DEVELOPMENT OF A MULTIPOLLUTANT VERSION OF THE COMMUNITY MULTISCALE AIR QUALITY (CMAQ) MODELING SYSTEM

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1. INTRODUCTION

One of the original ideas in developing the Community Multiscale Air Quality (CMAQ) modeling system was to provide a "one-atmosphere" approach for air quality modeling. In recent years, there has been increasing interest in modeling multipollutants, including criteria and hazardous air pollutants, in a single modeling framework for air quality management (Scheffe et al., 2007). To address this need and further advance the model to its one-atmosphere modeling capability, a multipollutant version of the CMAQ modeling system has been developed to predict ozone, particulate matter (PM), mercury, and 38 other hazardous air pollutants (HAPs) in a single configuration. The new model will support regional and urban studies that assess the potential co-benefits and effectiveness of various emission control programs such as the Clean Air Interstate Rule, Clean Air Mercury Rule, Clean Air Visibility Rule, and various onroad and nonroad mobile source rules. It will also support future assessment studies based on integrated HAPs and criteria pollutant national emission inventories. The multipollutant model was developed by modifying and merging algorithms for gas chemistry, aerosols, clouds, and emissions used in the mercury and HAPs versions of the CMAQ modeling system. The Carbon Bond 05 (CB05) chemical mechanism has been combined with the chemical reactions for chlorine, mercury, and HAPs, and implemented into the CMAQ modeling system. A normalization process was also performed to test the model and to insure that the multipollutant model is consistent with the original versions. Results suggest that consistency is achieved by including the emissions and chemistry of molecular chlorine (Cl_2) and hydrochloric acid (HCl) in each model version.

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2. MODEL DEVELOPMENT

CMAQ includes state-of-science capabilities for modeling multipollutant problems, including tropospheric ozone, fine particles, HAPs, acid deposition, and visibility degradation. However, the latest release of CMAQ (version 4.6 – CMAQv4.6) simulates mercury separately from other HAPs using different model configurations. The HAPs version of CMAQ (Hutzell et al., 2006; Luecken et al., 2006) includes 31 additional gas-phase species, 6 toxic metals, and diesel PM. The HAPs chemical mechanism selected for the multipollutant model supplements the Carbon Bond 05 (CB05) (Sarwar et al., 2007; Yarwood et al., 2005), with reactions for HAPs. The mercury version of CMAQ (Bullock and Brehme, 2006) includes elemental mercury, divalent gaseous mercury, and particulate mercury. The mercury version of CB05 includes reactions for mercury and chlorine chemistry. The cloud chemistry includes seven aqueous mercury chemical reactions. Both the HAPs and mercury models include modified versions of the aerosol module version 4 (aero4).

Constructing the multipollutant model was relatively straightforward. The effort merged chemical mechanisms and other algorithms from the HAPs and mercury models. The chemical mechanism (*cb04txhg_ae4_aq*) consists of 219 reactions, which includes 156 reactions from the

base CB05 mechanism, 21 reactions for chlorine chemistry, 38 reactions for gas-phase HAPs, and 4 reactions for mercury. There are 169 model species in the multipollutant model. Table 1 shows the number of species for each model configuration and shows the breakdown between gas-phase, aerosol, and non-reactive species. A fast chemical solver (*ebi_cb05txhg*) was created for the new mechanism. Multipollutant versions of the aerosol module (*aero4_txhg*) and aerosol emissions in the vertical diffusion modules (*eddy_txhg* and *acm2_txhg*) reflect the combined capabilities from HAPs and mercury. The multipollutant model uses the mercury version of the aerosol dry deposition module (*aero_depv2_hg*) since no special modifications were required for HAPs. The aqueous chemistry in the cloud module (*cloud_acm_txhg*) is largely based on the mercury version because of the extensive changes required for the mercury model. There were some inconsistencies in the chlorine chemistry and emissions between the HAPs and mercury model versions that will be demonstrated in the model tests in the following section, but these issues were addressed and resolved.

