Recent Developments in the CMAQ Modal Aerosol Module

Prakash Bhave, Chris Nolte, Jon Pleim, Donna Schwede, and Shawn Roselle

Atmospheric Sciences Modeling Division, Air Resources Laboratory, NOAA, Research Triangle Park, NC

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OBJECTIVES

- Summarize unique features of the AERO3 module.
- Highlight the aerosol-module updates in CMAQ v4.5.
- Describe new aerosol diagnostic tools released with CMAQ v4.5.

Unique Features of the AERO3 Module:

- *Inorganic Thermodynamics.* Incorporated the ISORROPIA module and improved its numerical stability (Nenes *et al*., 1998; Bhave *et al*., 2004a).
- *Secondary Organic Aerosol* (SOA). Revised treatment based on the absorptive-partitioning theory of Pankow (1994).
- *Heterogeneous Nitrate Production.* Added hydrolysis of $N_2O_{5\,(g)}$ by particle-phase liquid water, an important nighttime process (Riemer *et al*., 2003).
- *Aerosol Dry Deposition.* Updated the impaction term (Giorgi, 1986), resulting in enhanced deposition.
- *Computational Efficiency.* Developed efficient methods for calculating coagulation coefficients and partitioning semi-volatile organic compounds (Bhave *et al*., 2004a).
- *Source-Specific Emissions Speciation.* $PM_{2.5}$ emissions from each source category are speciated into elemental carbon, organic carbon, sulfate, nitrate, and other material, rather than applying a default profile to all sources.

Figure 1. Schematic representation of the size distribution and chemical composition of particulate matter in the AERO3 module.

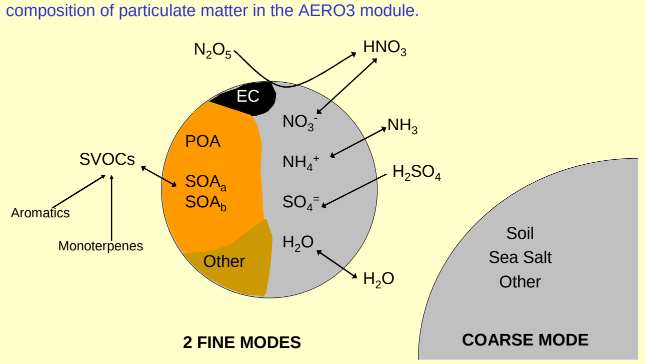


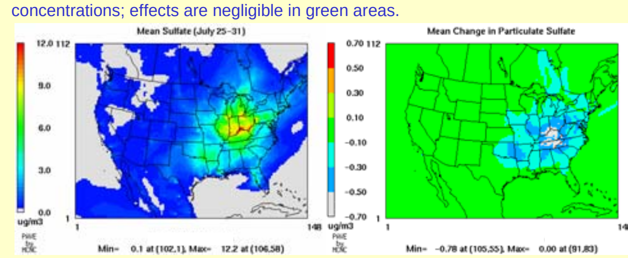
Table 1. Comparison of AERO3 with earlier work.

