Assessing Meteorological Variable and Process Relationships to Modeled PM2.5 Ammonium Nitrate and Ammonium Sulfate in the Central United States

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ABSTRACT

Many counties are required to submit an emissions control plan to the U.S. Environmental Protection Agency to reduce concentrations of particulate matter of less than 2.5 μm in diameter (PM2.5), which are dominated by ammonium sulfate and ammonium nitrate in the central United States. These control scenarios are simulated with photochemical models, which use emissions and meteorological variables to simulate PM2.5 formation, transport, and deposition. A monitor study was established in the central United States to measure simultaneously the PM2.5 sulfate ion, nitrate ion, ammonium ion, and chemical precursor species sulfur dioxide, nitric acid, and ammonia during 2004. These data, combined with nearby meteorological observations, provide an opportunity to assess whether meteorological variables or deposition processes may introduce systematic biases in PM2.5 ammonium sulfate and ammonium nitrate predictions. Skill in estimating total wet deposition is assessed by comparing model output with National Atmospheric Deposition Program monitors in the region. Meteorological variables that are important for mass transport (wind vector) and thermodynamic chemistry (temperature and relative humidity) compare well to observations. A model sensitivity, in which the temperatures in the inorganic chemistry module are adjusted to compensate for an underprediction bias, shows a minimal model response in predicted PM2.5 ammonium nitrate. The dry deposition of sulfur dioxide seems to have a systematic impact on ambient estimates of sulfur dioxide in the photochemical model. An attempt to correlate bias and error in meteorological variables to bias and error in PM2.5 species showed the most relationship between relative humidity and temperature and ammonium nitraite. Wet deposition of total sulfate, nitrate, and ammonium tend to be underpredicted in the winter months.

1. Introduction

Health studies have shown that premature death is statistically associated with exposure to particulate matter of less than 2.5 μm in diameter (PM2.5). Two of the largest chemical components of PM2.5 in the central United States include secondarily formed ammonium sulfate and ammonium nitrate (U.S. Environmental Protection Agency 2003). States with PM2.5 nonattainment 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. The SIPs will focus on reducing emissions of sulfur oxides (SO_x) and nitrogen oxides (NO_x), which form PM2.5 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 that treat the physical and chemical processes that result in PM2.5 formation, transport, and deposition.

Important meteorological processes that influence how well the photochemical model predicts PM2.5 ammonium sulfate and nitrate include mass transport, wet deposition, and dry deposition. Meteorological variables important for PM2.5 nitrate thermodynamic reactions include relative humidity and temperature. PM2.5 ammonium nitrate formation requires NO_x reaction by-product nitric acid availability, ammonia

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availability, and favorable meteorological conditions: cool temperatures and high humidity (Wexler and Seinfeld 1991). It is not well known how much influence meteorological inputs and meteorological processes within the photochemical model have on PM2.5 ammonium sulfate and ammonium nitrate predictions.

A monitor study was established in the central United States to measure simultaneously the PM2.5 sulfate ion, nitrate ion, ammonium ion, and chemical precursor species sulfur dioxide (SO_2), nitric acid (HNO_3), and ammonia (NH_3). These data, combined with nearby meteorological observations, provide an opportunity to assess whether meteorological variables may introduce systematic biases in PM2.5 ammonium sulfate and ammonium nitrate predictions. Wind speed and wind direction at stations near the ammonia monitor study are compared with observation data to assess how well mass transport is being characterized by the regulatory modeling system. Temperature and relative humidity are compared with observations taken near the ammonia study sites to assess how well these important variables are being represented in the modeling system.

Wet deposition and dry deposition are important removal processes in regional photochemical models, especially because these models are typically applied for continental-scale domains and annual simulation periods. Dry deposition velocity is not routinely measured in the United States. Dry deposition velocities reported in literature are compared with estimates by the photochemical model. Several model sensitivities are applied to determine the influence of precursor species dry deposition on predicted PM2.5 ammonium sulfate and ammonium nitrate. Wet deposition of total sulfate, total nitrate, and total ammonium is measured at many locations in the central and eastern United States as part of the National Atmospheric Deposition Program (NADP). These observation data are not collocated with ammonia monitor study sites but do allow for an assessment of the modeling system skill in the removal of total sulfate, total nitrate, and total ammonium through wet deposition processes in the same region. The NADP measurements also allow for an assessment of how modeled precipitation impacts modeled wet deposition of these species.

The relationships between PM2.5 ammonium nitrate and ammonium sulfate and important meteorological variables and deposition processes will be assessed using an annual 2004 photochemical modeling simulation. This will help to determine if PM2.5 ammonium sulfate, ammonium nitrate, and precursor species are poorly estimated because of meteorological factors. This type of assessment helps to build confidence that the modeling system is appropriately characterizing the important PM2.5 formation, transport, and removal processes. If meteorological factors are systemically affecting the photochemical model predictions of PM2.5 ammonium nitrate, ammonium sulfate, or key precursor species then the model may not respond appropriately to emissions adjustments and may overstate or understate the benefits of emissions control scenarios.

