APPLICATION OF THE CMAQ PARTICLE AND PRECURSOR TAGGING METHODOLOGY (PPTM) TO SUPPORT WATER QUALITY PLANNING FOR THE VIRGINIA MERCURY STUDY

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1. INTRODUCTION

CMAQ is being applied in this study to assess the contribution of mercury sources within Virginia and surrounding states to impaired waterways. A key component of this study is the use of the CMAQ Particle and Precursor Tagging Methodology (PPTM) which allows one to track the emission, dispersion, chemical reaction, and deposition of mercury from particular sources, source categories, or source regions throughout the simulation. The PPTM technique is being used to quantify the contributions of individual sources and source categories for a base year of 2001 and several future years. The modeling will be used to evaluate the effectiveness of emissions reductions expected as part of the Clean Air Mercury Rule (CAMR) and whether additional control measures will be needed in Virginia to meet applicable water quality criteria. Another important objective of the modeling analysis is to provide information that will enable VDEQ to conduct Total Maximum Daily Load (TMDL) studies for mercury of various Virginia waterways.

2. BACKGROUND

In the U.S., more than 8,500 individual bodies of water have been identified as mercury impaired and the primary source of mercury to these water bodies is believed to be atmospheric deposition. Mercury deposition affects the viability of aquatic ecosystems in a number of different ways. The sustainability of marine life, recreational and commercial fishing, and human health can be directly or indirectly affected by mercury deposition and the build up of mercury in lakes, streams, rivers, and wetland areas. In certain bodies of water such as those with low dissolved oxygen, high organic matter content, and low acidity, mercury deposition can lead to the formation and build up of the highly bio-accumulative form of mercury (methyl mercury).

Human exposure to mercury is most commonly associated with the consumption of contaminated fish. Due to measured high levels of mercury in fish, at least 44 U.S. states have, in recent years, issued fish consumption advisories. These advisories cover more than 2000 individual bodies of water and may suggest limits on the consumption of certain types of fish or recommend limiting or not eating fish from certain bodies of water because of unsafe levels of mercury contamination.

Within Virginia, fish consumption advisories have been issued for several bodies of water for which atmospheric deposition is thought to be the primary source of mercury. These are primarily located along the coastal plain, and have characteristics that are consistent with mercury methylation and bioaccumulation of mercury in fish.

Global, regional, and local sources of air mercury emissions contribute to the deposition, and understanding these contributions is an important step toward identifying measures that will effectively reduce mercury deposition and environmental mercury levels.

3. CONCEPTUAL MODEL

Analysis of observed mercury deposition, meteorological and emissions data as well as recent modeling results provides insight into the nature of mercury deposition in Virginia. The resulting conceptual model is being used to guide certain aspects of the modeling analysis including the modeling domain, sensitivity simulations, model evaluation, and PPTM sources as discussed in this section.

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There are three Mercury Deposition Network (MDN) monitoring sites in Virginia: Culpeper (located in central Virginia), Shenandoah National Park (in northwestern Virginia), and Harcum (near the Chesapeake Bay in coastal Virginia). Wet mercury deposition is monitored at these sites and has an annual cycle, with higher deposition amounts during the second and third calendar quarters.

A number of different meteorological factors influence wet mercury deposition at these sites. Key factors include precipitation, temperature, wind speed, and the potential for recirculation. There are different types of meteorological conditions and combinations of parameters that lead to high deposition.

Precipitation is an important mechanism for wet mercury deposition. Mercury wet deposition is correlated with rainfall, but rainfall amount does not fully explain the observed variations in deposition. This suggests that any examination of the sensitivity of CMAQ to the meteorological inputs should include but should not be limited to precipitation.

The period of record for the MDN sites in Virginia is limited to recent years, 2002 and later. However, for each of the Virginia MDN sites, it is possible to identify a longer term monitoring site (from a neighboring state) that has similar deposition characteristics to supplement the model performance evaluation for 2001.

Annual deposition amounts that have been adjusted to account for variations in meteorology are consistent with changes in the emissions for Virginia. Thus some sensitivity to changes in local emissions is expected in the modeling. For the Culpeper and Shenandoah sites, the adjusted deposition values indicate a slight downward trend.

Monitoring data and prior modeling results suggest that for all three Virginia sites, dry deposition is a significant contributing factor to total mercury deposition. This finding may also aid the evaluation of the modeling results.

4. OVERVIEW OF CMAQ PPTM

Version 4.6 of the CMAQ model is being used for this study. CMAQ supports the detailed simulation of the emission, chemical transformation, transport, and wet and dry deposition of elemental, divalent, and particulate forms of mercury.

