Atmospheric Environment 45 (2011) 5119-5130

Contents lists available at ScienceDirect

## Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

### Diagnosis of an underestimation of summertime sulfate using the Community Multiscale Air Quality model

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#### A R T I C L E I N F O

Article history: Received 24 February 2011 Received in revised form 8 June 2011 Accepted 10 June 2011

Keywords: Community Multiscale Air Quality Model Sulfate Cloud processing Model evaluation

#### ABSTRACT

We evaluate the simulations of SO<sub>2</sub> and sulfate using the Community Multiscale Air Quality model (CMAQ) version 4.6 with the observations over the United States in 2002. MM5 was used for meteorological simulations. While the general seasonal cycles of SO<sub>2</sub> and sulfate are simulated well by the model, we find significant systematic biases in the summer. The model low bias in sulfate is considerably more severe than the model bias in SO<sub>2</sub>. Both ACM and RADM schemes are used in the model to test the sensitivities of simulated sulfate to cloud processing. We carry out detailed modeling analysis and diagnostics for July 2002. Compared to satellite observations of cloud liquid water path, CMAQ cloud modules greatly overestimates convective (sub-grid) precipitating clouds, leading to large overestimation of sulfate wet scavenging. Limiting convective precipitating cloud fraction in the cloud modules to <10% and hence significantly reducing wet scavenging lead to much improved agreement between simulated and observed sulfate. The average lifetime of sulfate wet scavenging of sulfate does not necessarily lead to apparent problems in model simulations of sulfate wet deposition rate compared to surface observations. In general, there is still a lack of direct observational constraints from air quality monitoring measurements on model simulated cloud processing of SO<sub>2</sub> and sulfate.

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#### 1. Introduction

Understanding the tropospheric sulfur cycle is important because of its impacts on ecosystem (acid rain), air quality, and the radiation balance of the atmosphere. Human activities account for 60–80% of global emission of sulfur gases to the atmosphere (e.g., Chin et al., 2000). Oxidation of sulfur gases produces sulfate aerosols, which can directly influence the atmospheric radiation budget by scattering solar radiation. Sulfate aerosols also can indirectly affect the radiation budget through the modification of cloud properties (e.g., Charlson et al., 1992; Ramanathan et al., 2005). Three-dimensional chemical transport models that simulate the emissions, transports, chemical conversion, and dry and wet removal processes of sulfur are important tools for understanding their characteristics at global/regional scales, and for assessing their climatic and environmental effects (e.g., Chang et al., 1987; Chin et al., 2000; Kasibhatla et al., 1997; Barth et al.,

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1352-2310/\$ — see front matter  $\odot$  2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.atmosenv.2011.06.029

2000; Qian et al., 2001; Tan et al., 2002; Mebust et al., 2003; Yu et al., 2004; Eder and Yu, 2006; Huang et al., 2008; Appel et al., 2008).

Clouds are a key player regulating the production and loss of SO<sub>2</sub> and sulfate (e.g., Mueller et al., 2006, 2011). Dissolved SO<sub>2</sub> in-cloud droplets are oxidized by O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> to form sulfate. Evaporating clouds leave behind sulfate aerosols while precipitating clouds remove sulfate. Previous studies showed that aqueous-phase oxidation of SO<sub>2</sub> to sulfate makes a major contribution to sulfate in rain. Early theoretical studies (Saxena and Seigneur, 1986; Seigneur and Saxena, 1988) demonstrated the importance of aqueous-phase oxidation of SO<sub>2</sub> in determining ambient concentrations of sulfate. Daum et al. (1984) conducted aircraft measurements of the composition of cloud liquid water and interstitial air near Charleston, South Carolina. They found that the relative acidity of cloud water was much higher than that of the interstitial aerosols or of clear-air aerosols samples, indicating the occurrence of in-cloud acid formation. Prakash and Akula (1992) emphasized the role of non-precipitating clouds in producing ambient sulfate in summer. While precipitating clouds could be a source or sink of sulfate, non-precipitating cloud is solely a source of sulfate. Sulfate





concentrations simulated in a model therefore have a strong dependence on its cloud simulations.