2. Methods

a. Modeling system

The regulatory modeling system used to apply emissions control scenarios to support SIPs includes an emissions model, a photochemical model, and a meteorological model. The Comprehensive Air Quality Model with Extensions (CAMx), version 4.30, is a 3D photochemical transport model that uses state-of-the-science routines to model gas and particulate matter formation, transport, and removal processes (Nobel et al. 2002; Tanaka et al. 2003; Chen et al. 2003; Morris et al. 2004). Inputs to CAMx include initial and boundary concentrations, pollutant emissions, land use information, and meteorological variables (ENVIRON 2006). Inorganic chemistry is solved using the “ISORROPIA” thermodynamics module (Nenes et al. 1998; ENVIRON 2006). Wet deposition is treated with separate scavenging models for aerosols and gases. Gas scavenging is estimated as a function of gas solubility, gas diffusivity, cloud water content, and precipitation rate. Particle scavenging is a function of cloud water content, precipitation rate, and aerosol size. Dry deposition includes separate resistance models for aerosols and gases and is based on the model developed by Wesely (1989). Gas deposition velocities are a function of gas reactivity, gas solubility, gas diffusivity, meteorological conditions, and surface characteristics. Particle deposition velocities are estimated based on meteorological conditions, surface characteristics, and particle size (ENVIRON 2006).

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 2 weeks of spinup to minimize initial condition influence in the boundary layer. The initial and boundary conditions are based on monthly averaged species output from an annual (calendar year 2002) application of the Goddard Earth Observing System (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.

Meteorological input data for the photochemical

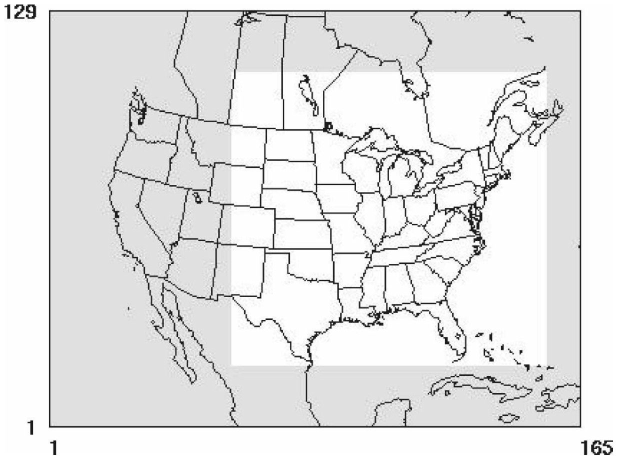

FIG. 1. MM5 and photochemical model domains.

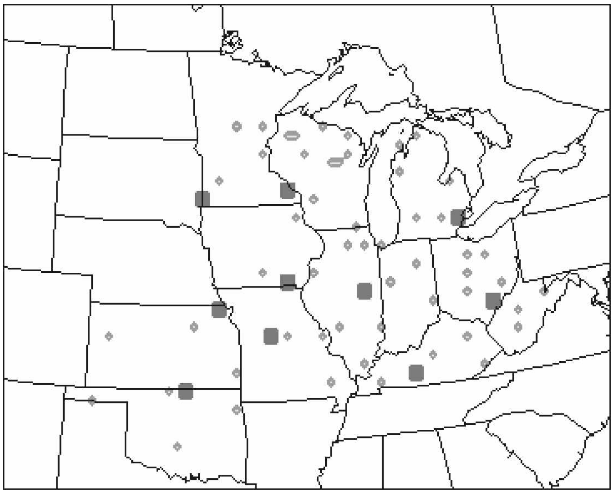

FIG. 2. Ammonia network monitor locations (squares) and NADP monitors used for wet deposition model performance (diamonds).

model simulations are generated using the fifth-generation Pennsylvania State University–National Center for Atmospheric Research Mesoscale Model (MM5), version 3.6.1 (Dudhia 1993; Grell et al. 1994). Important MM5 parameterizations and physics options include mixed-phase (Reisner 1) microphysics, the Kain–Fritsch 2 cumulus scheme, the rapid radiative transfer model, the Pleim–Chang planetary boundary layer (PBL), and the Pleim–Xiu land surface module. Analysis nudging for temperature and moisture is only applied above the boundary layer. Analysis nudging of the wind field is applied above and below the boundary layer. 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; Lake Michigan Air Directors Consortium 2004).