The CMAQ model includes three mercury (Hg) species; elemental mercury (Hg^0), reactive gaseous mercury (RGM), and particulate mercury (PHg). RGM and PHg are primarily comprised of divalent mercury.

Mercury simulation capabilities were first incorporated into the CMAQ model by adding gaseous and aqueous chemical reactions involving mercury to the CMAQ chemical mechanism (Bullock and Brehme, 2002). Since that time, the chemical mechanism has been further updated to include additional reactions and updated information on reaction rates. The most recent changes to CMAQ for mercury include an improved dry deposition algorithm and the incorporation of natural mercury emissions.

In addition to the state-of-the science chemical mechanism for mercury, other key features of the CMAQ model in simulating mercury deposition include state-of-the-science advection, dispersion and deposition algorithms, the latest version of the Carbon Bond chemical mechanism (CB05), and the CMAQ Particle and Precursor Tagging Methodology (PPTM).

PPTM for mercury (Douglas et al., 2006) provides detailed, quantitative information about the contribution of selected sources, source categories, and/or source regions to simulated mercury concentrations and (wet and dry) deposition. Mercury emissions from selected sources, source categories, or source regions are (numerically) tagged and then tracked throughout a simulation, and the contribution from each tag to the resulting simulated concentration or deposition for any given location can be quantified. By tracking the emissions from selected sources or source locations, the methodology also provides information on the fate of the emissions from these sources.

PPTM for mercury tracks emitted mass from its source through the modeling system processes. The emissions from each selected source, source category, or grouping are tagged in the simulation and each grouping is referred to as a “tag.” Typically, each tag includes all of the species necessary to keep track of the mercury emissions from a particular source or source grouping, but, the different species that comprise mercury emissions (e.g., elemental, divalent, and particulate) can also be tagged separately. The tagged species are differentiated from the regular species used in the CMAQ model by a suffix added to the species name. Each individual species from a given source or source grouping is tagged and the combination of all of the individual species represents the tag. As an example, in order to track the mercury emissions from waste incinerators, the species HG_t1, HGIIGAS_t1, and PHGI_t1, referring to elemental (HG), divalent (HGII), and particulate (PHG) emissions from incinerators, will be created. The "t" refers to tagging and the number one is the tag number. Collectively, these species (and the other species used in CMAQ to represent other forms of mercury, such as APHGI_t1 and APHGJ_t1) are referred to as the waste incinerator tag.

PPTM was developed to utilize model algorithms as much as possible to track simulated tag species concentrations. Processes that are linear, or independent of species, utilize the model algorithms to calculate the changes in species concentrations. An example of this type of process is advection. Other processes that are potentially non-linear or involve interactions with other species, are given a special treatment and are calculated for the overall (or base) species and apportioned to the tagged species. An example of this type of process is aqueous phase chemistry.

In the following section, we describe the methodology used to allocate changes to tags for each of the major processes in the CMAQ model.

4.1 Advection, Diffusion and Dry Deposition

Advection, diffusion and dry deposition of the tag species is accomplished using the standard algorithms in CMAQ. Deposition velocities for the tagged species are based on those for the corresponding standard species.

4.2 Gas Phase Chemistry

The current gas phase chemical mechanism in CMAQ causes a gradual conversion of elemental mercury (HG) to divalent forms in gas phase (HGIIGAS) and aerosol form (HGIIAER). There is no reaction to form elemental mercury from the other forms, and there are no reactions that form one type of divalent from the other. We have used this information to develop a simple method to allocate the divalent mercury formed during the gas phase chemistry step to the tags.

At the beginning of the gas phase chemistry step, the initial amount of HG, HGIIGAS, and HGIIAER are saved (HG_{init}, $HGIIGAS_{init}$, and $HGIIAER_{init}$). The initial amounts of each tag species are also saved. The gas phase chemistry module is called with the standard set of gas phase species (i.e., without tag species). Once the gas phase chemistry has completed a step, we calculate the following ratios:

$$HGG_{ratio} = (HGIIGAS - HGIIGAS_{init}) / HG_{init} \quad (1)$$

and

$$HGA_{ratio} = (HGIIAER - HGIIAER_{init}) / HG_{init} \quad (2)$$

where HGIIGAS and HGIIAER are the final values of the divalent forms of mercury. Effectively, these ratios give the amount divalent mercury of each form produced per unit elemental mercury.

The new concentrations for each tag species are then calculated as follows:

$$HGIIGAS_{s} = HGIIGAS_{init,s} + HG_{init,s}*HGG_{ratio} \quad (3)$$

$$HGIIAER_{s} = HGIIAER_{init,s} + HGinit,s*HGA_{ratio} \quad (4)$$

$$HG_{s} = HG_{init,s}*HG/HG_{init} \quad (5)$$

where s indicates the tag number and HG is the final concentration of elemental mercury.