Air quality simulation models, such as the Community Multiscale Air Quality model (CMAQ)http://www.epa.gov/AMD/CMAQ/ index.html, are a central component of the air quality management process at the national, state, and local levels. CMAQ is widely used to estimate aerosol production, distribution and impacts on air quality and ecosystems (e.g., Yu et al., 2004; Mueller et al., 2006; Eder and Yu, 2006; Appel et al., 2008). For this research, we evaluate CMAQ simulations using available chemical and meteorological observations in 2002 and examine in particular the effects of cloud modules in CMAQ on sulfate simulations.

#### 2. Observations and model description

#### 2.1. Model description

The modeling system consists of 3 components, MM5, SMOKE, and CMAQ. The CMAQ version 4.6 with the SAPRC99 chemical mechanism (Carter, 2000) and AERO4 aerosol module (Binkowski and Roselle, 2003) is used. The meteorological fields were assimilated using Penn State/NCAR MM5 (version 3.6.2) with four dimensional data assimilation (FDDA) (Stauffer and Seaman, 1990) using the NCEP reanalysis data (Grell and Stauffer, 1994; Kalnay et al., 1996) for 2002. The 148  $\times$  112 model-grid domain covers the contiguous United States and part of southern Canada and northern Mexico with a grid spacing of 36 km. There are 34 vertical layers in MM5 simulations. They are reduced to 19 layers in the Meteorology–Chemistry Interface Processor (MCIP) (version 2) for CMAQ simulations. We specified 19 vertical layers, of which 12 are below 1 km. The study period is from January to December 2002.

#### 2.1.1. Emissions

CMAQ emission inputs were prepared from the VISTAS inventory using the Sparse Matrix Operator Kernel Emissions (SMOKE) Modeling System (http://www.smoke-model.org/index.cfm) version 2.2. The VISTAS emission inventory was developed from the 1999 National Emissions Inventory (NEI) version 2 and scaled to 2002 (Barnard and Sabo, 2008). Source categories include biogenic sources by BEIS3, on-road mobile sources by MOBILE6, non-road mobile sources, area source, and stationary point sources. Actual electrical generating unit (EGU) data are used within the VISTAS domain. Fire emissions were recalculated for the southeastern states based on the updated fire records collected from state and federal fire agencies. Annual county-level fires emissions were allocated to each month based on VISTAS reported burn areas in each state as by Zeng et al. (2008).

#### 2.1.2. Cloud modules

Cloud convection is computed using either RADM or ACM cloud module. The sub-grid RADM cloud scheme in CMAQ was derived from the diagnostic cloud model in RADM version 2.6 (Chang et al., 1987, 1990; Dennis et al., 1993; Walcek and Taylor, 1986). The analytical mixing scheme has been replaced with a new mixing scheme based on the Asymmetrical Convective Model (ACM) that was originally developed for planetary boundary layer (PBL) mixing by Pleim and Chang (1992). The ACM scheme simulates a detraining convective plume by non-local transport from the source layer directly to each model layer within the convective layers. An important difference from the RADM cloud scheme is that the downward mixing in ACM is by gradual layer-by-layer compensatory subsidence. The RADM cloud scheme removes cloud coverage when the simulated mass flux over the 1 h time step exceeds the mass available below cloud. This artificial restriction of cloud coverage is eliminated in the ACM cloud scheme by setting a mixing time step according to mass flux constraints and iterating up to the lifetime of the cloud.

#### 2.2. Observation data sets and model evaluation metrics

#### 2.2.1. Surface observations

The data sets we used to evaluate CMAQ model performance include composition measurements from the Southern Aerosol Research and Characterization (SEARCH), the Speciation Trends Network (STN), the Interagency Monitoring of Protected Visual Environments (IMPROVE) and the Clean Air Status and trends Network (CASTNet), and wet deposition data from National Atmospheric Deposition Program (NADP). Fig. 1 shows the site locations of these observation networks.