	AERO	AERO2	AERO3
Primary Reference	Binkowski & Shankar (1995)	Binkowski & Roselle (2003)	this work
Host Air Quality Model	Regional Particulate Model (RPM) and prototype CMAQ versions	CMAQ versions 4.0 - 4.2.2	CMAQ versions 4.2.1 - 4.5
Size Distribution			
Lognormal Modes	nuclei (i), accumulation (j)	Aitken (i), accumulation (j), & coarse (c)	Aitken (i), accumulation (j), & coarse (c)
Moments			
Fine Modes (i, j)	0, 3, 6	0, 2, 3	0, 2, 3
Coarse Mode	NA	0, 3	0, 3
Standard Deviation			
Fine Modes (i, j)	Fixed	Variable	Variable
Coarse Mode	NA	Fixed	Fixed
Chemical Components			
Fine Modes (i, j)	SO_4, NH_4, H_2O	SO_4, NH_4, NO_3, POA, EC, SOA_a, SOA_b, H_2O, Other	SO_4, NH_4, NO_3, POA, EC, SOA_a, SOA_b, H_2O, Other
Coarse Mode	NA	soil, sea salt, other	soil, sea salt, other
Emissions			
Fine Modes (i, j) **- chemical speciation** **- mass distribution**	SO_4 only (i = 15%, j = 85%)	Default speciation for all sources OC, EC (i = 0.1%, j = 99.9%) SO_4 NO_3, other (j = 100%)	Source-specific speciation OC, EC (i = 0.1%, j = 99.9%) SO_4 NO_3, other (j = 100%)
Coarse Mode speciation	NA	90% soil, 10% other, no sea salt	90% soil, 10% other, no sea salt
Removal			
Dry Deposition	Slinn (1982)	Slinn (1982)	Giorgi (1986)
MIcrophysical Processes			
Cond./Evap.			
Fine Modes (i, j)	Condensation only	Instantaneous equilibrium	Instantaneous equilibrium
Coarse Mode	NA	None	None
Coagulation	analytic solution	i & j only - numerical quadrature	i & j only - analytic solution using tabulated correction factors
Nucleation	Kerminen & Wexler (1994)	Harrington & Kreidenweis (1998) Kulmala *et al*. (1998)	Kulmala *et al*. (1998)
Mode Merging	None	Aitken to accumulation	Aitken to accumulation
Chemical Processes			
Inorganic Equilibrium Module	MARS w. revised H_2O data	ARIES	ISORROPIA
Secondary Organics	None	condensation only	reversible partitioning
Heterogenous NO_3 Production	None	None	Riemer *et al*. (2003)

Significant Aerosol Updates in CMAQ v4.5:

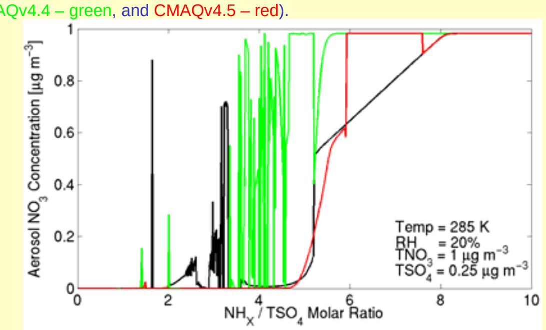
Aerosol Dry Deposition. The impaction term has been modified from the smooth-surface parameterization of Slinn (1982) to a parameterization that is more appropriate for vegetated surfaces (Giorgi, 1986), resulting in greater deposition velocities for accumulation-mode particles. Concentrations of all particulate species decline, but the effect on sulfate is most pronounced as shown in Figure 2. In addition, the impaction term was added for coarse particles and the resistance term was modified in accordance with Venkatram and Pleim (1999). The two latter changes have a negligible impact on model results for $PM_{2.5}$.

Figure 2. Effect of revised dry-deposition codes on sulfate concentrations in the lowest layer of a 36-km CMAQ domain. On left, CMAQ v4.5 result. On right, difference resulting from deposition updates while all other processes are held constant. Negative values show where the v4.5 code results in lower concentrations; effects are negligible in green areas.



