ATMOSPHERIC MERCURY SIMULATION WITH CMAQ VERSION 4.5.1

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1. HISTORY OF MERCURY MODELING WITH CMAQ

The first attempts to use the Community Multi-scale Air Quality (CMAQ) model for atmospheric mercury simulation were made in 2000 with the addition of two chemical reactions of mercury into an experimental version of the AQCHEM cloud-chemistry mechanism, 1) oxidation of mercury by ozone, and 2) spontaneous reduction of mercuric sulfite to form elemental mercury (Hg^0). This experimental version of AQCHEM continued to evolve and was operated independently outside of the full CMAQ framework as part of an intercomparison study of mercury chemistry models available at that time (Ryaboshapko *et al.*, 2002).

The first full-scale test applications of the CMAQ with mercury added were conducted in 2001. At that time, the spontaneous reduction of aqueous mercuric sulfite was thought to occur very rapidly ($\approx 0.6\ s^{-1}$) and a very small time increments was required for the solution of the aqueous chemistry simulation. This increased the computational demand of the CMAQ with mercury to many times that of the standard non-mercury model and the longest practical simulation episode was only a few days. Fortunately, subsequent chemical kinetics research (van Loon *et al.*, 2000) showed this reduction rate to be much slower ($\approx 0.01\ s^{-1}$). Using this slower kinetic rate, the addition of mercury to CMAQ model simulations required only a 30-40% premium in computing resources. This version of the CMAQ mercury model is described in Bullock and Brehme (2002).

During 2003 and 2004, the overall CMAQ model was reconfigured for greater computational efficiency. These general improvements came at just the right time. In 2004, the CMAQ mercury model was used for the U.S. EPA's development of the Clean Air Mercury Rule (CAMR). From 2004 to 2005, the EPA Office of Research and Development worked with the EPA Office of Air and Radiation to apply the CMAQ mercury model to simulate a number of retrospective and hypothetical full-calendar-year episodes.

During the CAMR model application process, minor refinements were made to the gaseous and aqueous chemical mechanisms for mercury. After the CAMR modeling was completed, new research suggested that elemental mercury could dry deposit to vegetation at a considerable rate. To account for this, another round of modifications were made to the mercury model in preparation for its first public release as part of CMAQ version 4.5.1 in March of 2006.

2. MERCURY-SPECIFIC MODIFICATIONS

The gaseous chemistry, aqueous chemistry and wet and dry deposition processes in the standard version of the CMAQ were modified to simulate atmospheric mercury. The gaseous chemistry mechanism including mercury is a modification of the CB-IV mechanism (Gery *et al.*, 1989; Gipson and Young, 1999) where four additional reactions shown in Table 1 have been added. Four mercury species were added to the model: elemental gaseous mercury (species name: HG), divalent gaseous mercury (species name: HGIIGAS), I-mode aerosol mercury (species name: APHGI), and J-mode aerosol mercury (species name: APHGJ).

Table 1. Gaseous mercury reactions

$Hg^0_{(g)} + O_{3(g)} \rightarrow$ 50% HGIIGAS, 50% APHG

$Hg^0_{(g)} + Cl_{2\,(g)} \rightarrow$ HGIIGAS

$Hg^0_{(g)} + H_2O_{2\,(g)} \rightarrow$ HGIIGAS

$Hg^0_{(g)} + OH_{(g)} \rightarrow$ 50% HGIIGAS, 50% APHG

Note: APHG includes both I-mode and J-mode mercury aerosols based on separate modeling of the modal aerosol production rates.

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It should be noted that “divalent gaseous mercury” is a term describing all chemically-stable oxidized gaseous compounds of mercury believed to exist in the atmosphere. No method currently exists to measure the ambient air concentrations of each of the individual mercury compounds that may exist. Instead, gaseous atmospheric mercury can be measured as two components; 1) elemental gaseous mercury which is rather inert, and 2) divalent gaseous mercury which is more water soluble and chemically reactive. Due to its special properties, divalent gaseous mercury is often referred to by the operational term “reactive gaseous mercury” or “RGM”.

