

## APPLICATION OF CMAQ ON HEMISPHERIC SCALES

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### 1. INTRODUCTION

The Community Multi-scale Air Quality (CMAQ) model has been applied to simulate a number of different air pollutants by environmental institutions and agencies all around the world. These applications have generally been on limited-area domains where estimation of the air concentration of pertinent pollutant species at the lateral boundaries is required.

Results from the recent North American Mercury Model Intercomparison Study (NAMMIS) (Bullock et al., 2008; 2009) suggest that prescribed lateral boundary air concentrations can lead to unrealistic simulation results if they are not consistent with the meteorological and chemical conditions of the CMAQ simulation. For example, if water-soluble pollutants are prescribed to exist at a boundary location where the CMAQ simulation indicates heavy rainfall, unrealistically large deposition fluxes will be simulated.

Mercury (Hg) is recognized as a global pollutant with a typical atmospheric lifetime on the order of months or years. However, certain forms of atmospheric Hg (e.g., oxidized gases) are known to deposit rather rapidly once they are emitted or formed in atmospheric chemical reactions. Thus, atmospheric Hg modeling has both long-range (global) and short-range (local/regional) components and provides an opportunity to investigate the effect of prescribed lateral boundary values that may be inconsistent with internal model processes.

To avoid inconsistent lateral boundary concentrations, this work has applied the CMAQ model on a domain covering the Northern Hemisphere to the extent that boundary fluxes are much less of a concern, at least for Hg species. We plan to eventually use hemispheric simulations and domain nesting to regional scales to study the effect of inconsistent boundary concentrations for a variety of pollutants. This paper describes our

initial 15-day hemispheric application of CMAQ for atmospheric Hg, which also involved simulation of ozone, acid deposition and particulate matter.

### 2. MODELING DOMAIN

The CMAQ was designed to work on any conformal map projection (i.e., where geometric shape is conserved). A polar stereographic projection was chosen to cover most of the Northern Hemisphere. We wanted to get far enough south so that boundary fluxes of Hg in CMAQ simulations would be significantly reduced. There was some concern that the meteorology of the Inter-Tropical Convergence Zone (ITCZ) near the Equator might be difficult to simulate. The US EPA worked with the UNC Institute for the Environment (UNC-IE) to develop a meteorological modeling domain covering all of the Northern Hemisphere north of 10°N. This was accomplished using a 149x149 array of 108-km grid cells on a secant latitude of 45°N. To isolate boundary effects in the meteorological modeling, the CMAQ domain was set back by 6 grid cells on all sides, resulting in a 137x137 grid cell array with corner cells near the equator and mid-lateral cells near 20°N. The CMAQ vertical domain was resolved using 34 layers defined in sigma-pressure coordinates with a model top at 100 hPa.

### 3. METEOROLOGICAL DATA

The meteorological input data for this study were produced by UNC-IE using version 3.0 of the Weather Research and Forecasting (WRF) - Advanced Research WRF (WRF-ARW) model. The WRF-ARW simulations used the 149x149 grid cell array described above with the same 34-layer vertical resolution as in CMAQ. The Pleim-Xiu (PX) surface layer, land cover and PBL schemes were used along with the RRTMG radiative transfer model. The WRF-ARW outputs were processed using MCIP version 3.4.1.

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UNC-IE encountered some difficulties when it first tried to process WRF-ARW outputs using MCIP and display the results with PAVE and VERDI. The problem was traced to the way MCIP was converting WRF header data to the I/O API format. MCIP has been modified to correct this problem. When a major “bug-fix” to WRF-ARW was published in late 2008, EPA and UNC-IE decided it was prudent to restart the meteorological modeling with the corrected WRF-ARW. UNC-IE eventually provided EPA with CMAQ-ready hemispheric meteorological data for the period from March 16 through 30, 2006.

#### 4. POLLUTANT EMISSION DATA

Emission data for anthropogenic SO<sub>x</sub>, NO<sub>x</sub>, VOC, PM, and CO were obtained from an on-line data base developed by NASA’s Arctic Research of the Composition of the Troposphere from Aircraft and Satellite (ARCTAS) project. This data base is global and provides 1°x1° spatial resolution. The data are in terms of annual fluxes, so no temporal resolution is provided and none was estimated for this work. The base year for this inventory is 2005 or 2006 depending on the pollutant. Hg emissions are also available from the ARCTAS data base, but without any physical or chemical speciation.

