

## Seasonality of speciated aerosol transport over the Great Lakes region

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[1] The Community Multiscale Air Quality model (CMAQ) is used to simulate aerosol mass and composition in the Great Lakes region of North America in an annual study for 2002. Model predictions are evaluated against daily and weekly average speciated fine particle (PM<sub>2.5</sub>) and bulk (PM<sub>2.5</sub> and PM<sub>10</sub>) mass concentration measurements taken throughout the region by the Interagency Monitoring of Protected Visual Environments (IMPROVE), Speciation Trends Network (STN), and Clean Air Status and Trends Network (CASTNet) monitoring networks, and number concentration is evaluated using hourly observations at a rural site. Through detailed evaluation of model-measurement agreement over urban and remote areas, major features of aerosol seasonality are examined. Whereas nitrate (winter maximum) and sulfate (summer maximum) seasonal patterns are driven by climatic influence on aerosol thermodynamics, seasonality of ammonium and organic mass (OM) is driven by emissions. Production of anthropogenic secondary organic aerosol (SOA) and summertime ozone formation both reach regional maxima over the southern Great Lakes, where they are also most strongly temporally correlated. Although primary OM is more prevalent, insufficient SOA formation leads to summertime OM underprediction of more than 50%. By comparing temporal patterns in aerosol species between model and observations, we find that elemental carbon, OM, and PM<sub>2.5</sub> are overly correlated in CMAQ, suggesting that the model misses chemical, transport, or emissions processes differentiating these constituents. In contrast, sulfate and PM<sub>2.5</sub> are not sufficiently correlated in CMAQ, although CMAQ simulates sulfate with a high level of skill. Performance relative to ad hoc regional modeling goals and previous studies is average to excellent for most species throughout the year, and seasonal patterns are captured.

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### 1. Introduction

[2] The Great Lakes of North America include among neighboring states and provinces some of largest cities in the United States and Canada: Chicago, Columbus, Detroit, Indianapolis, Milwaukee, Ottawa, and Toronto, among others. These population centers emit high levels of primary air pollutants and pollutant precursors, which interact with the complex meteorology associated with the large lakes, leading to persistent violations of the U.S. National Ambient Air Quality Standards (NAAQS) for both ozone (O<sub>3</sub>) and fine particulate matter (PM<sub>2.5</sub>) in many counties (U.S. Environmental Protection Agency, Nonattainment areas map—Criteria air pollutants, effective date of nonattainment designations June 2008, available at <http://www.epa.gov/air/data/nonat.html?us~USA~United%20States>). Understanding the chemical and meteorological processes controlling these pollutants allows for more efficient emissions control policy design, improved air quality forecasting, and

broader understanding of atmospheric chemical processes in coastal environments.

[3] The lakes, with their large volume and high heat capacity, have a dramatic influence on regional climate and air quality. The response of tropospheric O<sub>3</sub> to lake effect meteorology is pronounced, with maximum summertime ground level O<sub>3</sub> concentrations often located in the center of southern Lake Michigan and over Lake Erie. This above-lake buildup, and subsequent outflow to adjacent coastal areas, has been explained by the shallow, stable marine boundary layer and light southerly winds above the lake, which trap emissions close to the lake surface, enhancing photochemistry and directing polluted air back onshore [Lyons and Cole, 1976; Wolff *et al.*, 1977; Sillman *et al.*, 1993; Dye *et al.*, 1995; Hanna and Chang, 1995; Eshel and Bernstein, 2006]. Here, we examine the degree to which a chemical transport model (CTM) is able to adequately simulate speciated aerosols (PM) in this important region. Whereas O<sub>3</sub> is only a summertime problem, PM is a year-round pollutant in the upper midwestern United States and southern Canada, affected by summer photochemistry, winter storm systems, and seasonal patterns in emissions. Evaluating the degree to which a CTM can capture species-by-species seasonality, variability, and spatial patterns is a

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first step toward understanding how individual processes contribute to regional PM pollution.

[4] Studies to date have shown that about 80% of  $PM_{2.5}$  in the region is secondary, formed through condensation and chemical reactions among precursor species [Lee *et al.*, 2003; Kerr *et al.*, 2004; V. Rao *et al.*, Chemical speciation of  $PM_{2.5}$  in urban and rural areas in national air quality and emissions trends report, 2003, available at [http://www.epa.gov/air/airtrends/aqtrnd03/pdfs/2\\_chemspecofpm25.pdf](http://www.epa.gov/air/airtrends/aqtrnd03/pdfs/2_chemspecofpm25.pdf)]. In particular, secondary  $SO_4^{2-}$ ,  $NO_3^-$ , ammonium ( $NH_4^+$ ), and organic mass (OM) dominate in both urban and rural areas. On an annual basis, fine particulate levels in urban areas tend to be 30% higher than in rural areas, with the urban excess due mostly to carbonaceous aerosols (Rao *et al.*, emissions trends report, 2003). Multiple studies have attributed aerosol mass around the Great Lakes to emissions from motor vehicles as well as regionally dispersed secondary  $SO_4^{2-}$  and  $NO_3^-$  [Lee *et al.*, 2003; Sheesley *et al.*, 2004; Kim *et al.*, 2005, 2007; Buzcu-Guven *et al.*, 2007; Rizzo and Scheff, 2007; Zhao and Hopke, 2006; Zhao *et al.*, 2007]. On average, natural sources account for approximately 25% of observed aerosol mass, with 6% of observed  $PM_{2.5}$  mass contributed by salt and soil [Kim *et al.*, 2005; Malm *et al.*, 2004]. The less volatile oxidation products of biogenic emissions from forests and croplands contribute about 20% to OM at background sites [Malm *et al.*, 2004], and up to 100% in remote forested areas of the region [Sheesley *et al.*, 2004].

[5] The Great Lakes region has been included in larger spatial domains in numerous chemical transport modeling studies, particularly for model evaluation, but it has not been the focus of regional model aerosol studies to date. Mebust *et al.* [2003] established that summertime aerosol performance in the Community Multiscale Air Quality model (CMAQ) with a reactive aerosol module performed best for summertime  $SO_4^{2-}$ , with a negative bias for  $PM_{2.5}$  and its other components. In a model intercomparison between CMAQ and CAMx, Tesche *et al.* [2006] found that model bias for speciated aerosols was generally high in the winter and low in the summer, and that model performance was nearly identical on 12 km and 36 km grid systems in both models. G3go *et al.* [2006] find that CMAQ better simulates longer-term weekly fluctuations in  $SO_4^{2-}$  and  $NO_3^-$  concentrations than day-to-day variability. Phillips and Finkelstein [2006] found that CMAQ was particularly skillful in simulating annual and summertime patterns in  $SO_4^{2-}$ , including the continental summer maximum over Indiana and Ohio, and annual and winter  $NO_3^-$  but underestimated the intensity and extent of the summer continental  $NH_4^+$  maximum over Indiana and Ohio. Simulations with CAMx (K. Baker, Photochemical model performance for  $PM_{2.5}$  sulfate, nitrate, ammonium, and precursor species  $SO_2$ ,  $HNO_3$ , and  $NH_3$  at background monitor locations in the central and eastern United States, paper presented at 5th Annual CMAS Conference, Community Modeling and Analysis System, University of North Carolina, Chapel Hill, North Carolina, 16 October 2006) and PMCAMx [Gaydos *et al.*, 2007; Karydis *et al.*, 2007] found consistent agreement with daily observations of  $PM_{2.5}$  and its constituents. A climate sensitivity study of speciated aerosols in the region [Dawson *et al.*, 2007] found a strong response of  $PM_{2.5}$  to changes in temperature, mixing height, wind speed, and humidity in both winter and summer, along

with locally varying sensitivity to precipitation. Here, we diagnose CMAQ performance for a range of individual species, consider how these modeled distributions reflect atmospheric processes, and compare our results with earlier studies.

## 2. Data and Methods

[6] We employ CMAQ (v4.6) [Byun and Schere, 2006] using the Carbon Bond IV (CB-IV) lumped gas phase [Gery *et al.*, 1989] chemical mechanism, Regional Acid Deposition Model (RADM) aqueous chemistry [Chang *et al.*, 1987], advection by the piecewise parabolic method, and eddy diffusion. The CMAQ AE3 aerosol module employed consists of aerosol microphysics [Binkowski and Roselle, 2003] and the ISORROPIA (v1.7) aerosol equilibrium model [Nenes *et al.*, 1998], in which partitioning between gas and aerosol phases is a function of temperature and relative humidity. CMAQ employs a trimodal size distribution with lognormal Aitken, aggregation, and coarse modes. Speciated aerosols in the model do not grow to the coarse mode, and coarse mode particle types are treated as chemically inert.

[7] The secondary organic aerosol (SOA) scheme, based on the Secondary Organic Aerosol model [Schell *et al.*, 2001], accounts for SOA formation from the oxidation of alkenes, cresol, high-yield aromatics, low-yield aromatics, and monoterpenes, which form ten lumped, idealized semi-volatile gaseous SOA precursors that can subsequently condense onto particles. As implemented for CB-IV gas phase chemistry, SOA reactions are fully reversible (gaseous precursors can condense and evaporate) but SOA production from alkanes, olefins, and isoprene is not simulated. Many processes now known to affect SOA, including interactions with  $NO_x$  [e.g., Ng *et al.*, 2007] and  $SO_4^{2-}$  [e.g., Surratt *et al.*, 2007] and in-cloud processing [e.g., Lim *et al.*, 2005] are omitted. This treatment for the partitioning of organics between gas and particle phases, with outdated aerosol yields for modeled lumped VOC species and missing yields for important SOA formation pathways (isoprene, in particular), presents a structural limitation in simulating SOA, with an expected bias toward underprediction. Moreover, emissions initialized as primary organic aerosols cannot volatilize and then become SOA in this scheme, limiting the range for regional dispersion of primary organics before their wet and dry deposition.

[8] The study domain covers a  $2.23 \times 10^6$  km<sup>2</sup> region at  $36 \times 36$  km grid resolution and 14 vertical layers to the lower stratosphere (approximately 15 km). The analysis presented here considers a subset of data from a simulation of continental North America. CMAQ was run from December 2001 to December 2002, solving chemistry at 12-min intervals and saving results every hour. The annual modeling period was divided into 4 quarterly model runs, with 10 days of spin-up before each quarter.

[9] Emissions estimates for CMAQ were developed using the Sparse Matrix Operating Kernel for Emissions (SMOKE) [Houyoux *et al.*, 2000]. The data sets processed with SMOKE (v2.1) were obtained from U.S. Environmental Protection Agency's (EPA) 2001-based platform, version 1 [U.S. Environmental Protection Agency (EPA), 2005a]. This inventory is based on the 1999 National Emissions Inventory (NEI), with growth factors applied by Source Classification

Code, and augmented with national inventories for Canada (2000) and Mexico (1999). This NEI was used by EPA for analyses of the Clean Air Interstate Rule, Clean Air Visibility Rule (CAIR), and Clear Skies Legislation analysis. The 2001 NEI was the most recent complete national inventory publicly available at the time this work began. This emissions inventory represents the seasonality of aerosol and precursor emissions, but does not include day-specific emissions for 2002 for any anthropogenic sources. Fire emissions from wildfires, prescribed burns, and agricultural fires were estimated using 1996–2001 averages, which could lead to spatial and temporal errors in area emissions of  $\text{NO}_x$ , VOCs, and primary organic aerosols, for which biomass burning is a seasonally significant source, with corresponding impacts on secondary aerosol  $\text{NO}_3^-$  and SOA. Biogenic emissions were calculated from modeled meteorology using BEIS3 (v3.12).

