

Photochemical model performance for PM_{2.5} sulfate, nitrate, ammonium, and precursor species SO₂, HNO₃, and NH₃ at background monitor locations in the central and eastern United States

Kirk Baker^{a,b,*}, Peter Scheff^b

^a*Lake Michigan Air Directors Consortium, Rosemont, IL, USA*

^b*University of Illinois at Chicago, Chicago, IL, USA*

Received 26 October 2006; received in revised form 4 April 2007; accepted 4 April 2007

Abstract

Health studies have shown premature death is statistically associated with exposure to particulate matter <2.5 μm in diameter (PM_{2.5}). The United States Environmental Protection Agency requires all States with PM_{2.5} non-attainment counties or with sources contributing to visibility impairment at Class I areas to submit an emissions control plan. These emission control plans will likely focus on reducing emissions of sulfur oxides and nitrogen oxides, which form two of the largest chemical components of PM_{2.5} in the eastern United States: ammonium sulfate and ammonium nitrate. Emission control strategies are simulated using three-dimensional Eulerian photochemical transport models.

A monitor study was established using one urban (Detroit) and nine rural locations in the central and eastern United States to simultaneously measure PM_{2.5} sulfate ion (SO₄²⁻), nitrate ion (NO₃⁻), ammonium ion (NH₄⁺), and precursor species sulfur dioxide (SO₂), nitric acid (HNO₃), and ammonia (NH₃). This monitor study provides a unique opportunity to assess how well the modeling system predicts the spatial and temporal variability of important precursor species and co-located PM_{2.5} ions, which is not well characterized in the central and eastern United States.

The modeling system performs well at estimating the PM_{2.5} species, but does not perform quite as well for the precursor species. Ammonia is under-predicted in the coldest months, nitric acid tends to be over-predicted in the summer months, and sulfur dioxide appears to be systematically over-predicted. Several indicators of PM_{2.5} ammonium sulfate and ammonium nitrate formation and chemical composition are estimated with the ambient data and photochemical model output. PM_{2.5} sulfate ion is usually not fully neutralized to ammonium sulfate in ambient measurements and is usually fully neutralized in model estimates. The model and ambient estimates agree that the ammonia study monitors tend to be nitric acid limited for PM_{2.5} nitrate formation. Regulatory strategies in this part of the country should focus on reductions in NO_x rather than ammonia to control PM_{2.5} ammonium nitrate.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Photochemical model; Regional air quality; PM_{2.5}; Ammonia; Nitric acid; Sulfur dioxide

*Corresponding author. 9501 West Devon Avenue, Suite 701, Rosemont, IL 60018, USA. Tel.: +1 847 720 7881; fax: +1 847 720 7891.
E-mail address: baker@ladco.org (K. Baker).

1. Introduction

Two of the largest chemical components of PM_{2.5} in the eastern United States include secondarily formed ammonium sulfate and ammonium nitrate. States with PM_{2.5} 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 U.S. Environmental Protection Agency (EPA). The SIPs will focus on reducing emissions of sulfur oxides (SO_x) and nitrogen oxides (NO_x), which form PM_{2.5} sulfate and nitrate through physical processes and important chemical reactions including ammonia neutralization (Khoder, 2002).

Emission control strategies are modeled with three-dimensional Eulerian photochemical transport models. A comprehensive performance evaluation of the PM_{2.5} species and their precursors is helpful to determine if the model will appropriately predict PM_{2.5} after adjustments to primary emissions species. This type of evaluation in the central US has been problematic due to the lack of long-term co-located measurements of PM_{2.5} sulfate, nitrate, and ammonium ions and key precursor species including sulfur dioxide (SO₂), nitric acid (HNO₃), and ammonia (NH₃).

A group of monitors were operated from January through December 2004 using one urban (Detroit) and nine rural locations in the central and eastern United States (Fig. 1) to measure PM_{2.5} sulfate ion (SO₄²⁻), nitrate ion (NO₃⁻), ammonium ion (NH₄⁺), and PM_{2.5} precursor species sulfur dioxide, nitric acid, and ammonia. These samples were taken on a

once-in-6-day interval and have a 24-h averaging time. This ammonia monitor study provides a unique opportunity to assess how well the modeling system predicts the spatial and temporal variability of important precursor species and co-located PM_{2.5} 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 sulfate acidity and PM_{2.5} nitrate formation regime. The excess ammonia term is an indicator about whether PM_{2.5} nitrate ion formation is limited by the availability of ammonia or nitric acid. The DON gives an indication about whether PM_{2.5} sulfate ion is fully or partially neutralized with ammonium.

Error metrics between model predictions and observations and co-located observations of PM_{2.5} ions are compared to provide a model performance goal. This uses observation uncertainty as a context for a realistic model performance goal as an alternative to perfect statistical agreement and comparison with metrics estimated from other modeling studies. The bias metrics between PM_{2.5} ions and precursor species are examined for relationships to determine how much of the error in precursor model performance translates into error for co-located PM_{2.5} ion model estimates.

2. Methods

The Comprehensive Air Quality Model with Extensions (CAMx) version 4.30 is a three-dimensional Eulerian photochemical transport model that uses state-of-the-science routines to model particulate matter formation and removal processes (Nobel et al., 2002; Tanaka et al., 2003; Chen et al., 2003; Morris et al., 2004). The model is applied with ISORROPIA inorganic chemistry (Nenes et al., 1998), a semi-volatile equilibrium scheme to partition condensable organic gases between gas and particle phase (Strader et al., 1999), regional acid deposition model (RADM) aqueous-phase chemistry (Chang et al., 1987), and an updated carbon-bond IV (CB4) gas-phase chemistry module (Gery et al., 1989; Carter, 1996; ENVIRON, 2005). Inputs to CAMx include initial and boundary concentrations, meteorological variables, pollutant emissions, and land-use information.