Emission data for biogenic isoprene and terpene were obtained from an on-line database provided by the Precursors of Ozone and their Effects on the Troposphere (POET) project. These data also have a 1°x1° spatial resolution. Biogenic emissions from POET are specified on a monthly basis and the base year for the data is 2000.

Emission data for state-of-the-science atmospheric Hg modeling must provide information about the physical form (gas vs. aerosol) and the oxidation state for all significant Hg emissions. The first-ever global Hg emission inventory with this kind of speciation was recently developed by the Norwegian Institute for Air Research (NILU), the Arctic Monitoring and Assessment Programme (AMAP), and the Arctic Center, University of Groningen. It is available on-line providing 0.5°x0.5° spatial resolution and speciation in terms of gaseous elemental Hg (GEM), gaseous oxidized Hg (GOM) and particulate Hg (PHg). Some resolution of emission height based on industrial sector is also provided, but that was not used in this work. The base year for this inventory is 2000.

#### 5. SIMULATION RESULTS

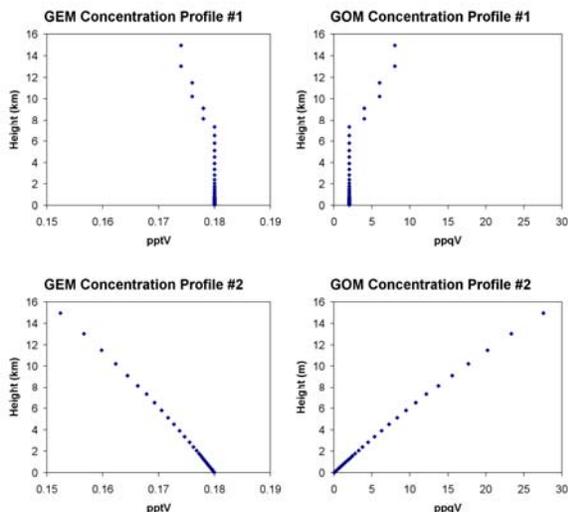


Fig. 1. Vertical concentration profiles of gaseous elemental mercury (GEM) and gaseous oxidized mercury (GOM) used for initial and lateral boundary conditions.

We applied a special multi-pollutant configuration of CMAQ version 4.7 where Hg was the only air toxic pollutant added to the base model for photo-oxidants, sulfur, nitrogen and particulate matter. As previously mentioned, CMAQ could only be applied on the hemispheric domain for a two-week period in late March of 2006. However, this simulation period was sufficient to demonstrate intercontinental transport of Hg and also highlight some additional technical obstacles that need to be overcome in the CMAQ treatment of atmospheric Hg cycling on hemispheric and global scales.

15-day simulations have been conducted using two different vertical profiles for initial and boundary concentrations for Hg species. Fig. 1 shows the concentration profiles used for GEM and GOM. The first set of vertical profiles had a discontinuous and modest decrease of GEM with height and a corresponding increase of GOM with height. The second set had profiles that were continuous with height, but the decrease of GEM and increase of GOM with height was more pronounced. In both cases, the initial and boundary concentrations of PHg were set to 17 pg m<sup>-3</sup> at all levels.

Two additional hemispheric simulations have been conducted using the second set of vertical profiles to test model sensitivity to changes in gaseous and aqueous Hg chemistry. The purpose for these tests was to determine the source of high GOM concentrations simulated near the surface in remote oceanic locations.

