USING CMAQ-AIM TO EVALUATE THE GAS-PARTICLE PARTITIONING TREATMENT IN CMAQ

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1. INTRODUCTION

The Community Multi-scale Air Quality model (CMAQ) aerosol component utilizes a modal representation, where the size distribution is represented as a sum of three lognormal modes. Though the aerosol treatment in CMAQ is quite advanced compared to other operational air quality models, various members of the CMAQ community have commented that improvements to the aerosol module should be made in order to bring it to the state of the science found in research-grade air quality models. Among the shortcomings noted are that (1) a trimodal representation is insufficient to resolve the aerosol size and composition distribution; (2) interactions of the gas phase with coarse particles, such as sea-salt, are neglected; and (3) the assumption of instantaneous equilibrium between gas-phase species and fine-mode aerosol is inaccurate. In the present study, we seek to understand the effects of the latter two assumptions on predicted fine-particle mass and chemical composition in regional-scale air quality models.

A sectional aerosol module that uses dynamic mass transfer rather than assuming instantaneous equilibrium between the gas and particle phases has been developed and integrated into the Community Multi-scale Air Quality model (CMAQ) (Zhang and Wexler, 2004). The resulting model, CMAQ-AIM, provides a useful platform to gauge the impact of certain assumptions made in the CMAQ aerosol module.

2. APPROACH

The CMAQ and CMAQ-AIM models are both applied to a continental United States domain over the month of July 2001. The models are run with 24 vertical layers and a horizontal grid cell size of 36 km. Both model simulations are begun on June 24, 2001, to provide a week of model "spin-up" to minimize the effect of initial conditions. For this modeling scenario, the CMAQ-AIM model takes about 5-7 times as long as CMAQ to execute.

The differences between the CMAQ and CMAQ-AIM models presented here are summarized in Table 1. A 2004 pre-release version of CMAQ is used with the SAPRC99 chemical mechanism and the AERO3 aerosol module. The CMAQ-AIM model is adapted from this same version of CMAQ, with the AERO3 module replaced by a module derived from the Aerosol Inorganic Model (AIM). CMAQ-AIM is used with nine size sections covering a range of particle diameter from 0.039–20 μm, whereas CMAQ treats the aerosol distribution as a superposition of three lognormal modes.

Table 1. Summary of differences between CMAQ and CMAQ-AIM models.

Feature	CMAQ	CMAQ-AIM
Size representation	modal	sectional
Mass transfer to fine PM	instantaneous equilibrium	dynamic
Mass transfer to coarse PM	none	dynamic
Thermodynamic module	ISORROPIA	AIM
Equilibrium state	metastable	stable
Sea salt	no	yes
$N_2O_5 \rightarrow HNO_3$ heterogeneous reaction	no*	no
Coagulation	yes	no

*N_2O_5 heterogeneous reaction is turned off in CMAQ for comparability with CMAQ-AIM.

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CMAQ-AIM uses three gas-to-particle transport schemes, termed Replacement Transport, Coupled Transport (Sun and Wexler, 1998), and Uncoupled Transport, to predict aerosol-phase mass and composition. Particle composition in different size sections is integrated over different time scales to efficiently treat the size-dependent differences in gas-to-particle mass transfer rates. Thus in CMAQ-AIM, particles in all size sections interact with the gas-phase species. In contrast, the coarse-particle mode in CMAQ does not interact with the gas phase, while the fine-particle modes (i.e., Aitken and accumulation) are assumed to be in instantaneous equilibrium with the gas phase.

In CMAQ-AIM, aerosol composition is adjusted dynamically in the direction of the most thermodynamically favorable state of the gas-aerosol system. Thus at very low ambient relative humidity (RH), a crystalline aerosol phase may be simulated in CMAQ-AIM. In CMAQ, it is assumed that all particles exist as metastable aqueous droplets irrespective of the ambient RH.

Sea-salt emission fluxes from the open ocean and surf zone are calculated using the parameterizations of Gong (2003) and de Leeuw et al. (2000), respectively, with relative-humidity-dependent size adjustments based on the polynomial expressions of Zhang et al. (2004). Sea-salt particles are emitted in all size sections of CMAQ-AIM greater than 0.08 μm diameter, with a peak in the mass distribution occurring between 5 and 15 μm, depending on the relative humidity. Sea-salt emissions are not included in the CMAQ simulations, but emission inputs of all other species are identical to the CMAQ-AIM simulation.

Because CMAQ-AIM does not include the formation of nitric acid by heterogeneous conversion of N_2O_5, the CMAQ AERO3 module was modified to turn off that reaction pathway. Both models can thus be expected to predict less total nitrate than the "standard" CMAQ configuration. The process of particle growth by coagulation is not treated in CMAQ-AIM.

