Chapter-14

MODELLING TRANSPORT AND TRANSFORMATION OF HG AND ITS COMPOUNDS IN CONTINENTAL AIR MASSES

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INTRODUCTION

It is known that atmospheric deposition contributes the majority of the Hg found in nearly all contaminated ecosystems, and in some cases it is the only source. In recent years, a number of numerical simulation models of atmospheric mercury have been developed to help understand the atmospheric pathway of mercury and to help formulate effective emission reduction strategies to reduce atmospheric deposition to specific nations, regions and watersheds (Cohen et al., 2004; Dastoor and Larocque, 2004; Christensen et al., 2003; Bullock and Brehme, 2002; Travnikov and Ryaboshapko, 2002; Berg et al., 2001; Lee et al., 2001; Petersen et al., 2001; Seigneur et al., 2001; Xu et al., 2000). Mercury deposition to specific fresh-water systems has been the subject of most interest as compared to deposition to oceanic areas, and the models used thus far for emission reduction strategy development have tended to be continental-scale models with oceanic areas at the model boundary.

Elemental Hg (Hg^0) emitted to air is believed to remain in the atmosphere for a period of time on the order of one year (Schroeder and Munthe, 1998). There are also a number of oxidized compounds of mercury known to exist in air. Most atmospheric mercury models simulate two additional species:

reactive gaseous mercury (RGM) and particulate Hg. These oxidized Hg species are more subject to atmospheric deposition than Hg^0 and they have significantly shorter atmospheric lifetimes (Schroeder and Munthe, 1998). Recent research has discovered certain phenomena in the Arctic (Schroeder et al., 1998) and at high altitude (Landis, 2004) that appear to involve atmospheric oxidation of Hg^0 on time scales of days or even hours, which would suggest the average atmospheric lifetime of Hg^0 emitted to air might be somewhat shorter than one year if that Hg^0 is transported to certain locations. Nonetheless, a lifetime of only 5 to 7 days would be required for significant intercontinental transport of Hg^0 to occur.

Thus, any model of atmospheric mercury in continental air masses must also consider the various forms of mercury being transported in from the marine environments at its lateral boundaries.

There are a few special considerations for modelling the behavior of Hg in continental air masses. First, the continents are where most humans live. Nearly all direct anthropogenic emissions of mercury occur in continental areas. Oxidized forms of mercury are more rapidly deposited from the atmosphere and a significant fraction of anthropogenic Hg emissions are in the oxidized form, especially those from combustion sources (Pacyna and Pacyna, 2002; Pacyna et al., 2003). Thus, the continents are where our industrial emissions have the most concentrated and significant impacts. Also, the surface underlying a continental air mass can be land or water, and land surfaces usually include vegetation which can have widely varying effects on atmospheric deposition processes depending on the season of the year. The effect of vegetation on atmospheric processes can even vary depending on current meteorological conditions or those in the recent past (e.g., leaf area index and evapotranspiration). Continental water bodies are not as deep as most oceans and their water temperatures can vary more widely from season to season. They also freeze and thaw more rapidly. Finally, unlike oceans, continents have topographic relief. Mountains and valleys can create complex atmospheric flow patterns that require fine-scale (spatial and temporal) modelling to resolve.

Since oceans cover two-thirds of the earth's surface, the behavior of mercury in marine environments is an important factor in its atmospheric lifetime and the concentration of the various forms of mercury in air and cloud water that might be expected at the horizontal boundaries of the continental-scale models. This chapter will focus on modelling mercury in continental air masses, but the importance of the marine environment to the global distribution of mercury and its eventual deposition to fresh-water systems should not be discounted.

