MODELING ATMOSPHERIC AEROSOLS IN WRF/CHEM

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1. INTRODUCTION

Modeling atmospheric aerosols requires appropriate representations of aerosol size distribution and microphysics in three-dimensional (3-D) air quality models (AQMs). The modal and sectional approaches are the two major approaches commonly used in AQMs to represent the particle size distribution. In the modal approach, the particle size distribution is approximated by several modes and particle properties are assumed to be uniform in each mode. In the sectional approach, the size distribution is discretized into sections and particle properties are typically assumed to be constant over particle size sections. A comprehensive aerosol module in AQMs should simulate all major aerosol microphysics including gas-particle mass transfer, thermodynamic equilibrium for both inorganic and organic species, nucleation (binary or ternary), coagulation, condensation, aerosol formation due to aqueous-phase and heterogeneous chemistry, aerosol scavenged by cloud droplets, and dry and wet deposition. Depending on the purpose of applications and available computational resources, not all these processes are treated in aerosol modules that are currently used in 3-D AQMs.

Large uncertainties exist in aerosol treatments in AQMs, causing differences in gas and aerosol predictions given the same model inputs and either the same or different gas-phase chemistry. In addition to differences in particle size representation (e.g., modal vs. sectional), other factors that may contribute to the discrepancies in model predictions may include differences in aerosol chemical and microphysical processes treated, and assumptions and numerical algorithms used for solving these processes. This is particularly true for aerosol modules that use the same size representation but with different microphysics. It is of interest to compare model results with different aerosol treatments to understand the major causes for discrepancies and identify possible areas of improvements for aerosol treatments. In this study, the NOAA's Weather Research and Forecasting/Chemistry (WRF/Chem) (Grell et al., 2005) prediction system is used as a host AQM to test and compare different aerosol modules in a retrospective mode.

2. AEROSOL MODULES IN WRF/CHEM

In this study, three aerosol modules are tested and compared. The first module is the Modal Aerosol Dynamics Model for Europe (MADE) (Ackermann et al., 1998) with the secondary organic aerosol model (SORGAM) of Schell et al. (2001) (referred to as MADE/SORGAM). The second module is the Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) (Zaveri et al., 2005a). The third module is the Model of Aerosol Dynamics, Reaction, Ionization and Dissolution (MADRID) (Zhang et al., 2004). The three modules differ in terms of size representation used, chemical species treated, assumptions and numerical algorithms used. Table 1 compares the major processes among the three aerosol modules.

MADE/SORGAM uses three lognormally-distributed modes to simulate particle size distribution. It uses a modified version of MARS of Binkowski and Shankar (1995) to simulate aerosol thermodynamic equilibrium for sulfate, nitrate, ammonium, and water. SORGAM is an absorptive secondary organic aerosol (SOA) module for hydrophobic condensable organic compounds. The formation of new sulfate particles from homogeneous binary nucleation is simulated using the approach of Kulmala et al. (1998). Coagulation and condensation are simulated using the modal approach of Binkowski and Shankar (1995). Gas-to-particle mass transfer is simulated using the full equilibrium approach of Binkowski and Roselle (2003) for two regimes that are based on the molar ratio of total ammonium to total sulfate, TNH4/TSO4: sulfate-poor (TNH4/TSO4 < 2) and sulfate-rich (TNH4/TSO4 ≥ 2).

MOSAIC uses currently eight size sections to represent the particle size distribution, although the size section number is flexible. It uses the Multicomponent Equilibrium Solver for Aerosols (MESA) and a new activity coefficient module Multicomponent Taylor Expansion Method (MTEM) to simulate aerosol thermodynamic equilibrium for sulfate, nitrate, ammonium, sodium, calcium, chloride, and water (Zaveri et al., 2005 b, c). Gas-to-particle mass transfer and condensation are treated using the Adaptive Time Split Explicit Euler Method (ASTEEM), which is a dynamic approach that solves the gas/particle partitioning among different size sections or group of sections with similar characteristics times. The ordinary differential equations for gas/particle partitioning are solved using an efficient time-splitting approach that does not require bulk

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equilibrium assumption or hybrid treatment. The current version of MOSAIC incorporated into WRF/Chem does not treat nucleation, coagulation, and SOA formation. A SOA module that treats the dynamic reversible absorption of 8 classes of SOA species (based on SORGAM) is being developed and incorporated into WRF/Chem.