Simulation of mercury also involves a treatment of aqueous chemistry with a special version of the AQCHEM routine, a treatment of aerosol dynamics with a special version of the AE3 code, and simulation of chlorine using the capability added with CMAQ version 4.5 (CMAS, 2005). The cloud chemistry mechanism in AQCHEM has been modified to include seven aqueous mercury chemical reactions as shown in Table 2.

Table 2. Aqueous mercury reactions

$Hg^0_{(aq)} + O_{3(aq)} \rightarrow Hg^{2+}_{(aq)}$ + products

$HgSO_{3\,(aq)} \rightarrow Hg^0_{(aq)}$ + products

$Hg(OH)_{2\,(aq)} + h\nu \rightarrow Hg^0_{(aq)}$ + products

$Hg^0_{(aq)} + OH_{(aq)} \rightarrow Hg^{2+}_{(aq)}$ + products

$Hg^{2+}_{(aq)} + HO_{2\,(aq)} \rightarrow Hg^0_{(aq)}$ + products

$Hg^0_{(aq)} + HOCl_{(aq)} \rightarrow Hg^{2+}_{(aq)}$ + products

$Hg^0_{(aq)} + OCl^-_{(aq)} \rightarrow Hg^{2+}_{(aq)}$ + products

A schematic diagram of the entire aqueous chemical system for mercury is shown in Figure 1. Aqueous Hg^{2+} species are partially bound to suspended carbon and isolated from the redox chemistry based on a method adapted from Seigneur *et al.* (1998). As mentioned above, some aqueous chemical reactions of mercury are faster than the non-mercury reactions previously in the model. The iterative solution criteria used to solve the aqueous chemical system were modified to maintain numerical stability and accuracy. Solution of the aqueous chemical model with mercury added still requires an increase in the number of time steps. However, the increase in CPU time for the entire model calculation is now only 10 to 20% depending on the fraction of finite volumes where cloud water is present.

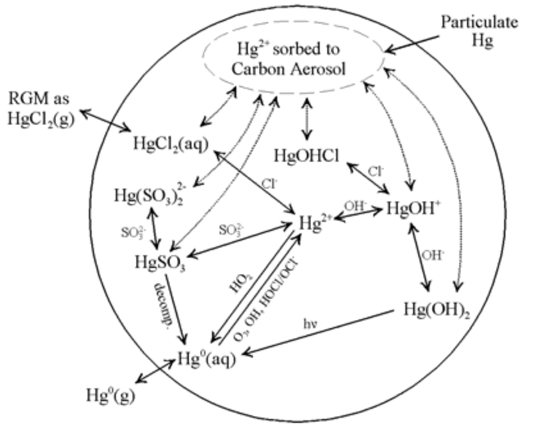

Figure 1. Schematic diagram of the aqueous mercury chemical system in CMAQ

3. MERCURY SCIENCE ADVANCES IN VERSION 4.5.1

CMAQ version 4.5.1 contains a number of science updates for mercury beyond those described in Bullock and Brehme (2002). These updates were made to reflect new information published in the peer-reviewed scientific literature and to address comments from peer review panels that are convened periodically to evaluate EPA and NOAA research programs.

The gaseous mercury chemistry described in Bullock and Brehme (2002) was modified as follows: (1) the Hg^0 reaction with hydrogen peroxide assumes the formation of 100% divalent gaseous mercury rather than 100% aerosol mercury; (2) the Hg^0 reaction with ozone assumes the formation of 50% divalent gaseous mercury and 50% aerosol mercury rather than 100% aerosol mercury; (3) the Hg^0 reaction with hydroxyl radical assumes the formation of 50% divalent gaseous mercury and 50% aerosol mercury rather than 100% aerosol mercury; and (4) the rate constant for the gaseous HG + OH reaction was lowered slightly to 7.7×10^{-14} cm^3 $molecules^{-1}$ s^{-1} based on the lower range of the kinetic rate constant estimated by Pal and Ariya (2004).