Boundary conditions represent pollution inflow into the model from the lateral edges and top of the

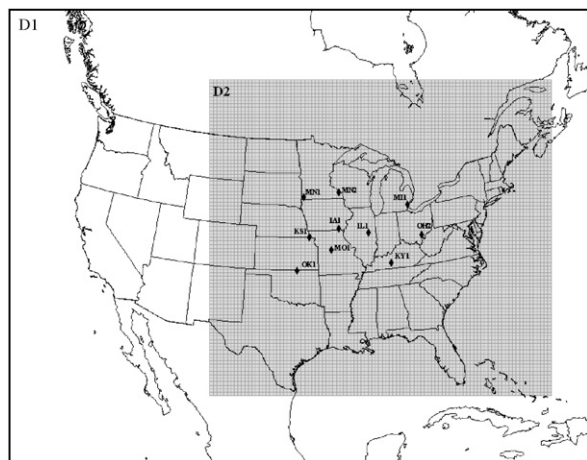


Fig. 1. CAMx 36-km modeling domain (D2) inside MM5 36-km domain (D1) and ammonia network monitor locations.

grid and initial conditions provide an estimation of pollution that already exists. The entire year of 2004 is divided into four separate simulations based on season: January to March, April to May, June to August, and September to December. Each season of the annual model simulation has 2 weeks of spin-up to minimize initial condition influence. The first-quarter simulation is initiated in mid-December 2003 to have an appropriate spin-up period. 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). The initial and boundary concentrations vary in the vertical and horizontal directions.

Emissions data are processed using the EMS-2003 emissions model (Janssen and Hua, 1998; 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 (Gery et al., 1989). 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; LADCO, 2004).

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 36 km² grid cells (Fig. 1). CAMx is applied with the vertical atmosphere resolved with 16 layers up to approximately 15 km above ground level.

Table 1
Monitor locations

Station name	Site code	IMPROVE site code	STN site code
Lake Sugema, IA	IA	LASU1	
Bondville, IL	IL	BOND1	
Sac and Fox Nation, KS	KS	SAFO1	
Mammoth Cave	KY	MACA1	
Allen Park, MI	MI	DETR1	261630001
Blue Mounds, MN	MN1	BLMO1	
Great River Bluffs, MN	MN2	GRR11	
Pleasant Green, MO	MO	ELDO1	
Athens, OH	OH2	QUC11	
Cherokee Nation, OK	OK	CHER1	

All ammonia study monitors are co-located with Interagency Monitoring of Protected Visual Environments (IMPROVE) monitors and the Detroit location is also co-located with a US EPA speciation trends network (STN) monitor (Table 1). Gases are converted to $\mu\text{g m}^{-3}$ using standard temperature and pressure. Observation data from monitors that are not co-located with the ammonia study monitors provide additional information about model performance. Other data sources include 64 monitors measuring nitrogen oxides (retrieved from US EPA's Aerometric Information Retrieval System) and 24 Clean Air Status and Trends Network (CASTNET) monitors measuring weekly concentrations of sulfur dioxide and nitric acid. Monitors from these networks are chosen to represent a region similar to the ammonia monitor study.

Metrics used to describe model performance include mean bias, gross error, fractional bias, and fractional error (US EPA, 2006; Boylan et al., 2006). In addition to these metrics (Table 2), the correlation coefficient (*r*) and the coefficient of determination (*r*²) are used to describe association between model and observation distributions. The bias and error metrics are used to describe performance in terms of the measured concentration units ($\mu\text{g m}^{-3}$) and the fractional metrics describe performance as a percent. The best possible model performance is when the metrics approach 0. The fractional metrics are bounded by 200%, which is considered very poor performance.

The photochemical model estimates represent a volumetric average over an entire grid cell. Observations represent concentrations at a specific location and some limited distance around the monitor location, which is a function of a species concentration gradient (Boylan et al., 2006). It is

not realistic to exactly match observed species concentrations at a specific location to a volumetric average model output, especially if the species is known to have large concentration gradients. Measurements have their own uncertainty due to biases and artifacts related to sampling and laboratory analysis methods. Studies have demonstrated that large differences exist between measurements of the same PM_{2.5} chemical species at co-located monitors (McDade et al., 2005; Boylan

et al., 2006). Consideration of uncertainties and spatial scale should be given when comparing model predictions and ambient measurements for model performance evaluation because neither one represents the absolute truth.

An indicator of whether PM_{2.5} 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 following equation are expressed in units of $\mu\text{mole m}^{-3}$:

$$\text{Excess ammonia} = \text{NH}_3 + \text{NH}_4^+ - 2\text{SO}_4^{2-} - \text{NO}_3^- - \text{HNO}_3.$$

When the excess ammonia term is <0 then PM_{2.5} nitrate formation would be ammonia limited and when the term is >0 then PM_{2.5} nitrate formation is nitric acid limited. The DON is estimated to determine whether sulfate is completely acidic, fully neutralized by ammonia, or in between. Concentrations are expressed as $\mu\text{g m}^{-3}$ in the DON equation.

$$\text{DON} = ([\text{NH}_4^+]/18 - [\text{NO}_3^-]/62) \times ([\text{SO}_4^{2-}]/96)^{-1}.$$

There are 2 moles of ammonium for every mole of sulfate when sulfate is fully neutralized in the form

Table 2

Performance/comparison metrics

$$\text{Mean bias} = \frac{1}{N \times M} \sum_{i=1}^N \sum_{j=1}^M (A_i^j - B_i^j)$$

$$\text{Mean error} = \frac{1}{N \times M} \sum_{i=1}^N \sum_{j=1}^M |A_i^j - B_i^j|$$

$$\text{Mean fractional bias} = \frac{1}{N \times M} \sum_{i=1}^N \sum_{j=1}^M \left(2 \times \frac{A_i^j - B_i^j}{A_i^j + B_i^j} \right)$$

$$\text{Mean fractional error} = \frac{1}{N \times M} \sum_{i=1}^N \sum_{j=1}^M \left| 2 \times \frac{A_i^j - B_i^j}{A_i^j + B_i^j} \right|$$

$$\text{Correlation coefficient } (r) = \frac{\left[\sum_{i=1}^n \sum_{j=1}^n (A_i^j - \bar{A})(B_i^j - \bar{B}) \right]}{\left[\sum_{i=1}^n \sum_{j=1}^n (A_i^j - \bar{A})^2 \sum_{i=1}^n \sum_{j=1}^n (B_i^j - \bar{B})^2 \right]^{1/2}}$$

A = photochemical model prediction; B = observation.