[10] Emissions of most primary aerosols and aerosol precursors in the Great Lakes region exhibit limited seasonality, as represented in NEI 2001. Regional aggregate monthly emissions of reactive aerosol precursors ( $\text{SO}_y$  and  $\text{NO}_y$ ) and primary fine (the sum of all directly emitted  $\text{PM}_{2.5}$  species) and coarse mode (unspecified) aerosols in the region all vary within a range of less than 12% between the highest and lowest months, with  $\text{SO}_y$  (2.1%) especially invariant. On a mass basis, total primary aerosol and precursor emissions in the average 36 km grid cell vary by less than 20% over the course of the year. The top 5% of emitting grid cells are even more invariant, with less than 8% range. Elemental carbon emissions exhibit much greater monthly range (33%), with a summer maximum and winter minimum. Ammonia ( $\text{NH}_3$ ) emissions peak in April and June in concert with the planting seasons for the region's two largest commodity crops, soybeans and corn. Thus, with the exception of EC and  $\text{NH}_4^+$ , seasonal cycles in aerosol concentrations are due primarily to changes in regional atmospheric conditions, including temperature, relative humidity, and ionic balance among aerosol species, rather than to temporal changes in emissions. Unless emissions estimates are greatly in error, this implies that seasonality in modeled aerosol concentrations, especially  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , is due to modeled chemical and thermodynamic processes.

[11] The Pennsylvania State University/National Center for Atmospheric Research mesoscale meteorological model (MM5) described by *Grell et al.* [1995, available at <http://www.mmm.ucar.edu/mm5/documents/mm5-desc-doc.html>] was used to develop gridded meteorology inputs to SMOKE and CMAQ. MM5 (v3.6.1) output was provided by the Lake Michigan Air Directors Consortium [*Baker, 2004*] over a continental 36 km  $\times$  36 km domain and processed for CMAQ by MCIP (v3.2). Results were tested and employed extensively by the Lake Michigan Air Directors Consortium and regional planning offices. Model evaluation [*Baker et al., 2005*; M. Abraczinskas et al., Characterizing annual meteorological modeling performance for visibility improvement strategy modeling in the southeastern United States, paper presented at 13th AMS Joint Conference on Applications of Air Pollution Meteorology with the Air and Waste Management Association, American Meteorological Society, Vancouver, British Columbia, Canada 2004; D. Olerud and A. Sims, MM5 2002 modeling in support of VISTAS (Visibility Improvement—State and Tribal Association), 2004, Baron Advanced Meteorological Systems, LLC,

Research Triangle Park, North Carolina, available at <http://www.baronams.com/projects/VISTAS>] indicated good performance for temperature, humidity, precipitation, and wind speed, with lower levels of agreement on wind direction. An MM5 study in the same region [*Zhong et al., 2005*] found that the model captures the general development and evolution of boundary layer inversions and lake–land breezes, although with errors in their strength and timing.

[12] Boundary conditions for the continental CMAQ domain were extracted from 2002 monthly mean concentration fields from the Model of Ozone and Related Tracers (MOZART) [*Horowitz et al., 2003*] incorporating aerosol physics described by *Tie et al.* [2001, 2005]. MOZART was run with 2002 reanalyzed meteorology from National Centers for Environmental Prediction Global Reanalysis [*Kalnay et al., 1996*]. Eleven gaseous and aerosol species with atmospheric lifetimes sufficient for intercontinental transport were taken from MOZART, including  $\text{O}_3$ ;  $\text{SO}_4^{2-}$ ;  $\text{NH}_4^+$ ;  $\text{NO}_3^-$ ; carbon monoxide (CO); elemental carbon (EC); organic carbon (OC); nitrogen dioxide ( $\text{NO}_2$ ); sulfur dioxide ( $\text{SO}_2$ ); ethane ( $\text{C}_2\text{H}_6$ ); propane ( $\text{C}_3\text{H}_8$ ); and acetone ( $\text{CH}_3\text{COCH}_3$ ).

[13] Model results were compared with 2002 observations from several national monitoring networks. Samples from the EPA Speciation Trends Network (STN) [*EPA, 2001*] every 3 or 6 days (depending on the site) and Interagency Monitoring of Protected Visual Environments (IMPROVE) [*Malm et al., 2004*] every 3 days, along with weekly observations from the Clean Air Status and Trends Network (CASTNet) [*Sickles and Shadwick, 2007*], provide aerosol concentration and speciation at representative urban, remote, and rural locations, respectively. For each network, all sites in the states of Illinois, Indiana, Minnesota, Michigan, Ohio, and Wisconsin were included in the study (40 STN, 14 CASTNet, 6 IMPROVE). The given citations detail the methods and uncertainty associated with each of the measurement protocols. In addition to reported uncertainties, as well as incommensurable reported speciation results due to differing techniques between the various networks [*e.g. Chow et al., 2004*], there are also known biases in measurements of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and carbonaceous aerosols [*Frank, 2006*]. Simulation of aerosol number concentration was assessed using hourly data from the Bondville, Illinois, NOAA Global Monitoring Division site, collocated with CASTNet and IMPROVE observations.

### 3. Model Performance Evaluation

[14] Aerosol seasonality is considered monthly and in the four seasons: January–March (JFM); April–June (AMJ); July–September (JAS); October–December (OND). Model predictions are compared with surface observations using model bias, error, normalized mean bias, normalized mean error, fractional bias (FB), fractional error (FE), and the coefficient of determination ( $r^2$ ) between predicted–observed pairings as performance metrics:

$$\begin{aligned} \text{Bias} &= \frac{1}{N} \sum_{i=1}^N (P_i - O_i) & \text{Error} &= \frac{1}{N} \sum_{i=1}^N |P_i - O_i| \\ \text{FB} &= \frac{2}{N} \sum_{i=1}^N \left( \frac{P_i - O_i}{P_i + O_i} \right) & \text{FE} &= \frac{2}{N} \sum_{i=1}^N \frac{|P_i - O_i|}{P_i + O_i} \end{aligned}$$

**Table 1.** CMAQ Monthly Performance for PM<sub>2.5</sub> and PM<sub>10</sub><sup>a</sup>

Month	PM <sub>2.5</sub>										PM <sub>10</sub> CASTNet				
	STN					IMPROVE					Obs	CMAQ	FB	FE	r <sup>2</sup>
	Obs	CMAQ	FB	FE	r <sup>2</sup>	Obs	CMAQ	FB	FE	r <sup>2</sup>					
Jan	14.71	19.56	0.42	0.44	53	6.31	10.26	0.31	0.43	86	8.68	12.12	0.16	0.40	85
Feb	11.12	13.97	0.30	0.47	52	4.91	6.86	0.26	0.42	71	6.68	8.08	0.06	0.36	71
Mar	11.70	13.88	0.17	0.39	63	6.24	7.57	-0.12	0.56	73	9.22	8.82	-0.35	0.67	54
Apr	12.31	11.27	-0.10	0.43	17	7.18	7.57	-0.08	0.43	45	10.86	8.58	-0.35	0.55	33
May	10.07	9.09	-0.03	0.42	34	6.85	6.13	-0.24	0.42	61	10.78	6.99	-0.55	0.64	56
Jun	17.97	15.36	-0.05	0.28	64	13.49	9.45	-0.42	0.51	55	19.21	10.49	-0.70	0.72	50
Jul	18.56	16.18	-0.05	0.31	36	13.22	9.78	-0.44	0.52	76	19.40	11.13	-0.74	0.77	58
Aug	14.07	13.26	0.11	0.32	55	9.24	9.09	-0.12	0.32	80	14.56	10.32	-0.49	0.54	82
Sep	14.21	16.79	0.20	0.34	66	9.33	11.34	0.14	0.39	74	14.07	12.90	-0.21	0.40	74
Oct	10.20	12.84	0.29	0.42	71	6.07	8.47	0.20	0.43	72	9.13	10.05	-0.07	0.41	72
Nov	12.02	13.87	0.18	0.37	54	6.27	9.32	0.32	0.45	68	8.37	10.90	0.16	0.38	62
Dec	17.37	21.94	0.31	0.46	59	7.02	11.22	0.44	0.55	78	9.65	12.83	0.19	0.44	73

<sup>a</sup>For Table 1 and all subsequent tables, model predictions are compared with surface observations at each observational network: IMPROVE, STN, and CASTNet. Monthly mean observations (Obs) are shown along with monthly mean predicted concentrations (CMAQ) in units of  $\mu\text{g}/\text{m}^3$ , along with fractional bias (FB), fractional error (FE), and  $r^2$  (%) for all predicted-observed pairings in that month: daily, every 3 days (STN); daily, every 3 days (IMPROVE); and weekly (CASTnet).

where  $P_i$  is the predicted value of the concentration at monitor  $i$ ,  $O_i$  is the observed concentration at monitor  $i$ , and  $N$  is the total number of prediction-observation pairings used for the comparison. Fractional bias and error are particularly useful model performance indicators because they are unitless, symmetrical (equally weighting positive and negative biases), and bounded: values for FB range between  $-2.0$  (extreme underprediction) and  $+2.0$  (extreme overprediction), while FE ranges between  $0.0$  and  $2.0$ . Values of FB that are equal to  $-0.67$  are equivalent to underprediction by a factor of 2, while values of FB that are equal to  $+0.67$  are equivalent to overprediction by a factor of 2. For Table 1 and Tables 3–8, we present monthly mean observed and modeled concentrations at each observational network, along with FB, FE, and  $r^2$  for all predicted-observed pairings in that month.

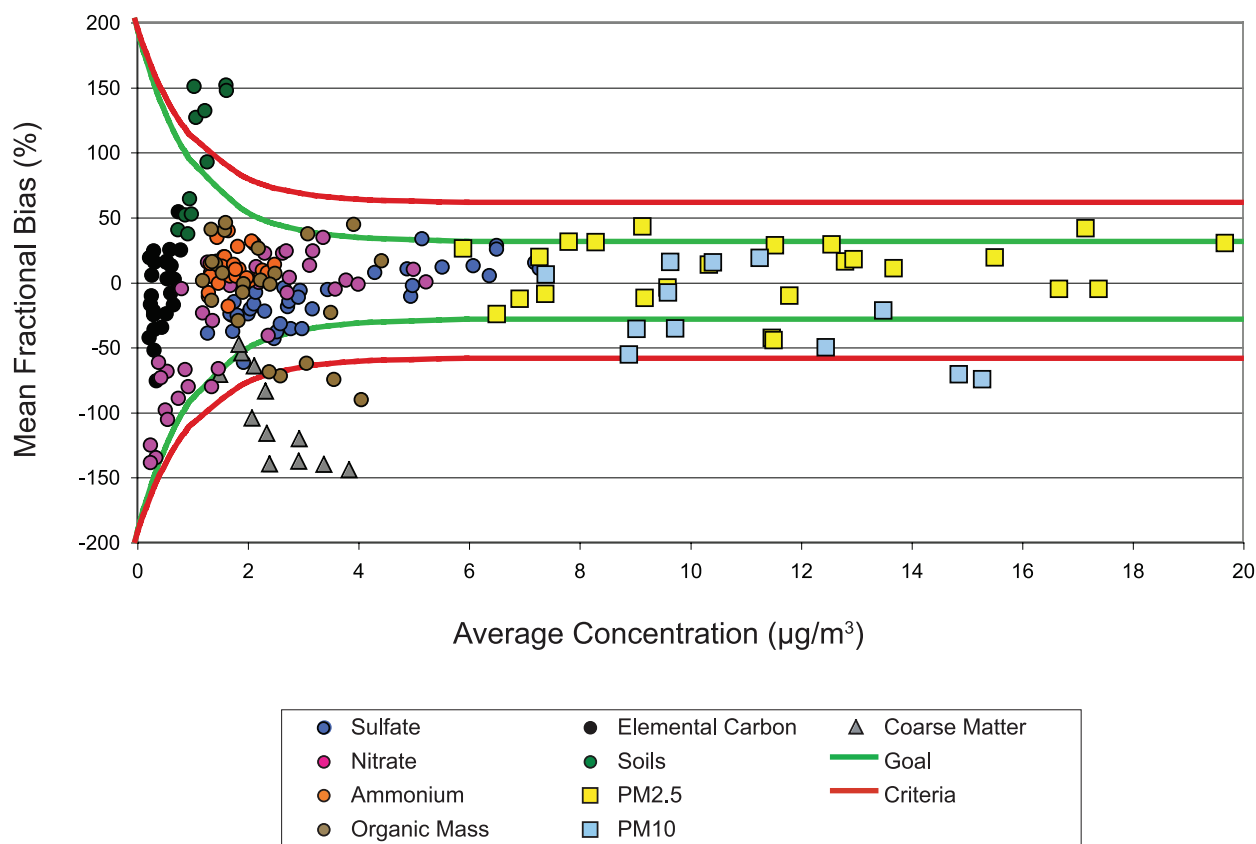
[15] Performance for all PM species at IMPROVE, STN, and CASTNet sites is summarized in Figure 1, a bugle plot [Boylan and Russell, 2006] displaying aggregate model fractional bias as a function of increasing concentration level. The plot also includes PM model bias performance goals ( $\pm 30\%$ ) and performance criteria ( $\pm 60\%$ ) suggested by Boylan and Russell [2006]. CMAQ captures relative month-to-month changes in PM<sub>2.5</sub> well, especially at STN sites, but predicts an annual maximum in winter, whereas STN and IMPROVE observations both indicate a summertime maximum (Table 1). From September to March, CMAQ captures month-to-month variability but consistently overpredicts PM<sub>2.5</sub> due to biases in  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , OM, and unspicified fine mass. CMAQ performance against STN PM<sub>2.5</sub> observations is much better from April to July, when CMAQ matches monthly mean values for the network very well (fractional bias  $\leq 0.1$ , error  $< 0.6 \mu\text{g}/\text{m}^3$ ). Modeled PM<sub>2.5</sub> variability at IMPROVE sites show a substantial underprediction of peak values (Figure 2) in June and July, explained by the low bias in summertime OM, and an overestimation of PM<sub>2.5</sub> in the winter, due mostly to overprediction in  $\text{NO}_3^-$ , OM, and unspicified mass (not shown).