In the IMPROVE network, samples of 24-h values every third day are collected on filters each week (on Wednesday and Saturday) beginning at midnight local time (Malm et al., 1994). The IMPROVE network data are available at 62 mostly rural sites over the US. In the SEARCH network, hourly or 24-h sulfate concentrations are available at eight sites, i.e., three rural sites (Yorkville, GA; Oak Grove, MS; Centreville, AL) and four urban sites (Jefferson Street, Atlanta; North Birmingham, AL; Gulfport, MS; Downtown Pensacola, FL) and Suburban Pensacola, FL (Hansen et al., 2003). The CASTNET samples are collected weekly on 3stage filter packs to analyze gases and particles at 87 sites in 40 states. The wet deposition data from the National Atmospheric Deposition Program (NADP) are computed by the precipitationweighted mean ion concentration for valid samples and total precipitation amount (http://nadp.sws.uiuc.edu:/NADP/). The monthly mean data are available at 311 sites over total US continent. STN data of 24-h values every third day are used to validate the model too at 223 sites. Some details regarding each of these networks (such as calibration standards, sampling methodology and frequency) can be found at http://www.epa.gov/geoss/eos/. The observed data contain uncertainties. In this study, we average the observations by time (monthly) and region. Furthermore, the model biases for sulfate are often quite large compared to the



Fig. 1. Site locations of the observation networks, the data from which were used in this study.



Fig. 2. Distribution of the 10 EPA regions.

difference of measurement by different networks (for example, to be shown in Fig. 10). Fig. 2 shows the map of 10 EPA regions, which we use to group measurement data for model comparison.

#### 2.2.2. Satellite observations

In addition to surface composition measurements, cloud water path and cloud fraction retrieved from four satellite instruments, Moderate Resolution Imaging Spectroradiometer (MODIS) onboard TERRA and AQUA satellites, AMSR (Advanced Microwave Scanning Radiometer) on AQUA satellite, TMI (TRMM Microwave Imager) are used to evaluate model simulations. The MODIS cloud data of TERRA and AQUA with its 2330 km viewing swath width provide daily global coverage. It acquires data in 36 high spectral resolution bands between 0.415 and 14.235 micron with spatial resolutions of 250 m (2 bands), 500 m (5 bands), and 1000 m (29 bands). We used channel 13 (0.6-14.2 µm) data. The level-3 MODIS daily global  $1^{\circ} \times 1^{\circ}$  grid average values of cloud water path and cloud fraction are used to evaluate corresponding model simulations. The water path data of AMSR and TMI are available only over the oceans. The standard deviation of the cloud fraction of these satellite data is  $\sim$  0.2, and standard deviation of water path of these satellite data is ~140 g m<sup>-2</sup>. The Terra satellite crosses the US at 10:00 am-1:00 pm local time, and the Aqua satellite crosses the US at 1:00 pm-4:00 pm local time. Model results are sampled in same time periods.

#### 2.2.3. Model evaluation metrics

Several statistical metrics are used here to compare the observed and predicted concentrations at surface stations. The root-mean square (RMS) absolute error RMS<sub>abs</sub> is computed as:

$$\text{RMS}_{\text{abs}} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (x_i - y_i)^2}$$

where  $x_i$  are observed data and  $y_i$  are modeled data. The RMS<sub>abs</sub> is a strict measure of absolute model bias against the observed aerosol concentrations. The second statistic parameter we examined is the relative root-mean square bias, RMS<sub>rel</sub>, which is computed from the relative, rather than absolute, bias for each cases,

$$\text{RMS}_{\text{rel}} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left(\frac{x_i - y_i}{x_i}\right)^2}$$

The relative root-mean square biases are calculated too. The mean relative bias (MRB) is calculated as:

$$MRB = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{x_i - y_i}{x_i} \right)$$

#### 3. Results and discussion

#### 3.1. Sulfate

Since particulate sulfate is one of the largest contributors to total PM<sub>2.5</sub> mass over the eastern United States especially in the summer, we begin our discussion by focusing on model evaluation with sulfate observations from the IMPROVE, CASTNet, STN, and SEARCH networks. We first compare the simulated and observed annual mean sulfate concentrations (Fig. 3). Two model simulations using RADM and ACM cloud modules are included. Table 1 lists the comparison results. For annual mean concentrations, model simulations are correlated with observations (R = 0.6-0.7). Both models show comparable performance and significantly underestimate sulfate concentrations. The model annual mean relative bias is ~25%.

To further understand the sulfate spatial distributions and seasonal cycle, we calculate and compare monthly mean sulfate in 10 EPA regions over the US continent. Fig. 4 illustrates the observed and simulated sulfate seasonal cycles in 10 EPA regions. The seasonal cycle of simulated sulfate is similar to the observations with high sulfate in summer and lower in winter (Rasch et al.,



Fig. 3. Observed and simulated annual mean sulfate concentrations of all available sites in 2002. The RADM (left panel) and ACM (right panel) cloud modules are used. The least-regression (solid) and 1:1 (dotted) lines are shown.