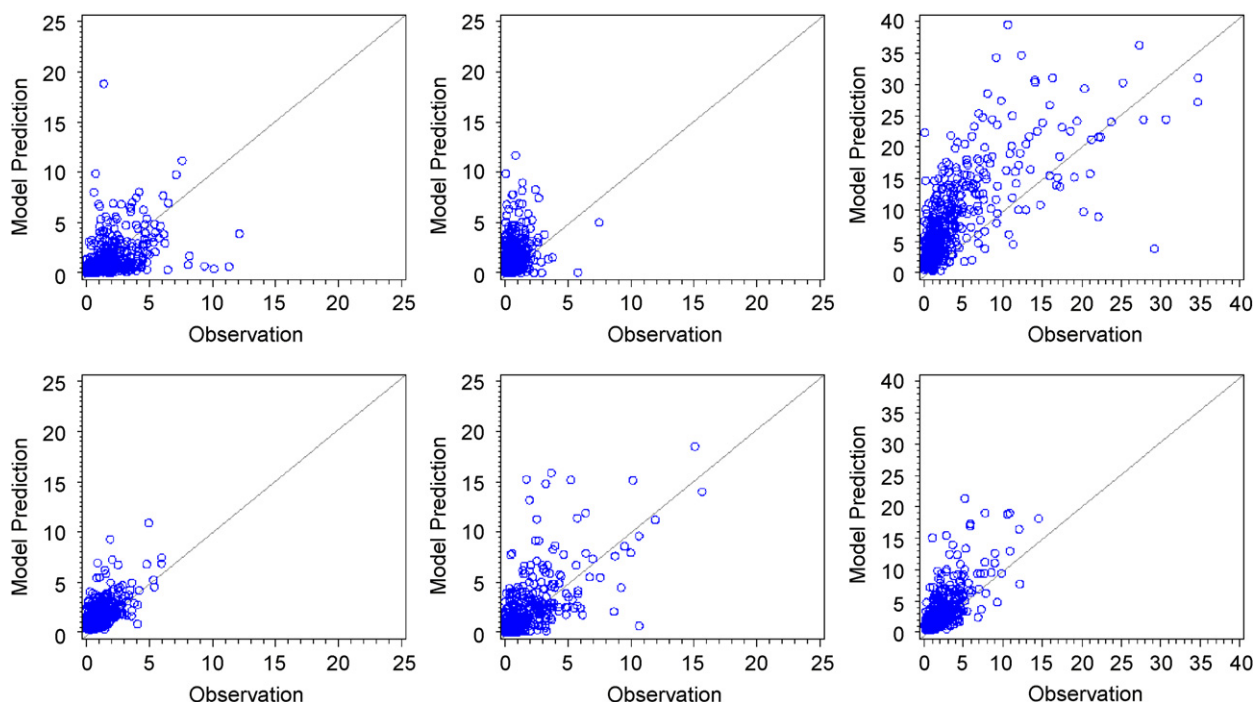


Fig. 2. Observations and model predictions of (top row left to right) NH_3 , HNO_3 , SO_2 , and (bottom row left to right) NH_4 , NO_3 , SO_4 ($\mu\text{g m}^{-3}$).

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. This equation assumes that nitrate is only neutralized by ammonia. This assumption is appropriate for these monitor locations, but may be too simplistic for other locations where nitrate is often neutralized by sodium or calcium.

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 ($\text{SO}_2 + \text{SO}_4^{2-}$), but good relationship between prediction–observation pairs (mean bias = $5.05 \mu\text{g m}^{-3}$ and $r^2 = 0.54$). This over-prediction is dominated by sulfur dioxide (mean bias = $4.00 \mu\text{g m}^{-3}$). Total nitrate ($\text{HNO}_3 + \text{NO}_3^-$) is slightly over-predicted by the model (mean bias = $1.22 \mu\text{g m}^{-3}$ and $r^2 = 0.28$). NH_X ($\text{NH}_3 + \text{NH}_4^+$) has little overall bias (mean bias = $0.13 \mu\text{g m}^{-3}$ and $r^2 = 0.13$). Scatter-plots in Fig. 2 shows all of the prediction–observation pairs for each of the species. The photochemical model does well at predicting concentrations of $\text{PM}_{2.5}$ species and NH_X .

The fractional bias metric estimated by station over all days is shown in Fig. 3 for total sulfate, total nitrate, and NH_X . In these box plots the 75th, 50th, and 25th percentiles of the distribution are shown by the top, middle, and bottom bars of the box. The circle inside the box is the mean and any values outside the box are outside the 25th to 75th percentile distribution. The fractional bias distributions for total sulfate show little variation by site. NH_X bias metric distributions are centered near 0 for most sites, indicating an appropriate amount of ammonium in the model. The bias metrics for the OK and MN1 sites tend to be below 0 and suggest possible deficiencies in the ammonia emission inventory for these locations. Total nitrate fractional bias distributions are close to 0 for the most north-western sites (IA, KS, MN1, and MO). One exception is the MN2 site, which shows an over-prediction bias for total nitrate and NH_X . The MN2 monitor has a unique siting on top of the Mississippi River bluffs in southeast Minnesota. It is likely that the 36-km grid cells do not adequately capture the micro-scale meteorology at that location. The distributions of total nitrate bias is consistently well above 0 for sites closest to the Ohio River Valley.