[16] CMAQ calculates PM<sub>10</sub> as the sum of PM<sub>2.5</sub>, coarse mode soil and crustal material, and other unspicified coarse mode material; sea salt aerosol is negligible over the region

in both CMAQ and source-apportioned observations [Kim *et al.*, 2005]. Regional PM<sub>10</sub> is consistently underestimated from March through September at the rural IMPROVE sites, with CMAQ's unspicified coarse mode aerosols, which comprise 30% of simulated PM<sub>10</sub> mass, contributing a consistent negative bias. Tesche *et al.* [2006] attribute the negative PM<sub>10</sub> bias over the eastern United States to CMAQ's simulation of all speciated aerosols in Aitken and accumulation modes only. We add that the high concentrations of coarse soil material observed in the region throughout the year represent large real-world reservoirs of salts (particularly calcium carbonate and sodium chloride) whose roles in catalysis and ionic reactions with speciated inorganic aqueous and aerosol species are not simulated in this implementation of CMAQ. As crustal cations represent important sinks for aqueous nitric acid ( $\text{HNO}_3$ ), this limitation suggests a high bias in ambient gaseous and aqueous  $\text{HNO}_3$  and may indirectly increase simulated concentrations of nitrogenous species (including  $\text{NH}_3$ ,  $\text{NO}_3^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{N}_2\text{O}_5$ ) while impacting the equilibrium partitioning among them. Sectional aerosol modeling, which resolves aerosols and their chemistry in explicit size bins, is required to model coarse particle speciation, improve performance potential for PM<sub>10</sub>, and model the ultragiant particles that have been documented downwind of the Great Lakes [Lasher-Trapp and Stachnik, 2007].

[17] Considering performance independent of concentration, fractional bias and fractional error results are summarized in Table 2 according to four levels of performance suggested by Morris *et al.* [2005]: excellent, FB  $\pm 15\%$  and FE  $> 35\%$ ; good, FB  $\pm 30\%$  and FE  $> 50\%$ ; average, FB  $\pm 60\%$  and FE  $> 75\%$ ; problematic, FB  $> \pm 60\%$  and FE  $> 75\%$ . We note that performance is good or excellent for 91 of 168 species-month-network pairs (52%), and only problematic for 23 (14%). When aggregated to seasonal profiles taking into account all observations at all networks, only the underestimation of low  $\text{NO}_3^-$  concentrations in spring and summer (Figure 3) is problematic with respect to contemporary performance standards. Overall, performance for aerosol seasonality in our 2002 simulation is encouraging, especially considering that biomass burning emissions were not specific

## CMAQ Monthly Performance (2002)



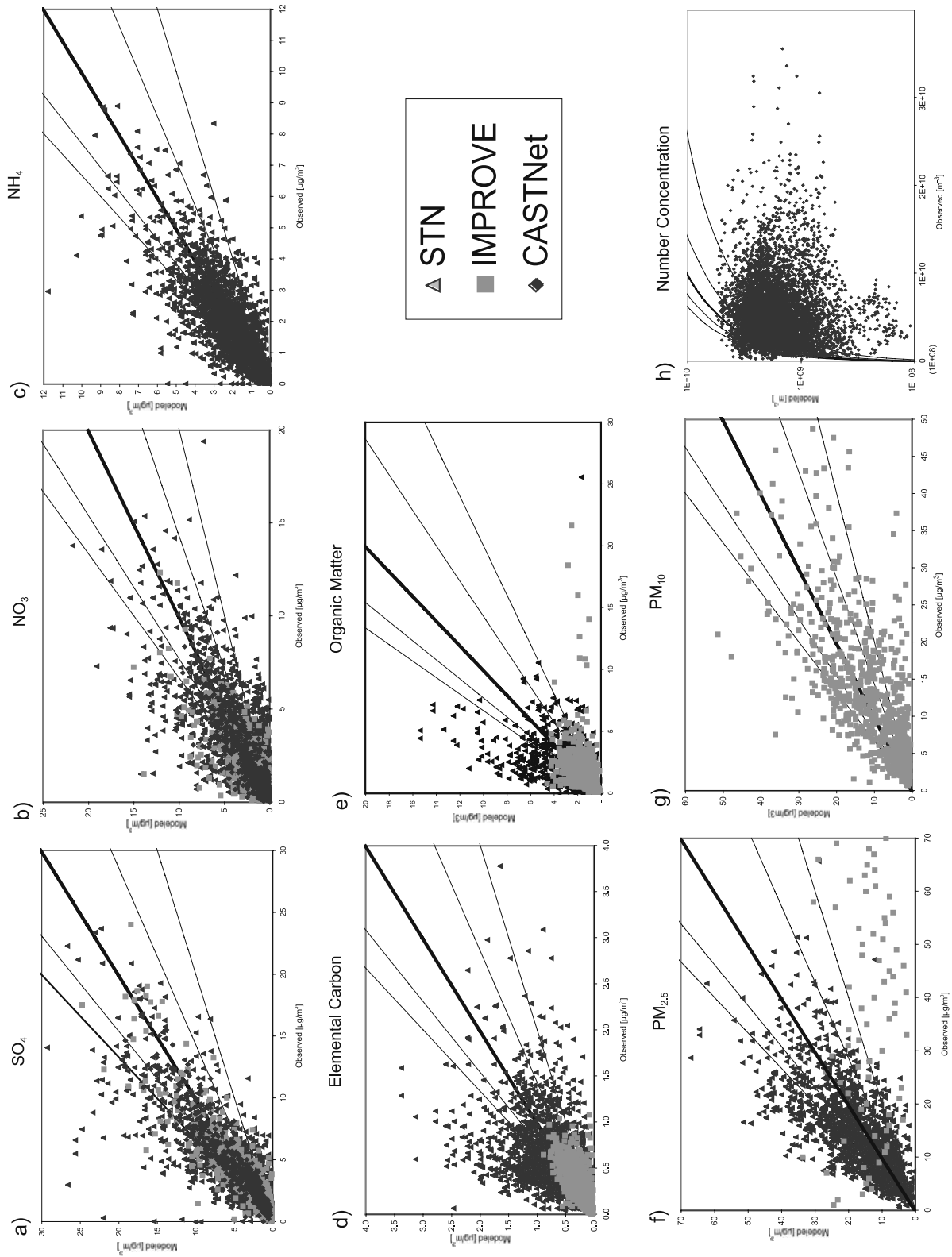
**Figure 1.** The 2002 CMAQ performance for all aerosol species across the IMPROVE, STN, and CASTNet networks, comparing monthly average concentrations ( $\mu\text{g}/\text{m}^3$ ) with mean fractional bias (%). Graph includes sulfate, nitrate, ammonium, organic mass, elemental carbon, soil matter, and coarse matter, as well as aggregate  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ . Lines reflect the  $\pm 30\%$  “goal” (green) and  $\pm 60\%$  “criteria” (red) levels for acceptable regional model performance in simulating aerosols, as defined by *Boylan and Russell* [2006].

to our study year. We note that while  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{PM}_{2.5}$  achieve classification of “good” when all networks’ observations are aggregated seasonally, no CMAQ modeled species can be classified as good or excellent at every network for every month of the year.

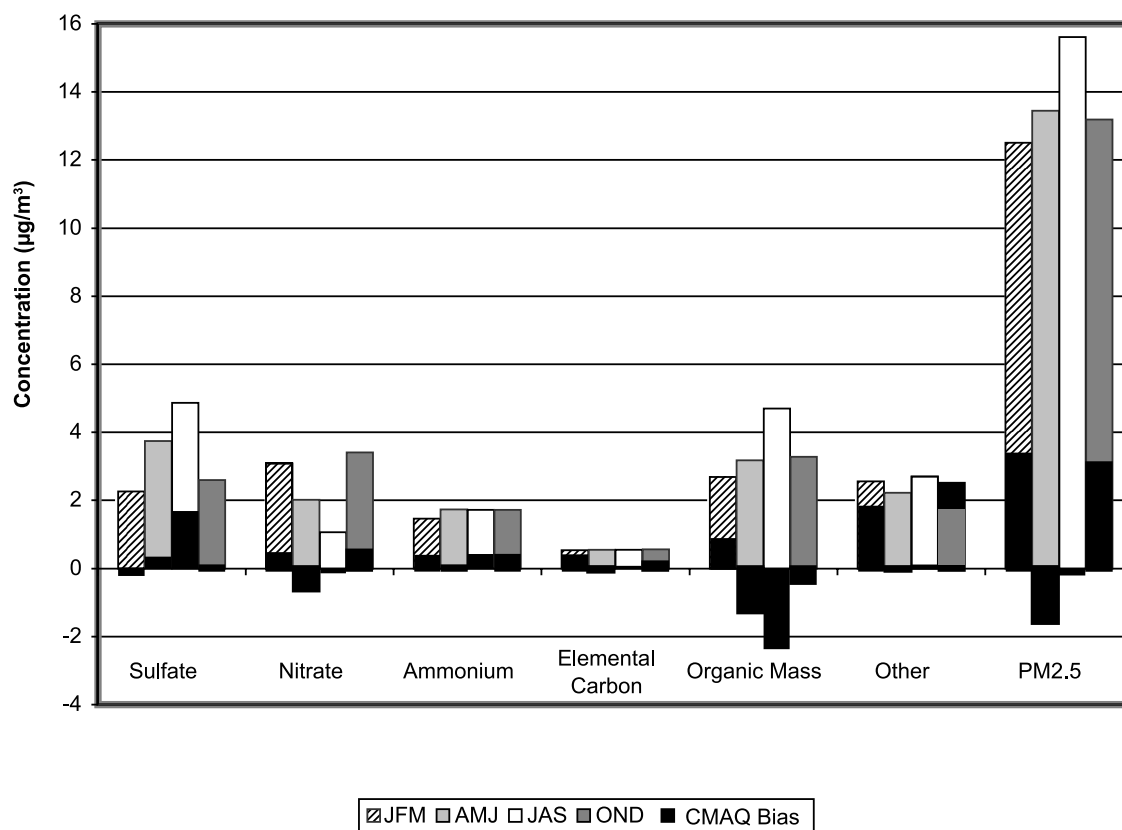
[18] A comparison of simulated seasonal mean  $\text{PM}_{2.5}$  speciation versus that measured at the STN network monitors in the study domain is presented in Figure 3. Despite errors in the total  $\text{PM}_{2.5}$  mass, modeled seasonal speciation profiles are generally consistent with observations, including the summertime maximum in  $\text{SO}_4^{2-}$  and wintertime maximum in  $\text{NO}_3^-$ . While there are biases in their concentrations, the relative abundances of EC and  $\text{NH}_4^+$  are especially well simulated, with regionally averaged seasonal predictions of their percentage contribution to total  $\text{PM}_{2.5}$  mass of 3.5% to 4.2% (EC) and 11.0% to 13.0% ( $\text{NH}_4^+$ ). These fractional contributions never differ from observed estimates of  $\text{PM}_{2.5}$  speciation by more than 1.2% and 2.8%, respectively, and EC contribution to  $\text{PM}_{2.5}$  is within 0.1% in summer and fall. The relative abundance of organic matter is very well simulated at urban sites in winter (observed fraction = 21.4%, modeled fraction = 21.6%), but erroneous throughout

the rest of the year. The overprediction of  $\text{SO}_4^{2-}$  in summer and fall, underprediction of OM from April to December, and overprediction of unspiciated CMAQ fine particle mass in fall and winter contribute most significantly to total  $\text{PM}_{2.5}$  biases.