Table 1. Number of Modeled Species by Chemical Mechanism

Mechanism	Gas-phase	Aerosol	Non-reactive	Total Species *(total transported)*
Base CB05 *cb05_ae4_aq*	56	34	12	102 *(79)*
CB05 w/chlorine *cb05cl_ae4_aq*	62	34	11	107 *(82)*
CB05 w/mercury *cb05hg_ae4_aq*	65	36	11	112 *(88)*
CB05 w/HAPs *cb05cltx_ae4_aq*	73	58	33	164 *(141)*
CB05 Multipollutant *cb05txhg_ae4_aq*	76	60	33	169 *(147)*

3. MODEL TESTS

For this study, model simulations were tested for the period of July 22-31, 2001. The modeling domain covered the continental U.S. with 36 km x 36 km grid resolution and 14 vertical layers. Meteorological data were prepared using the fifth-generation Penn State-NCAR Mesoscale Model (MM5) system (Grell et al., 1994). Initial and boundary conditions were set to clean conditions (default profile data). Emissions data were created by merging existing emissions files from previous HAPs and mercury model studies; both are based on the 1999 National Emissions Inventory (NEI) for criteria air pollutants (CAPs) and HAPs, while estimates for natural emissions of elemental mercury from land, oceans and volcanoes were obtained from the work of Seigneur et al. (2004). Simulations were performed with models for HAPs, mercury, multipollutant, CB05 with chlorine chemistry, and base-CB05.

3.1 Initial Results

Some of the largest differences in results between the different model configurations (HAPs, mercury, multipollutant, and CB05 with chlorine chemistry) were related to chlorine species. Figures 1 and 2 show the 10-day average Cl_2 concentrations for the HAPs model and multipollutant model, respectively. Note that the scales are different in both plots. The most striking feature in comparing these figures is that Cl_2 concentrations are several orders of magnitude smaller in the HAPs model than in the multipollutant model. In the HAPs model, Cl_2 and HCl emissions were zeroed out to keep ozone (O_3) predictions consistent with the base CB05 model. Comparing O_3 between the HAPs and multipollutant models showed differences as large as 36 ppb in Utah, because of differences in each model's treatment of Cl_2 emissions.

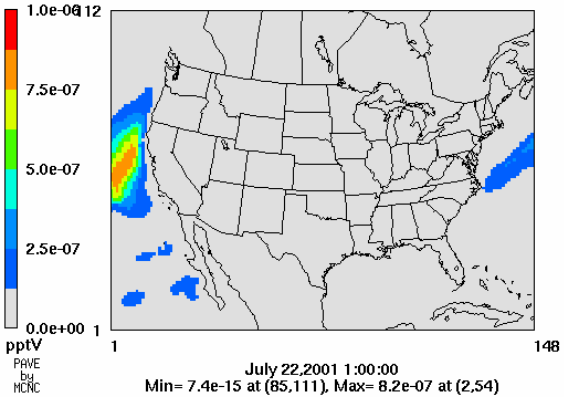

Fig. 1. 10-day average Cl_2 concentrations from the HAPs model simulation.

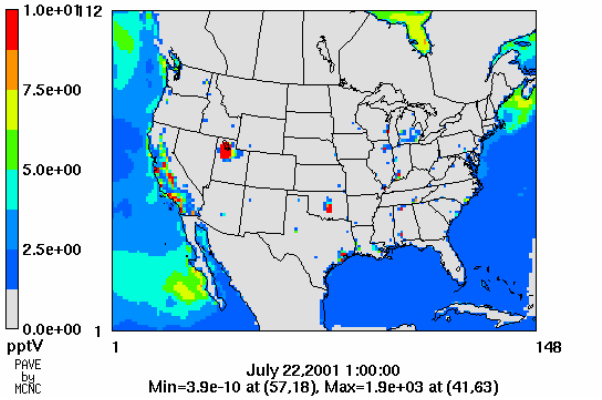

Fig. 2. 10-day average Cl_2 concentrations from the multipollutant model simulation (mercury and CB05 with chlorine chemistry models show nearly identical results).