 $\begin{array}{l} \textbf{Table 1} \\ \textbf{Linear regression parameters, root-mean square errors (RMS_{abs}, RMS_{rel}) and mean relative biases (MRB) between simulated and observed annual mean sulfate concentrations. Either the RADM or ACM cloud scheme is used in the model. \end{array}$ 

Model	R	Slope	Intercept (µg m <sup>-3</sup> )	RMS <sub>abs</sub> (µg m <sup>-3</sup> )	RMS <sub>rel</sub>	MRB
RADM	0.70	0.40	0.65	1.70	0.55	-0.24
ACM	0.62	0.35	0.74	1.82	0.56	-0.25

2000). Simulated regional distribution is also reasonable, higher sulfate in the eastern US (EPA regions 2–5) where anthropogenic SO<sub>2</sub> emissions are high, and lower in the West (EPA regions 8–10) where anthropogenic SO<sub>2</sub> emissions are low. Same as in Fig. 3, monthly mean model sulfate is lower in almost all regions, except in the Northwest (EPA region 10), and is lower than observations in most seasons, except in winter. There are many factors that can influence the sulfate simulations including SO<sub>2</sub> emissions, gas and aqueous-phase conversions, dry and wet depositions, and transport. We will diagnose the reasons for the model underestimation of sulfate after presenting SO<sub>2</sub> results.

We note here that after completing this study, we have conducted a modeling study using the newer CMAQ version 4.7 with WRF version 3.2.1 assimilated meteorological field. The simulated sulfate is much improved although the monthly mean relative low bias in July still remains (-0.29 comparing to -0.62 for standard ACM run see Table 2). Diagnosing the detailed difference between WRF and MM5 (e.g., Zhao et al., 2009) and between CMAQ version 4.6 and 4.7 is beyond the scope of this work. We only focus on diagnosing the underestimation of sulfate using available observations in this study.

#### 3.2. SO<sub>2</sub>

We compare first the SO<sub>2</sub> seasonal cycles in 10 EPA regions (Fig. 5). Oxidation of SO<sub>2</sub> to sulfate is more active in summer than in winter. Concentrations of SO<sub>2</sub> show the opposite seasonal cycles compared to sulfate, i.e., higher in winter and lower in summer. The model captures the observed seasonal variations but tends to overestimate SO<sub>2</sub> in winter. In wintertime, vertical and horizontal transport is a major factor affecting SO<sub>2</sub> concentrations since chemical oxidation is slow. The higher concentrations may be an indication of error in the simulated vertical mixing, for example. We did not explore further the reasons for winter SO<sub>2</sub> biases in this study because the model bias of SO<sub>2</sub> is considerably less than sulfate (except in EPA region 10). Relative to the large model underestimates of sulfate, simulated SO<sub>2</sub> concentrations in the summer are in reasonable agreement with the observations. The SO<sub>2</sub> concentration agreement between the model and observations does not suggest that there are no errors in the chemical conversion and hence the loss of SO<sub>2</sub>. However, it does indicate that the conversion of SO<sub>2</sub> to sulfate is less likely to be the cause of the simulated bias of sulfate. The concentrations of SO<sub>2</sub> reflect the balance between SO<sub>2</sub> emissions and loss. In the summer, gas and aqueous-phase conversion of SO<sub>2</sub> to sulfate is the major loss. A bias of the SO<sub>2</sub> loss (and therefore sulfate source) would indicate a bias of the SO<sub>2</sub> source since the concentrations of SO<sub>2</sub> are reasonably



Fig. 4. Observed and simulated monthly mean sulfate concentrations in 10 EPA regions (Fig. 2). The observations are shown in solid line, CMAQ simulation with ACM in dot line, and CMAQ simulation with RADM in dash line.

# Table 2 Linear regression parameters, root-mean square errors (RMS<sub>abs</sub>, RMS<sub>rel</sub>), and mean relative biases (MRB) of monthly mean sulfate between simulated and observed annual mean sulfate concentrations for July, 2002.