[19] To better evaluate the processes controlling CMAQ representation of  $\text{PM}_{2.5}$  and its component species we examine seasonal spatial patterns for each compound. Seasonality of spatial patterns in simulated  $\text{PM}_{2.5}$  mass is rather limited, as shown in Figure 4. We focus on areas with modeled  $\text{PM}_{2.5}$  concentrations close to or in excess of  $15 \mu\text{g}/\text{m}^3$ , the current annual average limit for  $\text{PM}_{2.5}$  under the NAAQS. Seasonal average concentrations of approximately  $15 \mu\text{g}/\text{m}^3$  are characteristic over a wide area in all seasons, but the spatial extent of this area is smallest in spring (AMJ), extending from southeastern Wisconsin, southern Michigan, and eastern Illinois into Indiana, Ohio, and neighboring states. In other seasons, the extent of the  $15 \mu\text{g}/\text{m}^3$  or greater region is wider, extending furthest west in autumn (OND), and reaching the highest concentrations throughout Indiana (the state with most persistent high regional  $\text{PM}_{2.5}$ ) in summer (JAS). Seasonal mean concentrations in excess



**Figure 2.** Scatterplots show monthly mean CMAQ model predictions versus aerosol mass concentrations ( $\mu\text{g}/\text{m}^3$ ) at STN and IMPROVE sites for (a)  $\text{SO}_4$ ; (b)  $\text{NO}_3$ ; (c)  $\text{NH}_4$ ; (d) elemental carbon; (e) organic matter; (f)  $\text{PM}_{2.5}$ ; (g)  $\text{PM}_{10}$ ; and (h) CMAQ model predictions versus aerosol number concentrations at the Bondville, Illinois, CASTNet site.



**Figure 3.** Seasonal average concentrations of  $PM_{2.5}$  and components in  $\mu\text{g}/\text{m}^3$ , as measured at the STN measurement sites in the study region. CMAQ performance is shown as bias relative to these observed values on a seasonal basis.

of 25–30  $\mu\text{g}/\text{m}^3$  are seen in the Chicago area year-round (lowest in AMJ). Spatial patterns in seasonal averages of  $PM_{2.5}$  follow those of  $\text{NH}_4^+$  (Figure S1 in the auxiliary material<sup>1</sup>), with a correlation coefficient  $r > 0.94$  between the regional maps for all four seasons. As  $\text{NH}_3$  emissions in the region are ascribed predominantly to agriculture, this consistently close spatial relationship between  $\text{NH}_4^+$  and total  $PM_{2.5}$  mass reinforces the importance of rural area sources in the regional aerosol burden throughout the year. Seasonal spatial patterns in  $PM_{10}$  (not shown) are very similar to  $PM_{2.5}$  but with wider regions of Indiana and Illinois exhibiting concentrations of  $\sim 25 \mu\text{g}/\text{m}^3$  and higher in winter, summer, and fall, and even more intense local urban hot spots than appear in Figures 4a–4d.

### 3.1. Sulfate ( $\text{SO}_4^{2-}$ )

[20] Like total  $PM_{2.5}$ ,  $\text{SO}_4^{2-}$  (Figure 5) shows a regional spatial signal with a minimum over the forested, lightly populated areas north of Lake Superior to maxima downwind of Chicago and in the Ohio River Valley (ORV). A regional cloud of  $\text{SO}_4^{2-}$  is found over the southeastern portions of the region throughout the year, with a minimum in winter and a maximum in summer, with wide areas in southern Illinois, southern Indiana, and southern Ohio with concentrations from 9 to 11  $\mu\text{g}/\text{m}^3$ . These areas of high  $\text{SO}_4^{2-}$  have been extensively attributed to coal-fired power plants in the ORV

[e.g., Kim *et al.*, 2007; Zhao *et al.*, 2007]. Additional major sources include local emissions from metal smelting and refining operations, as well as urban plumes from Chicago, St. Louis, and other major cities.

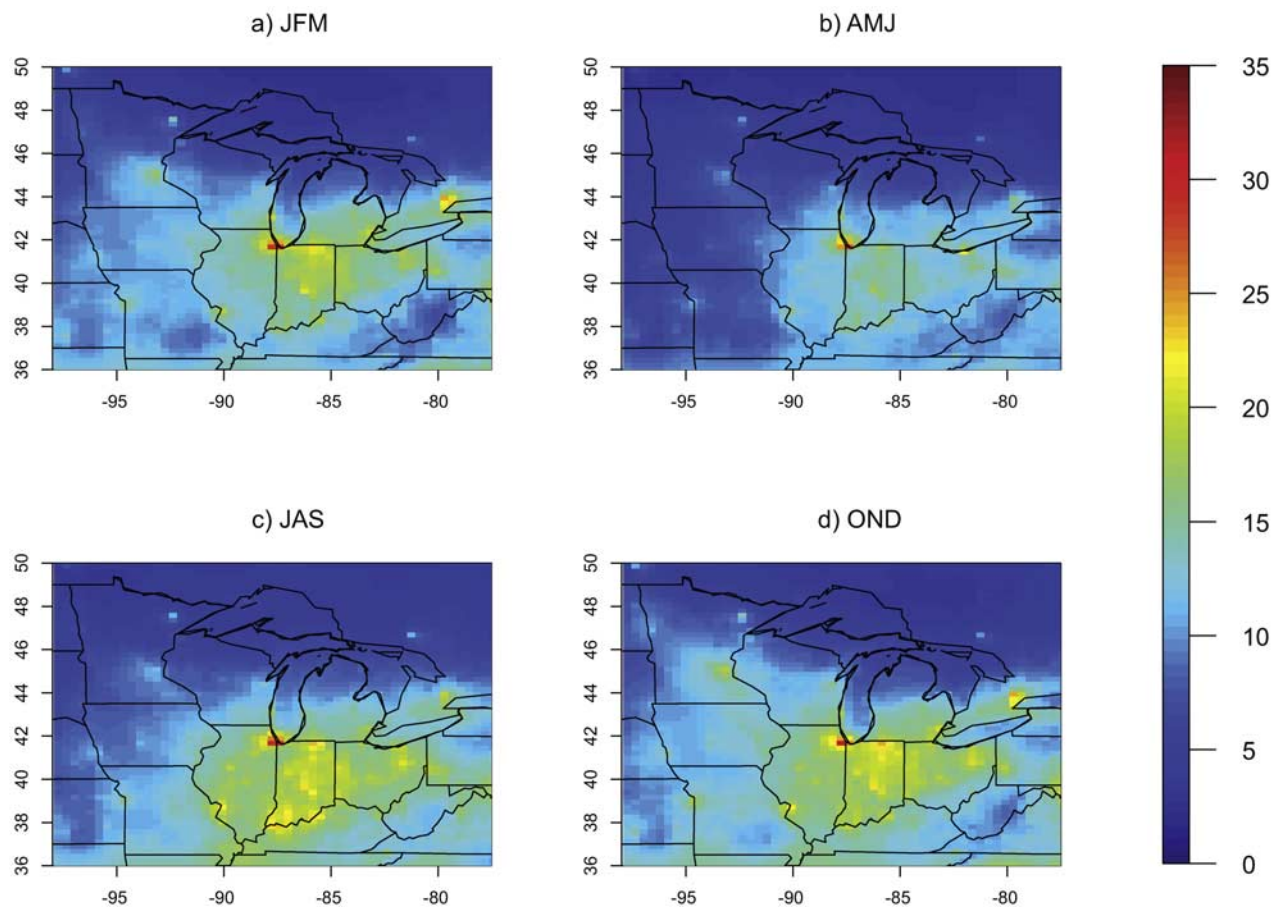
[21] Monthly variations in  $\text{SO}_4^{2-}$  performance are shown in Table 3. Observations at all sites exhibit peak values in June and July with a secondary peak in September, a pattern which CMAQ captures at the IMPROVE sites better than at CASTnet or STN. Overall, sulfate is consistently underpredicted in winter and overpredicted in summer (especially at urban sites), as also found by Tesche *et al.* [2006]. Since there is limited seasonality in primary emissions, and trends in model performance are consistent throughout the winter and summer, these seasonal biases are likely due to modeled representation of equilibrium partitioning between  $\text{SO}_4^{2-}$ ,

**Table 2.** Seasonal Average CMAQ Performance<sup>a</sup>

	JFM	AMJ	JAS	OND
Sulfate	Good	Good	Good	Good
Nitrate	Good	Problematic	Problematic	Good
Ammonium	Good	Good	Good	Good
Elemental carbon	Average	Average	Good	Average
Organic mass	Average	Average	Average	Average
$PM_{2.5}$	Good	Good	Good	Good
$PM_{10}$	Good	Average	Average	Average

<sup>a</sup>Excellent, fractional bias  $\pm 15\%$  and fractional error 35%; good, fractional bias  $\pm 30\%$  and fractional error 50%; average, fractional bias  $\pm 60\%$  and fractional error 75%; problematic, fractional bias  $> \pm 60\%$  and fractional error  $> 75\%$ .

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2008JD010598.



**Figure 4.** CMAQ simulated  $\text{PM}_{2.5}$  ( $\mu\text{g}/\text{m}^3$ ) in the lowest model layer, shown for each season: (a) JFM; (b) AMJ; (c) JAS; (d) OND.

aqueous sulfuric acid, and gaseous  $\text{SO}_2$ , rather than to biases in deposition or emissions. On an annual basis, CMAQ tends to overestimate low concentrations ( $<1 \mu\text{g}/\text{m}^3$ ) and underestimate the occurrence of concentrations in the range of  $2\text{--}7 \mu\text{g}/\text{m}^3$ .