The meteorological fields output by MM5 are prepared for use by the photochemical model with processing utilities. These programs translate certain meteorological parameters from the MM5 grid to the photochemical grid. In addition, these processors estimate vertical diffusivity coefficients that are not explicitly output by MM5. The MM5–CAMx, version 4.4, utility was used to translate MM5 output to CAMx input (Kemball-Cook et al. 2004). The vertical diffusivity coefficients are based on the O'Brien (1970) vertical diffusivity algorithm and have a minimum value of 0.1 $m^2 s^{-1}$. This scheme takes the PBL height output by MM5 and creates a well-mixed atmosphere inside the PBL.

All models are applied with a Lambert projection centered at (40°N, 97°W) and true latitudes at 33° and 45°N (Fig. 1). The photochemical modeling domain consists of 97 cells in the x (north–south) direction and 90 cells in the y (east–west) direction covering the central and eastern United States with square 36-km grid cells. The meteorological modeling domain covers the continental United States with 165 cells in the x direction and 129 cells in the y direction with square 36-km grid cells. MM5 resolves the vertical atmosphere up to 15 km above ground level with 34 layers. CAMx, version 4, (CAMx4) is applied with the vertical atmosphere resolved with 16 layers up to approximately 15 km above ground level. The near-surface layers are matched one to one between MM5 and CAMx4, and upper levels are collapsed from MM5 to CAMx4 to improve computational efficiency. All models are applied for the entire calendar year of 2004 for comparison with observation values.

b. Observation data

A monitor study was established using mostly rural locations (nine rural and one urban) in the central United States to measure simultaneously the PM2.5 sulfate ion ($SO_4^{=}$), nitrate ion (NO_3^-), ammonium ion (NH_4^+), and chemical precursor species sulfur dioxide, nitric acid, and ammonia (Fig. 2). These samples have a 24-h averaging time and were taken on a once-in-6-days schedule. Samples collected for the entire year of 2004 have been validated and made available by the Lake Michigan Air Directors Consortium and Central Regional Air Planning Association.

Hourly meteorological observations for surface temperature, wind direction, wind speed, and dewpoint temperature are available from the National Center for Atmospheric Research's Techniques Data Laboratory U.S. and Canada surface hourly observations data ar-

TABLE 1. Meteorological stations near ammonia network (AMN) sites.

AMN station	Meteorological station	Distance (mi)	Distance (km)	Distance (grid cells)
IA	KFFL	23.1	37.2	1.0
IA	KMPZ	27.9	44.9	1.2
IL	KCMI	6.4	10.3	0.3
KS	KFNB	8.2	13.2	0.4
KY	KBWG	23.7	38.1	1.1
MI	KDTW	7.0	11.3	0.3
MN1	KFSD	29.0	46.7	1.3
MN1	KPQN	19.4	31.2	0.9
MN2	KONA	3.9	6.3	0.2
MO	KDMO	10.7	17.2	0.5
OH2	KPKB	35.7	57.4	1.6
OK	KWLD	11.5	18.5	0.5
OK	KPNC	14.4	23.2	0.6

chive (dataset ds472.0). The temperature and dewpoint temperature are used to estimate relative humidity. Meteorological monitor locations closest to ammonia monitor study locations are shown in Table 1. The meteorological observations are averaged at each hour where multiple sites are near an ammonia study monitor.

The National Atmospheric Deposition Program monitor sites collect weekly measurements of precipitation and wet deposition of NO_3^- and $SO_4^=$ anions and NH_4^+ cation. NADP sites measure wet deposition as mass per volume (mg L^{-1}), and the photochemical model outputs mass per area (g ha^{-1} or mole ha^{-1}). The observations are converted to mass per area using NADP-measured precipitation. NADP monitors (number N of monitors = 55) in the central United States are used to examine model performance in estimating precipitation and wet deposition of total sulfate, total nitrate, and total ammonium (Fig. 2). Dry deposition is not routinely measured in the United States. A comparison of model estimates of dry deposition velocity with published values gives an indication about whether the modeling system is appropriately removing mass through dry deposition processes.

c. Prediction–observation metrics

Metrics used to describe quantitatively the accuracy of the model variables: bias, error, fractional bias, fractional error, correlation coefficient, and total wind displacement are shown in Table 2 (U.S. Environmental Protection Agency 2006; Boylan et al. 2006). The wind displacement is the difference between the end points of the modeled and observed wind vectors. The observed wind vector is calculated using wind speed and wind direction. The modeling system wind field variables are the **U** and **V** vector components so that no conversion is necessary. The difference is estimated in kilometers and then divided by the size of the grid cell (36 km) to estimate the equivalent wind displacement in terms of grid cells. Wind field performance is best when the wind displacement approaches 0. The bias

TABLE 2. Model performance/comparison metrics, where A is model prediction, B is observation, **U** and **V** are wind vector components, N is the number of monitors, and M is the number of observation–prediction pairs.