GENERAL MODELLING CONCEPTS

Numerical simulation models for air pollutants are developed with the intent that they address all of the current knowledge regarding emission sources, transport and diffusion, chemical and physical transformations, and removal processes. However, many of the meteorological processes known to affect mercury occur on rather small spatial and temporal scales (e.g., convective clouds) and it is currently impractical to model them in full detail over continental model domains, much less the entire global mercury cycle. A compromise between model domain size and temporal/spatial resolution is required. As the calculating power of computing equipment has increased, this compromise has become less difficult. However, it is still necessary to use limited-area models in order to simulate atmospheric mercury at the level of spatial detail required to resolve the atmospheric flow patterns (e.g., land/sea-breeze circulations) and cloud elements in which important mercury transport and transformations are known to occur. Albert Einstein is quoted as having said "Make everything as simple as possible, but not simpler."

This advice certainly applies to modelling atmospheric mercury. But, with our scientific understanding of atmospheric mercury continuing to evolve, the level of spatial/temporal detail necessary to resolve all important processes may change with each new discovery.

The individual atmospheric mercury models that have been developed thus far fall across a wide range of the simple-complex scale. Models that encompass the entire global domain of the mercury cycle must simulate several years in order to accumulate a global background air concentration of Hg^0 and they tend to neglect small-scale air circulations, planetary boundary layer (PBL) structure, and cloud-water physicochemistry in their simulations. Those models that manage to resolve these complex atmospheric processes in high detail are only applicable up to the regional spatial scale, at best, and can only be used to simulate a few weeks or months of time on the most powerful computing systems. This compromise between model complexity and domain size is made based on a desire to minimize "modelling uncertainty", which occurs when the model is not accurately treating accepted scientific fact in its calculation of a numerical simulation.

A different type of uncertainty that must always be considered when atmospheric mercury modelling is applied, especially for assessment purposes, is "scientific uncertainty". This is true regardless of the complexity of the models being used or the quality of their input data. Some future scientific discovery regarding sources of atmospheric mercury, its atmospheric composition or behavior, or its modes of deposition could make the results of any modelling assessment performed today scientifically indefensible and obsolete. Modelling for the purposes of scientific research is performed in anticipation of such discoveries, and it plays an important role in the support and direction of the field research through which these discoveries may be made. Model simulations are also used to develop public policy, and this implies a certain level of confidence in the current science that should not be misunderstood. Policy decisions are made with the best information available at the time, and mercury policy decisions are no exception. Our current scientific understanding of atmospheric mercury is incomplete and improved knowledge will lead to more complete scientific certainty. As the noted historian Daniel Boorstin once said, "The greatest obstacle to discovery is not ignorance - it is the illusion of knowledge."

BASIC SIMULATION MODEL STRUCTURES

There are two basic types of numerical model structures currently being used for the simulation of long-range atmospheric mercury transport and deposition, Lagrangian and Eulerian.

Lagrangian modelling

In Lagrangian modelling, the model's reference frame moves with the entity or substance being modeled. Individual parcels of air and the mercury contained in them are resolved and their motion and physicochemical processes are simulated based on pre-defined meteorological information. Usually, these parcels are defined as originating at the location of each air emission source in the inventory being used. They are "released" from each source at specific time intervals with the mercury mass loading in each parcel upon release determined by multiplying the time interval by the mercury emission flux rate for the source in question. Modelers commonly refer to these as "puff" models. Rather than the continuous pollution elements that are simulated by Gaussian-plume models for short-range single-source applications, Lagrangian models simulate a train of discrete emission parcels that, when totaled together, resemble a continuous plume.

Chemical and physical reactions of mercury are simulated in most Lagrangian models one parcel at a time with no interaction with the other pollutant parcels present in the simulation. If one parcel contains twice the amount of mercury as a second one under the same meteorological conditions and with the same air concentrations for all other reactants, the simulated rate of all reactions and depositions for the first parcel will be exactly twice those for the second one. This “linear” chemistry assumption is currently acceptable for atmospheric mercury simulation because; 1) the chemical and physical reactions of mercury that have been identified thus far have all been found to be either first-order or zero-order reactions, and 2) the concentrations of mercury are normally so much smaller than the concentrations of its reactants that significant depletion of reactants does not occur. However, many of the chemical species known to react with mercury are the products of photochemical reactions that are known to be non-linear. Therefore, Lagrangian modelling is dependent on some sort of previous determination of the air concentrations of these reactants. Also, limited-area modelling with a Lagrangian modelling framework requires the simulation of synthetic sources to account for mercury transporting or diffusing into the model domain across the lateral and top boundaries.