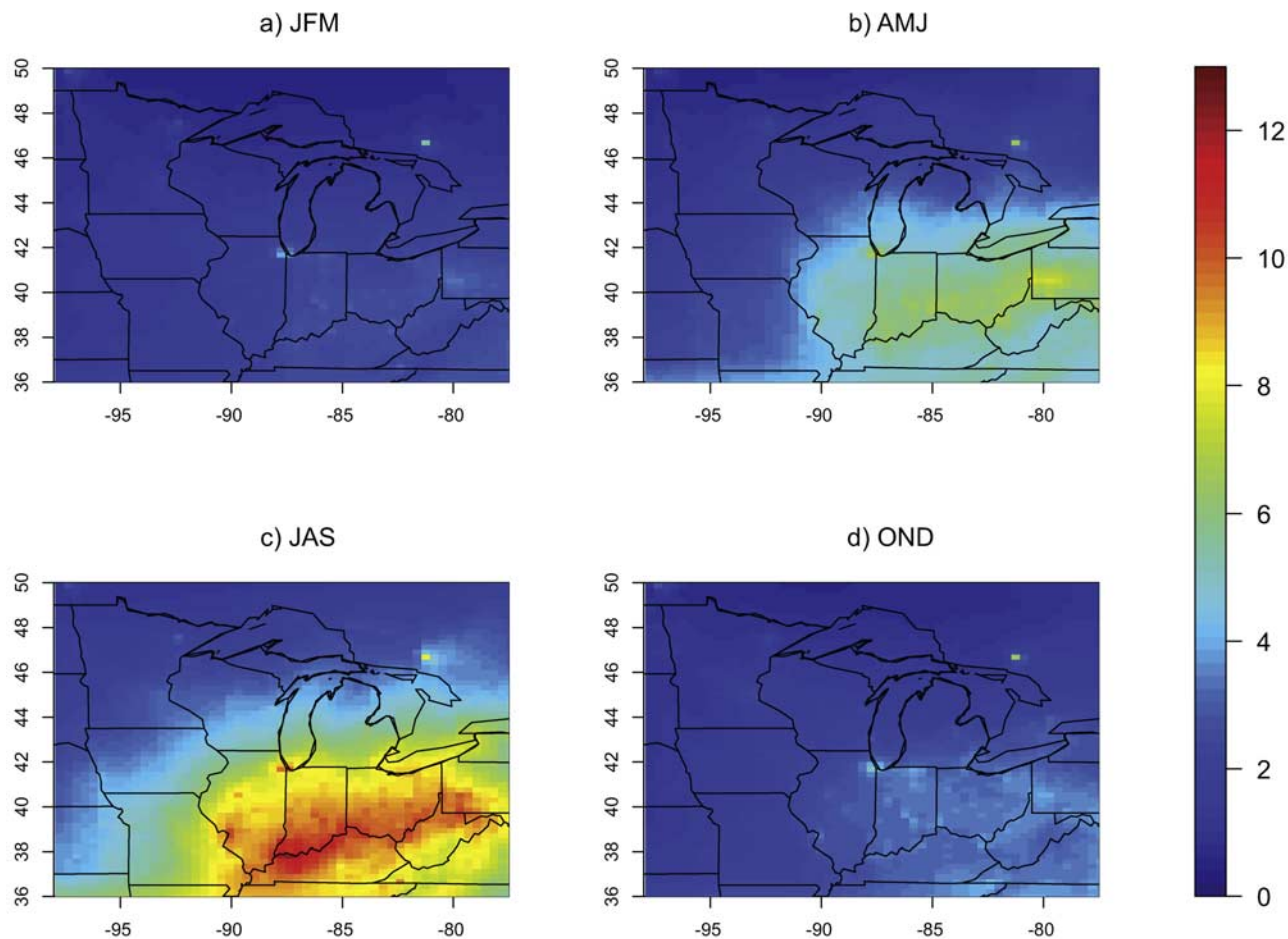
[22] Simulated daily and weekly variability in  $\text{SO}_4^{2-}$  concentration is well correlated with observations, with annual time series for all sites yielding  $r^2 > 80\%$  for CASTNet and IMPROVE. Urban STN sites had a lower daily  $r^2$  value of 68% on an annual basis, as local condensation of urban  $\text{SO}_2$  emissions is less correlated with meteorological variability than regionally transported background  $\text{SO}_4^{2-}$ . Weekly time series of average concentrations across CASTNet sites in the region (Figure 7a) show that CMAQ simulates the pronounced episodic variability in the regional  $\text{SO}_4^{2-}$  burden throughout the year, but with a consistent high bias in the summer.

### 3.2. Nitrate ( $\text{NO}_3^-$ )

[23] Figure 6 shows seasonal patterns in surface  $\text{NO}_3^-$  concentrations, which exhibit a seasonality almost exactly opposite that of  $\text{SO}_4^{2-}$ , with maximum concentrations in fall (OND) and winter (JFM). As simulated in CMAQ,  $\text{NO}_x$  emissions from urban sources condense as they are transported, leading to  $\text{NO}_3^-$  maxima downwind of Chicago and Detroit in the winter. In spring and summer, when higher temperatures cause  $\text{NO}_y$  to partition mostly to the gas phase,

local peaks in aerosol  $\text{NO}_3^-$  are evident over the large metropolitan areas of the region, with only trace amounts in rural and remote areas. In fall, and to a less pronounced degree in winter, regional background  $\text{NO}_3^-$  is not consistently advected across the southern lakes (Michigan, Huron, and Erie), so above-lake concentrations are noticeably lower than surrounding regional air (Figure 6d).

[24] Nitrate's seasonality, with a December peak and August minimum, is adequately simulated. However, CMAQ also includes an anomalous secondary peak in March, with an average overprediction in excess of  $0.9 \mu\text{g}/\text{m}^3$  across each of the networks. This bias, the largest for any month, is greatest at urban STN sites ( $1.17 \mu\text{g}/\text{m}^3$ ), but more significant at IMPROVE sites, where the error represents an overprediction in excess of 80%. Table 4 highlights an overprediction in winter at all networks, consistent with the study by Mathur *et al.* [2008]. Despite overprediction in winter and underprediction in summer, model bias is only conclusively beyond the range of reported IMPROVE measurement uncertainty for the high concentrations found in March, November, and December, when such measurement uncertainty would also be at a minimum under winter conditions [Karlsson *et al.*, 2007]. Possible reasons for these discrepancies between CMAQ and observations of aerosol  $\text{NO}_3^-$  include the equilibrium gas-aerosol partitioning in ISORROPIA, insufficient uptake of  $\text{HNO}_3$  by coarse mode



**Figure 5.** CMAQ simulated  $\text{SO}_4^{2-}$  ( $\mu\text{g}/\text{m}^3$ ) in the lowest model layer, shown for each season: (a) JFM; (b) AMJ; (c) JAS; (d) OND.

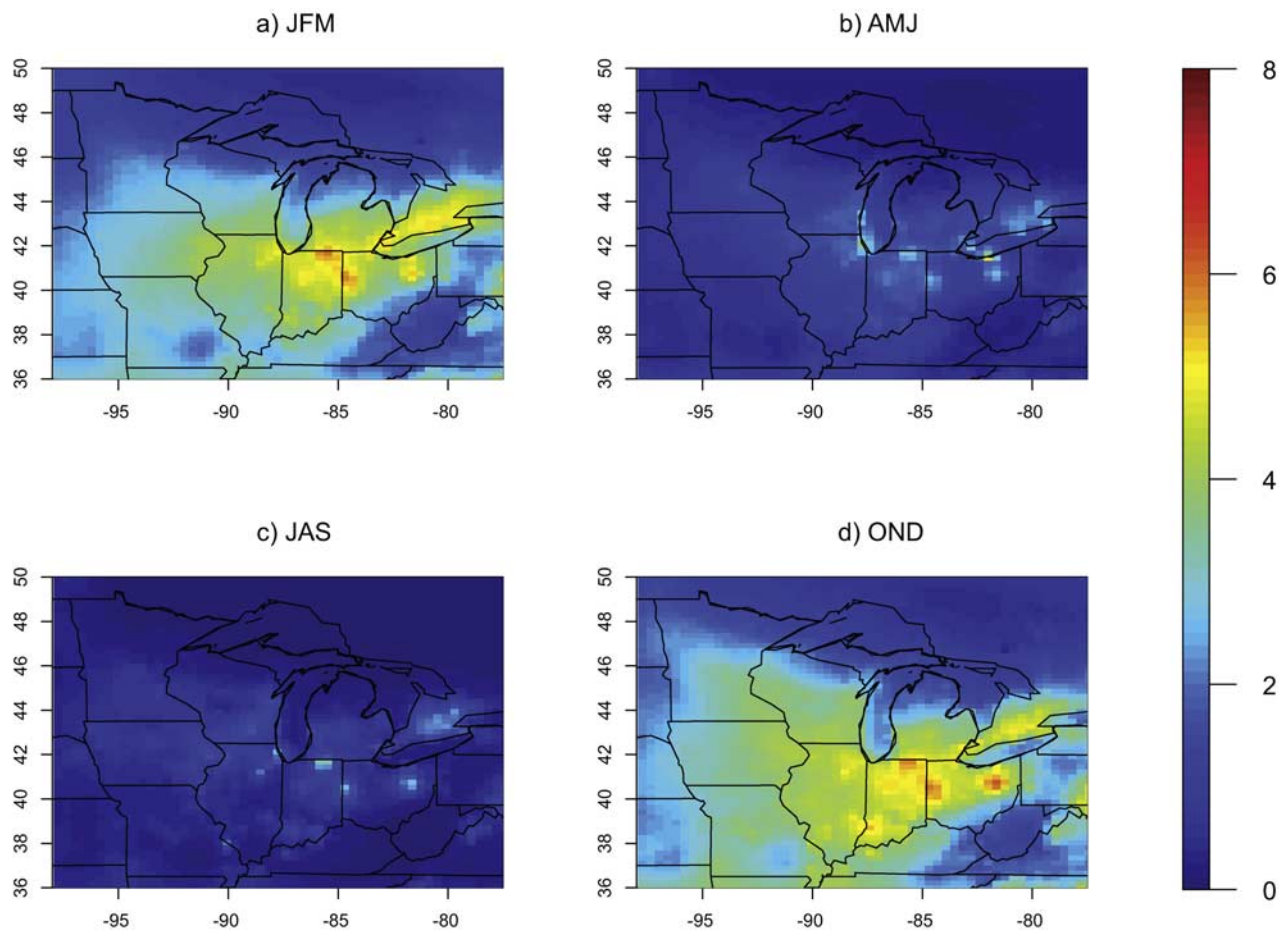
aerosols, heterogeneous reactions on the surface of aerosols, insufficient modeled wet deposition through snow, and measurement uncertainties for total (gaseous + aerosol)  $\text{NH}_3/\text{NH}_4^+$  and total (aerosol and aqueous) sulfuric acid/ $\text{SO}_4^{2-}$  [Yu et al., 2005]. However, the appearance of these high biases only in the winter, when  $\text{NO}_x$  emissions most readily condense to  $\text{NO}_3^-$  at low temperatures and ambient humidity levels, likely indicates that in these preferential climatic conditions the known high bias for  $\text{NO}_x$  in estimated

emissions from point [Frost et al., 2006] and area sources [Hudman et al., 2008] directly flows through to  $\text{NO}_3^-$  concentrations, to a degree that cannot be mediated by partitioning of the excess to  $\text{HNO}_3$  and gaseous reactive nitrogen species as in other seasons. High biases in winter  $\text{NH}_3$  emissions and subsequent conversion of excess  $\text{NH}_3$  to  $\text{NO}_3^-$  could also be a factor. Daily and weekly variability in  $\text{NO}_3^-$  observations is simulated in CMAQ with less fidelity than  $\text{SO}_4^{2-}$ , with  $r^2$  of 58% for STN (daily), 63% for

**Table 3.** CMAQ Monthly Performance for Sulfate<sup>a</sup>

Month	STN					IMPROVE					CASTNet				
	Obs	CMAQ	FB	FE	$r^2$	Obs	CMAQ	FB	FE	$r^2$	Obs	CMAQ	FB	FE	$r^2$
Jan	2.14	2.11	-0.07	0.39	38	1.93	1.50	-0.37	0.47	61	2.21	1.78	-0.24	0.27	58
Feb	1.89	1.71	-0.25	0.41	65	1.41	1.10	-0.38	0.52	63	1.87	1.52	-0.25	0.32	52
Mar	2.75	2.39	-0.31	0.51	46	2.30	1.52	-0.61	0.64	79	3.17	2.37	-0.35	0.36	80
Apr	3.16	2.77	-0.35	0.57	37	2.72	2.20	-0.43	0.51	67	3.31	2.99	-0.20	0.32	69
May	2.66	2.80	-0.14	0.47	55	2.51	2.52	-0.38	0.56	75	3.30	3.57	-0.05	0.23	92
Jun	5.42	6.71	0.13	0.39	77	4.82	5.05	-0.10	0.45	84	6.57	7.78	0.16	0.24	91
Jul	5.45	7.51	0.26	0.41	62	4.82	5.12	-0.02	0.34	86	6.79	7.72	0.11	0.21	87
Aug	4.10	6.17	0.34	0.49	59	3.91	4.65	0.08	0.41	79	5.55	7.41	0.29	0.33	80
Sep	5.06	5.94	0.12	0.42	73	4.34	5.4	0.11	0.43	83	6.10	6.61	0.06	0.18	76
Oct	2.47	2.82	-0.03	0.41	82	2.00	2.19	-0.16	0.43	72	2.86	3.01	-0.06	0.26	79
Nov	2.47	2.11	-0.22	0.40	37	1.76	1.57	-0.24	0.43	60	2.22	1.84	-0.20	0.24	80
Dec	2.87	2.94	-0.11	0.44	24	1.84	1.64	-0.14	0.51	64	2.94	2.47	-0.18	0.26	71

<sup>a</sup>See Table 1 footnote for details.