Model	R	Slope	Intercept (µg m <sup>-3</sup> )	$\begin{array}{c} RMS_{abs} \\ (\mu g \ m^{-3}) \end{array}$	RMS <sub>rel</sub>	MRB
ACM	0.80	0.49	-0.32	3.15	0.62	-0.62
ACM15	0.87	0.90	-0.54	1.10	0.36	-0.32
ACM10	0.85	0.97	-0.60	0.83	0.34	-0.28
RADM	0.85	0.58	-0.23	2.59	0.52	-0.52
RADM15	0.87	0.85	-0.45	1.29	0.37	-0.34
RADM10	0.87	0.90	-0.45	1.02	0.33	-0.29

simulated. There is no evidence for large overestimates of  $SO_2$  emissions in the summer. Therefore, one is compelled to assume that the source of sulfate from  $SO_2$  oxidation is reasonably simulated in the model.

#### 3.3. Sulfate wet deposition

Wet deposition of sulfate dominates its removal (Barth et al., 2000; Chin et al., 1996); dry deposition of sulfate is insignificant (to be shown in Table 4). The NADP wet deposition data are calculated by the precipitation-weighted mean ion concentrations for valid samples and total precipitation amount at the sites, and monthly mean sulfate wet deposition data are reported. In order to investigate if the model low bias in simulated sulfate in summer is related to wet deposition, here we compare simulated sulfate wet deposition rates to the NADP observations. Fig. 6 shows observed

and simulated monthly mean sulfate wet deposition rates in the 10 EPA regions. Interestingly, simulated sulfate wet deposition rates are reasonable good, except in the EPA eastern regions of 2-5 in summer. The overestimates tend to be higher in using the ACM scheme than the RADM scheme. The overestimated sulfate wet deposition rates in these regions in summer may be an indicator of model bias in precipitation. However, we note that the wet deposition rates do not provide a direct constraint on sulfate concentrations. Since the sulfate lifetime is relatively short in summer (to be shown in Table 4), there is an approximate balance between local sulfate production and loss. Therefore the amount of wet deposition is largely controlled by the sulfate production rate from SO<sub>2</sub> oxidation.

Having said that, we note that the recent work by Appel et al. (2010) evaluated in detail the depositions of sulfate, ammonia, and nitrate in CMAQ for 5 years using surface observations. They used CMAQ version 4.7 with the updated ACM2 scheme, so the results cannot be compared directly to this work. Some results from that study are however, relevant. They found a general high bias in convective precipitation and sulfate wet deposition in the summer. A higher resolution (12 km) model in their study showed an even higher bias than the 36-km resolution model. To correct for the high wet deposition bias, they applied an adjustment assuming that wet deposition of sulfate is linearly correlated (1:1) to precipitation amount. Our analysis suggests a more complicated relationship. Table 4 and Fig. 11 will show that wet deposition of sulfate is more sensitive to convective cloud in the ACM scheme than the RADM scheme. In the ACM scheme, convective cloud not only affects wet deposition but also the production of sulfate (via



Fig. 5. Same as Fig. 4 but for SO<sub>2</sub>.



Fig. 6. Same for Fig. 4 but for sulfate wet deposition rates. The observations were obtained from the NADP program.

aqueous-phase oxidation of SO<sub>2</sub>). For the purpose of this work, i.e., correcting the low bias in simulated sulfate concentrations in the summer, we find that sulfate concentrations are much more sensitive to convective cloud than sulfate wet deposition rates (Figs. 10 and 11 and Table 4).

#### 3.4. Sensitivity of sulfate simulations to cloud

Previous analysis suggests that the production and loss rates of sulfate do not appear to have large biases. The significant bias in sulfate simulations therefore likely resides in the timescales of production and loss pathways (i.e., the rate "constants"). For sulfate, cloud is not only a major loss pathway through wet scavenging, but also a source through heterogeneous production in aqueous phase (Hegg and Hobbs, 1981; Daum et al., 1984; Saxena and Seigneur 1986). Heterogeneously produced sulfate contributes to ground level concentrations when it mixed down to the ground from cloud level (Prakash and Akula, 1992). We will focus our model sensitivity analysis of cloud effects in July, when convective clouds occur frequently and model bias is large.