3. RESULTS

Model results shown here are averages of the 744 instantaneous, hourly outputs over the entire month of July 2001. Predicted SO_4^{2-} concentrations are shown in Figs. 1a and 1b. Difference plots (CMAQ-AIM minus CMAQ) for total NO_3^-, NH_4^+, NO_3^-, and HNO_3 are shown in Figs. 2-5. The CMAQ results for aerosol-phase

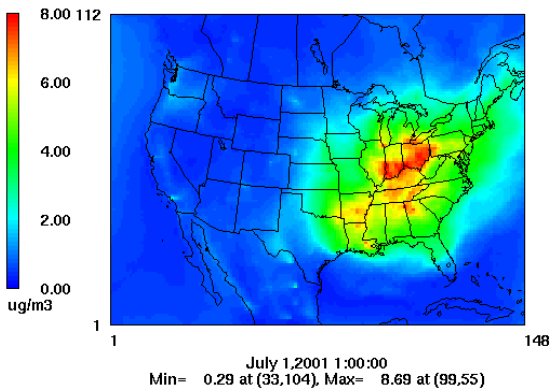

Fig. 1a. Aerosol sulfate concentrations (sum of i and j modes) predicted by CMAQ, averaged over July 2001.

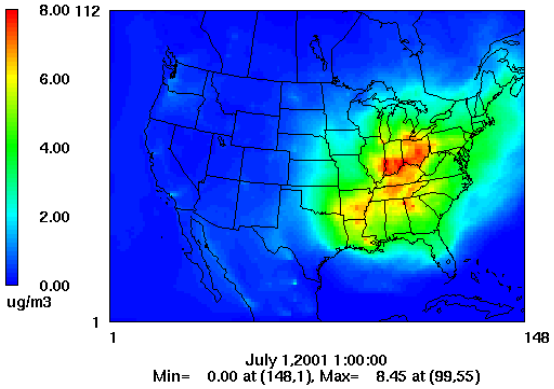

Fig. 1b. Aerosol sulfate concentrations (sum of first 6 size bins) predicted by CMAQ-AIM, averaged over July 2001.

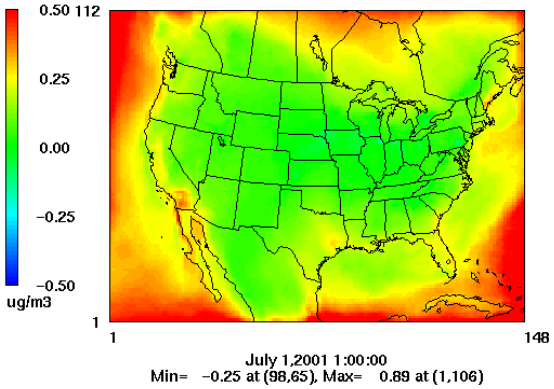

Fig. 2 CMAQ-AIM minus CMAQ total nitrate concentrations, averaged over July 2001.

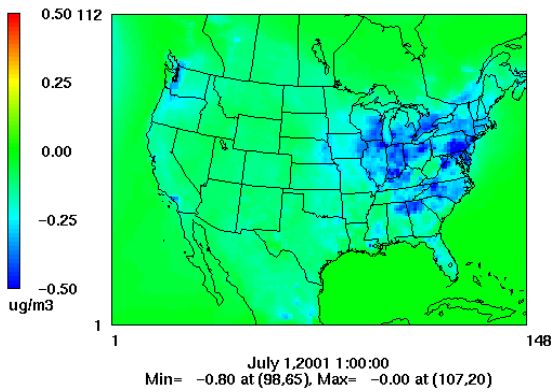

Fig. 3. CMAQ-AIM minus CMAQ NH_4^+ concentrations, averaged over July 2001.

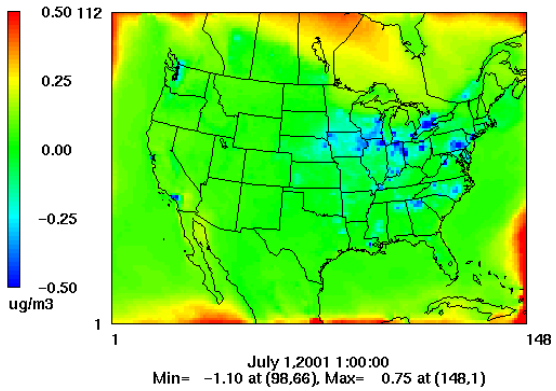

Fig. 4. CMAQ-AIM minus CMAQ NO_3^- concentrations, averaged over July 2001.