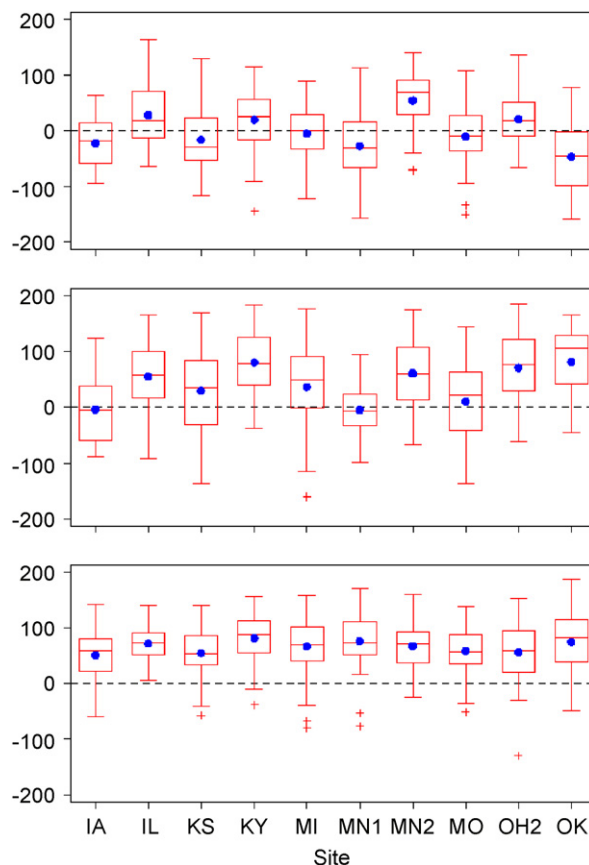


Fig. 3. NH_X (top), total nitrate (middle), and total sulfate (bottom) fractional bias (%) distributions over all days by site.

The fractional bias metrics normalize large and small concentrations, making seasonal trends in model performance more discernable. NH_X fractional bias is minimal for most summer and spring months (Fig. 4). The fractional bias distributions by month for NH_X show that the modeling system does not have enough NH_X in the winter and too much in the late fall months. Ammonia emissions are annual totals that are allocated to each month based on known temporal information, from 2002 in this application, so moving some of the emissions from the fall into the late winter months would not change total emissions but would likely improve model performance. This suggests the monthly allocation of total annual ammonia emissions may need to be adjusted to more appropriately represent 2004 ammonia-related emissions activity. Gas-phase ammonia is often under-predicted when particulate ammonium and sulfate is over-predicted. The excess sulfate in the model keeps ammonium in the particulate phase when it

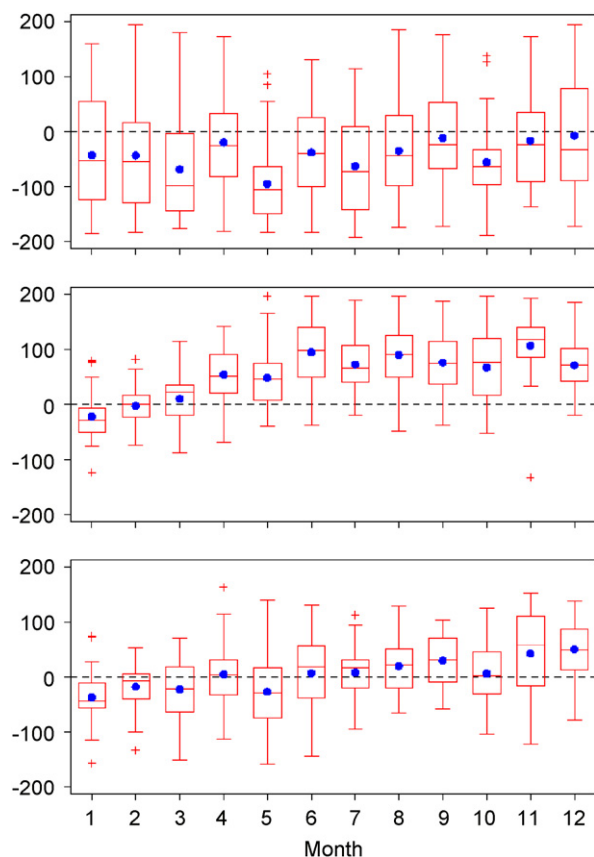


Fig. 4. Fractional bias (%) distributions over all sites by month for ammonia (top), PM_{2.5} ammonium ion (middle), and NH₄X (bottom).

should be in the gas phase or available to potentially neutralize nitrate.

Total nitrate fractional bias distributions by month show a clear tendency for the modeling system to over-predict in the warmer months (Fig. 5). PM_{2.5} nitrate ion fractional bias is minimal during the coldest months when concentrations are highest. Nitric acid is over-predicted during the summer and fall seasons. However, nitric acid concentrations at the ammonia monitor study may be under-measured. The manual denuder system used by most sites in the study has been shown to under-measure nitric acid compared to the commercial honeycomb denuder system used at a few sites in the study (Tsai et al., 2000; Baker and Scheff, 2006a). Monthly averaged nitric acid concentrations at 24 Midwest CASTNET monitors and nine ammonia study monitors show very little seasonal variability. The modeling system shows a clear over-prediction tendency during the warmest months for nitric acid compared to CASTNET and