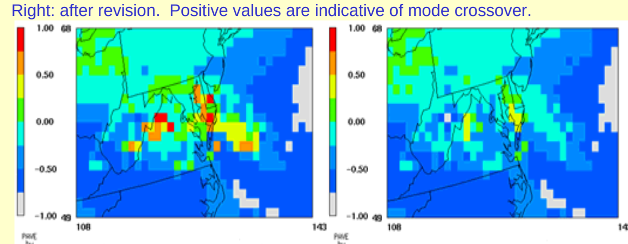
ISORROPIA Numerical Stability. The AERO3 module was updated to include ISORROPIA version 1.5 with October 2003 revisions of the Zdanovskii-Stokes-Robinson (ZSR) correlation parameters. Use of these updated parameters smoothes out the discontinuities in CMAQv4.4 reported by Bhave et al. (2004a), as shown in Figure 3. In addition to the ZSR parameter updates, a bug was fixed in the retrieval of Kusik-Meissner binary activity coefficients within ISORROPIA v1.5. Still, some numerical discontinuities are encountered in upper layers of CMAQ v4.5 simulations (Young and Pleim, 2005). Further improvements in numerical stability may be warranted at high-elevation and in wintertime conditions.

Figure 3. Variation in particulate nitrate as a function of total ammonia at fixed temperature, relative humidity, total-nitrate concentration, and sulfate concentration, in box-model tests of different versions of ISORROPIA (CMAQv4.3 – black, CMAQv4.4 – green, and CMAQv4.5 – red).



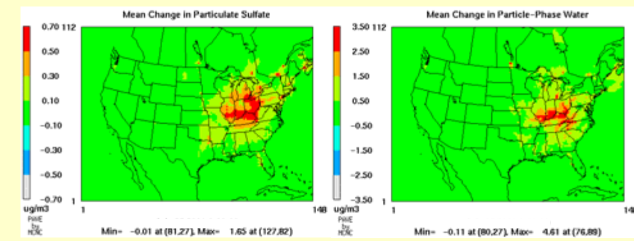
Mode Merging. An error in the mode-merging section of the aerosol-processes subroutine was fixed, thereby eliminating the most extreme cases of "mode crossover" (instances where the Aitken-mode diameter grows larger than the accumulation mode) as shown in Figure 4. Some minor crossover still occurs in CMAQv4.5, warranting further investigation.

Figure 4. Effect of mode-merging revision on the most extreme occurrences of mode crossover — measured as $\log_{10}(D_{g,Aitken}/D_{g,accum})$ — in the lowest layer of a July 22–31 simulation on a 36-km contiguous U.S. domain. Left: before revision. Right: after revision. Positive values are indicative of mode crossover.



H_2SO_4 Emissions. An error in the conversion of gas-phase H_2SO_4 emissions into sulfate was fixed, resulting in enhanced particulate sulfate concentrations in regions with high H_2SO_4 emissions (e.g., Ohio River valley). The effect of this code revision on sulfate negates the effects of the dry-deposition modifications described earlier (compare right panel of Figure 2 with left panel of Figure 5). Due to the hygroscopicity of sulfate, particle-phase water increases significantly with the revised code, as shown in the right panel of Figure 5. This error was reported by Jinyou Liang of the California Air Resources Board and, later, by Atmospheric Environmental Research, Inc.

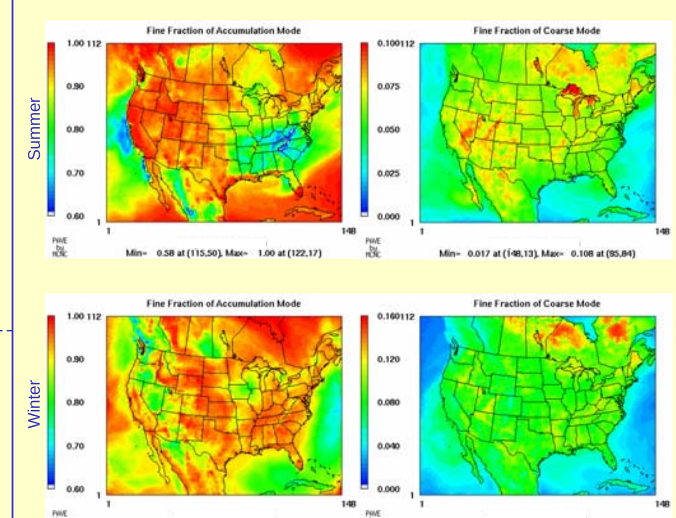
Figure 5. Effects of the revised H_2SO_4-emissions conversion on 7-day average particulate sulfate (left) and particle-phase water (right) concentrations in the lowest layer of a 36-km domain (July 25 – 31, 2001). Positive values indicate that concentrations increase in the revised code; effects are negligible in green areas. Note the differences in scale.