**Figure 6.** CMAQ simulated  $\text{NO}_3^-$  ( $\mu\text{g}/\text{m}^3$ ) in the lowest model layer, shown for each season: (a) JFM; (b) AMJ; (c) JAS; (d) OND.

IMPROVE (daily), and 75% for CASTNet(weekly), based on annual time series. Weekly time series at CASTNet (Figure 7b) indicate that CMAQ captures both the weekly average concentrations and the high degree of week-to-week variability in winter, but is inconsistent during the spring and fall and cannot simulate the weekly variability at low concentrations in the summer.

### 3.3. Ammonium ( $\text{NH}_4^+$ )

[25] Ammonium in the Midwest is dominated by dispersed area  $\text{NH}_3$  emissions from agricultural fertilizers, including anhydrous  $\text{NH}_3$  and manure spreading. These agricultural patterns are most evident in summer (Figure S1). Local enhancement by conversion of  $\text{NO}_x$  and  $\text{HNO}_3$  to  $\text{NH}_4^+$ , balancing excess urban  $\text{SO}_4^{2-}$ , leads to urban peaks of comparable magnitude throughout the year, especially in the vicinity of Chicago, and industrial areas of Indiana and Ohio in winter and fall.

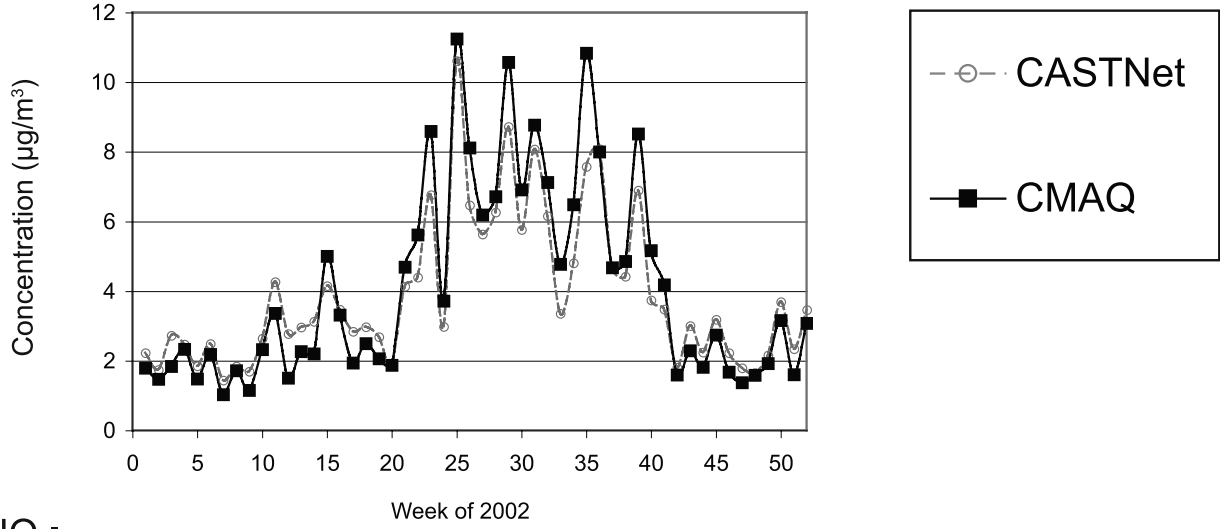
[26] While seasonality in  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  is the result of seasonal climate differences determining the condensation rates of relatively constant precursor emissions,  $\text{NH}_4^+$  has no simple seasonal cycle, driven instead primarily by the seasonality of agricultural practices. Here, the  $\text{NH}_3$  emissions inventory and its seasonal variation is a critical factor, and Gilliland *et al.* [2006] demonstrated through inverse modeling with CMAQ that the NEI 2001 inventory used is

reasonable, but may be slightly biased high in winter and low in summer. Our CMAQ simulation of  $\text{NH}_4^+$  is quite skillful throughout the year, more so in weekly observations at the rural CASTNet sites than for 24-h samples in urban areas, as shown in Table 5. In general, CMAQ FB and FE for  $\text{NH}_4^+$  are consistently the lowest of any aerosol species in the region throughout the year, with CASTNet FB < 0.10 in nine of twelve months. We note that in our simulation, there is no apparent seasonality to CMAQ bias, although CASTNet  $\text{NH}_4^+$  FB and FE are unusually high in October. The complicated monthly variations in  $\text{NH}_4^+$  concentrations are captured well by CMAQ, although monthly variability in response to the cycle of agricultural emissions is exaggerated. Ammonium time series correlation with observations was similar to  $\text{NO}_3^-$ , with  $r^2$  of 63% (STN) and 70% (CASTNet). On a regional average basis, episodic variability in CASTNet  $\text{NH}_4^+$  is simulated very skillfully, with erroneous predictions of weekly trends for only a few weeks in spring and fall (Figure 7c).

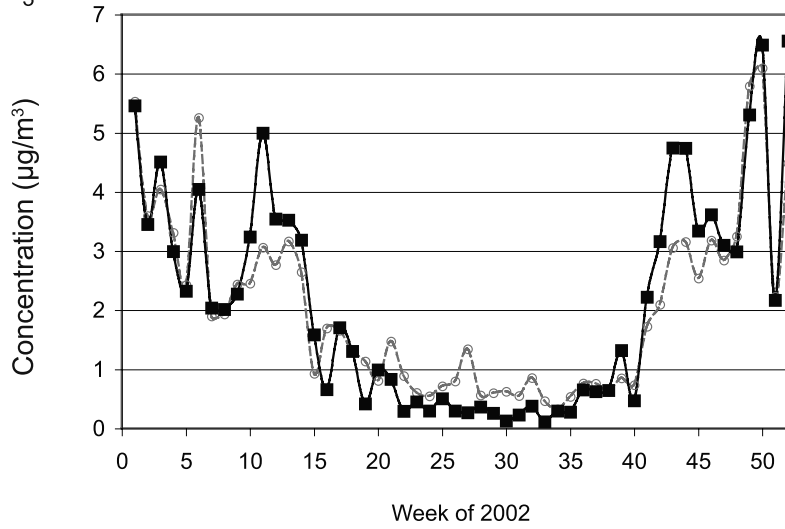
### 3.4. Carbonaceous Aerosols

[27] Both elemental carbon (EC) and organic carbon (OC) are simulated in CMAQ. EC is a nonreactive primary pollutant dominated by emissions in urban areas. Organic carbon, calculated as the total mass of organic aerosols (i.e., organic mass, OM), is composed of directly emitted

a)



b)  $\text{NO}_3^-$



c)

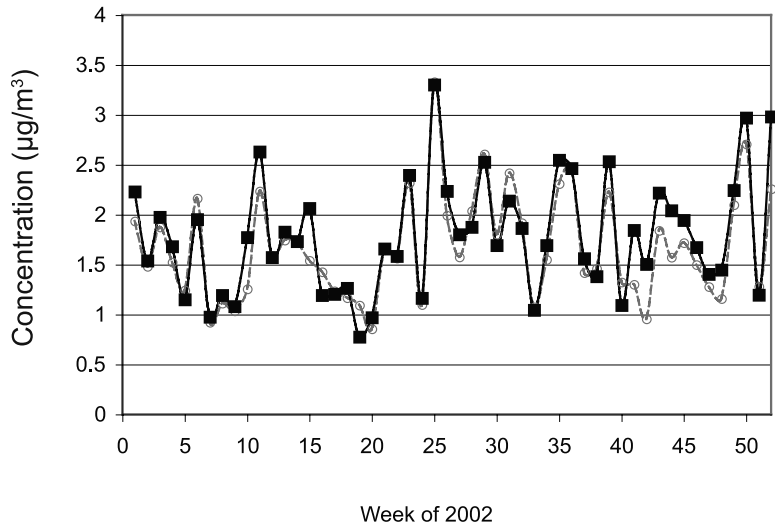


Figure 7. Observed and simulated weekly surface concentrations ( $\mu\text{g}/\text{m}^3$ ) averaged across all CASTNet sites in the region: (a)  $\text{SO}_4^{2-}$ ; (b)  $\text{NO}_3^-$ ; (c)  $\text{NH}_4^+$ .

**Table 4.** CMAQ Monthly Performance for Nitrate<sup>a</sup>

Month	STN					IMPROVE					CASTNet				
	Obs	CMAQ	FB	FE	r <sup>2</sup>	Obs	CMAQ	FB	FE	r <sup>2</sup>	Obs	CMAQ	FB	FE	r <sup>2</sup>
Jan	3.96	4.00	-0.01	0.35	61	1.85	2.41	0.13	0.58	64	3.77	3.75	0.02	0.21	74
Feb	2.73	2.67	-0.07	0.50	58	1.16	1.37	0.16	0.64	70	2.88	2.60	0.04	0.32	80
Mar	2.58	3.75	0.25	0.57	50	1.11	1.99	0.20	0.81	52	2.86	3.83	0.35	0.45	49
Apr	2.56	2.15	-0.40	0.73	35	1.09	1.26	-0.23	0.89	43	1.65	1.69	-0.02	0.47	43
May	1.83	1.08	-0.66	0.89	14	0.69	0.38	-1.05	1.19	10	1.09	0.62	-0.67	0.82	16
Jun	1.65	1.01	-0.80	1.03	8	0.51	0.15	-1.34	1.40	12	0.67	0.39	-0.68	0.93	4
Jul	1.01	0.80	-0.80	1.09	5	0.30	0.15	-1.38	1.53	6	0.74	0.25	-0.98	1.11	6
Aug	0.97	0.5	-0.89	1.12	29	0.32	0.14	-1.25	1.39	4	0.56	0.27	-0.73	0.95	19
Sep	1.21	1.49	-0.29	0.79	58	0.32	0.43	-0.61	1.11	46	0.76	0.82	-0.04	0.75	2
Oct	1.90	2.46	0.01	0.62	64	1.06	1.57	0.08	0.87	76	2.16	3.07	0.23	0.42	76
Nov	3.42	3.71	-0.05	0.46	58	1.94	2.65	0.23	0.59	55	2.95	3.27	0.14	0.27	59
Dec	4.91	5.51	0.01	0.43	67	2.31	3.05	0.25	0.55	77	4.75	5.21	0.10	0.26	68

<sup>a</sup>See Table 1 footnote for details.

(primary) OC, as well as secondary organic aerosols (SOA) from both biogenic and anthropogenic precursor emissions. We compared concentrations of carbonaceous aerosols to measurements identifying the contributions of EC and OC to total carbon by employing the NIOSH thermal optical transmittance analytical protocol at STN sites and the thermal optical reflectance technique at IMPROVE sites. We compared reported EC directly, without adjusting for artifacts arising from differences in these analytical techniques [Chow *et al.*, 2004]. We compared model OM with blank-corrected IMPROVE fine organic mass, and STN OM adjusted according to the Speciated Modeled Attainment Test protocol [EPA, 2007] to account for measurement artifacts.

[28] Elemental carbon concentrations are highest in all seasons near urban areas, with limited transport from these emissions hot spots. As shown in Table 6, simulated urban concentrations, captured by the STN network sites, are representative throughout most of the year, although there is a strong positive bias in the winter, peaking in January at  $0.52 \mu\text{g}/\text{m}^3$ . This bias has been suggested as an emissions overestimate by Lane *et al.* [2007] and supported by Karydis *et al.* [2007]. In all seasons, regional background concentrations from area sources and long-range transport are less than half of urban levels. Rural concentrations from the IMPROVE sites are underestimated from May through October, but winter performance is very good: network-wide mean concentrations are within  $0.02 \mu\text{g}/\text{m}^3$  in November, December, February, and March. In the daily observational pairings, monthly average network-wide mean bias is within

$0.05 \mu\text{g}/\text{m}^3$  from November through April, and December mean bias is less than  $0.002 \mu\text{g}/\text{m}^3$ . The improved correlation between CMAQ and observations at the IMPROVE network (49%) versus STN (27%) indicates that large-scale transport processes affecting rural areas are better simulated than local emissions and dispersion from urban areas.