An important limitation of the CMAQ mercury model previous to the v4.5.1 release was its lack of any explicit treatment for the exchange of Hg^0 gas between the air and various underlying surfaces. It was assumed that dry deposition of Hg^0 was relatively slow and was effectively compensated by the gaseous evasion of previously deposited mercury. This assumption was supported by the general observation of a stable global average concentration of Hg^0 in air.

More recently, chamber studies have demonstrated the ability of many types of vegetation to absorb or release Hg^0 at a considerable rate depending on environmental conditions. While the factors controlling the balance of deposition and recycling of mercury may still not be completely understood, simulation modeling can provide a valuable tool for further scientific development. Thus, these separate and opposing fluxes were added to the model using the limited process information available today.

Dry deposition of Hg^0 gas was added to the model with deposition velocity (V_d) values provided from the Meteorological-Chemical Interface Processor version 3.1 (MCIP v3.1). Important variables affecting the dry deposition of gases include molecular diffusivity, water solubility and vapor pressure. The molecular diffusivity of Hg^0 is obtained from Massman (1999) and its water solubility and vapor pressure are accounted for using a Henry's law constant from Clever *et al.* (1985).

The uptake of a gaseous substance to any surface is limited to some degree by the concentration of that substance already present in the surface materials. The current CMAQ model structure is not capable of simulating dynamic reservoirs of mercury in soils, water bodies and vegetation. To treat this limiting factor for dry deposition of Hg^0 to vegetation, a mesophyll resistance term was added to MCIP v3.1 in addition to the existing stomatal resistance term. A value of 5000 sec m^{-1} for mesophyll resistance was determined through model experimentation to achieve dry deposition velocities during the growing season in the experimentally observed range of 0.01 to 0.2 cm s^{-1} (Lin *et al.*, 2006).

Water bodies, both fresh and saline, tend to be supersaturated with dissolved Hg^0 and thus represent a net emission source of Hg^0 rather than a deposition sink (Rolphus and Fitzgerald, 2001 and references cited therein). For water bodies, the dry deposition velocity for Hg^0 is simply set to zero and evasion of Hg^0 is treated separately as described below.

Earlier versions of the CMAQ mercury model could simulate emissions of Hg^0 gas from naturally mercuriferous soils and geologic formations as defined by input data. Estimates of these natural Hg^0 emissions for development and testing of CMAQ version 4.5.1 were obtained from Seigneur et al. (2001). These first-time fluxes into the global mercury cycle are relatively small compared to the recycling emissions of mercury from soils, water bodies and vegetation from previous atmospheric deposition which is also included in the work of Seigneur et al. (2001). If dry deposition of Hg^0 is treated, then recycling of previously deposited mercury must also be treated or model simulations will exhibit unrealistic depletion of Hg^0 air concentrations.

Atmospheric mercury deposition through both wet and dry processes is largely in the form of oxidized mercury. However, some fraction of deposited mercury is continually recycled to air mostly in the form of Hg^0 (Ericksen *et al.*, 2006 and references cited therein). Since we do not yet have the means to simulate dynamic reservoirs of mercury in surface materials, a rather simple approach to mercury deposition recycling is used. Previous CMAQ simulations of atmospheric mercury based on the previous "zero-sum" assumption for the effect of dry deposition and recycling of Hg^0 were used to determine annual total deposition flux patterns for mercury in all forms. The recycling fraction of deposited mercury was set to one-half based on previous modeling by Seigneur et al. (2001). This annual flux of recycling mercury in the form of Hg^0 was temporally scaled to the hourly surface skin temperature and hourly incoming solar radiation flux values obtained from MCIP to estimate recycled mercury emission rates for each hour of the simulation period. The recycling fraction of one-half was found to provide model simulations which show little or no long-term depletion of Hg^0 in the interior parts of the model domain relative to locations near the boundary. This is admittedly a rather arbitrary calibration of the model. However, no other method appears to be available given the current state of the science.