Eulerian modelling

In Eulerian modelling, the model’s reference frame is fixed and the entity or substance being modeled moves through this reference frame. Eulerian models are often referred to as “fixed grid” models. The atmosphere is defined as a three-dimensional stationary array of finite volume elements. Physical and chemical variables in the model are simulated as if they each have only one value all throughout a particular volume element at any particular point in time.

Transport and diffusion of atmospheric constituents are simulated by transfers from one volume element to another, normally to an adjacent element except when special techniques are employed to negate artificial numerical diffusion. Eulerian modelling has been used since the mid 20th century to simulate physical meteorology. Nearly all current weather forecast models use this type of modelling framework. Over the years, meteorological modelers have striven to reduce the size of the volume elements to better resolve pressure, wind, temperature, humidity and clouds as they exist in the real atmosphere, knowing that volume averaging of these physical parameters was a primary source of modelling uncertainty in their simulations. The same is true for atmospheric chemistry modelling. Simulating a single air concentration for each chemical constituent throughout the entire expanse of a large volume element obviously deviates from reality.

The numerical methods used to simulate the motion of a substance from one volume element to another require that this motion or diffusion be calculated in small increments of time. These "time steps" must be kept below a certain length to avoid instabilities in the mathematical calculations that can cause artificial numerical errors to amplify. Reducing all three dimensions of the volume elements by one-half creates eight times as many volume elements to simulate. It also requires that the time step for pollutant transport be reduced by one-half, resulting in another doubling of the calculations required to simulate a particular period of time. In essence, doubling the fineness of the model's spatial resolution produces a 16-fold increase in the number of calculations that have to be made.

Regardless of these difficulties, an Eulerian modelling framework is required for the realistic simulation of complex, non-linear chemistry. Even where simple chemistry is involved, if a pollutant is released to air from a large number of sources, or is released from a diffuse source over a large area (e.g., oceanic emissions), an Eulerian modelling framework may be the most efficient option due to the large number of discrete pollutant parcels that a Lagrangian model would have to track and simulate.

MERCURY EMISSIONS INTO CONTINENTAL AIR MASSES

As mentioned before, most direct anthropogenic emissions of mercury occur in continental areas, and a significant fraction of anthropogenic emissions are in the oxidized forms that deposit from the atmosphere most rapidly. Model simulations of the atmospheric fate and transport of mercury suggest that the speciation of the mercury emissions governs mercury deposition patterns in industrial source areas, while in remote areas the atmospheric chemistry of mercury determines those deposition patterns (Pai et al., 1999). Clearly, it is important to ensure that numerical models of atmospheric mercury include a proper treatment of mercury transformations, but in continental air masses the speciation of emissions is more important than anywhere else. When modelling mercury deposition from continental air masses, an accurate inventory of industrial emissions of oxidized mercury is most critical to achieving accuracy in the simulated wet and dry deposition of total mercury to nearby sensitive watersheds.

Because of the strong diel (day-night cycle) fluctuations in the PBL structure of continental air masses, the transport and diffusion characteristics of any air pollutant emitted into them are highly dependent on the time of day and height of the emission. When daytime surface heating is at a maximum, strong convective vertical mixing occurs between the surface and the PBL top which may be 2 km or more above the surface. Under these conditions, even pollutant emissions from tall stacks can rapidly mix down to the surface and lead to localized increases in air contaminant concentrations. However, vertical homogenization of the air within this deep PBL tends to rapidly dilute pollutant air concentrations. Therefore, deep and rapid mixing with the PBL formed under conditions of strong solar heating does not necessarily lead to the highest surface-level air concentrations near emission sources.