As discussion above, our two standard simulations are CMAQ4.6 with ACM cloud module, and CMAQ4.6 with RADM cloud module. We conduct model simulations using two different sub-grid cloud schemes (RADM and ACM). We note here that cloud effects may not be the only factor leading to the model bias. Cloud oxidation in the CMAQ model also has large uncertainties (Mueller et al., 2011). Kondo et al. (in press) suggested that the RADM scheme tends to overestimate wet scavenging of aerosols in the accumulation mode since below cloud washout is treated as in-cloud rainout. Two cloud modules of ACM and RADM are

discussed in above section, detailed analysis of RADM and ACM schemes is beyond the scope of this work. The ad-hoc modification we implemented in this work by limiting convective precipitating cloud fractions should therefore not be treated as a mechanistic approach to improve the cloud scavenging schemes in CMAQ.

Further we compare standard model simulated cloud water path with satellite observations in July 2002 in Fig. 7. Cloud water path is the vertical column of cloud water in the atmosphere. The observations by MODIS (onboard TERRA and AQUA), AMSR, and TMI are described in Section 2.2. Generally MODIS data are higher than AMSR and TMI over the ocean. However, the disagreement among the satellite products are much less than the large overestimates in the model using either the ACM or RADM cloud module (see Fig. 7), which could result in a high bias in wet deposition of sulfate.

To correct sulfate bias, we did two sensitivities. One is the standard CMAQ4.6 with the ACM cloud module while limiting subgrid convective precipitating cloud fraction to <10% <15% (denoted ACM10 and ACM15). The second one is the standard CMAQ4.6 with the RADM cloud module while limiting sub-grid convective precipitating cloud fraction to <10% or 15% (denoted RADM10 and RADM15). We limit only the convective precipitating cloud fraction because the simulated water path is dominated by convective clouds in the ACM scheme (Fig. 8). The same is true for the RADM scheme (not shown). After limiting the convective precipitating cloud fraction, the high bias in-cloud water path is much reduced in the sensitivity simulation compared to the standard simulation, resulting in better agreement with the satellite observations (Fig. 7).

#### Cloud Water Path in July 2002



Fig. 7. Comparison of simulated monthly mean water path with satellite observations for July 2002. The Terra satellite crosses the US over the intervals about 10:00 am-1:00 pm local time and Aqua crosses the US in the intervals about 1:00 pm-4:00 pm local time. Model results are averages from same time periods. RADM10 and ACM10 denote that convective precipitating clouds are limited to <10% in the RADM and ACM cloud module, respectively.

We further compared model simulated cloud fractions, which mainly reflect large-scale resolved clouds, compared to satellite observations (Fig. 9). While overestimating cloud water path, but the models with both RADM and ACM schemes clearly underestimate cloud fraction particularly over regions without convective clouds. Mueller et al. (2011) also suggested that CMAQ cloud cover has a low bias over the U.S. based on surface observations. Analysis of Figs. 7–9 implies that the model overestimates convective clouds but underestimates large-scale resolved clouds.

By limiting the convective precipitating cloud fraction to <10% based on the comparisons of Figs. 7 and 8, the wet scavenging of sulfate is much reduced in the model, which will impact sulfate

Resolved and convective cloud Water Path



Fig. 8. Simulated monthly mean water path distributions of convective (left) and resolved (right) clouds using the ACM cloud module for July 2002. Convective clouds are computed in CMAQ but large-scale "resolved" clouds are obtained from MM5 and used in CMAQ.

simulations in the model. It is indeed the case. Fig. 10 shows that the large and systematic underestimates of sulfate in the model are much reduced in the sensitivity simulations (RADM10 and ACM10). Table 2 shows the regression statistics between observed and simulated sulfate for the standard and sensitivity simulations. Not surprisingly, the regression slope increases from 0.49 to 0.97, and absolute RMS decrease from 3.15 to 0.83 from the standard ACM scheme to ACM10, respectively; the slope increases from 0.58 to 0.90, and the absolute RMS decreases from 2.59 to 1.02 from the standard RADM scheme to RADM10, respectively.

The effects of limiting convective precipitating cloud fraction on simulated sulfate wet deposition are not as drastic as the sulfate concentrations (Fig. 11) since the amount of sulfate wet deposition is constrained less by sulfate concentrations but more by sulfate production rates. This point becomes more apparent in the budget analysis below. Nonetheless, significant reduction of simulated wet deposition of sulfate is evident for the simulation using the ACM cloud module (when the deposition rate is >0.5 kg S ha<sup>-1</sup>). The reduction brings the model results closer to the observations. The effect on the simulations using the RADM scheme is minor.