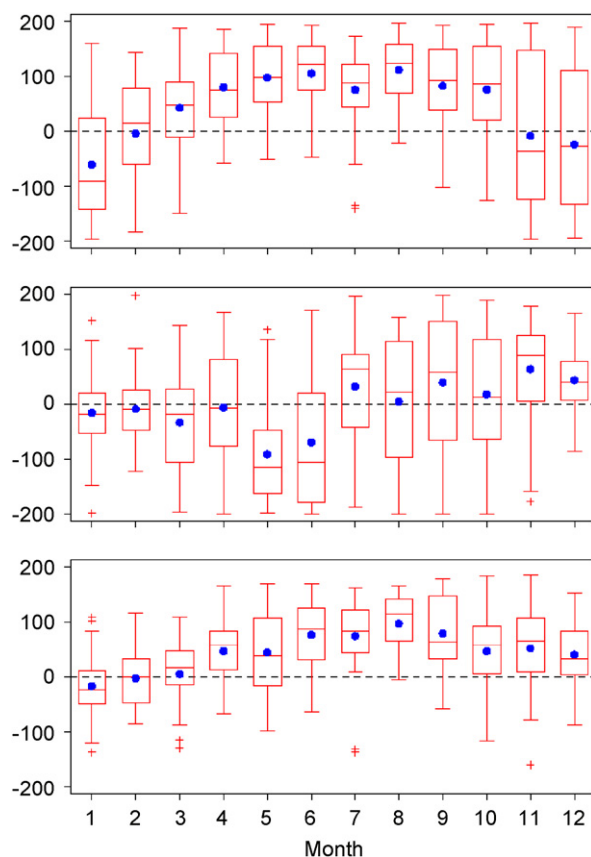


Fig. 5. Fractional bias (%) distributions over all sites by month for nitric acid (top), PM_{2.5} nitrate ion (middle), and total nitrate (bottom).

ammonia study monthly averaged observations. Monitors that measure NO_x are typically situated in areas with high emissions such as urban areas and near stationary point sources. The mean fractional bias for NO_x is examined by month to give an indication about whether the model is significantly over or understating NO_x concentrations. Fractional bias for NO_x does not show a strong seasonal trend, but is lowest in April at −22.1% and highest in November at 15.6%. Nine of 12 months have an average fraction bias between ±10%, suggesting that NO_x is not being over- or under-stated to a large degree in the model. The minimal bias for NO_x coupled with over-predictions of nitric acid in the summer months indicates that the model may be generating too much nitric acid though photochemical reactions or summer deposition processes are not appropriately characterized.

Total sulfate is over-predicted in the modeling system during the entire annual simulation, which is largely due to sulfur dioxide over-predictions

(Fig. 6). The large bias for only sulfur dioxide suggests that PM_{2.5} sulfate formation in the model is often limited by oxidant availability and not always by sulfur dioxide availability in the eastern and central United States. Particulate phase sulfate is under-predicted in January, has little bias in February, and is then over-predicted the rest of the year. Model predictions for sulfur dioxide are also over-predicted when compared to monthly averaged sulfur dioxide concentrations at 24 Midwest CAST-NET monitors. Emissions of sulfur dioxide are dominated by electrical generating units that have continuous emissions monitors that track emission rates. The high confidence in emissions estimates suggests that sulfur dioxide model over-prediction is more likely due to meteorological processes in the photochemical model. An evaluation of model estimated sulfur dioxide dry deposition velocity suggests that dry deposition processes are not removing sulfur dioxide quickly enough from the model (Baker and Scheff, 2006b). The grid resolu-

tion of the modeling may have some relationship to a systematic over-prediction. A finer grid scale might improve the resolution of large sulfur dioxide plumes, particularly in areas like the Ohio River Valley where there are many facilities emitting large amounts of sulfur dioxide. Since sulfate is systematically over-predicted at monitors located far away from the Ohio River Valley, it seems unlikely that grid resolution would be a sole reason for systematic sulfate over-predictions.

Excess ammonia is an indicator term used to describe PM_{2.5} 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 (Fig. 7). PM_{2.5} nitrate formation is limited by nitric acid availability when the excess ammonia term is >0 and limited by ammonia when the term is <0 . The modeling system usually agrees with the observed formation regime, but tends to be ammonia limited more often than seen in observations. This result is not entirely unexpected since the modeling system slightly under-predicts ammonia and nitric acid may be under-measured at the ammonia study monitors (Tsai et al., 2000; Baker and Scheff, 2006a). The modeling system correctly predicted ammonia limited conditions for 21 samples, correctly predicted nitric acid limited conditions for 224 samples, and incorrectly predicted the PM_{2.5} nitrate formation regime for 133 (35%) samples. The modeling system matched the observed PM_{2.5} nitrate formation regime for 65% of the samples ($N = 378$). The model performance for the excess ammonia term does not show any discernable seasonal trends.

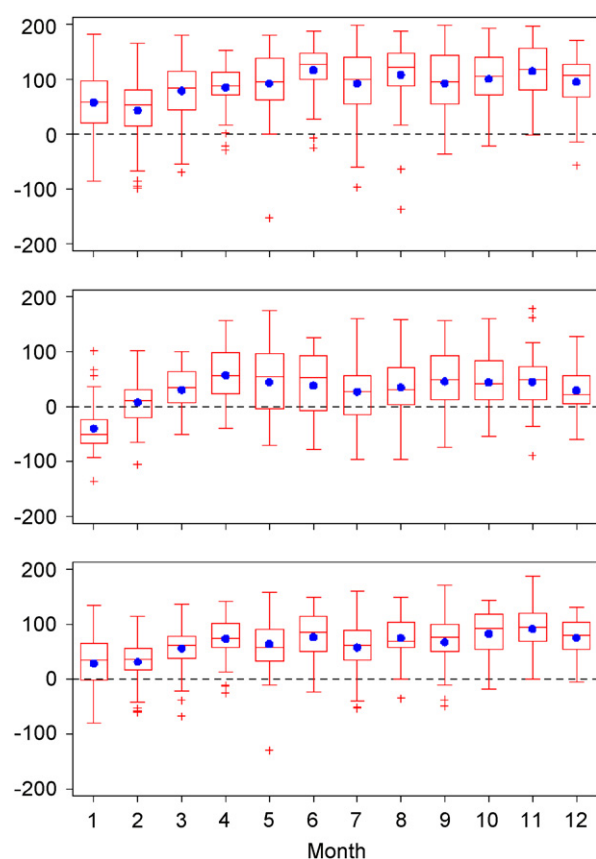


Fig. 6. Fractional bias (%) distributions over all sites by month for sulfur dioxide (top), PM_{2.5} sulfate ion (middle), and total sulfate (bottom).