Under the opposite conditions of nighttime surface cooling, a vertically stratified nocturnal boundary layer develops over the surface. Emissions near the surface within this shallow layer of temperature inversion (increasing temperature with height) will not be mixed vertically and will remain near the surface. Winds also tend to be rather light within this nocturnal boundary layer, leading to high pollutant concentrations in the locality of an emission source. Elevated and buoyant emissions which are released or rise above the top of this nocturnal boundary layer will exhibit vertical mixing to some degree dependent on the PBL structure left behind from the previous day, but downward mixing will be limited by the top of the nocturnal inversion layer. Under this condition, pollutant emissions can travel very long distances aloft during the night with little or no surface-level air concentration from the source in question.

Similar vertical thermal structures can exist in marine air masses, but they are rarely as intense and do not have such strong diel cycles as those found in continental air masses. For this reason, simulations of pollutant transport and diffusion in continental air masses depend more strongly on detailed information regarding the time of day and effective stack height, which is the sum of physical stack height and plume rise, of pollutant emissions.

A variety of mercury emission inventories have been developed, but only a portion of them are useful for numerical simulation modelling applications. Inventories where the emission flux is defined as national totals, or as totals for large political regions like state or provinces, are rarely useful for atmospheric simulation modelling. The spatial resolution of emissions information provided in this form is simply insufficient. In a technical sense, these emission inventories are simply data sets which are used as inputs to numerical simulation models and are not really a part of the models themselves. Nonetheless, the various assumptions and simplifications that are made during the course of compiling these emission inventories can have profound effects on the results of model simulations. Emission sources are nearly always grouped or categorized based on industrial activity or physical characteristics of the emission source. But the definitions for these groups and categories of sources can vary quite significantly between individual inventories. Instead of describing the emissions of Hg^0, RGM and particulate Hg for each source, most current inventories provide only total mercury emission rates. The critical estimation of the speciation of those mercury emissions are usually left for the modeler to perform based on the type or category of the source in question. Beginning with their 1999 base year, mercury emission inventory developers at the U.S. EPA began to prescribe speciation profiles for each source type and category in their inventory.

To be used for simulation purposes, mercury emission inventories must contain descriptions of each major source of mercury providing its geographic coordinates (e.g., latitude and longitude) for locating the source within the modelling domain and exhaust characteristics (e.g., stack height, exhaust temperature) for estimating the effective height of emission in addition to basic mercury emission flux rates. Most emission inventories provide no temporal resolution at all for the emission flux rates and simply provide a single mass per time quantity for each source element in the inventory. Rarely do these inventories provide an indication of the fraction of the total emissions applicable to each hour of the day, day of the week, or month/season of the year. Smaller anthropogenic sources of mercury that are not accounted for individually during inventory development are typically described as "area sources" and are accounted for as a group for each state, province, or other political division. Since the geographic size and shape of these political divisions may vary widely, the modeler is faced with a spatially allocation problem that has no standard solution. Sometimes the geometric centroid of the political division is used as the simulated emission point for a single integrated area source. Sometimes the flux rate indicated for the area source is spatially distributed among the model grid points or grid cells falling within the boundaries of the political division. Whatever the case, the spatial resolution of the emission inventory is usually inferior to that of the model and additional modelling uncertainty results from the spatial allocation.