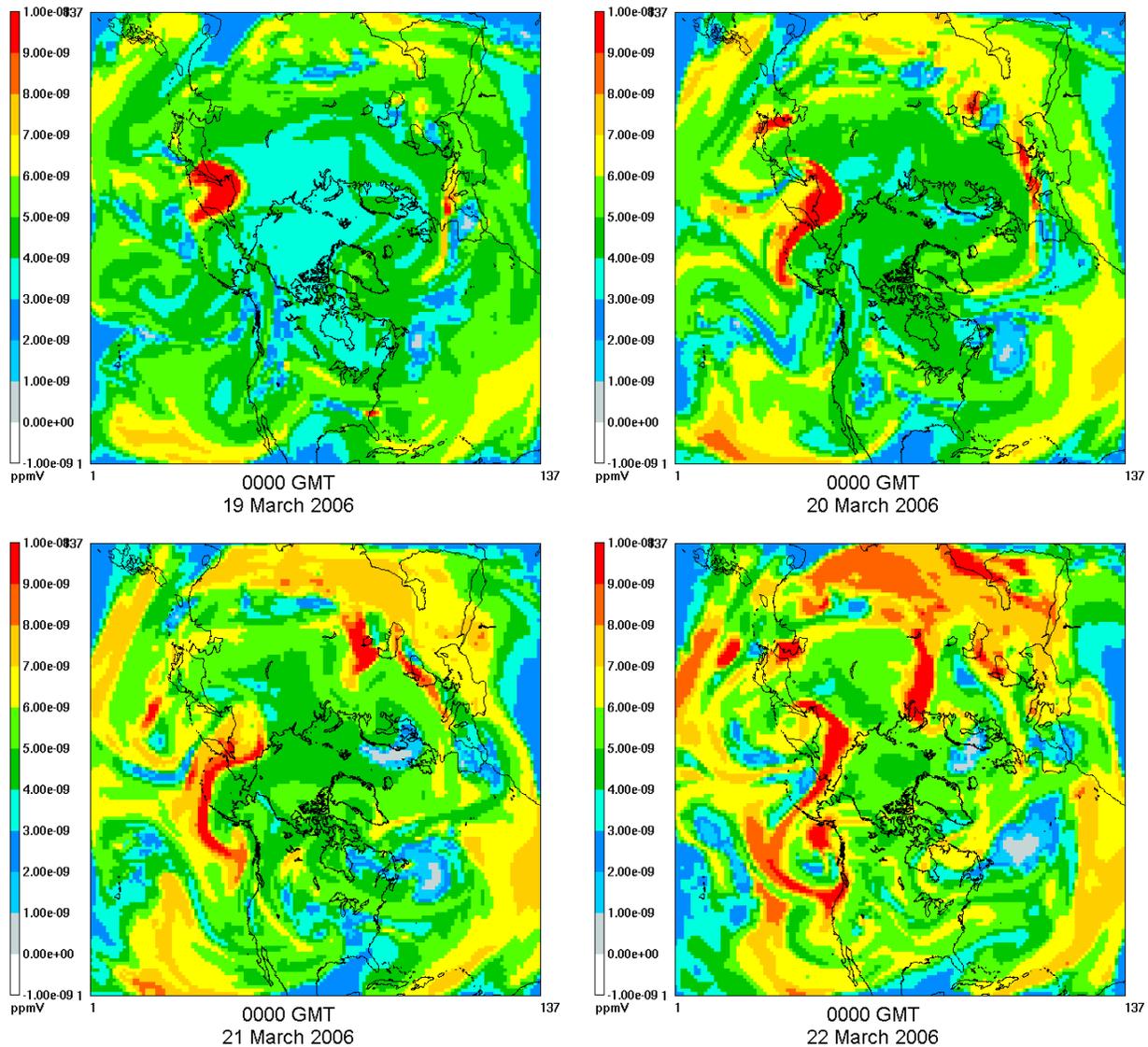


Fig. 2. Simulated concentration of gaseous oxidized mercury in layer 26 at 24-hour intervals showing trans-Pacific transport from Asia to North America.

### 5.1 Intercontinental Transport

Atmospheric Hg emissions in Asia have often been cited as a significant source of Hg deposition to the U.S. It has long been known that emissions of GEM all around the globe contribute to a nearly ubiquitous air concentration of 1.0 to 1.5 ng m<sup>-3</sup> for that particular Hg species. However, atmospheric deposition of GEM is rather slow compared to the other species of Hg. The main concern is the possibility for emissions of GOM (and possibly PHg) to be transported across the Pacific Ocean with subsequent deposition to North America.

Because GOM is readily deposited from air to any underlying surface, its transport near the surface should be terminated rather quickly. Thus, long-range transport of GOM at altitudes above the planetary boundary layer has always been the main concern. Fig. 2 shows results from the first CMAQ simulation which demonstrates transport across the Pacific of an air mass laden with ROM. Other less obvious examples of long-range GOM transport can be found in a variety of locations. The results shown here are from layer 26 of the model, which corresponds to an altitude of around 6000 m above sea level.