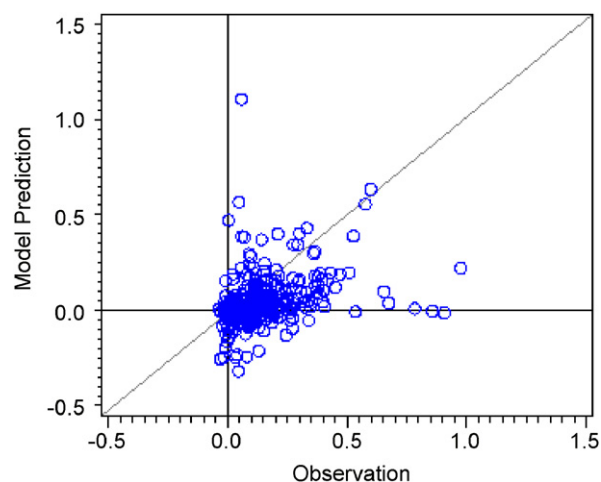


Fig. 7. Excess ammonia indicator term ($\mu\text{mole m}^{-3}$).

In general, the modeling system and ambient observations tend to agree on whether PM_{2.5} nitrate formation is nitric acid or ammonia limited, which improves confidence that the modeling system estimates of PM_{2.5} nitrate ion will respond appropriately to changes in precursor emissions.

The modeling system performance in predicting the DON by ammonia is shown in Fig. 8. Measured DON ranges outside the expected value of 0–2 because of reduced measurement precision at low concentrations and occasional samples where nitrate may be neutralized by an ion other than ammonium. PM_{2.5} sulfate is almost always completely neutralized by ammonia in the modeling system. Observations suggest PM_{2.5} sulfate is fully neutralized to ammonium sulfate during January, February, and March and exists in the form of ammonium bisulfate in the summer months. This suggests there should be more free ammonia or less NH_x in the photochemical model. This type of scenario would potentially improve performance to some degree for ammonia and PM_{2.5} ammonium ion. Sulfate acidity indirectly provides information about how well the modeling system estimates regional ammonia concentrations. This is useful because many monitors routinely measure PM_{2.5} sulfate, nitrate, and ammonium ions but do not measure ammonia. Since sulfate tends to be formed regionally and transported, the DON provides some insight into how well ammonia is characterized by the modeling system over a broad regional and temporal scale that will only include a relatively small amount of measurements.

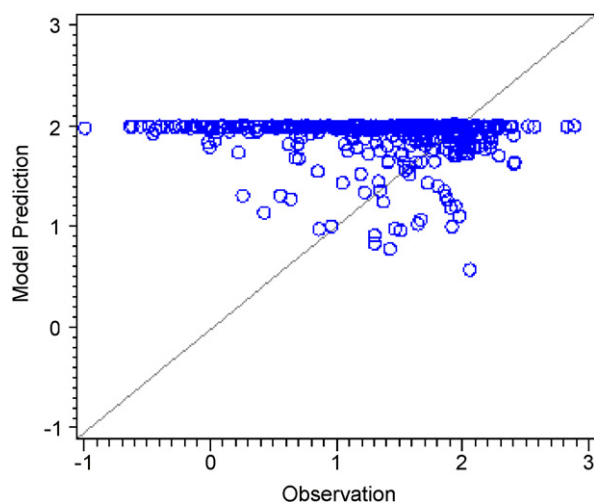


Fig. 8. Degree of sulfate neutralization by ammonia (no units).

Model performance metrics are useful to quantitatively assess the skill of the model in predicting observations. 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 of the PM_{2.5} species taken at the ammonia study sites with measurements taken from co-located monitors. The co-located observation metrics are estimated over January–December 2004 to match the modeling simulation time period. Table 3 shows the relationship between the model predictions and observations and co-located observations quantified with the coefficient of determination (r^2). 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. 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 that model–observation relationships approaching 0.7–0.8 reflect good model performance. Error and fractional error model performance metrics are compared to the same metrics used to describe co-located observations in Table 3. The model performance error is slightly lower when comparing model estimates of PM_{2.5} sulfate and nitrate ions directly to IMPROVE observations. The error and fractional error for PM_{2.5} sulfate ion

Table 3
Model-observation and co-located observation error and fractional error metrics

Metric	Species	Model–Obs ^a	Model–Obs ^b	Obs ^a –Obs ^b
Error	NO_3^-	1.2	1.0	0.50 ± 0.08
Error	SO_4^{2-}	1.5	1.2	0.75 ± 0.11
Error	NH_4^+	0.9		0.44 ± 0.11
Fractional error	NO_3^-	85.9	84.7	45.0 ± 3.9
Fractional error	SO_4^{2-}	52.1	39.4	33.4 ± 2.7
Fractional error	NH_4^+	66.8		42.4 ± 8.2
r^2	NO_3^-	0.43	0.46	0.77
r^2	SO_4^{2-}	0.47	0.56	0.71
r^2	NH_4^+	0.34	0.52	0.72

^aAmmonia network.

^bIMPROVE network.

for model estimates compared to IMPROVE observations are very close to the error for PM_{2.5} sulfate ion between the ammonia and co-located IMPROVE network observations.

The relationship in model–observation bias for the PM_{2.5} species and precursors is examined using the correlation coefficient (Table 4) to determine whether bias in precursor species directly translates into bias for PM_{2.5} species. Relationships in model performance bias between PM_{2.5} species are also shown in Table 4. These correlation coefficients compare the bias metric distributions over all sites and days for a pair of species. A number close to 1.0 indicates a strong relationship in the bias metric between a pair of species and a number close to 0.0 indicates no relationship. A strong relationship is seen between model–observation bias for PM_{2.5} sulfate ion and PM_{2.5} ammonium ion and also between PM_{2.5} nitrate ion and PM_{2.5} ammonium ion. This makes sense since these ions are chemically coupled in the atmosphere. Sulfur dioxide bias has a fairly weak relationship with PM_{2.5} sulfate ion bias, which is interesting since a more direct relationship might be expected between SO₂ and SO₄^{2−}. Nitric acid bias and ammonia bias is weakly associated with bias in the PM_{2.5} species. These weak relationships between precursor species and particulate species indicate model performance for precursor gases does not directly translate into model bias for the particulate species in the same ambient sample. This likely reflects the different time scales of particulate formation and regional transport.