There is one strictly terrestrial mercury air emission source type that can be significant in comparison to industrial sources and is sometimes considered natural, but is in fact largely anthropogenic; that being forest fires (Friedli et al., 2003; Friedli et al., 2001). Not only are many forest fires intentionally set, but much of the mercury emitted from them is actually anthropogenic mercury accumulated in forest soils from atmospheric deposition over the decades or centuries since the last forest fire at that location. Intentional agricultural fires (prescribed burning) also fall into this category, but in this case there is good reason to expect the amount of mercury accumulated in the underlying soils to be less important than in forest fires due to the shorter accumulation period since the last burning. Being a combustion source, one might expect a significant fraction of the mercury emitted from these fires to be in oxidized form. However, recent measurements of Hg emitted from forest fires in the Cascade Mountains in Washington State showed 95% or more to be in the form of Hg^0 gas with the remainder found in the particulate fraction of the smoke (Friedli et al., 2003).

There is currently no comprehensive mercury emission inventory for modelers to account for individual forest and agricultural fires in their simulations, and no generally-accepted method to estimate long-term average emission rates from such sources. This is certainly a subject in need of additional research.

Emissions of mercury to continental air from water bodies, soils, and vegetation are also anthropogenic to a large degree since much of the mercury in those media was deposited over time from anthropogenic sources. However, nearly all of these emissions are believed to be in the form of Hg^0 (Vette et al., 2002; Grigal, 2002). Truly natural emissions of mercury from geologic formations are also believed to be mostly Hg^0 (Gustin et al., 2002). Continental-scale modelling has shown that industrial Hg^0 emissions do not add significantly to the Hg^0 air concentration except in intense source regions and the effect of Hg^0 air concentrations on the simulated deposition of total mercury is mostly influenced by the air concentration at the lateral model boundaries (U.S. EPA, 1997). Except where natural substrates are exceptionally rich in mercury, it follows that natural emissions of Hg^0 may also be factored into continental-scale modelling by the background Hg^0 air concentration. Nonetheless, the processes that govern the exchange of mercury between the atmosphere and the various natural surfaces below it need to be studied and understood so that, eventually, these processes and sources of natural and recycled mercury can be included more explicitly in atmospheric modelling.

ATMOSPHERIC MERCURY CHEMISTRY

Nearly all contemporary models of atmospheric mercury attempt to simulate generally the same gas-phase reactions in air and aqueous-phase reactions in cloud water that have been identified and studied through laboratory investigation. Some of these chemical reactions were first identified and studied many years ago, but modern laboratory techniques developed only in past few years have allowed much improved determination of the rate of these reactions under various conditions. Some models ignore the slower, less significant reactions of mercury in order to concentrate efforts on simulating the reactions that are believed to be most important (Ryaboshapko et al., 2002). Laboratory investigation of mercury chemistry is continuing and it sometimes results in significantly revised estimates of reaction rate for particular reactions and considerable debate among the modelling community as to which rate determination to accept as most accurate.

In just the past few years, a number of scientific papers have been published describing chemical reactions of mercury in air and in cloud water. Some provide information about chemical reactions that were suspected for some time to occur in the atmosphere, but for which no reaction rate determinations had been published before (Ariya et al., 2002). Some suggest significantly different values for reactions rates that had been published previously (Van Loon et al., 2000). One even suggests the existence of an unusual form of water-soluble mercury that had never been considered before, a Hg^0-SO_2 complex (Van Loon et al., 2001), while another provides evidence that a chemical reaction previously included in many atmospheric mercury models does not actually occur in atmospheric water (Gårdfeldt and Jonsson, 2003).

Atmospheric measurements taken in recent years have identified previously unknown chemical phenomena regarding mercury. It is only since the late 1990's that gaseous elemental mercury depletion events (GEMDEs) have been recognized to occur in northern Canada (Schroeder et al., 1998). Subsequent research has improved our understanding of GEMDEs and has found them to occur at various circumpolar locations (Lindberg et al., 2002; Ebinghaus et al., 2002; Sommar et al., 2004). We are only just now beginning to understand how GEMDEs occur and how they may influence the global cycling of mercury (Bottenheim et al., 2002). Ongoing observations of RGM and particulate Hg at high altitude, both aloft and on mountain tops, suggest that chemical oxidation of mercury is occurring on in the middle and/or upper atmosphere for reasons that are not yet understood (Landis, 2004).

