INCORPORATION OF THE MODEL OF AEROSOL DYNAMICS, REACTION, IONIZATION AND DISSOLUTION (MADRID) INTO CMAQ

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1. INTRODUCTION

Recent reviews of the current status of three-dimensional (3-D) air quality models for PM[1, 2] have suggested that existing 3-D models have several limitations in their treatment of aerosols that should be addressed before they can provide reliable results in a policy or regulatory context. Accordingly, we present here the development of a new model for the treatment of PM processes, its incorporation into a 3-D host model, the Community Multiscale Air Quality model (CMAQ), and its application to the Los Angeles basin.

CMAQ was selected as the host air quality model following a review of several existing models[3]. CMAQ is a 3-D grid-based air quality model that was developed by the U.S. Environmental Protection Agency (EPA)[4]. The version used here is the August 2000 version as released by EPA.

The new modules incorporated into CMAQ include the Model of Aerosol Dynamics, Reaction, Ionization, and Dissolution (MADRID)[5] and the Carnegie-Mellon University (CMU) aqueous-phase chemical kinetic mechanism[6]. In addition, some existing modules of CMAQ were modified either to be compatible with the new modules or to provide better representation of atmospheric processes[7].

2. FORMULATION OF MADRID

MADRID simulates the chemical composition of PM and the dynamics of the particle size distribution. First, we conducted comprehensive reviews of existing aerosol modules[2, 8, 9]. Next, the selected modules were integrated and, if warranted, modified, to constitute a coherent framework for the simulation of atmospheric PM

ISORROPIA[10] is used to simulate the thermodynamics of inorganic PM species in MADRID. ISORROPIA treats sulfate, nitrate, ammonium, sodium, chloride and water and solves the thermodynamic equilibria of the various chemical species in the gas, liquid and solid phases.

Two formulations of MADRID are available that differ by their treatment of secondary organic aerosol (SOA) formation.

The formulation of MADRID 1 uses an empirical representation of SOA formation that is based on data obtained in smog chamber experiments[11, 12]. The MADRID 1 formulation for SOA includes two anthropogenic VOC precursors, which are characterized as one with low SOA yield (XYL) and one with high SOA yield (TOL). The SOA products were added to the products of the reactions of these two species with OH. We use twelve biogenic precursors of SOA. The Clausius-Clapeyron equation is used to account for the temperature dependence of the saturation vapor pressure. Values of 88 kJ/mole and 175 kJ/mole are used for the enthalpy of vaporization of condensable products from terpenes and aromatics (< C10) and sesquiterpenes, respectively[14, 15].

The formulation of MADRID 2 is based on a mechanistic representation of SOA formation using a detailed gas-phase chemical kinetic mechanism[16] and an advanced treatment of SOA formation that accounts for both hydrophilic and hydrophobic SOA[17]. Ten surrogate SOA compounds are used in MADRID 2. The formulation of the gas/particle partitioning for hydrophobic compounds follows an absorption approach. For hydrophilic compounds, SOA interact with inorganic species via ISORROPIA.

The modal approach is used to represent the particle size distribution in the original CMAQ. A sectional approach is used in MADRID to represent the particle size distribution. The processes that govern aerosol dynamics include coagulation, nucleation (i.e., the formation of new particles), growth due to condensation, shrinkage due to volatilization and the mass transfer of chemical species between the bulk gas phase and the particle surface. Coagulation is neglected because its time scale is long compared to those

of other processes. The other processes are treated explicitly in MADRID.

One option in MADRID is to use only two particle size sections to represent the particle size distribution. The most common approach is to select two size sections that represent fine and coarse particles. In this option, gas/particle mass transfer is the only aerosol dynamic process that is relevant in the case of a two-section representation. When a multi-sectional (i.e., more than two) representation is selected, new particle formation, growth by condensation, shrinkage by volatilization and gas/particle mass transfer are simulated.

The parameterization of McMurry and Friedlander[18] is used to simulate the nucleation of new sulfate particles. The moving-center technique[19] is used to simulate condensational growth. (Note that this process is simulated only when more than two particle size sections are selected by the user). This technique minimizes numerical diffusion and allows the simultaneous tracking of particulate mass and particulate number. Particles are not always at equilibrium with the gas phase. The algorithm of Capaldo et al.[20] is used to treat mass transfer explicitly for particles above 2.15 μm; it assumes full equilibrium for particles below that threshold size.

3. APPLICATION OF CMAQ-MADRID

The 3-D air quality model, CMAQ-MADRID, described above was applied to simulate the 27-28 August 1987 episode in the Los Angeles basin. A comprehensive data base of the Southern California Air Quality Study (SCAQS) is available that provides data needed for model inputs and evaluation. This episode has been used earlier for the evaluation of PM air quality models[2] and, therefore, it provides a convenient benchmark.

The meteorological fields were simulated using the meteorological mesoscale model MM5 with four-dimensional data assimilation. This MM5 simulation has been used in previous air quality simulations[21, 22]. A post-processing step was added to develop a diagnostic 4-D field of mixing heights using aloft data available throughout the basin.

Emissions of gases and particles generally follow Pai et al.[21] The total PM mass emissions were obtained from Meng et al.[23] and the PM chemical speciation was obtained from Jacobson et al.[24] PM emissions were assigned to sections according to the default size distribution of CMAQ[4]. Initial (IC) and boundary conditions (BC) for gases follow Pai et al. [21]

A two-section representation of the particle size distribution was used. For MADRID 1, we selected the CBM-IV gas-phase chemistry. MADRID 2 uses the Caltech Atmospheric Chemistry Mechanism (CACM). Heterogeneous reactions were simulated following Jacob[25].