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

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

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

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

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

$$\text{Wind displacement (km)} = \frac{1}{NM}\sum_{i=1}^{N}\sum_{j=1}^{M}(A\mathbf{U}_i^j - B\mathbf{U}_i^j + A\mathbf{V}_i^j)(3600\ \text{s h}^{-1} \times 1\ \text{h} \times 1\ \text{km}/1000\ \text{m})$$

TABLE 3. Mean model performance metrics.

Metric	Variable	N	Mean	Std dev
Bias	Temperature (°F)	86 474	−0.49	5.16
Bias	Relative humidity (%)	86 373	−0.71	15.06
Bias	Wind speed (m s^{-1})	76 480	0.34	1.40
Error	Temperature (°F)	86 474	3.82	3.51
Error	Relative humidity (%)	86 373	11.50	0.76
Error	Wind speed (m s^{-1})	76 480	1.12	0.91
Fractional bias	Temperature (°F)	86 474	−0.11	1.03
Fractional bias	Relative humidity (%)	86 373	−2.12	23.74
Fractional bias	Wind speed (ms)	76 480	9.09	36.62
Fractional error	Temperature (°F)	86 474	0.75	0.72
Fractional error	Relative humidity (%)	86 373	17.41	16.27
Fractional error	Wind speed (m s^{-1})	76 480	28.69	24.50
Wind displacement (km)		74 612	18.01	15.19
Wind displacement (grid cells)		74 612	0.50	0.42

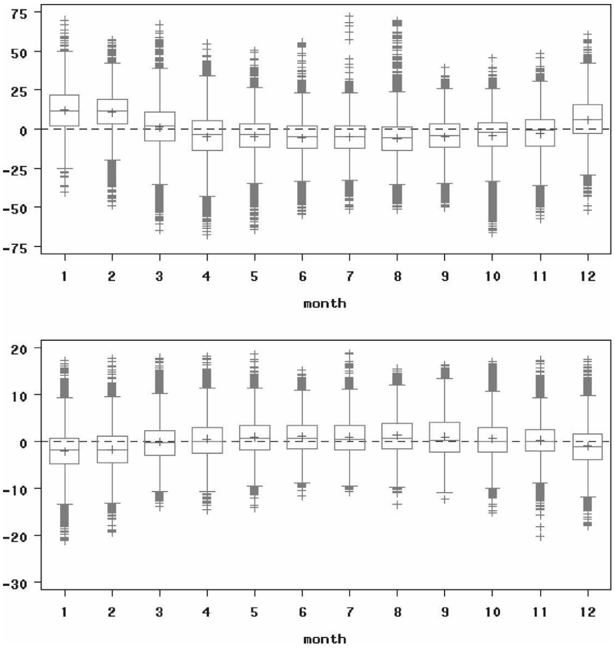

FIG. 3. Bias metric by month: (top) relative humidity (%) and (bottom) temperature (°F).

and error metrics are used to describe performance in terms of the measured units, 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.

3. Results and discussion

a. Formation and transport

Model performance metrics for temperature, relative humidity, wind speed, and total wind displacement are shown in Table 3. These metrics are the mean metrics over all stations and hours. The minimum wind speed reported by observation stations is 1.54 m s^{-1}. The meteorological model does not have a minimum estimate of wind speed. The wind speed bias was estimated using only predictions (hereinafter the word "prediction" designates model output, even if based on historical model inputs and episodes, rather than being a true prediction in real time) and observations greater than 1.54 m s^{-1} to determine whether the minimum reporting value affects model performance results. The mean bias when these values are not included is 0.33 m s^{-1} (N = 68 521) as opposed to 0.34 m s^{-1} (N = 76 480) when all values are included in the metric estimate. The relatively small number of hours with very calm wind conditions means the wind speed measurement limitation has minimal impact on overall model performance.

The distribution of the bias metric over all monitor locations by month is shown in Fig. 3 for relative humidity and temperature. The distribution of the bias metric over all days by monitor location for relative humidity and temperature is shown in Fig. 4. The mean bias for relative humidity is near zero during the spring through autumn months and positive (overprediction) during the coldest months. Temperature is slightly underpredicted during the coldest months and slightly overpredicted during the warmest months. Temperature and relative humidity bias distributions by site show that most sites tend to have slightly overpredicted temperatures and little relative humidity bias. The one exception is the MN2 location, which has an overprediction bias for relative humidity and an underprediction bias for temperature. The MN2 site (KONA) is located on top of the Mississippi River bluffs in southeast Minnesota, and the horizontal resolution of the model may not be capturing microscale meteorological behavior at this location.