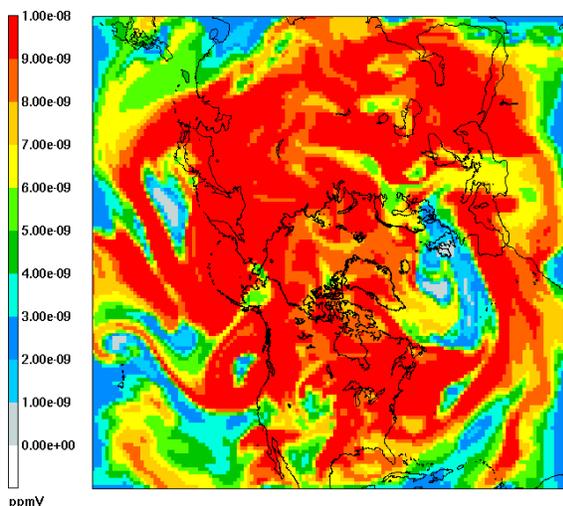


Fig. 3. Map of GOM concentrations in layer 26 near the end of the first simulation showing the influx of low concentrations at the lateral boundaries.

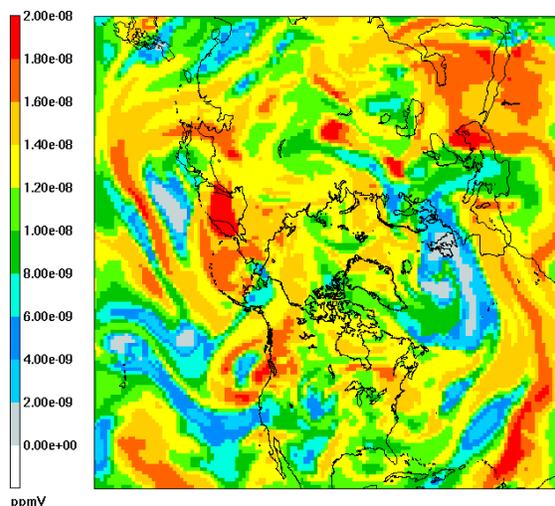


Fig. 4. Map of GOM concentrations in layer 26 near the end of the second simulation showing boundary influx concentrations similar to those in the interior.

## 5.2 Boundary effects

Measurements and global model simulations have generally indicated higher concentrations of GOM at higher altitudes with an opposite relationship for GEM. The first set of initial and boundary values was designed to reflect this. However, towards the end of the first 15-day simulation, it became apparent that the CMAQ model was not simulating the same general vertical distribution of GEM vs. GOM as was defined in that first set of boundary values.

Fig. 3 shows an obvious lateral boundary influx of low GOM concentrations in layer 26 (~6000 m ASL) compared to what CMAQ simulated for interior portions of the domain.

Three separate global models used to define boundary conditions for a recent atmospheric mercury modeling study indicated GOM concentrations of up to  $700 \text{ pg m}^{-3}$  ( $8 \times 10^{-8}$  ppmV) near the 100 hPa level (Bullock et al., 2008). The second set of initial and boundary concentrations was developed to better match these values.

Fig. 4 shows the result of using the second set of boundary values. Note that the concentration scale has been doubled from that used in Fig. 3. Boundary influx concentrations are similar to those within the interior of the domain at the end of the 15-day simulation. However, in this case the boundary values were found to be too high in the

top model layer. CMAQ did not simulate a continuing increase of GOM to the top of the model like the global models. This may be because CMAQ does not extend as high to simulate the effect of stratospheric ozone on mercury oxidation as the global models do.

## 5.3 Surface-level RGM in marine air

In the first two simulations, some rather high concentrations of GOM were noted near the surface over remote oceanic areas. Attendant low GEM concentration suggested some sort of chemical oxidation was the cause. A test was conducted where the simulated reaction of GEM with atomic chlorine (added in CMAQ v4.7) was slowed by a factor of 100. This had only a minor effect. In a second test, the aqueous chemistry was changed to allow the reaction of all dissolved species of  $\text{Hg}^{2+}$  with  $\text{HO}_2$ . With CMAQ v4.7, only the free  $\text{Hg}^{2+}$  ion was involved in this mercury-reducing reaction. However, the method employed in the only rate determination for this reaction (Pehkonen and Lin, 1998) used the changing concentration of total  $\text{Hg}^{2+}$  to estimate the kinetic rate (Lin, personal communication).