Emission of Hg^0 gas from vegetation has also been observed, usually when the ambient air concentration of Hg^0 is at or below the long-term average for the site in question. This potential emission source has been simulated using output data derived from a special version of the Biogenic Emissions Inventory System (BEIS) described in Lin *et al.* (2005). For each horizontal grid cell, whenever the hourly rate of emissions from vegetation estimated from the BEIS exceeded the hourly value obtained from the recycling mercury flux estimation described above, the BEIS-derived guidance was used as the recycling flux estimate.

All natural and recycling anthropogenic mercury emissions for CMAQ v4.5.1 applications are estimated during pre-processing before the model simulation is calculated. The methods of estimation used during the model development and testing are quite elementary and are by no means the only methods that could be employed for future applications. There are plans for future versions of CMAQ to simulate air-surface exchanges of mercury as a two-way dynamic process once the controlling factors are better understood.

4. TYPICAL MODEL APPLICATION PROCESS

The CMAQ v4.5.1 model code can be retrieved from the CMAS website. The mercury version of the CMAQ Chemical Transport Model (CCTM) is part of the v4.5.1 public release of March 2006. The CCTM requires four types of input files: J-value files, meteorology, emissions and initial condition/boundary condition (IC/BC) files.

J-value ASCII character files, one per simulation day, contain data for the photolytic gas reactions. The reactions in these files are calculated by the routine JPROC, which requires input data tables for each reaction. The reactions in J-value files must match the photolytic reaction names in the CCTM.

Meteorology files are in binary NETCDF format, created by MCIP. Several files are needed per model day; some are 3-dimensional, some are 2-dimensional, and one is for the lateral boundary only, depending on the meteorological variable in question. The user must ensure that all of the variables needed for the CCTM are included in the proper files, since MCIP has gone through revisions which have changed the output variable lists as model requirements have changed. Meteorology files can cover a larger area than the horizontal model domain since the CCTM can horizontally window the meteorological data. The user must ensure that the vertical sigma levels are consistent with the other input files.

Emissions files are also in NETCDF format and are created by SMOKE, with one file per simulation day. For the mercury CCTM, emissions need to include the CB-IV criteria species plus the emitted mercury species (HG, HGIIGAS, APHGI) and molecular chlorine gas (CL2). Emissions of recycling mercury from water bodies, soils and vegetation present a special problem that must be considered when dry deposition of Hg^0 is simulated. No standard method exists for estimating these emissions, but future version of CMAQ may be able to treat them as internal model processes.

IC/BC files can be static (temporally constant) values based on assumed vertical profiles of air concentration or time-variable based on previous larger-scale modeling. These data must match the modeling domain; the CCTM cannot extract the proper data elements from a larger set. The internal start time of these NETCDF files must either be time independent, or the time must correspond to the model day that is being executed. The user can apply the same time-independent IC/BC files repeatedly for different model days, or apply different IC/BC files for different model days. The initial condition file is only used at model start up, and the model output concentration file is used as the initial conditions to start the next model day.

After the input files are established, the user sets up the shell script to run the CCTM. For typical applications at the U.S. EPA, part of the script runs another script to ensure all the meteorology, emissions and IC/BC files exist, and exits if not. This script also assigns the inputs to the appropriate environment variables that the CCTM is expecting for that file, as listed in the FILES_CTM.EXT include code. The CCTM is set to execute one model day at a time, usually in a loop in the script. For each day, the script must also include “setenv” statements to specify a horizontal grid definition file (e.g., setenv GRIDDESC griddesc.dat) and a vertical grid template file from which to extract the layering parameters (e.g., setenv LAYER_FILE GRIDCRO3D_$model_day). Any 3-dimensional meteorology file can be used for the vertical grid template file.

5. MERCURY IN CMAQ VERSION 4.6

For CMAQ v4.5.1, the mercury model operates only with the CB-IV gas-phase chemical mechanism and the "AERO3" (AE3) aerosol module. For the CMAQ v4.6 code release, we will extend the mercury modeling treatments described above to work with the CB05 gas-phase chemical mechanism and the "AERO4" (AE4) aerosol module. The functionality of the mercury codes will also be coordinated with the special codes of the air toxics version of the CCTM so that a comprehensive one-atmosphere “model of everything” might be developed.

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