New Aerosol Diagnostic Tools in CMAQ v4.5:

$PM_{2.5}$ Calculations. A new subroutine has been added to the AERO3 module to calculate the volume fraction of each mode that is composed of particles smaller than 2.5μm aerodynamic diameter. Following the methodology of Jiang et al. (2005), these new diagnostic variables facilitate a more rigorous calculation of $PM_{2.5}$ than the summation of Aitken and accumulation modes. Summer and winter 36-km simulations with these new diagnostic variables indicate that, on average, 10–15% of the coarse mode falls within the $PM_{2.5}$ size range and up to 40% of the accumulation mode exceeds 2.5 μm in aerodynamic diameter.

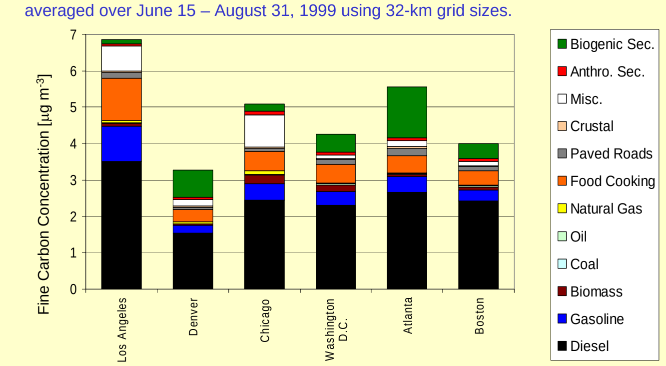
Figure 6. Fractions of the accumulation mode (left) and coarse mode (right) in the $PM_{2.5}$ size range. Upper panels display summer averages (July 25–31, 2001) and lower panels display winter averages (January 4–10, 2001) in the surface layer.



Sulfate Tracking. CMAQv4.5 includes an optional diagnostic model configuration that provides detailed information on the modeled sulfur budget. This model version tracks sulfate production from the gas-phase and the five aqueous-phase chemical reactions, as well as contributions from direct emissions and initial and boundary conditions. Each of the tracked species is advected, diffused, processed through clouds, and deposited (both wet and dry) individually. This is a valuable tool for probing the nonlinear nature of atmospheric sulfate production.

Primary Carbon Source Apportionment. New codes released with CMAQ v4.5 provide users the option to track the contributions of elemental carbon and primary organic carbon from up to 10 different source categories or source regions. A detailed description of this model option is provided by Bhave et al. (2004b).

Figure 7. Example of the carbon source-apportionment results at selected cities, averaged over June 15 – August 31, 1999 using 32-km grid sizes.



FUTURE DIRECTIONS

- *Transition to AERO4*. Version 4.5 of CMAQ contains the final update of the AERO3 module. It will not be supported beyond v4.6. A prototype version of the AERO4 module is released in v4.5, so users may transition to the new aerosol module during the coming year. All of the updates described here have been incorporated in AERO4.
- *Sea Salt*. The main scientific enhancement in AERO4 is the treatment of sea-salt emissions and chemistry. Preliminary results from the AERO4 module are provided by Shankar et al. (2005).
- *Secondary Organic Aerosol*. A significant collaborative effort between NOAA and EPA scientists is underway to revamp the SOA module in a future release of CMAQ. Details about this effort are provided by Offenberg et al. (2005).