MADRID also uses the sectional approach with any number of size sections. It uses ISORROPIA of Nenes et al. (1998) to simulate the thermodynamics of major inorganic aerosol species. SOA formation is treated using two formulations: an empirical representation (referred to as MADRID 1) that is based on a reversible absorption theory and smog chamber data, and a mechanistic representation (referred to as MADRID 2) that simulates both hydrophilic and hydrophobic particles. Nucleation of sulfuric acid and water vapor is simulated using the approach of McMurry and Friedlander (1979) that accounts for the competition between nucleation and condensation. Gas/particle mass transfer is simulated with three algorithms: the CIT bulk equilibrium approach that assumes full equilibrium between gas and aerosol phases, the CMU hybrid approach that treats mass transfer explicitly for coarse particles and assumes full equilibrium for fine particles, and the dynamic approach that solves the full aerosol dynamic equation (Hu et al., 2005). In the CIT bulk equilibrium approach, the condensation is implicitly treated by allocating the transferred mass to different size sections based on condensational growth law. Condensation is explicitly simulated in the CMU hybrid approach and the dynamic approach. The growth of particles over sections with fixed size boundaries in all three approaches is simulated using the moving-center scheme of Jacobson (Jacobson, 1997). The current version of MADRID in WRF/Chem does not treat coagulation.

MADE/SORGAM and MOSAIC have been incorporated and tested in WRF/Chem (Grell et al., 2005; Fast et al., 2005). They have been coupled with different gas-phase chemistry. In WRF/Chem, MADE/SORGAM is coupled with Regional Acid Deposition Mechanism version 2 (RADM2) of Stockwell et al. (1990) and the Regional Atmospheric Chemistry Mechanism (RACM) of Stockwell *et al.* (1997). MOSAIC is coupled with the Carbon-Bond mechanism Version Z (CBM-Z) of Zaveri and Peters (1999). In the EPA Community Multiscale Air Quality (CMAQ) modeling system – MADRID (i.e., CMAQ-MADRID) (Zhang et al., 2002, 2004), MADRID 1 is coupled with RADM2 and CBM-IV, and MADRID 2 is coupled with the Caltech Atmospheric Chemical Mechanism (CACM) of Griffin et al. (2002). As an initial step, MADRID 1 is coupled with the CBM-Z mechanism, permitting the use of the same gas-phase chemistry for intercomparison of MADRID and MOSAIC. Although the two modules are based on the sectional approach, differences exist in the chemical species/processes treated and numerical algorithms used.

3. TESTBED, MODEL SETUP and EVALUATION PROTOCOLS

A 5-day episode (12 UTC 28 August through 12 UTC 2 September of 2000) from the Texas Air Quality Study (TexAQS-2000) in the southern U.S. is selected as a testbed in this study. The TexAQS-2000 was carried out around the Houston area where the exceedance of the NAAQS 120 ppb O_3 standard occurs most frequently and VOC reactivities are typically much higher than other urban areas in the U.S. The concurrent ground-based, rooftop and aircraft measurements, coupled with several national long-term monitoring programs such as the EPA's supersite for PM measurements, create a data base that is sufficiently comprehensive to rigorously test integrated air quality models for O_3 and PM. Measurements of meteorological conditions, gaseous (NO_x, NO_y, O_3, SO_2, CO, CO_2, and HNO_3) and PM (mass, number, and size distribution) were made (e.g., Neuman et al., 2002; Brock et al., 2003). During the 5-day period, high afternoon O_3 mixing ratios (> 100 ppb) were often observed in the Houston metropolitan area, which was resulted largely from local anthropogenic and biogenic emissions (Jiang and Fast, 2004). The horizontal grid spacing used in the simulations is 12-km. The initial conditions, boundary conditions, and emissions are the same ones as the WRF/Chem simulations with MOSAIC described in Fast et al. (2005).