Total wind displacement is shown in Fig. 5 in terms of gridcell equivalents to characterize wind field performance relative to the modeling grid scale. The MN2 monitor location has the best performance for wind field, which is interesting because it has the worst performance for temperature and relative humidity. The MI, IL, and MO sites show the poorest performance for

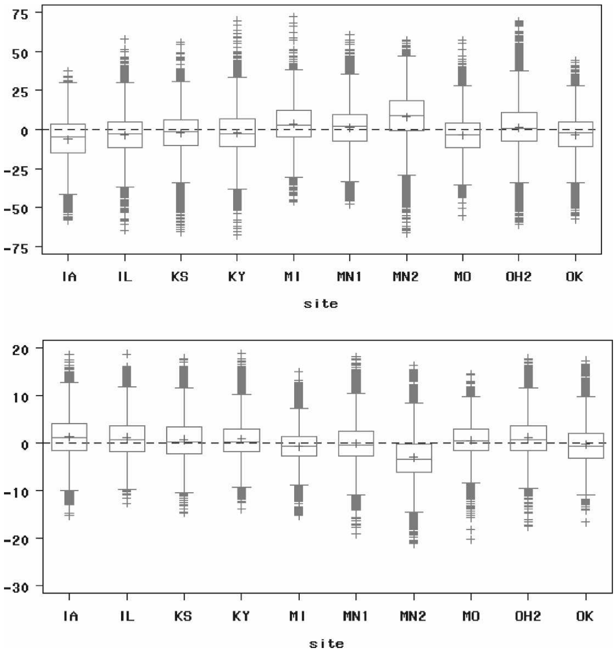

FIG. 4. As in Fig. 3, but by site.

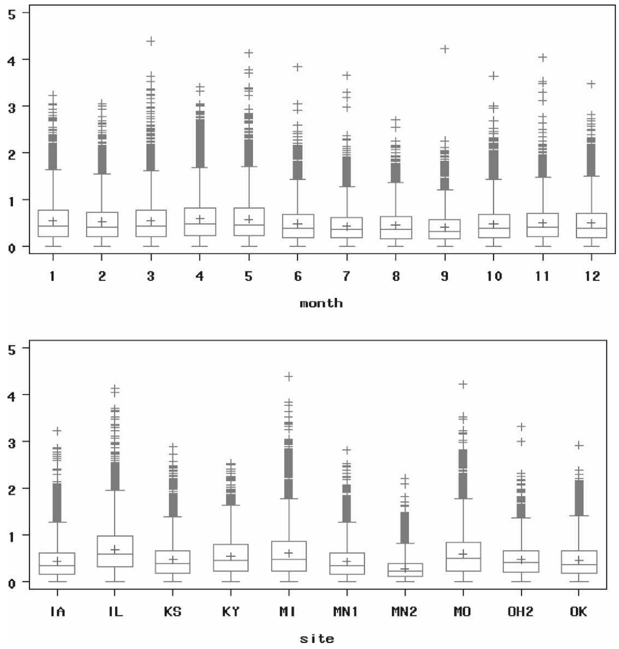

FIG. 5. Wind displacement (gridcell equivalents) by (top) month and (bottom) site.

total wind displacement. However, the 75th-percentile wind displacement is not above 1 gridcell equivalent at any of the monitor locations, which suggests that the horizontal wind vector error is smaller than the scale of the modeling simulation and wind field performance is good. This good performance for the wind speed is not entirely the result of applying analysis nudging in the boundary layer. Previous sensitivities applying MM5 with a variety of boundary layer and land surface schemes in the central U.S. region showed much better wind field performance using the Pleim–Chang PBL and Pleim–Xiu land surface module than any other combination of boundary layer and land surface options (Johnson 2003; Lake Michigan Air Directors Consortium 2004).

Table 4 shows the correlation between bias and error performance metrics for meteorological inputs (temperature, RH, and wind speed) and photochemical output chemical species: $SO_4^{=}$, NO_3^-, NH_4^+, SO_2, HNO_3, and NH_3. These relationships are estimated for all ammonia network sites by month. Table 4 shows estimated r^2 values greater than 0.20. Stronger relationships are certainly possible but might not be realistic because meteorological conditions alone do not cause ammonium nitrate and sulfate formation and representation of emissions and chemistry are also important. The strongest relationships between meteorological variable bias and error and chemical species bias and error are during the autumn and winter months. The most notable relationships between model performance bias metrics include temperature and NH_x (NH_3 + NH_4^+), relative humidity and NH_4^+, temperature and HNO_3, and relative humidity and HNO_3. These are not cause–effect relationships, but it suggests that model performance for temperature and relative humidity is most important for PM2.5 ammonium nitrate formation in the colder months. An alternative way to discern relationships between model performance for relative humidity, temperature, and PM2.5 nitrate ion includes an examination of mean bias when PM2.5 nitrate ion is

TABLE 4. Meteorological metrics correlated to photochemical species metrics. Here Temp is temperature, RH is relative humidity, and WS is wind speed.