REFERENCES

Bhave, P.V., S.J. Roselle, F.S. Binkowski, C.G. Nolte, S. Yu., G.L. Gipson, and K.L. Schere, 2004a, CMAQ aerosol module development: Recent enhancements and future plans. *3rd Annual CMAS Models-3 User's Conference, October 18-20, 2004, Chapel Hill, NC,* Paper 6.8.

Bhave, P.V., G.A. Pouliot, and M. Zheng, 2004b, Source apportionment of primary carbonaceous aerosol using the Community Multiscale Air Quality model. *Preprints, 27th NATO/CCMS International Technical Meeting on Air Pollution Modeling and its Applications, October 24-29, 2004, Banff, Alberta, Canada*. NATO/CCMS, 25–32.

Binkowski, F.S. and U. Shankar, 1995, The regional particulate matter model 1. Model description and preliminary results, *J. Geophys. Res.*, 100: 26191–26209.

Binkowski, F.S. and S.J. Roselle, 2003, Models-3 Community Multiscale Air Quality (CMAQ) model aerosol component 1. Model description, *J. Geophys. Res.*, 108(D6), 4183, doi:10.1029/2001JD001409.

Giorgi, F., 1986, A particle dry deposition scheme for use in tracer transport models, *J. Geophys. Res.*, 91: 9794–9806.

Harrington, D.Y. and S.M. Kreidenweis, 1998, Simulations of sulfate aerosol dynamics, part I, model description, *Atmos. Environ*., 32: 1691–1700.

Jiang, W., S. Smyth, E. Giroux, H. Roth, and D. Yin, 2005, Differences between CMAQ fine mode particle and $PM_{2.5}$ concentrations and their impact on model performance evaluation in the Lower Fraser Valley, *Atmos. Environ*., in press.

Kerminen, V.-M. and A.S. Wexler, 1994, Post-fog nucleation of H_2SO_4-H_2O particles in smog, *Atmos. Environ*., 28: 2399–2406.

Kulmala, M., A. Laaksonen, and L. Pirjola, 1998, Parameterization of sulfuric acid/water nucleation rates, *J. Geophys. Res.*, 103: 8301–8307.

Nenes, A., S.N. Pandis, and C. Pilinis, 1998, ISORROPIA: A new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols, *Aquatic Geochemistry*, 4:123-152.

Offenberg, J., E. Edney, M. Lewandowski, M. Jaoui, P. Bhave, C. Nolte, and G. Sarwar, 2005, Development and evaluation of an improved SOA representation in the CMAQ model. 4th *Annual CMAS Models-3 User's Conference, September 26-28, 2005, Chapel Hill, NC,* Late-breaking poster.

Pankow, J.F., 1994, An absorption model of the gas/aerosol partitioning involved in the formation of secondary organic aerosol, *Atmos. Environ.*, 28:189-193.

Riemer, N., H. Vogel, B. Vogel, B. Schell, I. Ackermann, C. Kessler, and H. Hass, 2003, Impact of the heterogeneous hydrolysis of N_2O_5 on chemistry and nitrate aerosol formation in the lower troposphere under photosmog conditions, *J. Geophys. Res.*, 108(D4), 4144, doi:10.1029/2002JD002436.

Shankar, U., P.V. Bhave, and J.M. Vukovich, 2005, Implementation and initial applications of sea salt aerosol emissions and chemistry algorithms in the operational CMAQ. 4th *Annual CMAS Models-3 User's Conference, September 26-28, 2005, Chapel Hill, NC,* Poster P.6.

Slinn, W.G.N., 1982, Predictions for particle deposition to vegetative canopies, *Atmos. Environ.*, 16: 1785–1794.

Venkatram, A. and J. Pleim, 1999, The electrical analogy does not apply to modeling dry deposition of particles, *Atmos. Environ.*, 33: 3075–3076.

Young, J. and J. Pleim, 2005, Layer dependent advection in CMAQ. 4th *Annual CMAS Models-3 User's Conference, September 26-28, 2005, Chapel Hill, NC,* Poster P.15.