4.3 Aerosol Dynamics

Two aerosol dynamics processes are simulated for mercury in CMAQ: 1) the formation of particulate mercury via gas phase reaction of elemental mercury, and 2) the transition of some fraction of the Aitken mode particulate mercury to accumulation mode particulate mercury.

The rate of formation of particulate mercury from gas phase reactions is determined, as described above, in the gas phase chemistry, for both the overall particulate mercury and for each of the particulate mercury tags.

The rate of accumulation of Aitken-mode particles into accumulation-mode particles is calculated by CMAQ for all particles. The rate is then applied to each of the constituent particulate species, including particulate mercury. In order to determine the changes in particulate mercury for each of the tags, each equation for particulate mercury has been emulated for the tag species.

4.4 Cloud Processes

Wet scavenging of pollutants and aqueous-phase chemistry are applied for both convective and resolved clouds by CMAQ. In PPTM, the tagged species concentrations are updated following the cloud scavenging and removal processes.

For the purpose of calculating the scavenging of each of the tag species, it is assumed that the fraction of each tag species removed will be the same as the fraction of the corresponding overall species removed. The scavenging is calculated as usual for the standard CMAQ species. After the scavenging, the fraction of each mercury species removed is calculated.

The aqueous chemistry is called in the usual way for standard species including mercury, and the concentrations of the standard species are updated. The aqueous chemistry routine is called again to calculate the chemical changes for each tag.

5. CMAQ/PPTM MODELING FOR THE VIRGINIA MERCURY STUDY

5.1 Application Procedures

The CMAQ model is being applied for the calendar year 2001. Selection of the simulation period considered meteorological and emissions database availability and meteorological representativeness.

The modeling domain includes a 36-km resolution outer grid and a 12-km inner grid. The outer grid encompasses the entire contiguous U.S. as well as portions of Canada and Mexico and, therefore, all or nearly all mercury emissions sources in North America. The inner grid covers the eastern two-thirds of the U.S. with a horizontal grid resolution of 12 km. Thus, the modeling domain supports 12-km horizontal grid resolution over Virginia.

The emissions inventory incorporates the latest mercury emission data for point sources in Virginia (for 2002 and 2005). Mercury emissions for all other areas and source categories were obtained from Version 3 of the 2002 National Emissions Inventory (NEI).

5.2 Preliminary Results

A baseline simulation and two preliminary PPTM simulations have been completed to date. The first PPTM run examines the contribution to mercury deposition from mercury sources in Virginia and compares this with the contribution from all sources outside of the state. The second run examines the contributions from 1) Electric Generating Unit (EGU) sources in Virginia 2) EGU sources in the remainder of the 12-km domain, and 3) all other mercury sources in the 12-km domain. Figure 1 shown simulated wet and dry mercury deposition for baseline simulation for the month of July for the 12-km domain.

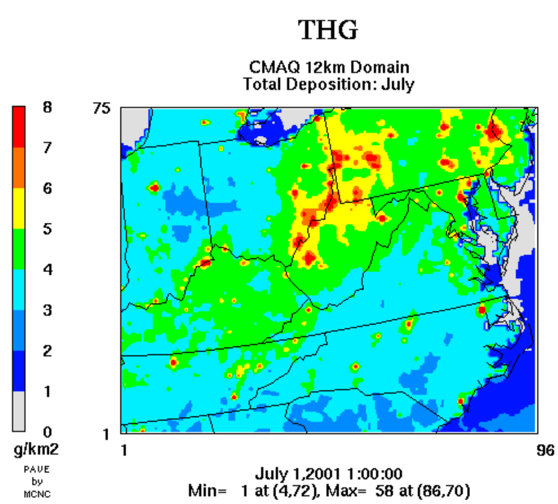

Fig. 1. Simulated wet and dry total mercury deposition for July 2001. .

Additional CMAQ and PPTM results will be displayed and discussed at the conference, with emphasis on the use of the CMAQ PPTM tool for the assessment of mercury deposition and to support environmental decision making.

6. REFERENCES

Bullock, O.R. and Brehme, K.A. 2002. Atmospheric mercury simulation using the CMAQ model: formulation description and analysis of wet deposition results. *Atmos. Environ.* 36, 2135–2146.

Douglas, S., T. Myers, and Y. Wei. 2006. “Implementation of Mercury Tagging in the Community Multi-scale Air Quality Model.” Prepared for the U.S. EPA, OAQPS, Research Triangle Park, North Carolina. Prepared by ICF International, San Rafael, California (06-051).