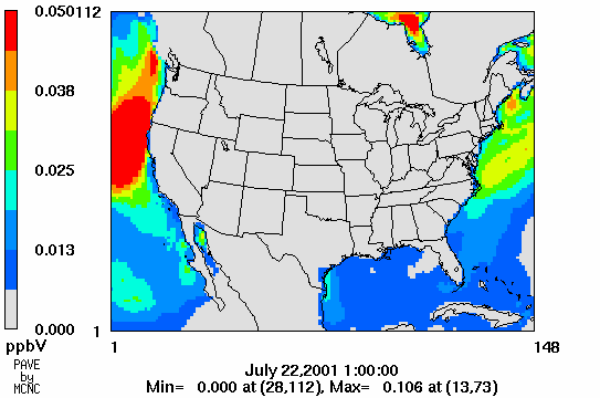

Fig. 3. 10-day average HCl concentrations from the HAPs model simulation.

Figures 3 and 4 show the 10-day average HCl concentrations for the HAPs and CB05 with chlorine chemistry models. In the HAPs model simulation, HCl concentrations are highest over the oceans. Contrast this to the CB05 with chlorine chemistry model results and differences are noted in Utah, California, and over the open ocean. The differences in HCl between these model results derive mostly from the HAPs model not including Cl_2 emissions. Although the chlorine chemistry in the HAPs model is nearly identical to the CB05 with chlorine model, it does include an additional gas-phase reaction of HCl with hydroxyl radical (OH):

$$HCl + OH \rightarrow Cl + H_2O \qquad (1)$$

This reaction was added to the HAPs model to be consistent with the loss processes included for other gas-phase HAPs. The reaction also may be important in controlling Cl concentrations over polluted coastal areas (Keene et al., 2007). For the most part, the impact of this reaction on HCl concentrations is negligible.

Figure 5 shows very different results for the mercury model simulation; HCl concentrations are much higher for the mercury model over the interior U.S. (especially over the Ohio valley). There was an unintended feedback of HCl and aerosol Cl^- in the mercury model that resulted from a background value set in the aqueous chemistry model for Cl^-.

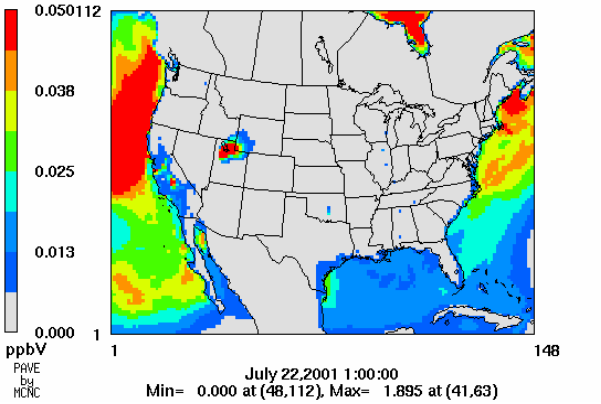

Fig. 4. 10-day average HCl concentrations from the CB05 with chlorine chemistry model simulation.

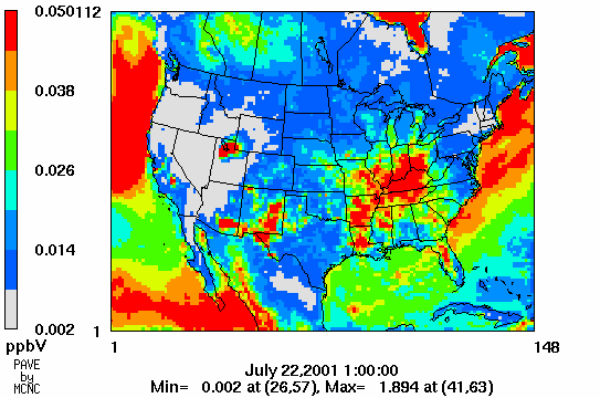

Fig. 5. 10-day average HCl concentrations from the mercury model simulation.