Figure 5 shows that reacting all dissolved  $\text{Hg}^{2+}$  instead of only the free ion results in a significant reduction in GOM concentrations in marine air near the surface.

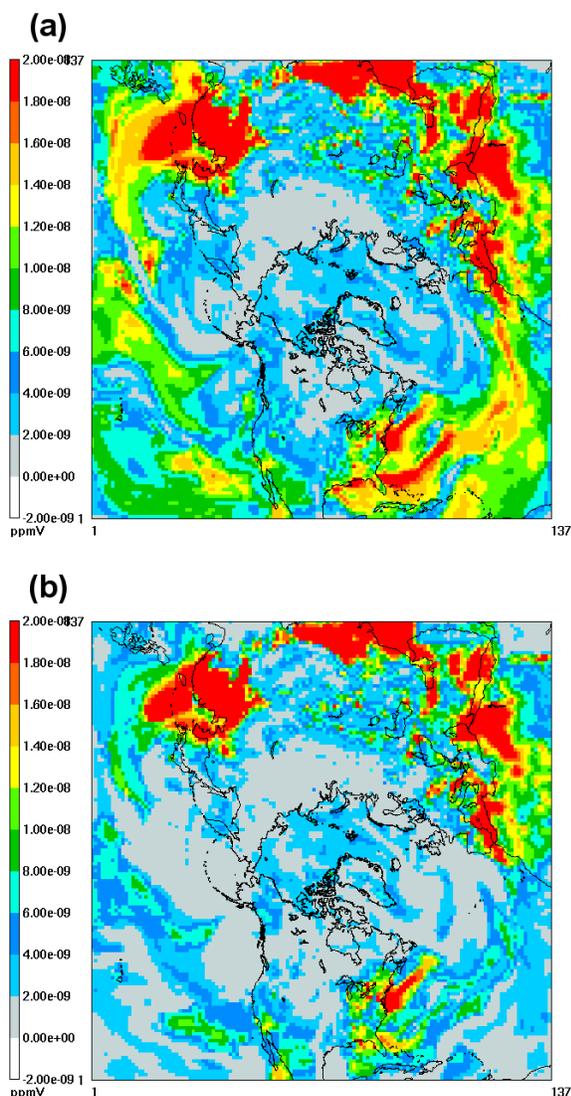


Fig. 5. Simulated GOM concentration in layer 1 after 15 days where (a) aqueous HO<sub>2</sub> reacts only with free Hg<sup>2+</sup> ions and (b) aqueous HO<sub>2</sub> reacts with all dissolved Hg<sup>2+</sup>.

## 6. SUMMARY

This work has demonstrated that CMAQ can be applied for hemispheric-scale modeling using a horizontal domain based on a polar stereographic projection. Simulations on this domain show evidence of intercontinental transport of oxidized forms of Hg. However, evaluation of simulated deposition of Hg and the fraction attributable to this intercontinental transport has not yet been performed.

This work has also shown that, even with lateral boundaries between 0° and 20°N, cross-boundary flows can still be significant and vertical

concentration profiles applied at the boundary need to be chosen with care. Further work is underway to push these boundaries even closer to the equator where cross-boundary flows should be reduced further.

The lack of a continued upward gradient with height for simulated GOM near the top of model suggests that stratospheric chemistry needs to be included. Further work is underway to raise the model top to 50 hPa.

Finally, this work has shown that certain changes to the aqueous mercury chemistry in CMAQ v4.7 may need to be reconsidered. The reduction of aqueous Hg<sup>2+</sup> to Hg<sup>0</sup> by reaction with HO<sub>2</sub> has been deemed unlikely to be important under normal atmospheric conditions (Gårdfeldt and Jonsson, 2003) and this reaction was scaled down considerably in CMAQ v4.7. However, it seems obvious from the results shown here that some similar reaction is required to maintain a reasonable reduction-oxidation balance for Hg.

## 7. REFERENCES

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