4. Conclusion

Model performance is quite good for PM_{2.5} sulfate ion, PM_{2.5} nitrate ion, and PM_{2.5} ammonium ion. Performance for precursor species sulfur

dioxide, nitric acid, and ammonia is not as strong as the performance for the PM_{2.5} species based on bias and error model performance metrics. Sulfur dioxide is systematically over-predicted by the modeling system at each monitor location. Sulfur dioxide emissions are dominated by large electrical generating utilities and the emissions estimates are good, which suggests that deposition mechanisms are not efficiently removing sulfur dioxide in the model. The modeling system usually predicts sulfate as fully neutralized to ammonium sulfate, which does not compare well with observations in the warmer months when sulfate is usually observed as ammonium bisulfate.

Nitric acid measurement uncertainty makes it difficult to discern if the model over-predictions, particularly in the summer, are the result of a model process deficiency. The over-prediction of nitric acid in the summer should have minimal impact on regulatory applications since the warm temperatures do not favor PM_{2.5} ammonium nitrate formation. PM_{2.5} nitrate under-prediction in the winter months may be partly symptomatic of PM_{2.5} sulfate over-predictions. The PM_{2.5} sulfate ion is keeping ammonia sequestered that would otherwise be free to react with nitric acid and form PM_{2.5} ammonium nitrate (Khoder, 2002). Model performance for NH_x is quite good, but the monthly bias metric indicates that using year-specific ammonia activity data is important for NH_x emissions estimates. The minimal bias for NH_x is encouraging since States have much less experience in developing ammonia emission inventories compared to sulfur dioxide and nitrogen oxides, which have been previously compiled to support acid rain and ozone regulations.

The modeling system is being used to support the regional haze rule which considers the highest 20% observed days and will likely be used to support future regulatory applications focusing on the proposed 24-h PM_{2.5} NAAQS. These types of applications mean that performance is important when particulate concentrations are highest. Model performance for PM_{2.5} sulfate ion is best in the summer (fractional bias = 36%, $r^2 = 0.57$) when ambient concentrations are highest. PM_{2.5} nitrate ion performance has a mean fractional bias of −19% and 41% in the winter and fall seasons, respectively. The prediction–observation pairs for PM_{2.5} nitrate ion are well correlated for winter ($r^2 = 0.49$) and fall ($r^2 = 0.39$) seasons. The days with the lowest concentrations are important for regional haze modeling applications that must

Table 4
Bias correlations for all sites and days

	NH ₃	NO ₃ [−]	HNO ₃	SO ₂	SO ₄ ^{2−}	NH ₄ ⁺
Mean	−0.44	0.39	0.91	4.00	1.01	0.65
STD	1.95	2.05	1.62	4.80	2.24	1.09
N	515	488	497	559	537	478
NH ₃	1.00	0.36	−0.16	−0.01	0.03	0.25
NO ₃ [−]		1.00	0.03	0.22	0.23	0.77
HNO ₃			1.00	0.45	0.36	0.28
SO ₂				1.00	0.27	0.31
SO ₄ ^{2−}					1.00	0.66
NH ₄ ⁺						1.00

consider the 20% best days and the annual PM_{2.5} NAAQS that considers all days. The model predicts little PM_{2.5} nitrate in the summer when concentrations are lowest and performs well for PM_{2.5} sulfate in the winter.

PM_{2.5} 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 PM_{2.5} nitrate will respond appropriately to changes in precursor emissions. Regulatory strategies in this part of the country should focus on reductions in NO_x rather than in ammonia to control PM_{2.5} ammonium nitrate. PM_{2.5} sulfate ion is well predicted by the modeling system even though sulfur dioxide is consistently over-predicted. This over-prediction is likely in part due to the modeling system not removing sulfur dioxide quickly enough through deposition processes and not due to emissions (Baker and Scheff, 2006b). Overall, the modeling system performs well at predicting PM_{2.5} ammonium sulfate and ammonium nitrate and seems appropriate for regulatory modeling applications. However, it is important to continue to examine model performance for these chemical species and their precursors to continue to improve model estimates of these species.

The ammonia monitor or any future similar study would be even more valuable for model performance evaluation if routine measurement of nitrogen oxides is included with the other species. Ultimately, nitric acid starts out in the atmosphere as nitrogen oxides so it would be useful to ensure that the modeling system is performing well in these predominantly rural monitor locations rather than using urban and source-related data for making this type of comparison. Future work to quantify the improvement in model performance due to the use of a finer grid resolution over the central and eastern United States would compliment the analysis presented here. A clear understanding of the uncertainty related to grid resolution for PM_{2.5} ammonium sulfate, ammonium nitrate, and precursor species would help focus efforts toward improving model processes and inputs.

Acknowledgment

This project would not have been possible without the emissions modeling work done by Mark Janssen at Lake Michigan Air Directors Consortium.