CAMx	MM5	N	r^2	Month
Error NH_4^+	Error RH	37	0.36	1
Error NH_4^+	Error Temp	30	0.30	11
Error NH_3	Error Temp	35	0.30	1
Error SO_2	Error RH	45	0.27	3
Bias NH_4^+	Bias Temp	30	0.27	11
Bias NO_3^-	Bias Temp	43	0.25	12
Error HNO_3	Error Temp	30	0.25	12
Bias HNO_3	Bias RH	26	0.24	11
Error NO_3^-	Error WS	26	0.23	9
Bias SO_2	Bias RH	35	0.23	11
Bias HNO_3	Bias Temp	35	0.23	1
Bias NH_4^+	Bias RH	45	0.21	2
Error $SO_4^{=}$	Error Temp	36	0.21	11
Error HNO_3	Error WS	26	0.20	11

TABLE 5. Mean bias for key meteorological variables when daily PM2.5 nitrate ion bias is below −0.5, between −0.5 and 0.5, and above 0.5.

Metric	Daily bias NO_3^- condition		
	<-0.5	>-0.5 and <0.5	>0.5
N	104	234	150
Bias NO_3^- (μg m^{-3})	−1.51	−0.04	2.38
Bias RH (%)	1.42	−2.12	0.03
Bias temperature (°F)	−0.19	0.77	−1.47
Bias wind speed (m s^{-1})	0.42	0.37	0.16

TABLE 6. Error (μg m^{-3}) performance metric (winter months) for two sensitivity model simulations. Here SENS1 is the ammonia deposition adjustment, and SENS2 is the ISORROPIA temperature adjustment.

Species	N	BASE	SENS1	SENS2
NH_3	133	0.81	0.75	0.81
NO_3^-	135	1.24	1.50	1.26
HNO_3	128	0.54	0.49	0.55
SO_2	135	4.01	3.98	4.01
$SO_4^=$	136	1.01	1.06	1.01
NH_4^+	135	0.50	0.60	0.50

underpredicted, is near zero bias, and is overpredicted (Gilliam et al. 2004). Table 5 shows the mean bias for important meteorological variables for different conditions of PM2.5 nitrate ion bias. When PM2.5 nitrate ion is overpredicted, temperature is underpredicted and relative humidity bias is near zero. When PM2.5 nitrate ion is underpredicted, the temperature bias is near zero and the relative humidity bias is overpredicted. The wind speed bias is highest when PM2.5 nitrate ion is underpredicted, which suggests that winds may be dispersing precursor emissions too efficiently and not leaving the appropriate mix for PM2.5 nitrate formation.

Temperatures are slightly underpredicted during the winter months by several degrees Fahrenheit. A sensitivity test was performed in which the temperature that is used by the inorganic chemistry module in the photochemical model was increased by 1 K. The mean error metric by species for this model sensitivity is shown in Table 6. This attempt to compensate for the low temperature bias during the coldest months had a minimal impact on modeled PM2.5 nitrate ion estimates. This test suggests that the 1-K temperature error is not large enough to systematically bias PM2.5 ammonium nitrate predictions at these monitor locations.

b. *Wet deposition*

Observed and predicted wet deposition for total nitrate, total sulfate, and total ammonium is shown in Fig. 6. The modeling system tends to underpredict the higher observed amounts of total ammonium and total nitrate wet deposition. Total sulfate shows more scatter in model estimates when compared with the highest amounts of observed total wet deposition. Performance metrics fractional bias and fractional error for total sulfate, total nitrate, and total ammonium are shown in Table 7 by season. The total wet deposition for all three species tends to be underpredicted during the coldest months and to have a bias closer to zero during the warmer months.

Observations and predictions of weekly precipitation totals at NADP sites have the strongest correlation during January, February, and March ($r^2 = 0.67$) and the weakest relationship during June, July, and August ($r^2 = 0.29$). Precipitation fractional bias is slightly greater than 0 for each season (Table 7), suggesting that the modeling system may tend to overestimate precipitation—in particular, in the summer when the fractional error is highest. The total sulfate, total nitrate, and total ammonium wet deposition tends to be underpredicted, even though precipitation has a tendency to be overpredicted.

This result suggests that ambient concentrations may be underestimated during the colder months or that wet deposition processes are not removing these species efficiently enough during the colder months. Total ammonium and total nitrate have a negative fractional bias for predicted ambient concentrations in the winter months. Total sulfate does not have a negative bias in the winter, which suggests that frozen precipitation is not efficiently removing this species. In the case of total nitrate and total ammonium, the underprediction of winter wet deposition is likely a combination of underestimated ambient concentrations and frozen precipitation not efficiently removing these species.

c. *Dry deposition*

Dry deposition is not explicitly measured on a routine basis, and therefore a comparison of total dry deposition is not possible. The dry deposition velocity estimated by the photochemical model for key PM2.5 precursor gas species is compared with dry deposition velocities reported in literature. Land use characteristics are important in dry deposition, and so reported deposition velocities over agriculture and forest land use types are the most relevant for comparison with the values estimated by the photochemical deposition model at the ammonia monitor study sites. All monitor sites besides the MI (Detroit, Michigan) location are dominated by forest and agricultural land use.