Cloud Fraction in July 2002

**Fig. 9.** Monthly mean cloud fraction comparison between satellite observed and simulated data in July 2002. The observations by MODIS are used here. The Terra satellite crosses the US over the intervals about 10:00 am-1:00 pm local time and Aqua crosses the US over the intervals about 1:00 pm-4:00 pm local time. Model results are averages from same time periods.

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Fig. 10. Observed and simulated monthly mean sulfate for July 2002. The top panel shows the model results with the standard RADM and ACM cloud modules and the bottom panel shows the results when convective precipitating clouds is limited to <10%. The least-regression (solid red) and 1:1 (dotted black) lines are shown.



Fig. 11. Same as Fig. 10 but for sulfate wet deposition rate. The observations from the NADP program were used. The left column shows the model results with the standard RADM and ACM cloud modules and the right column shows the results when convective clouds are limited to <10%.



Fig. 12. Same as Fig. 11 but for monthly mean SO<sub>2</sub> concentrations.

Table 3 Simulated  $SO_2$  deposition rates and column burden for July 2002 over the US domain.

dep. Wet dep $m^{-2} hr^{-1}$ ) (µg $m^{-2}$	p. Total dep. $(\mu g m^{-2} hr)$	$ \begin{array}{c} \text{Column} \\ (\text{mg m}^{-1}) \end{array} $
4 7.28	36.82	3.47
7 3.83	35.20	3.80
7 3.20	35.07	3.91
5 5.62	33.57	2.78
6 1.56	33.62	3.51
2 116	34 38	3 73
	$\begin{array}{ccc} \text{dep.} & \text{Wet dep}\\ \text{m}^{-2}\text{hr}^{-1}) & (\mu\text{g m}^{-2}\\ 4 & 7.28\\ 7 & 3.83\\ 7 & 3.20\\ 5 & 5.62\\ 6 & 1.56\\ 2 & 1.16\\ \end{array}$	$\begin{array}{cccc} \text{dep.} & \text{Wet dep.} & \text{Total dep.} \\ n^{-2}  \text{hr}^{-1}) & (\mu g  m^{-2}  \text{hr}^{-1}) & (\mu g  m^{-2}  \text{hr}^{-1}) \\ 4 & 7.28 & 36.82 \\ 7 & 3.83 & 35.20 \\ 7 & 3.20 & 35.07 \\ 5 & 5.62 & 33.57 \\ 6 & 1.56 & 33.62 \\ 2 & 1.16 & 34.38 \\ \end{array}$

The effect of cloud scavenging of sulfate does not affect significantly the model simulations of surface SO<sub>2</sub> (Fig. 12). The decrease of aqueous-phase oxidation of SO<sub>2</sub> by limiting convective precipitating cloud fraction increases SO<sub>2</sub> concentrations slightly, still in reasonably good agreement with the observations. When convective precipitating cloud fraction is limited to <10%, the SO<sub>2</sub> total deposition decreases with dry deposition increasing and wet deposition decreasing, and column burden increases (Table 3). However, the overall effect on SO<sub>2</sub> is relatively small compared to sulfate (next section).

3.5. Sulfate budgets of sensitivity simulations

Clouds affect both the production and loss of sulfate. We summarize the sulfate budget for standard and sensitivity simulations in Table 4. When convective precipitating cloud fractions are limited to 10% or 15%, the aqueous-phase production decreases, gas-phase production increases, wet deposition decreases, and dry deposition increases. Note that the removal of sulfate is almost solely from wet scavenging, while both aqueous-phase and gasphase production is important for sulfate production. Consequently, sulfate concentrations, column burden, and lifetime increases when both wet scavenging and aqueous-phase production is reduced by limiting convective precipitating cloud fraction to 10 or 15%. The ACM cloud scheme estimates more aqueous-phase production and removal than the RADM scheme. However, the two schemes produce quite similar results when convection cloud fraction is limited; the aqueous-phase production is about 60% more than gas-phase production. Even though the aqueous-phase production is larger, the contributions to column sulfate by aqueous-phase production is slightly less than gas-phase production because wet scavenging is collocated with aqueous-phase production. This result is consistent with Barth et al. (2000).