[29] The regional spatial extent of total modeled OM is very similar to the patterns in EC, but with concentrations 5 to 10 times greater (Table 7). In January, when modeled and observed OM is dominated by primary emissions, the spatial correlation ( $r$ ) between monthly mean EC and OM concentrations reaches 0.97. Overall, seasonal variation in the regional burden of OM is poorly represented in CMAQ. Modeled OM is positively biased in winter, and negatively biased in summer. The summertime underprediction is likely due to the CMAQ's insufficient SOA formation at high temperatures and relative humidity. Modeled and observed daily time series vary widely in skill from month to month, with monthly  $r^2$  ranging from 3% to 36% (STN) and 1% to 72% (IMPROVE). Despite these problems, OM concentrations are simulated in spring and fall with very little bias ( $\text{FB} < 0.10$ ) in both urban and remote areas.

[30] In comparing model and measured organic aerosols, it is necessary to convert measured OC to match the total calculated OM. We employ the conventional value of 1.4 to inflate OC measurements to modeled OM, consistent with the IMPROVE methodology and prior observational studies in the region [e.g., Offenberg and Baker, 2000]. Since CMAQ employs an internal conversion factor of 1.2 to convert OC

**Table 5.** CMAQ Monthly Performance for Ammonium<sup>a</sup>

Month	STN					CASTNet				
	Obs	CMAQ	FB	FE	r <sup>2</sup>	Obs	CMAQ	FB	FE	r <sup>2</sup>
Jan	1.66	1.95	0.28	0.41	63	1.61	1.71	0.05	0.15	77
Feb	1.21	1.40	0.15	0.44	63	1.31	1.30	0.05	0.22	74
Mar	1.52	1.95	0.14	0.41	66	1.71	1.95	0.11	0.23	68
Apr	1.69	1.58	-0.18	0.45	38	1.42	1.49	0.00	0.24	57
May	1.29	1.27	-0.07	0.50	40	1.30	1.25	-0.10	0.26	74
Jun	2.22	2.45	0.08	0.36	77	2.15	2.24	0.04	0.29	68
Jul	1.85	2.36	0.30	0.48	43	2.06	1.99	0.02	0.26	63
Aug	1.43	1.85	0.40	0.57	57	1.74	1.81	0.05	0.23	68
Sep	1.90	2.22	0.32	0.47	77	1.92	2.01	0.04	0.20	72
Oct	1.21	1.65	0.35	0.53	70	1.40	1.74	0.20	0.32	62
Nov	1.68	1.85	0.11	0.38	61	1.42	1.62	0.13	0.17	74
Dec	2.28	2.66	0.14	0.38	69	2.12	2.38	0.10	0.19	85

<sup>a</sup>See Table 1 footnote for details.

**Table 6.** CMAQ Monthly Performance for Elemental Carbon<sup>a</sup>

Month	STN					IMPROVE				
	Obs	CMAQ	FB	FE	r <sup>2</sup>	Obs	CMAQ	FB	FE	r <sup>2</sup>
Jan	0.47	0.99	0.55	0.64	26	0.25	0.31	0.25	0.33	87
Feb	0.45	0.71	0.26	0.54	16	0.20	0.22	0.20	0.39	65
Mar	0.45	0.61	0.03	0.52	29	0.24	0.22	-0.16	0.39	67
Apr	0.54	0.49	-0.24	0.55	13	0.25	0.24	-0.10	0.45	12
May	0.47	0.38	-0.34	0.57	21	0.26	0.15	-0.42	0.51	66
Jun	0.66	0.63	-0.17	0.50	26	0.45	0.21	-0.75	0.76	20
Jul	0.55	0.65	0.13	0.48	33	0.36	0.24	-0.52	0.64	43
Aug	0.47	0.56	0.17	0.49	33	0.34	0.24	-0.36	0.45	67
Sep	0.64	0.67	0.03	0.45	40	0.33	0.25	-0.24	0.39	80
Oct	0.58	0.60	-0.08	0.54	34	0.32	0.24	-0.22	0.40	55
Nov	0.44	0.60	0.16	0.54	31	0.25	0.25	0.06	0.32	71
Dec	0.65	0.90	0.25	0.55	36	0.31	0.30	0.16	0.39	66

<sup>a</sup>See Table 1 footnote for details.

to OM in the model, we inflate CMAQ modeled primary OM output by 1.167 to ensure consistency with the 1.4 factor applied to observations (i.e.,  $1.2 \times 1.167 = 1.4$ ), following EPA [2005b, 2005c]. This OM/OC ratio is considerably lower than that estimated by recent studies, including  $1.81 \pm 0.07$  observed by Bae *et al.* [2006a] in St. Louis; 1.5–1.9 found in upstate New York [Bae *et al.*, 2006b];  $1.7 \pm 0.2$ , the annual average at 38 IMPROVE sites [Malm and Hand, 2007]; and 1.6 (urban) and 2.1 (nonurban) recommended by Turpin and Lim [2001]. It is, however, within the wide 1.1–1.9 range suggested by Chen *et al.* [2006] for August conditions in the eastern United States. This variation in OC/OM ratios suggests that a more sophisticated algorithm should be deployed for the interpretation of model predictions of OM, and the application of a single conversion factor may contribute to the negative bias in our predicted OM. Still, uncertainty associated with the OM/OC factor does not explain the very poor representation of seasonal and daily variability.

[31] One advantage of model-based aerosols analysis is the ability to estimate primary and secondary contributions to OM, and identify the sources of these aerosols. Consistent with previous studies by Yu *et al.* [2007] and Karydis *et al.* [2007], we find that OM in the Midwest is dominated by the primary component, with the contribution of primary to total OM varying seasonally from 52% in June to 70% in January. Accurate representation of the sources and formation pathways of SOA remains a challenge, and our chemical mechanism in CMAQ, like that of most contemporary global and regional CTMs, currently underestimates SOA [e.g., Bhave *et al.*, 2007; Zhang *et al.*, 2006a, 2006b]. Because there are no routine SOA measurements in this region, we compare our SOA performance with that of other published regional studies. Robinson *et al.* [2007] found SOA account for more than 80% of summertime OM in PMCAMx except in urban areas. Other analyses using chemical mass balance [Sheesley *et al.*, 2004; Subramanian *et al.*, 2007] suggest that most OM is of secondary origin throughout the year in the eastern United States, with primary OC greater than or equal to SOA only in winter.

[32] In our simulations, biogenic SOA contributes more than 50% of OM in the forested and lightly populated north of the region throughout the year, but usually contributes less than 25% of OM in polluted areas. This is consistent with a national radiocarbon analysis of IMPROVE data

from December 2004 to February 2006 [Schichtel *et al.*, 2008] that found more than 90% of fine particle carbon in northern parts of the region is contemporary (emphasizing biomass burning), while in the south more than 55% is of fossil origin in both winter and summer. In that analysis, the southern Great Lakes region is the most widespread area of the continental United States where fossil sources of carbon are more important contributors to total carbon mass than contemporary carbon throughout both urban and rural areas. During the spring and summer growing seasons, CMAQ OM north of Lake Superior is nearly all biogenic, and biogenic SOA contributes more than 80% of total carbon mass and 40–55% of seasonal average PM<sub>2.5</sub>. Anthropogenic SOA also exhibits strong seasonality, but with different spatial and temporal patterns, largely driven by photochemical activity. Like O<sub>3</sub>, anthropogenic SOA is photochemically produced in spring and summer over Lake Erie and Lake Michigan, particularly near urban plumes. Thus, O<sub>3</sub> and anthropogenic SOA are highly correlated over the Great Lakes in the summer (Figures S2, S3, and S4). Although anthropogenic SOA and O<sub>3</sub> in the Midwest are produced by similar processes, only a small fraction of simulated summertime above-lake PM<sub>2.5</sub> (<3%) is due to SOA. Over Lake Michigan, JAS average modeled PM<sub>2.5</sub> is composed mostly of SO<sub>4</sub><sup>2-</sup> (40–60%), with NH<sub>4</sub><sup>+</sup>, primary OM, and unspiciated mass each contributing 10–20%.

[33] Summertime OM is strongly underpredicted at sites in western Michigan, however, supporting the finding [Robinson *et al.*, 2007] that traditional SOA modules such as CMAQ's SORGAM underestimate this anthropogenic SOA production over the Great Lakes. Summertime biogenic SOA is also underestimated throughout the region due to the absence of SOA formation from isoprene photooxidation, which recent modeling studies have indicated would represent an increase over our simulated SOA of 50% [Lane and Pandis, 2007] to 100% [Zhang *et al.*, 2007; Liao *et al.*, 2007; van Donkelaar *et al.*, 2007] of simulated SOA in this region. The model also excludes several recently discovered SOA formation pathways, such as anthropogenic NO<sub>x</sub> and SO<sub>4</sub><sup>2-</sup> catalyzing SOA formation, as well as processes affecting SOA that have yet to be identified. In addition, there are likely biases in biogenic and anthropogenic area emissions of OM and its VOC precursors. Therefore, although SOA from biomass burning is less important to OM and total carbon in the region than in nearly every other area of the

**Table 7.** CMAQ Monthly Performance for Organic Mass<sup>a</sup>

Month	STN					IMPROVE				
	Obs	CMAQ	FB	FE	r <sup>2</sup>	Obs	CMAQ	FB	FE	r <sup>2</sup>
Jan	3.21	4.58	0.45	0.61	27	1.27	1.86	0.41	0.46	72
Feb	2.76	3.39	0.38	0.68	14	1.13	1.51	0.41	0.50	47
Mar	2.07	2.29	0.27	0.70	15	1.13	1.20	0.02	0.45	44
Apr	2.40	2.03	0.02	0.71	3	1.24	1.58	0.15	0.50	1
May	2.11	1.68	-0.07	0.61	21	1.51	1.15	-0.13	0.51	33
Jun	5.01	2.09	-0.74	0.78	23	3.70	1.45	-0.71	0.73	13
Jul	5.92	2.16	-0.90	0.93	17	3.31	1.44	-0.68	0.72	13
Aug	4.12	1.98	-0.62	0.69	23	2.10	1.52	-0.29	0.45	21
Sep	4.06	2.92	-0.23	0.48	17	1.97	1.85	-0.01	0.37	43
Oct	2.59	2.36	0.07	0.57	36	1.49	1.56	0.08	0.40	29
Nov	2.58	2.20	-0.01	0.50	32	1.32	1.36	0.16	0.42	43
Dec	4.66	4.14	0.17	0.61	27	1.29	1.88	0.46	0.57	48

<sup>a</sup>See Table 1 footnote for details.

continental United States, limited model SOA formation pathways, the initial partitioning of organic emissions to primary organic aerosols, and errors in the timing and magnitude of biomass burning events through the use of a climatological average emissions inventory all lead to errors in the seasonality and day-to-day variability of OM concentrations.

### 3.5. Aerosol Number Concentration

[34] Hourly observations of aerosol number concentration at Bondville, Illinois, were compared with CMAQ predictions of the sum of Aitken, accumulation, and coarse lognormal modes. Bondville is a village roughly 5 km west of the Champaign-Urbana metropolitan area, and <1 km from an interstate highway. It is impacted by representative levels of regional background pollution, with lesser local influences from copper smelting, metal plating, and limestone [Buzcu-Guven *et al.*, 2007]. In this environment, CMAQ simulates number concentration to the correct order of magnitude, but with a consistent negative bias (Figure 2 and Table 8). The correct order of magnitude is the only aspect of number concentration at Bondville adequately reproduced in CMAQ. Observed seasonality is not simulated and number concentration is underpredicted in all months but September. Although our underprediction is obvious, in fact CMAQ performs better here than in other CMAQ studies simulating number concentration in Atlanta, Georgia [Park *et al.*, 2006] and the Pacific Northwest (R. A. Elleman *et al.*, CMAQ aerosol number and mass evaluation for Pacific Northwest, paper presented at Models-3 User's Workshop, Community Modeling and Analysis System, University of North Carolina, Chapel Hill, North Carolina, 2004), which both found frequent underprediction by factors of 10 to 1000. The observed distribution for number concentration at Bondville is closer to Gaussian than the lognormal found for mass concentrations (Figure S5). CMAQ's trimodal system, lacking an ultrafine mode that would disperse mass across a greater number of particles, thus underpredicts aerosol abundance.