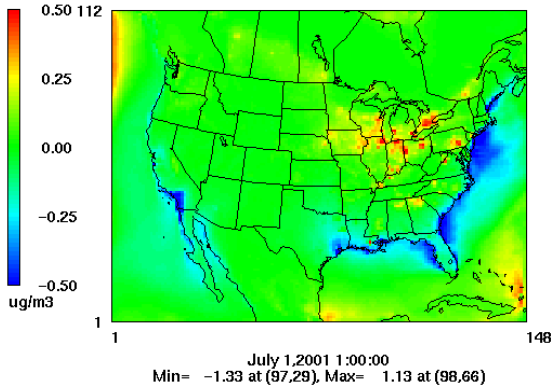

Fig. 5. CMAQ-AIM minus CMAQ HNO_3 concentrations, averaged over July 2001.

species are the sum of the Aitken and accumulation modes; for CMAQ-AIM, the sum of the first six size bins, corresponding to particles smaller than 2.5 μm diameter, is used. We recognize that the sum of the Aitken and accumulation modes is not exactly equivalent to summing the first six size bins (Jiang, 2002), but this approach should be adequate for bringing out important features of the model differences.

As can be seen from Figs. 1a and 1b, average sulfate concentrations predicted by CMAQ and CMAQ-AIM are very similar. Differences in total nitrate, computed as the sum of aerosol nitrate and the nitrate mass fraction of HNO_3, are plotted in Fig. 2. Note that for this figure, all CMAQ-AIM size sections are used, i.e., coarse NO_3^- is included. As can be seen from Fig. 2, total nitrate concentrations predicted by the two models are also very similar. Similarities in total nitrate and sulfate are expected due to the fact that both models employ the same gas-phase emissions and chemical reaction mechanism.

3.1 Effect on Gas-Particle Partitioning

Relative to CMAQ, CMAQ-AIM predicts lower concentrations of NH_4^+ (Fig. 3) and NO_3^- (Fig. 4) aerosol in the Midwest and in much of the eastern U.S., and correspondingly higher concentrations of HNO_3 (Fig. 5) and NH_3 (not shown). This is likely due to the assumption of instantaneous equilibrium in CMAQ. In CMAQ-AIM, HNO_3 and NH_3 partition gradually into the aerosol phase, which may account for the differences seen here.

3.2 Effect of sea-salt emissions.

As can be seen from Fig. 5, CMAQ-AIM predicts lower concentrations of HNO_3 in southern California and along the Atlantic and gulf coasts. This is likely due to the sea-salt emissions in CMAQ-AIM being allowed to interact with the gas phase. Gas-phase HNO_3 can be transferred to the aerosol and displace Cl^- to form sodium nitrate particles and HCl. This process is not treated in CMAQ.

4. FUTURE WORK

The impact of including heterogeneous sea-salt reactions on the aerosol composition and size distribution will be examined directly by running CMAQ-AIM without sea-salt emissions. In addition, we plan to develop an aerosol module as similar as possible to the one in CMAQ except that it will use a sectional representation. Both models will be compared against an observational dataset. These future studies should facilitate an evaluation of assumptions made within the CMAQ aerosol

module and prioritization of future model development efforts.

5. REFERENCES

De Leeuw, G.; Neele, F.P.; Hill, M.; Smith, M.H.; Vignati, E., 2000. Production of sea spray aerosol in the surf zone. *J. Geophys. Res.*, 105(D24), 29,397-29,409.

Gong, S.L., 2003. A parameterization of sea-salt aerosol source function for sub- and super-micron particles. *Global Biogeochemical Cycles*, 17(4), doi:10.1029/2003GB002079.

Jiang, W.; Yin, D. Mathematical formulation and consideration for converting CMAQ modal particulate results into size-resolved quantities. Presented at the AMS Fourth Conference on Atmospheric Chemistry, 2002.

Sun, Q.; Wexler, A.S., 1998, Modeling urban and regional aerosols—Condensation and evaporation near acid neutrality. *Atmos. Environ.* 32: 3527-3531.

Zhang, K.M.; Knipping, E.M.; Wexler, A.S.; Bhave, P.V.; Tonnesen, G.S., 2004. Size distribution of sea-salt emissions as a function of relative humidity. *Atmos. Environ.,* in review.

Zhang, K.M.; Wexler, A.S., 2003. Further development of the Community Multi-scale Air Quality Model with Aerosol Inorganic Module (CMAQ-AIM). Report to the University Corporation for Atmospheric Research.

The research presented here was performed under the Memorandum of Understanding between the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Commerce's National Oceanic and Atmospheric Administration (NOAA) and under agreement number DW13921549. Although it has been reviewed by EPA and NOAA and approved for publication, it does not necessarily reflect their policies or views.