1. Introduction

The sulfur chemistry in the Community Multiscale Air Quality (CMAQ) model (version 5.0) has been updated. Here, we describe the updates to sulfur chemistry and compare model predictions obtained with CMAQv4.7.1 and CMAQv5.0.

2. Methodology

Air quality simulations were performed for January and July 2002 using CMAQv4.7.1 (Foley et al., 2010) and CMAQv5.0. The modeling domain covered the continental US using 36-km horizontal grid resolution and contained 24 vertical layers. The off-line photolysis option was used for both simulations. The non-urban as well as the urban minimum eddy diffusion coefficient has been revised in CMAQv5.0. For this study, both coefficients in CMAQv5.0 were replaced with the values in CMAQv4.7.1. Monthly mean boundary values were used for both simulations.

Meteorological fields were obtained from the PSU/NCA/NCMMS system (Grell et al., 1994 (version 3.5). Anthropogenic emissions were obtained from the National Emissions Inventory. Biogenic emissions were estimated using the Biogenic Emissions Inventory System version 3.14 (Schwede et al., 2005).

3. Sulfur chemistry in CMAQv5.0

A number of updates have been implemented in CMAQv5.0 that directly impact sulfate production potential. In CMAQv5.0, BURROKAT (Froutzkias and Nenes, 2007) was implemented, along with an updated treatment and tracking of crustal species (e.g., Ca, Mg, and trace metals) and aerosol (e.g., Fe, Mn). These species impact aqueous-phase oxidation of SO(V) to SO(IV) by altering the pH and ionic strength of the droplets, and, in the case of Fe and Mn, also affect Fe(III)/Mn(II) metal-catalyzed aqueous-phase sulfur oxidation.

The CB05 mechanism in CMAQ contains one gas-phase chemical reaction for SO oxidation. The rate constant for the reaction in CMAQv5.0 has been updated using the 2006 NASA/JPL recommendation. The gas-phase reaction for the SO oxidation is now consistent between the CB05 and SAPRC07 mechanisms.

Additionally, CMAQ contains five aqueous-phase chemical pathways for SO oxidation involving (1) H2SO, (2) O3, (3) methylhydroxyl peroxide (MHP), (4) peroxyacetic acid (PAA), and (5) metal catalysis. Rate constants for all pathways (except metal catalysis) have been updated following Jacobson (1997).

In previous versions of the CMAQ model, sulfate production via the above reaction was calculated using the prescribed background concentrations of 0.01 μg/m3 for Fe(III) and 0.005 μg/m3 for Mn(II). As CMAQv5.0 contains predictions of Fe and Mn, these tracked concentrations are now used to estimate Fe(III) and Mn(II) values for the metal catalyzed oxidation pathway. To estimate aqueous-phase Fe(III) and Mn(II) concentrations from total (activated) aerosol iron and manganese, the solubility and oxidation state of these species need to be estimated. Iron solubility and oxidation state is highly variable and dependent on a number of factors including origin of the aerosol and time of day, with more soluble iron aerosol found in anthropogenic source regions compared to areas with high levels of natural dust emissions (Alexander et al., 2009; Seifert et al., 1998). Manganese is typically more soluble than iron and exists mainly as Mn(II) in cloud liquid droplets; whereas iron cycles diurnally, and exists mainly as Fe(II) during the day and Fe(III) at night (Alexander et al., 2009). In CMAQv5.0, the solubility of iron and manganese is kept constant at 10% and 50%, respectively (Alexander et al., 2009). All dissolved manganese is assumed to be Mn(II), and Fe(III) is assumed to be 90% of the dissolved Fe at night and 10% during the day. Note that while only Fe(III) and Mn(II) impact the SO(IV) oxidation rate, all Fe and Mn in the activated droplets is subjected to scavenging/deposition.

4. Results

Monthly mean surface sulfate concentrations obtained with CMAQv4.7.1 along with the predicted sulfate concentration difference between the two models are presented in Figure 1. The impact in January is mixed. CMAQv5.0 predictions increase in some locations while decrease in other locations compared to those with CMAQv4.7.1. The maximum increase in sulfate occurs just south of Lake Michigan where metal concentrations are relatively high.

Normalized mean bias and normalized mean error for sulfate obtained with CMAQv4.7.1 and CMAQv5.0 are shown in Table 1. Normalized mean bias obtained with CMAQv5.0 improved in both January and July. Normalized mean error was similar for both models, with CMAQv5.0 having slightly lower relative error in July and higher in January compared to CMAQv4.7.1.

5. Summary

CMAQv5.0 has been updated to include the latest gas-phase and aqueous-phase SO oxidation rates, as well as an expanded list of explicitly tracked species, including crustal species and trace metals. On a monthly average basis, the absolute impacts on simulated sulfate concentrations are relatively small though not insignificant, and in certain regions and at shorter timescales, more significant impacts are simulated. Higher absolute differences were simulated in January, with the model updates leading to higher monthly average concentrations in some areas (e.g., near Chicago) and lower concentrations in others (e.g., the Northeastern U.S). July showed a more widespread average increase of sulfate throughout the domain due to CMAQv5.0 updates. Model performance statistics for sulfate generally improved with CMAQv5.0. We plan to examine the impact of additional chemical reactions and meteorological conditions on sulfate in the future.

6. References


Normalized mean bias and normalized mean error for sulfate obtained with CMAQv4.7.1 and CMAQv5.0 are shown in Table 1. Normalized mean bias obtained with CMAQv5.0 improved in both January and July. Normalized mean error was similar for both models, with CMAQv5.0 having slightly lower relative error in July and higher in January compared to CMAQv4.7.1.

Table 1: Normalized mean bias and normalized mean error for sulfate obtained with CMAQv4.7.1 and CMAQv5.0.

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