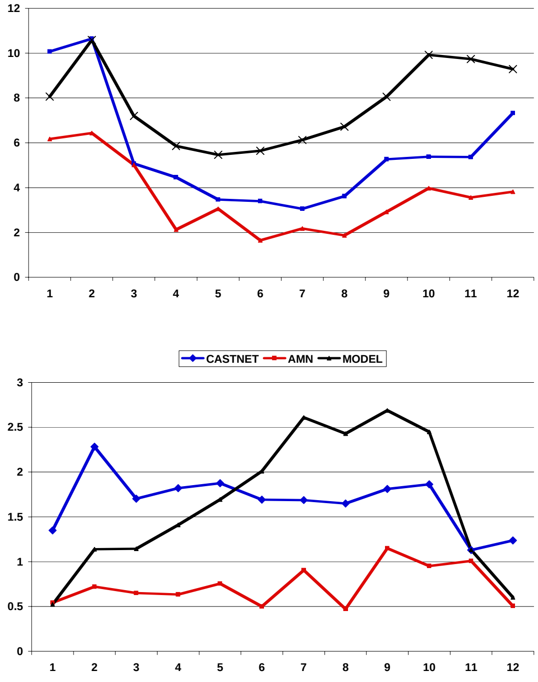

Figure 6. Monthly concentrations of SO_2 (top) and HNO_3 (bottom)

The modeling system appears to over-predict SO_2, particularly in the late summer and early fall months. It also shows that SO_2 tends to be under-estimated at ammonia network monitors and performance compared to these observations might make SO_2 performance to appear unrealistically degraded. The ammonia network monitors also appear to under-measure nitric acid. Model estimates of nitric acid fall in line with the observed values in the colder months and are higher during the warmer months.

Excess ammonia is an indicator term used to describe PM2.5 nitrate formation in terms of ammonia or nitric acid limitation. Excess ammonia predicted by the modeling system is compared to the same term estimated with observed data (Figure 7).

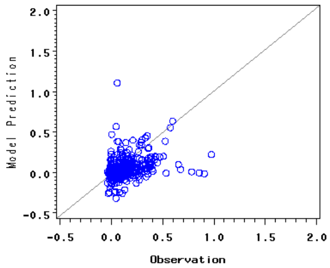

Figure 7. Excess Ammonia Indicator Term

PM2.5 nitrate formation is limited by nitric acid availability when the excess ammonia term is greater than 0 and limited by ammonia when the term is less than 0. The modeling system tends to be nitric acid limited more often than seen in observations. This result is not entirely un-expected since the modeling system slightly under-predicts ammonia and nitric acid is under-measured. In general, the modeling system and ambient observations tend to agree on whether PM2.5 nitrate formation is nitric acid or ammonia limited. This improves confidence that the modeling system estimates of PM2.5 nitrate ion will respond appropriately to changes in emissions pre-cursors.

The modeling system performance in predicting the degree of sulfate neutralization by ammonia is shown in Figure 8.

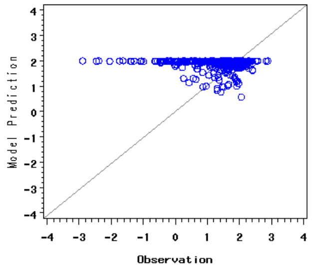

Figure 8. Degree of sulfate neutralization by ammonia

PM2.5 sulfate is almost always completely neutralized by ammonia in the modeling system. Observations suggest PM2.5 sulfate tends to be partially neutralized by ammonia, not usually fully neutralized to ammonium sulfate. This suggests there should be more free ammonia gas in the photochemical model and less PM2.5 sulfate and PM2.5 ammonium. This type of scenario would potentially improve model performance to some degree for all 3 of these species.

Model performance metrics are useful to quantitatively assess the skill of the model in predicting observations. It is unrealistic to expect the modeling system to predict observations with any more precision than which they can be measured. Observation collection methods are not perfect and an estimate of measurement uncertainty provides a useful benchmark for comparison to model performance metrics. Observation error is estimated by comparing measurements taken at the ammonia network sites with measurements taken from co-located networks that include IMPROVE and STN.

Table 3 shows the relationship between the model predictions and observations and co-located observations. The co-located observation relationship provides an upper-bound benchmark for model performance that is much more realistic than the mathematical perfect relationship of 1.

Table 3. Model-Observation and Co-located observation r^2 values

	Model-Obs		Obs-Obs	
Species	N	RSQ	N	RSQ
NO3	487	0.44	463	0.77
SO4	536	0.49	510	0.71
NH4	477	0.35	103	0.72
SO2	558	0.52	42	0.86

Model estimates are well associated with observations. The weakest relationship between model estimates and observations is for NH_4^+. The variability between co-located observations suggests model-observation relationships approaching 0.7 to 0.8 reflect excellent model performance. This also suggests an r^2 of 1.0 would be impossible to achieve given the inherent variability between co-located observations. Error and fractional error model performance metrics are compared to the same metrics used to describe co-located observations in Table 4.

Table 4. Model-Observation and co-located observation error and fractional error metrics

Metric	Species	Model-Obs[1]	Model-Obs[2]	Obs-Obs
Error	NO3	1.2	1.0	0.5
Error	SO2	4.5		3.4
Error	SO4	1.5	1.2	0.8
Error	NH4	0.9		0.4
Frac Error	NO3	85.9	84.7	45.1
Frac Error	SO2	96.6		39.0
Frac Error	SO4	52.1	39.4	33.4
Frac Error	NH4	66.8		42.5

[1] *model v. ammonia network*

[2] *model v. IMPROVE network*

The error and fractional error between the model estimates of PM2.5 nitrate and sulfate ions and IMPROVE network observations are also shown in Table 4. The model performance error is lower when comparing model estimates of PM2.5 sulfate and nitrate ions to IMPROVE observations. The error and fractional error for PM2.5 sulfate ion for model estimates compared to IMPROVE observations are very close to the error between the ammonia and co-located IMPROVE network observations. The error metrics for SO_2 are higher than for $SO_4^=$, NO_3^-, or NH_4^+. However, the error estimated between co-located samples of SO_2 is also higher compared to $SO_4^=$, NO_3^-, and NH_4^+. A evaluation of model performance comparing SO_2 error to the error for other species might lead to a conclusion that performance for SO_2 is poor relative to these species, but relative to the error in co-located SO_2 measurements it is estimated as well as NO_3^-, $SO_4^=$, and NH_4^+.

4. CONCLUSION

Model performance is quite good for PM2.5 sulfate ion, PM2.5 nitrate ion, and PM2.5 ammonium ion. Performance for pre-cursor species sulfur dioxide, nitric acid, and ammonia is good but not as strong as the performance for the PM2.5 species. The pre-cursor species performance is better than quantified against the ammonia monitor network observations for sulfur dioxide and nitric acid as these species seem to be under-measured by the network. Sulfur dioxide is systematically over-predicted by the modeling system. SO_2 emissions are dominated by large electrical generating units and the emissions estimates are very good, which suggests deposition removal mechanisms are not efficiently removing SO_2 in the model. Ammonia tends to be under-predicted by the modeling system, especially during the winter and early spring months.

PM2.5 nitrate formation is usually limited by the availability of nitric acid at these monitor locations based on the observation data. The model estimates of the excess ammonia indicator tend to agree with the observed estimate and improves confidence that model PM2.5 nitrate will respond appropriately to changes in pre-cursor emissions. Regulatory strategies will likely focus on reductions in NO_X rather than ammonia to control PM2.5 ammonium nitrate so the modeling system matches up well to the intended application purpose.

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