[35] Spatial distribution in simulated aerosol number concentration is consistent with bulk aerosol mass concentrations of PM<sub>2.5</sub> and PM<sub>10</sub> but with less pronounced seasonality. Number concentration throughout the region is dominated by secondary SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>, and the dispersion of number concentration is highly correlated with the sum of these

species ( $r = 0.80$ ), and more so than for either species alone. Smelting operations, evident in the localized maximum in northeast Minnesota in Figure 4 near taconite mining and processing facilities, generate local enhancement due to new SO<sub>4</sub><sup>2-</sup> particles comparable to the highest urban peaks over Chicago and Toronto.

### 4. Modeled and Observed Relationships Among Aerosol Species

[36] Relationships between time series of speciated aerosols offer unique insight into the composition of multi-species aerosol conglomerations, and highlight where the dynamics of different species are controlled by the same physical processes. For instance, ammonium sulfate and bisulfate are the most prevalent ionic aerosols in the region (K. Baker, presented paper, 2006), and the relatively high correlation between NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> in observed daily STN ( $r^2 = 67\%$ ) and CASTNet ( $r^2 = 62\%$ ) time series reflect the shared fate of ammonium sulfate particles. The lower correlation between OC and insoluble EC at STN sites ( $r^2 = 31\%$ ) reflects the different removal processes and characteristic lifetimes. Comparison of correlation relationships between species in model and measurements illustrates the extent to which model processes accurately reflect observed processes. Moreover, chemical mass balance source apportionment in

**Table 8.** CMAQ Monthly Performance for Aerosol Number Concentration at Bondville, Illinois<sup>a</sup>

Month	IMPROVE					
	Obs	CMAQ	FB	FE	r <sup>2</sup> (Daily)	r <sup>2</sup> (Hourly)
Jan	5.41	2.34	-0.73	0.76	14	4
Feb	5.60	1.71	-0.95	0.96	23	10
Mar	6.42	2.26	-0.91	0.96	4	2
Apr	6.59	1.36	-1.17	1.18	36	6
May	7.51	1.47	-1.24	1.25	38	7
Jun	7.21	1.57	-1.16	1.16	7	0
Jul	7.12	1.54	-1.13	1.14	12	3
Aug	3.53	1.71	-0.51	0.60	4	5
Sep	2.38	2.58	0.21	0.61	2	1
Oct	5.27	1.97	-0.79	0.85	28	1
Nov	3.86	1.98	-0.57	0.68	16	2
Dec	4.44	1.89	-0.78	0.79	0	5

<sup>a</sup>See Table 1 footnote for details. Observed and modeled number concentrations in 10<sup>9</sup> particles/m<sup>3</sup>. FB and FE calculated from hourly values; r<sup>2</sup> (%) shown for hourly and daily time series.

the region [Lee *et al.*, 2003] has identified a chemical signature for interaction between secondary organic and inorganic aerosols, due to as yet unidentified chemical and/or physical processes, that might be identified in a mechanistic model.

[37] Ionic balance implies that variability in the total mass of anionic aerosols ( $\text{NO}_3^{2-} + \text{SO}_4^{2-}$ ) would be very highly correlated with variability in  $\text{NH}_4^+$ , and this is the case throughout the year in both observed (94% CASTNet, 96% STN) and simulated (84%, 91%) time series. The slightly weaker correlations in CMAQ are surprising, as model inorganic chemistry without speciated coarse mode soil cations should be more simply balanced among these species. The ionic complex of  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  also shows weaker than expected connections in CMAQ throughout the year, although simulation of episodic spikes across the CASTNet monitors (e.g., weeks 6, 11, and 25) are even stronger in CMAQ than observations (Figure 7). Correlations between mass concentrations in CMAQ (36% CASTNet, 51% STN) are lower than in observations (62%, 67%). Although  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  concentrations are less correlated than expected, interestingly, the errors in these two species are highly correlated, as evident in Figure 7, where in weeks 15–17 the two species move from overestimate to underestimate in unison. The normalized biases of contemporaneous predictions of  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  at CASTNet sites show an  $r^2 = 71\%$ . Similarly, the normalized errors between these two species are correlated with  $r^2 = 74\%$ . These strong links between both species' error further suggest that incomplete or erroneous processes consistently impact both species at the same times. As model processes are changed or added, we suggest that this pairing may be a particularly useful metric for evaluating incremental improvements in chemical transport model performance. Nitrate and  $\text{SO}_4^{2-}$  are completely uncorrelated, as would be expected, while nitrate and ammonium are weakly correlated in both model and observations. Daily correlation for  $\text{SO}_4^{2-}$  with  $\text{PM}_{2.5}$  is about one third weaker in CMAQ (57% IMPROVE, 42% STN) than in observations (80%, 64%), but much stronger for  $\text{NO}_3^-$  and  $\text{PM}_{2.5}$  (38% IMPROVE, 49% STN, compared to observations of 9%, 23%). The simulated relationship between  $\text{NH}_4^+$  and  $\text{PM}_{2.5}$  (86% STN) is consistent with observations (75%). These temporal associations, when viewed in light of model bias, suggest that despite uncertainty in emissions sources [Simon *et al.*, 2008], the chemical transport of  $\text{NH}_4^+$  as part of a multispecies regional aerosol complex is being adequately simulated with confidence. The weaker relationships of  $\text{SO}_4^{2-}$ , which is simulated correctly as an independent pollutant, imply that other chemicals interacting with  $\text{SO}_4^{2-}$  are not well simulated, and/or that the interactions themselves are not captured.

[38] We find that the relationships between OC, EC, and  $\text{PM}_{2.5}$  are much stronger in CMAQ than observations. EC and  $\text{PM}_{2.5}$  are much more strongly correlated in CMAQ (82% IMPROVE, 69% STN) than observations (64%, 22%). The same tendency is found for OC and  $\text{PM}_{2.5}$ : model comparison showed 49% IMPROVE, 68% STN, and observed correlations were 7%, 43%, respectively. Moreover, EC and OC are also more closely linked to each other as modeled (57%, 84%) than observed (45%, 31%), although stronger relationships (91%) have been observed in suburban Maryland in winter (L. W. A. Chen *et al.*, Observation of carbonaceous

aerosols and carbon monoxide at a suburban site: Implication for an emission inventory, paper presented at 10th International Emissions Inventory Conference, U.S. Environmental Protection Agency, Denver, Colorado, 1–3 May 2001). Daily correlations with  $\text{PM}_{2.5}$  in CMAQ are higher for EC and OC than for  $\text{SO}_4^{2-}$ , and close to  $\text{NH}_4^+$ , the species which Bell *et al.* [2007] found to be most closely correlated with total  $\text{PM}_{2.5}$  mass in detrended daily data across the United States.

[39] These results suggest that CMAQ underestimates, or simply does not simulate, the real-world processes that differentiate the transport and variability of OC, EC, and the secondary inorganics that contribute most to  $\text{PM}_{2.5}$ . The problem is greatest at urban sites near emissions sources, but also evident at remote sites, suggesting that subgridscale chemistry and dispersion are not entirely responsible for the missed processes. Rather, the ubiquitous overcorrelation between these species implies that important chemical or physical processes are not captured. Robinson *et al.* [2007] demonstrate that a dynamic aging and partitioning scheme for SOA and its low-volatility gas-phase precursors significantly enhances modeled SOA contribution to total OM in our study region, and produces a more realistic spatial representation of SOA. Our findings that EC and OM are overly correlated in both space and time in a traditional model are consistent with the suggestion by Robinson *et al.* [2007] that partitioning of primary organic aerosols could reduce these errors in the simulation of OM.

## 5. Conclusion

[40] We applied the CMAQ model to simulate aerosol speciation and dynamics over the Great Lakes region in an annual study for 2002. Our aim in this evaluation was to examine the skill of CMAQ over this region of varied emitting activities and complex meteorology, and build understanding of chemical and physical processes controlling aerosol distribution over the upper midwestern United States and southern Canada. In this area,  $\text{PM}_{2.5}$  is a year-round air quality problem, driven by  $\text{NO}_3^-$  in the winter,  $\text{SO}_4^{2-}$  in the summer, and  $\text{NH}_4^+$ , OM, EC and other components year round. Overall,  $\text{PM}_{2.5}$  concentrations are lowest in the springtime, and lowest in regions away from major cities and the industrial facilities of the ORV. The shallow boundary layer above the Great Lakes in the spring (cool lake, warm land) enhances SOA formation as a byproduct of enhanced near-surface  $\text{O}_3$ . This enhancement persists into the summer (JAS), but the lake effect is less pronounced as the water and land temperature equalize. In the fall (warm lake, cool land), circulations around the lakes lead to above-lake minima, most notable in maps of  $\text{NO}_3^-$  and total  $\text{PM}_{2.5}$ . Anthropogenic emissions of aerosols and their precursors are shown to have little seasonality, highlighting the importance of seasonal climate variability in aerosol concentrations.

[41] We find that CMAQ performance is good or average for most speciated aerosols at three representative observational networks. The model shows the greatest errors in simulating low spring and summer  $\text{NO}_3^-$  concentrations, as well as unspicated fine and coarse aerosol mass. These species-by-species comparisons indicate general overestimates of  $\text{PM}_{2.5}$  in fall and winter months, and overestimate of  $\text{PM}_{10}$  in summer months. Overall performance statistics

are generally comparable to prior modeling studies in larger spatial domains covering eastern North America, with some notable exceptions. We find CMAQ 2002 annual performance for  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and OM much improved over *Tesche et al.* [2006], but differences in emissions, meteorology, and model configuration contribute uncertainty as to the source of this improvement. Our errors in  $\text{NO}_3^-$  are comparable to errors in  $\text{SO}_4^{2-}$  for most of the year, consistent with the study by *Karydis et al.* [2007], but differ from other recent modeling studies [e.g., *Tesche et al.*, 2006; *Yu et al.*, 2005] which find that  $\text{SO}_4^{2-}$  is simulated much better than  $\text{NO}_3^-$ . Sulfate performance is superior to that found with PMCAMx using the same meteorology [*Karydis et al.*, 2007], while July OM [*Gaydos et al.*, 2007; *Karydis et al.*, 2007] is considerably less skillful, likely due to our study's insufficient biomass burning emissions and limited SOA formation pathways. Skill in simulating OM for other seasons, and ratios of primary to secondary OM are highly consistent with the results of *Karydis et al.* [2007], despite different representations of SOA. Bias and daily correlations with observations at IMPROVE sites for  $\text{SO}_4^{2-}$ , OC,  $\text{PM}_{2.5}$ , and  $\text{PM}_{10}$  are slightly improved over an earlier CMAQ study using the same aerosol mechanism in June [*Mebust et al.*, 2003], while summertime  $\text{NO}_3^-$  remains substantially underpredicted. Seasonal spatial patterns in  $\text{PM}_{2.5}$  are similar to those simulated in PMCAMx by *Karydis et al.* [2007], *Gaydos et al.* [2007], and *Dawson et al.* [2007] but differ in extent and intensity.

[42] We analyze time series of simulated and observed concentrations to evaluate whether CMAQ is capturing the physical and chemical processes that link and/or differentiate aerosol species. We find that CMAQ underestimates the correlation between  $\text{SO}_4^{2-}$  and  $\text{PM}_{2.5}$ , which, combined with an independent evaluation of  $\text{SO}_4^{2-}$  showing simulation skill, suggest that interactions between  $\text{SO}_4^{2-}$  and other  $\text{PM}_{2.5}$  constituents are not adequately captured. In contrast, EC, OC, and  $\text{PM}_{2.5}$  are overly correlated, indicating that CMAQ is missing important processes that distinguish the emissions, chemistry, and transport of carbonaceous aerosols. To understand why modeled chemical and physical processes diverge from the observed atmospheric system, process analysis, data assimilation, and adjoint studies would be excellent techniques to apply to the relationships among speciated aerosols in this region.

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