Figure 1 shows a comparison between the observed and predicted chemical compositions of $PM_{2.5}$ in Riverside on 27 August and 28 August 1987. Although both models underpredict $PM_{2.5}$ concentrations at this site (MADRID 1 by 7% and 42% and MADRID 2 by 15% and 50% for 27 and 28 August, respectively), they reproduce the relative composition quite well. Nitrate is the dominant component observed, followed by the "other" category, which includes seasalt, soil dust and other unclassified components. The top components are reproduced accurately in the MADRID 1 simulation. Lower nitrate concentrations were predicted in MADRID 2 on 28 August. As a result, the "other" category surpasses nitrate as the dominant component. The relative abundances of sulfate and ammonium are reproduced quite accurately, while EC is underrepresented in both models. A major difference between the two models, as noted above, is the predicted OC fraction. MADRID 2 predicts OC to be about 10% of total $PM_{2.5}$, while MADRID 1 predicts about 4 to 5% OC in Riverside.

4. CONCLUSION

We have presented the development and initial application of a new 3-D air quality model for PM, CMAQ-MADRID. This model combines a state-of-the-science representation of the major processes that govern the chemical composition and size distribution of PM in the atmosphere with numerical robustness of the corresponding algorithms. CMAQ-MADRID was applied to simulate an air pollution episode in the Los Angeles basin. The chemical composition of PM was well reproduced by the model except that SOA formation was underpredicted. The treatment of SOA formation is still a major source of uncertainties and additional fundamental studies will be required to improve our ability to predict SOA concentrations.

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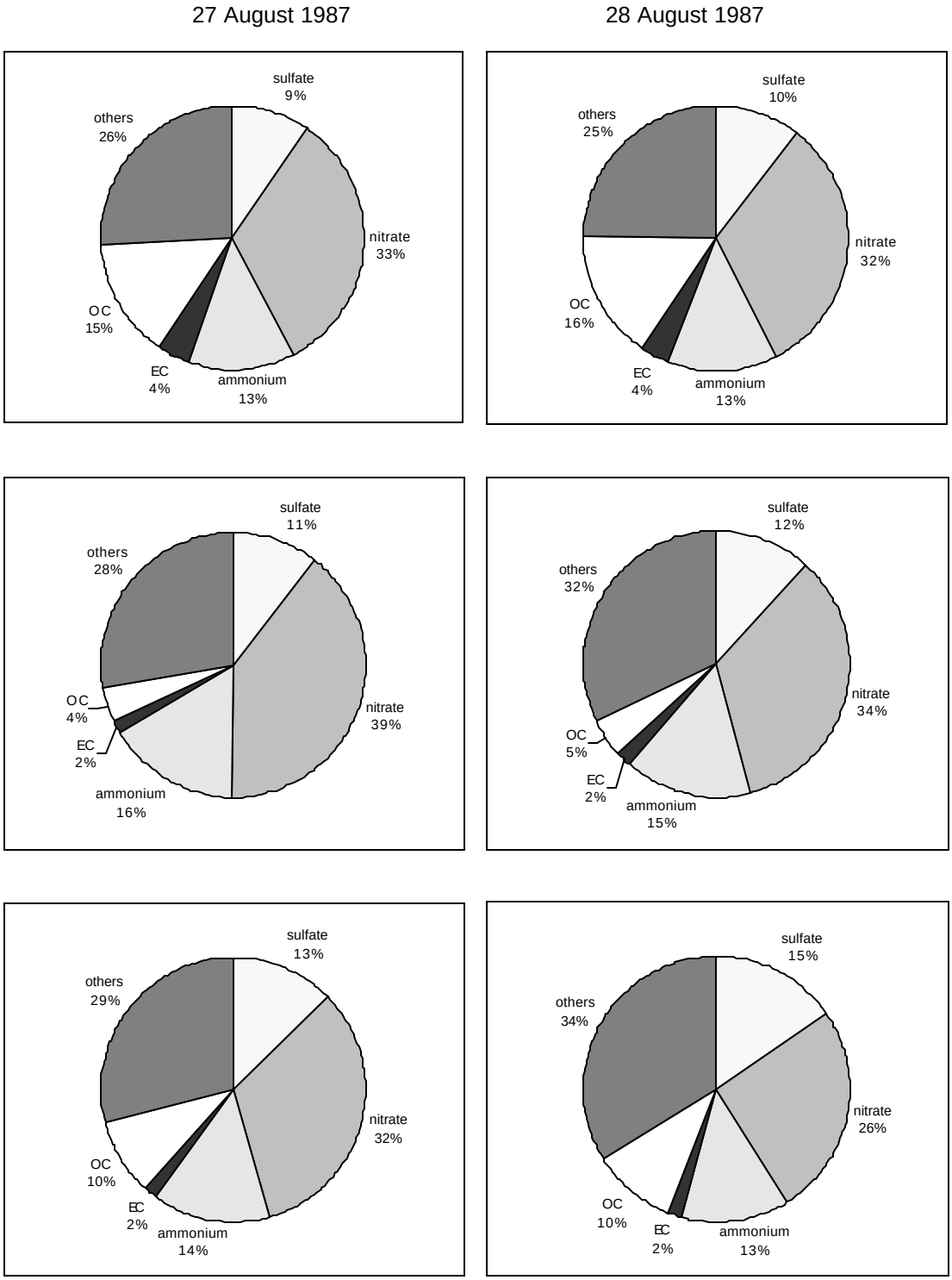

Fig. 1 Comparison of observed and predicted $PM_{2.5}$ chemical compositions in Riverside, CA on 27 and 28 August 1987: observations (top), CMAQ-MADRID 1 (middle), and CMAQ-MADRID 2 (bottom).