These new and revised chemical rate determinations and observations of unexplained atmospheric phenomena are certainly keeping the chemistry formulations of atmospheric mercury simulation models in a state of uncertainty and change. This should be considered a good thing, as it indicates progress is being made in developing our understanding of the behavior of atmospheric mercury and the sources most likely responsible for observed atmospheric mercury deposition and ecosystem contamination in continental areas.

MODELLING MERCURY WITH THE COMMUNITY MULTI-SCALE AIR QUALITY MODEL

The Community Multiscale Air Quality model (CMAQ) is an Eulerian type model used to simulate the transport, transformation and deposition of air pollutants and their precursors (Byun and Ching, 1999). The pollutants simulated by the standard version of CMAQ include tropospheric ozone, acidic and nutrient substances, and aerosol matter of various composition and particle size. The standard version was used as the basis for development of the mercury version of CMAQ (CMAQ-Hg) which has been applied to simulate continental domains in North America and Europe. A complete description of all special CMAQ model formulations for the simulation of atmospheric mercury is given in Bullock and Brehme (2002). Basic transport and diffusion simulation in the CMAQ-Hg was kept the same as in the standard CMAQ. All pollutant species normally simulated by the standard CMAQ are also simulated in CMAQ-Hg along with mercury and molecular chlorine gas. Descriptions of the standard CMAQ are found in Byun and Ching (1999).

The CMAQ-Hg modelling domain is variable in size and spatial resolution. Horizontal spacing of grid points in mercury simulations performed thus far has been 36 km in both dimensions. Two vertical layer structures have been employed using 14 and 21 layers of varying thickness from the surface to the 10 kPa pressure level, with the finest resolution near the surface. All CMAQ-Hg simulations performed thus far have used the Carbon Bond-IV (CB-IV) gaseous chemistry mechanism from the standard model plus special chemistry treatments for mercury and molecular chlorine gas which is a significant oxidizing agent for mercury in air and cloud water. Meteorology has been defined using the Fifth-Generation Pennsylvania State University / National Center for Atmospheric Research (NCAR) Mesoscale Model (Grell et al., 1994), commonly referred to as "MM5", employing the surface energy flux and the planetary boundary layer model of Pleim and Xiu (1995).

The CMAQ-Hg simulates mercury in three separate forms; (1) gaseous Hg^0, (2) RGM, and (3) particulate Hg. Particulate Hg is resolved in two particle size modes; the super-fine Aitken mode and the fine-particle accumulation mode. A treatment for coarse-mode particulate Hg is currently under development. Four gas-phase oxidation reactions for mercury are simulated in the CMAQ-Hg as shown in Table 1. The Hg^{2+} products of these reactions are modeled in CMAQ-Hg as either RGM or particulate Hg based on the vapor pressure of the compounds that are assumed to be produced.

Reduction of Hg^{2+} species to Hg^0 is simulated only in the cloud chemistry mechanism. While some chemical reduction of Hg^{2+} to Hg^0 may occur in the gas phase, the mechanism and rate for this type of reaction remains poorly understood. In general, gas-phase reactions of mercury appear to be of minor importance to its oxidation state as compared to its aqueous-phase reactions.

Chlorine photolysis is known to occur at a rather rapid rate, similar to nitrogen dioxide, a gas-phase species simulated in the standard CMAQ and in CMAQ-Hg. The Cl_2 photolysis rate in CMAQ-Hg is referenced to the CMAQ photolysis rate for NO_2 with a proportionality factor of 0.295. This referencing is based on efforts at the University of Texas to expand the CB-IV mechanism to include Cl_2 and is based on their analysis of updated actinic flux data for Cl_2 and NO_2 (Finlayson-Pitts and Pitts, 2000).