Few recent observations have been made of sulfur

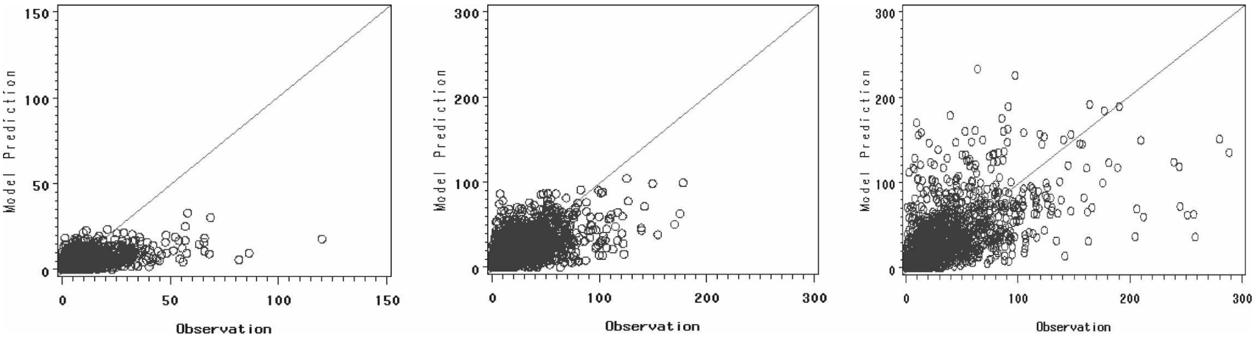

FIG. 6. Wet deposition (kg km^{-2}) for (left) total ammonium, (middle) total nitrate, and (right) total sulfate.

dioxide deposition velocities (Wesely and Hicks 2000). Field studies have shown that sulfur dioxide deposition velocities are typically higher than those for ozone (Wesely and Hicks 2000). Previous research shows that measured ozone deposition velocities range from 0.0 to 1.0 cm s^{-1} for maize and from 0.0 to 1.5 cm s^{-1} for soybeans (Wesely and Hicks 2000). This agrees fairly well with the minimum and maximum (0.0 and 1.1 cm s^{-1}) ozone deposition velocity estimated for agricultural land use in the photochemical model. The dry deposition model estimates for the ammonia monitor study locations have an annual mean of 0.36 cm s^{-1} for sulfur dioxide and 0.33 cm s^{-1} for ozone. The modeled dry deposition velocity estimates for sulfur dioxide and ozone are fairly similar, and ozone deposition velocities seem appropriate when compared with literature values. This suggests that sulfur dioxide deposition velocities may be underpredicted by the photochemical model. Sulfur dioxide concentrations estimated by the photochemical model tend to be overpredicted. The sulfur dioxide dry deposition velocity estimated by the photochemical model was increased by a factor of 2 for the annual 2004 simulation to determine whether this perturbation would improve model performance for ambient sulfur dioxide.

Figure 7 shows the fourth-quarter seasonal average concentration (μg m^{-3}) difference in sulfur dioxide concentrations between a standard model simulation and when sulfur dioxide dry deposition velocities were multiplied by a factor of 2. When sulfur dioxide dry deposition velocities are systematically increased by a factor of 2, sulfur dioxide–modeled concentrations drop regionally and model performance for sulfur dioxide improves. Model performance metrics for sulfur dioxide and PM2.5 sulfate ion are shown in Table 8. These metrics are estimated for the standard photochemical simulation (BASE) and for the sensitivity test in which sulfur dioxide dry deposition velocities are increased by a factor of 2 (SO2 SENS). Model estimates of sulfur dioxide tend to move closer to the observed concentrations when sulfur dioxide deposition velocities are systematically increased. The model predictions for PM2.5 sulfate ion do not change as much but also move closer to observed values. This sensitivity results in improved sulfur dioxide and PM2.5 sulfate ion performance and no change for any other species estimated by the model. This indicates additional formulations may be needed in the photochemical dry deposition model to increase sulfur dioxide deposition velocities.

Ammonia deposition was perturbed during October, November, and December because the modeling system underpredicts ambient ammonia and overpredicts particulate nitrate. This sensitivity provides additional information about the influence of the surface resistance term in estimated ammonia concentrations. Lowering the surface resistance term in the dry deposition module effectively decreases deposition and increases ambient concentrations. Model performance for ammonia improves slightly with the deposition adjustment, and performance for PM2.5 nitrate and ammo-

TABLE 7. Model performance metrics for wet deposition and precipitation.