Figure 6 shows the average HCl concentrations for the multipollutant model. For this model, the aqueous chloride ion concentration was reduced by 4 orders of magnitude to minimize the feedback into the model species. Hydrochloric acid emissions were included and results show a direct impact over the Eastern U.S. (modeled HCl concentrations are higher than simulated by the other model configurations). In the 1999 NEI, the major emissions sources for HCl are coal-fired utility boilers. HCl emissions were included to provide the aqueous chemistry routine with simulated Cl^- instead of relying on background values.

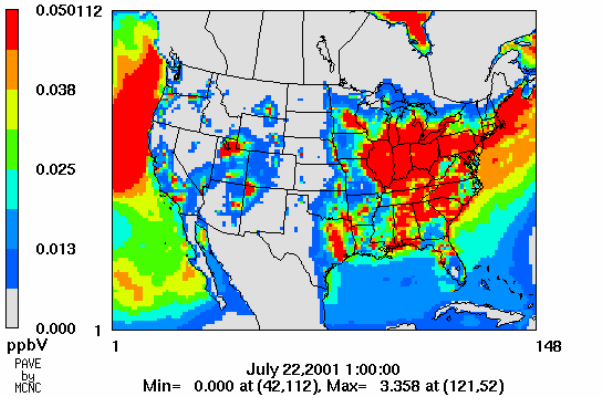

Fig. 6. 10-day average HCl concentrations from the multipollutant model simulation with aqueous chemistry modification and with HCl emissions included.

3.2 Normalization

Based on the initial testing, differences in chlorine treatment were identified in each of the CMAQ model versions. The following changes have been implemented in CMAQ and are planned to be included in the next release of the model.

1) Molecular chlorine emissions will be included in the HAPs model.

2) For all model versions that have chlorine chemistry, HCl emissions will be included.

3) The background chloride ion concentration in aqueous chemistry has been reduced to minimize artificial feedbacks into gas and aerosol species. This only affects the mercury and multipollutant versions of the model.

4) The chemical reaction of HCl with OH will be included in the mercury and CB05 with chlorine chemistry models to have a consistent set of reactions across all model versions.

The test cases were rerun using the updated model codes. Results for the 10-day test period showed that hourly O_3 concentrations for different model configurations (multipollutant, HAPs, mercury, and CB05 with chlorine chemistry) agreed to within ±0.5 ppb. Hourly sulfate aerosol concentrations agreed to within ±1 μg/m^3. Table 2 compares the average elapsed time for different configurations of the model for the test cases presented in the study. Results are shown for simulations using two gas-phase chemical solvers, Rosenbrock (ros3) and Euler Backward Iterative (ebi). Note that the elapsed-time for each simulation roughly scales with the number of transported species for each model (compare with Table 1).

Table 2. Average Elapsed Time (minutes) per Simulation Day for Different Model Configurations[1]

Model	Chemical Solver	
	ros3	ebi
Base CB05	19.9	16.6
CB05 w/chlorine chemistry	22.2	18.9
CB05 w/mercury	23.8	20.7
CB05 w/HAPs	33.7	30.7
CB05 Multipollutant	35.9	32.0

[1]Simulations were performed on an SGI-Altix 4700 supercomputer using 8 processors per run.

4. CONCLUSIONS

A multipollutant version of CMAQ has been developed and tested. Initial applications and evaluation are underway, and may indicate other refinements are necessary before this model is released to the public. The multipollutant model is planned to be included in the next official release in the fall of 2008. Based on the initial tests we have conducted, the CB05 mechanism with chlorine chemistry would be the base model configuration in the next model release to achieve consistent results across model configurations.

DISCLAIMER

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 DW13921548. This work constitutes a contribution to the NOAA Air Quality Program. Although it has been reviewed by EPA and NOAA and approved for publication, it does not necessarily reflect their policies or views.

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