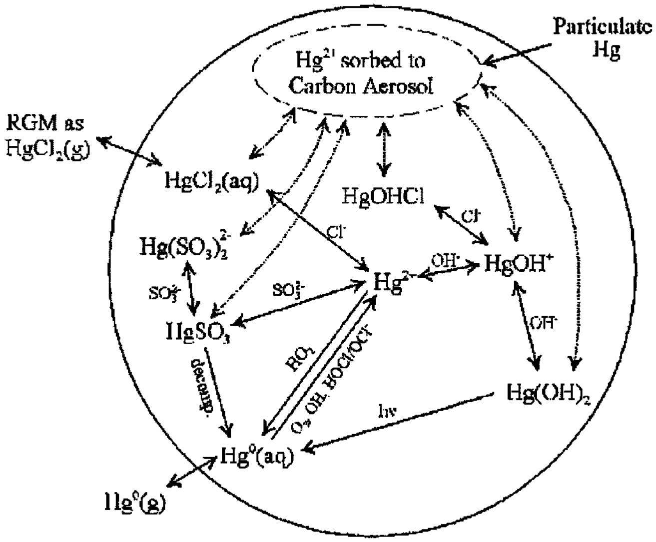

Figure 1. Schematic representation of the aqueous mercury chemical mechanisms.

The cloud chemistry mechanism for mercury in CMAQ-Hg is illustrated in Figure 1. It simulates gas/liquid partitioning, aqueous chemistry and reversible sorption of Hg^{2+} complexes to elemental carbon aerosol (ECA) suspended in cloud water, and was developed based on the approach of Pleijel and Munthe (1995). This aqueous chemistry mechanism involving Hg^0, the Hg^{2+} ion, and six Hg^{2+} compounds is simulated simultaneously with the pre-existing aqueous chemistry from the original CMAQ. Gas/liquid partitioning of Hg^0 and RGM is simulated using Henry's law equilibrium assumptions. RGM is assumed to partition based on the Henry's constant for mercuric chloride ($HgCl_2$).

Particulate mercury is assumed to be completely incorporated into cloud water and composed of Hg^{2+} sorbed to ECA at the start of the CMAQ operator splitting technique that is employed to simulate cloud chemistry and wet deposition (Byun and Ching, 1999). All aqueous chemical reactions for mercury and their rate constants are shown in Table 1.

Table 1. Chemical reactions for mercury and their rate constants used in CMAQ model.