		Fractional bias (%)				Fractional error (%)			
Season	*N*	NO_3^-	$SO_4^=$	NH_4^+	Precipitation	NO_3^-	$SO_4^=$	NH_4^+	Precipitation
Winter	496	−73	−91	−113	10	92	108	122	52
Spring	535	−27	−9	−50	13	64	64	81	58
Summer	493	−14	14	−19	14	70	74	78	74
Autumn	458	−28	−48	−64	0	68	81	87	50

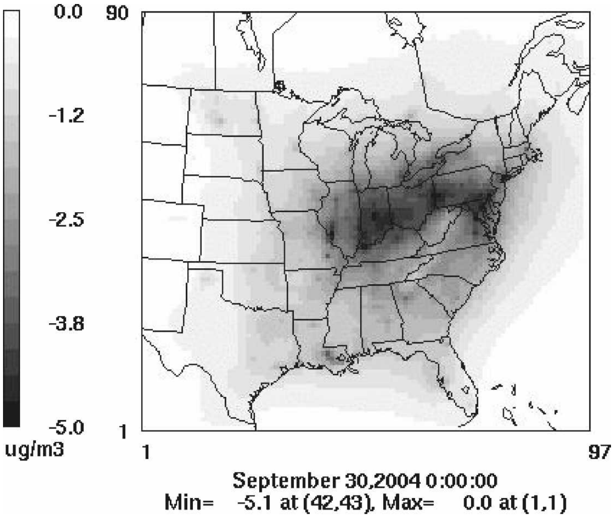

FIG. 7. Difference between quarter-4 average SO_2 concentration ($\mu g\ m^{-3}$) for standard run − SO_2 velocities × 2.0.

nium ions worsens (Table 6; SENS1). Dry deposition velocity for ammonia does not appear to be a systematic cause of poor model performance for ammonia, PM2.5 ammonium sulfate, or PM2.5 ammonium nitrate in the winter.

4. Conclusions

The meteorological variables temperature and relative humidity are important for correction partitioning of nitric acid between the gas and particulate phases. Modest correlations are seen between temperature, humidity, and PM2.5 ammonium nitrate bias and error metrics during the coldest months. A model sensitivity test that compensated for a tendency of the modeling system to underpredict temperature in the coldest months resulted in very little difference in model predictions. The temperature and relative humidity do not seem to be systematically degrading model performance for PM2.5 ammonium nitrate, ammonium sulfate, or precursor species. Transport is well represented in the modeling system because the wind displacement metric is usually less than 1 gridcell equivalent. This suggests that precursors are being moved around the chemical transport model appropriately and that the wind field is not a source of systematic error in chemical species prediction.

TABLE 8. Performance metrics for ambient SO_2 and $SO_4^=$.

Metric	Species	N	BASE	SO2 SENS	Units
Bias	SO_2	559	4.0	2.2	$\mu g\ m^{-3}$
Bias	$SO_4^=$	537	1.0	0.7	$\mu g\ m^{-3}$
Error	SO_2	559	4.5	3.1	$\mu g\ m^{-3}$
Error	$SO_4^=$	537	1.5	1.3	$\mu g\ m^{-3}$
Fractional bias	SO_2	559	90.1	68.1	%
Fractional bias	$SO_4^=$	537	31.3	23.5	%
Fractional error	SO_2	559	96.6	80.8	%
Fractional error	$SO_4^=$	537	52.1	49.0	%

Weekly total precipitation performance is good at central U.S. NADP monitor locations and does not seem to systematically affect wet deposition model estimates. Total nitrate, total sulfate, and total ammonium wet deposition are underpredicted by the modeling system in the coldest months at NADP monitor locations, which indicates that wet deposition processes may not be removing these chemical species efficiently enough during the coldest months.

The systemic increase in sulfur dioxide deposition velocity improved ambient sulfur dioxide and PM2.5 sulfate ion performance and did not change any of the other species. The dry deposition of sulfur dioxide does seem to have a systematic impact on ambient estimates of sulfur dioxide in the photochemical model. The photochemical model may not always respond appropriately to emissions adjustments if too much sulfur dioxide is in the model. The deposition model should be examined to determine how sulfur dioxide deposition velocities may be improved. A field experiment showed that sulfur dioxide deposition velocities increase in the presence of ambient ammonia (Cape et al. 1998). Because ammonia exists in the central United States in concentrations comparable to sulfur dioxide, the presence of ambient ammonia would increase sulfur dioxide deposition velocities and would help to minimize the apparent deposition velocity underpredictions in the model. The adjustment to the surface resistance term used for estimating ammonia dry deposition velocity systematically increased ammonia concentrations but made performance for PM2.5 ammonium nitrate worse.

Overall, meteorological variables and processes do not seem to be systematically degrading model performance for PM2.5 ammonium sulfate and nitrate with the exception of sulfur dioxide dry deposition and winter wet deposition. This type of evaluation provides a direction for future model development and improvement. It also establishes a level of model performance for key meteorological variables that allows the photochemical model to appropriately predict PM2.5 ammonium sulfate, ammonium nitrate, and key precursor species.

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