References

- Baker, K., Scheff, P., 2006a. Spatial and temporal variability in ambient concentrations of PM_{2.5} sulfate, nitrate, ammonium and precursors SO₂, HNO₃, and NH₃ in the Midwest United States. December 2006, submitted for publication.
- Baker, K., Scheff, P., 2006b. Assessing meteorological variable and process relationships to modeled PM_{2.5} ammonium nitrate and ammonium sulfate in the central United States. December 2006, submitted for publication.
- Bey, I., Jacob, D., Yantosca, R., Logan, J., Field, B., Fiore, A., Li, Q., Liu, H., Mickley, L., Schultz, M., 2001. Global modeling of tropospheric chemistry with assimilated meteorology: model description and evaluation. *Journal of Geophysical Research* 106, 23,073–23,096.
- Blanchard, C.L., Roth, P.M., Tanenbaum, S.J., Ziman, S.D., Seinfeld, J.H., 2000. The use of ambient measurements to identify which precursor species limit aerosol nitrate formation. *Journal of the Air & Waste Management Association* 50, 2073–2084.
- Boylan, J.W., Odman, M.T., Wilkinson, J.G., Russell, A.G., 2006. Integrated assessment modeling of atmospheric pollutants in the southern Appalachian Mountains: part II. Fine particulate matter and visibility. *Journal of the Air & Waste Management Association* 56, 12–22.
- Carter, W.P., 1996. Condensed atmospheric photooxidation mechanisms for isoprene. *Atmospheric Environment* 30, 4275–4290.
- Chang, J.S., Brost, R.A., Isaksen, I.S.A., Madronich, S., Middleton, P., Stockwell, W.R., Walcek, C.J., 1987. A three-dimensional eulerian acid deposition model: physical concepts and formulation. *Journal of Geophysical Research* 92, 14,681–14,700.
- Chen, K.S., Ho, Y.T., Lai, C.H., Chou, Y.M., 2003. Photochemical modeling and analysis of meteorological parameters during ozone episodes in Kaohsiung, Taiwan. *Atmospheric Environment* 37, 1811–1823.
- Dudhia, J., 1993. A nonhydrostatic version of the Penn State/NCAR mesoscale model: validation tests and simulation of an Atlantic cyclone and cold front. *Monthly Weather Review* 121, 1493–1513.
- ENVIRON International Corporation, 2005. User's Guide Comprehensive Air Quality Model with Extensions (CAMx) Version 4.20. ENVIRON International Corporation, Novato, CA <www.camx.com>.
- Gery, M.W., Whitten, G.Z., Killus, J.P., Dodge, M.C., 1989. A photochemical kinetics mechanism for urban and regional scale computer modeling. *Journal of Geophysical Research* 94, 925–956.
- Goebe, M.D., Strader, R., Davidson, C.I., 2003. An ammonia emission inventory for fertilizer application in the United States. *Atmospheric Environment* 37, 2539–2550.
- Grell, G.A., Dudhia, J., Stauffer, D., 1994. A description of the Fifth Generation Penn State/NCAR Mesoscale Model (MM5). NCAR Technical Note, NCAR TN-398-STR.
- Jacob, D.J., Park, R., Logan, J., 2005. Documentation and evaluation of the GEOS-CHEM simulation for 2002 provided to the VISTAS Group.
- Janssen, M., Hua, C., 1998. Emissions Modeling System-95 User's Guide <<http://www.ladco.org/emis/guide/ems95.html>>.

- Johnson, M., 2003. Meteorological Modeling Protocol: Iowa Department of Natural Resources 2002 Annual MM5 Application.
- Khoder, M.I., 2002. Atmospheric conversion of sulfur dioxide to particulate sulfate and nitrogen dioxide to particulate nitrate and gaseous nitric acid in an urban area. *Chemosphere* 49, 675–684.
- Lake Michigan Air Directors Consortium, 2004. Meteorological Modeling Protocol For Application to PM_{2.5}/Haze/Ozone Modeling Projects <<http://www.ladco.org/tech/photo/photochemical.html>>.
- McDade, C.E., White, W.H., Hyslop, N.P., Solomon, P.A., Klamser-Williams, T., Crumpler, D., Egeghy, P., 2005. Comparison of aerosol data from the STN and IMPROVE networks. Presented at the AAAR Specialty Conference: Particulate Matter, Supersites Program & Related Studies, Atlanta, GA, 11 February 2005.
- Morris, R.E., Mansell, G., Tai, E., 2004. Air quality modeling analysis for the Denver early action ozone compact. Prepared for Denver Regional Air Quality Council, Denver, CO.
- Nenes, A., Pandis, S.N., Pilinis, C., 1998. ISORROPIA: a new thermodynamic equilibrium model for multiphase multi-component inorganic aerosols. *Aquatic Geochemistry* 4, 123–152.
- Nobel, C.E., McDonald-Buller, E.C., Kimura, Y., Lumbley, K.E., Allen, D.T., 2002. Influence of population density and temporal variations in emissions on the air quality benefits of NO_x emission trading. *Environmental Science and Technology* 36, 3465–3473.
- Pinder, R.W., Strader, R., Davidson, C.I., Adams, P.J., 2004. A temporally and spatially resolved ammonia emission inventory for dairy cows in the United States. *Atmospheric Environment* 38, 3747–3756.
- Strader, R., Lurmann, F., Pandis, S.N., 1999. Evaluation of secondary organic aerosol formation in winter. *Atmospheric Environment* 33, 4849–4863.
- Strader, R., Peckney, N.J., Pinder, R.W., Adams, P.J., Goebes, M., Ayers, J., Davidson, C.I., 2005. The CMU Ammonia Emission Inventory. Available at <<http://www.cmu.edu/ammonia>>.
- Tanaka, P.L., Allen, D.T., McDonald-Buller, E.C., Chang, S., Kimura, Y., Mullins, C.B., Yarwood, G., Neece, J.D., 2003. Development of a chlorine mechanism for use in the CAMx regional photochemical model. *Journal of Geophysical Research* 108, 4145.
- Tsai, C.J., Perng, S.B., Chiou, S.F., 2000. Use of two different acidic aerosol samplers to measure acidic aerosols in Hsinchu, Taiwan. *Journal of the Air & Waste Management Association* 50, 2120–2128.
- US Environmental Protection Agency, 2006. Guidance on the use of models and other analyses for demonstrating attainment of air quality goals for ozone, PM_{2.5}, and regional haze, Draft 3.2, September 2006.
- Wilkinson, J., Loomis, C., Emigh, R., McNalley, D., Tesche, T., 1994. Technical Formulation Document: SARMAP/LMOS Emissions Modeling System (EMS-95). Final report prepared for Lake Michigan Air Directors Consortium (Des Plaines, IL) and Valley Air Pollution Study Agency, Sacramento, CA, 1994.