The surface measurements for gas and aerosol species obtained from TCEQ are used to evaluate model predictions. Both traditional measures such as the normalized mean bias (NMB) and the normalized mean gross error (NMGE), and new metrics such as the normalized mean bias factor (NMBF) and the normalized mean error factor (NMEF) are calculated. The performance of MADRID is evaluated against MADE/SORGAM and MOSAIC. Discrepancies between predictions and observations and among model results are analyzed.

4. PRELIMINARY RESULTS

The simulations are being conducted with eight processors on the NCSU's IBM blade center linux clusters. For MADRID simulation, the CIT bulk equilibrium approach is used, and the SOA module is unactivated. Figure 1 shows the spatial distribution of the 24-hr average $PM_{2.5}$ concentrations predicted on 29 August (central daylight time (CDT)), 2000. While the $PM_{2.5}$ concentrations from MOSAIC are slightly higher than those from MADRID, both results are generally consistent in terms of the synoptic pattern and "hot spots". Figure 2 compares the 2-day time series plots of hourly $PM_{2.5}$ concentrations predicted by both modules against the observational data at five sites in the vicinity of Houston: Conroe C65 (CONR, north of Houston), Houston East C1 (HOEA, near the ship channel), Channelview C15/A115 (CHAN, just north of the ship channel), Houston Deer Park 2 C35/C1001/A139 (DRPA, just south of the ship channel), Deer Park, TX, and Galveston Airport C34/A109/X152 (GALC, near coast). The simulation results from both modules are quite similar during most time periods with differences less than 1 $\mu g\ m^{-3}$ (within 10%). The differences are between 1-7.3 $\mu g\ m^{-3}$ (10-29%) for a few hours, with relatively large differences occurring at HOEA/CHAN (15-29.2%) and DRPA (20-28.8%) between 3-6 p.m. CDT 29 August. Simulations with both modules overpredict the 24-hr average $PM_{2.5}$ concentrations at DRPA, but give better agreement overall at other sites.

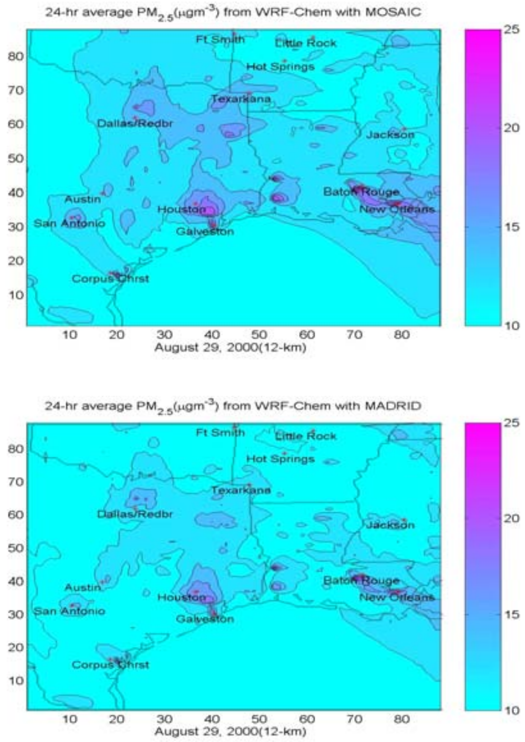

Figure 1. The spatial distribution of the 24-hr average $PM_{2.5}$ concentrations predicted by WRF/Chem with MOSAIC (Top) and MADRID (bottom) on 29 August (CDT), 2000.