Tuble 1	
Sulfate budgets for July 2002 over the US domain	n.

Model	Production $(\mu g m^{-2} hr^{-1})$		$\begin{array}{cc} \mbox{Production} & \mbox{Dep. frm aq. phase prod.} \\ (\mu g \ m^{-2} \ hr^{-1}) & (\mu g \ m^{-2} \ hr^{-1}) \end{array}$		Dep. frm gas-phase prod. ( $\mu g \ m^{-2} \ hr^{-1}$ )		Column (mg m <sup>-2</sup> )		Lifetime (days)	Export (%)
	Aq.	Gas	Wet	Dry	Wet	Dry	Aq.	Gas		
ACM	139.9	53.18	124.4	0.89	47.54	1.26	2.0	2.3	1.0	10
ACM15	101.7	56.64	83.53	2.21	36.16	2.10	4.1	4.2	2.8	21
ACM10	87.23	57.60	70.99	2.42	32.78	2.29	4.6	4.8	3.6	25
RADM	97.57	49.85	86.79	1.50	40.58	1.73	3.0	3.4	2.0	11
RADM15	86.68	53.70	72.52	2.04	35.80	2.19	3.9	4.4	3.1	20
RADM10	82.05	54.50	66.73	2.18	33.62	2.32	4.3	4.8	3.6	23

By limiting the convective precipitating cloud fraction, simulated column sulfate burden increases by 50–100%. Even more drastic, the lifetime of sulfate increases from 1 or 2 days to 3.6 days. As a result, a much larger fraction of sulfate (>20% compared to 10% in the standard model) is exported out of the U.S. domain. Sulfate production and deposition decrease, and sulfate column and sulfate residence time increase by limiting convective precipitating cloud fraction (Table 4). The longer sulfate lifetime simulated in the ACM10 and RADM10 simulations is more consistent with previous modeling studies by Gary and Chang (1997), Quinn and Bates (2003), Barth et al. (2000), Chin et al. (2000); Koch et al. (1999), and Pham et al. (1995).

#### 4. Conclusions

SO<sub>2</sub> and sulfate simulated using the CMAQ model version 4.6 are evaluated with the observations over the United States in 2002. While the general seasonal cycles of SO<sub>2</sub> and sulfate are reproduced by the model, we find systematic low biases for sulfate in the summer. We note that the low bias is reduced by 50% when using CMAQ version 4.7 with WRF meteorological fields; the reason for the improvement is unclear. To diagnose the low biases in CMAQ version 4.6 with MM5 meteorological fields, both ACM and RADM schemes are used to test the sensitivities of simulated sulfate to cloud processing. We carry out detailed modeling analysis and diagnostics for July 2002. Compared to satellite observations of cloud liquid water path, we found a large high bias of estimated (sub-grid) convective clouds, leading to large overestimation of sulfate wet scavenging. Limiting convective precipitating cloud fraction in the cloud modules and hence significantly reducing wet scavenging leads to much improved agreement between simulated and observed sulfate. Model simulations show that aqueous-phase production of sulfate is much larger than gas-phase production, and it is more then 60% of total production, but their contributions to sulfate column are about same since sulfate removal is dominated by wet scavenging. The average lifetime of sulfate in the model increases from 1-2 days to 3-4 days and column burden increases 50-100% by limiting convective precipitating cloud fraction to <10% for July.

In this study, we find that simulated surface SO<sub>2</sub> concentrations are not nearly as sensitive to model cloud modules as sulfate. We show that a potential model problem of excessive wet scavenging of sulfate does not necessarily lead to apparent problems in model simulations of sulfate wet deposition rate compared to surface observations. In general, there is still a lack of direct observational constraints from air quality monitoring measurements on model simulated cloud processing of SO<sub>2</sub> and sulfate. Field experiments with targeted aircraft and surface observations in addition to air quality monitoring measurements will be needed to improve our ability to simulate cloud processing of pollutants.

#### Acknowledgments

This work was supported by the Southern Company. S. Mueller was supported by the Tennessee Valley Authority. We thank two anonymous reviewers for the suggestions and comments, particularly for the suggestion of examining the WRF-CMAQ (v4.7) simulation results.

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