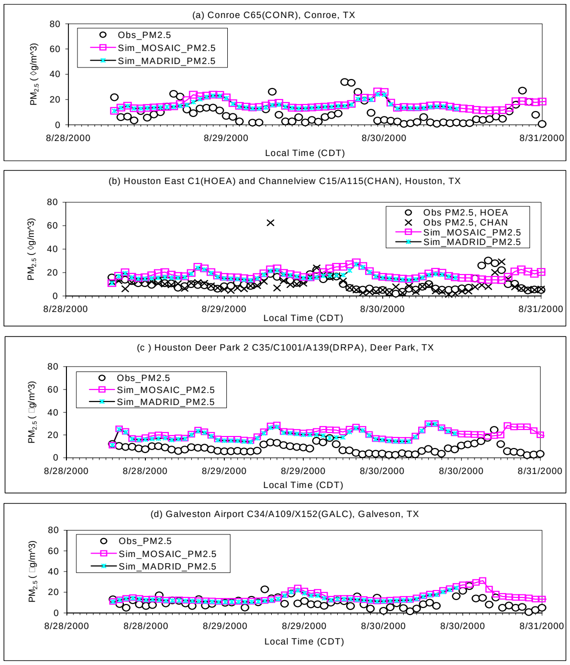

Figure 2. The time series of observed and predicted 24-hr average $PM_{2.5}$ concentrations predicted by MOSAIC and MADRID at (a) CONR; (b) HOEA and CHAN (both sites fall into the same model grid cell); (c) DRPA, Deer Park, TX; and (d) GALC.

5. CONCLUDING REMARKS

MADRID has been incorporated into WRF/Chem and is being compared with two existing aerosol modules in WRF/Chem: MADE/SORGAM and MOSAIC in terms of spatial and temporal distributions. The model predictions are being compared against available observational data. Statistics will be calculated to provide a quantitative overall assessment of the model/module performance. Discrepancies and their likely causes between predictions and observations and among results with three different aerosol models will be identified. The initial focus of the evaluation is the mixing ratios of gas-phase species and the mass concentrations of $PM_{2.5}$ and its inorganic composition. The evaluation will be extended to predicted SOA, particle number and size distributions, once the modules for SOA formation and coagulation are incorporated into the current version of MOSAIC and MADRID in WRF/Chem. A more rigorous evaluation that includes all these key elements will provide a complete understanding of differences in aerosol treatments and the resultant discrepancies in model predictions, as well as necessary improvements for accurate model predictions.

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Table 1. Gas-phase mechanisms and aerosol modules in WRF/Chem.

Process	**MADE/SORGAM**	**MOSAIC**[1]	**MADRID**[1]
Gas-phase mechanism	RADM2, RACM	CBM-Z	CBM-Z
Aerosol processes			
size distribution	Three modes over 0.01 – 10 µm	Eight sections over 0.039 – 10 µm	Eight sections over 0.0216 – 10 µm
inorganic species	Thermodynamic equilibrium for sulfate, nitrate, ammonium, and water with MARS-A	Thermodynamic equilibrium for sulfate, nitrate, ammonium, sodium, calcium, chloride and water with MESA-MTEM	Thermodynamic equilibrium for sulfate, nitrate, ammonium, sodium, chloride and water with ISORROPIA
organic species	Reversible absorption parameterization for products of 8 classes of VOC precursors	Dynamic reversible absorption of 8 classes of secondary organic aerosol (SOA) species (based on SORGAM mechanism)	MADRID 1: Reversible absorption for 38 condensable species MADRID 2: Reversible absorption & dissolution for 42 condensable VOCs grouped into 5 hydrophobic and 5 hydrophilic surrogate SOA species)
nucleation	Binary homogeneous nucleation of sulfuric acid	None	Binary homogeneous nucleation of sulfuric acid
coagulation	Modal approach	None	None
condensational growth/shrinkage by volatilization	Modal approach	Sectional approach with ASTEEM	Sectional approach with the implicit or explicit approach + the moving center method
gas/particle mass transfer	Full equilibrium approach with two chemical regimes: sulfate-poor and sulfate-rich	Dynamic approach with ASTEEM	1. Full equilibrium approach 2. Hybrid approach 3. Dynamic approach

[1] The current versions of MOSAIC and MADRID incorporated into WRF/Chem do not simulate SOA.