No.	Reaction	k or K	Ref.
Gaseous-phase reaction of Hg			
RG1	$Hg^0_{(g)} + O_{3(g)} \quad TPM$	3.0×10^{-20} cm^3 molecules^{-1} s^{-1}	1
RG2	$Hg^0_{(g)} + Cl_{2(g)} \quad RGM$	4.8×10^{-18} cm^3 molecules^{-1} s^{-1}	2
RG3	$Hg^0_{(g)} + H_2O_{2(g)} \quad TPM$	8.5×10^{-19} cm^3 molecules^{-1} s^{-1}	3
RG4	$Hg^0_{(g)} + OH_{(g)} \rightarrow TPM$	8.7×10^{-14} cm^3 molecules^{-1} s^{-1}	4
Aqueous-phase reactions of Hg			
RA1	$Hg^0_{(aq)} + O_{3(aq)} \rightarrow Hg^{2+}_{(aq)}$ + products	4.7×10^7 M^{-1} s^{-1}	5
RA2	$HgSO_{3(aq)} \rightarrow Hg^0_{(aq)}$ + products	$T \times e^{((31.971 \times T)-12595)/T}$ s^{-1}	6
RA3	$Hg(OH)_{2(aq)} + h\nu \rightarrow Hg^0_{(aq)}$ + products	6.0×10^{-7} s^{-1} (maximum)†	7
RA4	$Hg^0_{(aq)} + OH_{(aq)} \rightarrow Hg^{2+}_{(aq)}$ + products	2.0×10^9 M^{-1} s^{-1}	8
RA5	$Hg^{2+}_{(aq)} + HO_{2(aq)} \rightarrow Hg^0_{(aq)}$ + products	1.1×10^4 M^{-1} s^{-1}	9
RA6	$Hg^0_{(aq)} + HOCl_{(aq)} \rightarrow Hg^{2+}_{(aq)}$ + products	2.09×10^6 M^{-1} s^{-1}	10
RA7	$Hg^0_{(aq)} + OCl^-_{(aq)} \rightarrow Hg^{2+}_{(aq)}$ + products	1.99×10^6 M^{-1} s^{-1}	10
Aqueous-phase chemical equilibria for Hg			
E1	$Hg^{2+} + SO_3^{2-} \leftrightarrow HgSO_3$	2.0×10^{-13} M	11
E2	$HgSO_3 + SO_3^{2-} \leftrightarrow Hg(SO_3)_2^{2-}$	4.0×10^{-12} M	11
E3	$Hg^{2+} + 2Cl^- \leftrightarrow HgCl_2$	1.0×10^{-14} M^2	12
E4	$Hg^{2+} + OH^- \leftrightarrow HgOH^+$	2.51×10^{-11} M	11
E5	$HgOH^+ + OH^- \leftrightarrow Hg(OH)_2$	6.31×10^{-12} M	11
E6	$HgOH^+ + Cl^- \leftrightarrow HgOHCl$	3.72×10^{-8} M	11
Henry's equilibria for Hg			
H1	$Hg^0_{(g)} \Leftrightarrow Hg^0_{(aq)}$	1.1×10^{-1} M atm^{-1}	13
H2	$HgCl_{2(g)} \Leftrightarrow HgCl_{2(aq)}$	1.4×10^6 M atm^{-1}	14

† Rate constant for RA3 is scaled to the cosine of solar zenith angle

References: (1) Hall (1995); (2) Calhoun and Prestbo (2001); (3) Tokos et al. (1998); (4) Sommar et al. (2001); (5) Munthe (1992); (6) Van Loon et al. (2000); (7) adapted from Xiao et al. (1994); (8) Lin and Pehkonen (1997); (9) Pehkonen and Lin (1998); (10) Lin and Pehkonen (1998); (11) Smith and Martell (1976); (12) Lin and Pehkonen (1999); (13) Sanemasa (1975); (14) Lindqvist and Rodhe (1985)

Chemical equilibria used in the aqueous mechanism are also in Table 1, as are the Henry's constants used for gas/liquid partitioning. Sorbed aqueous Hg^{2+} complexes are not subject to aqueous chemical reduction to the elemental form and subsequent out gassing from cloud droplets (Seigneur et al., 1998). Thus, sorption to ECA can affect the amount of mercury in cloud water subject to removal by precipitation.

Upon completion of the CMAQ operator splitting function for cloud chemistry and wet deposition, all aqueous chemical species are transferred back to the gas phase for the simulation of transport and dry deposition. This transfer is necessary because the current versions of the CMAQ and CMAQ-Hg have no explicit simulation of cloud water transport. Cloud water concentration is estimated at the beginning of each aqueous chemistry time loop based on the previous MM5 meteorological model simulation. Given the assumptions of Henry's equilibrium for all gaseous species and complete incorporation of particulate Hg into cloud water at the beginning of the cloud chemistry time loop, the effect on the aqueous chemistry simulation from this transfer to the gas phase is minimal. Methods for explicit simulation of the transport of cloud water and its chemical constituents by the CMAQ modelling system are currently under development. In the mean time, dissolved Hg^0 is transferred as gaseous Hg^0, all dissolved Hg^{2+} species are transferred collectively as RGM, and all Hg^{2+} species sorbed to ECA are transferred collectively as particulate Hg.

It should be noted that emissions of sea salt aerosol and other sources of chloride ion (Cl^-) in cloud water are not yet defined for the standard version of CMAQ. A minimum aqueous Cl^- concentration of 1.0×10^{-3} g l^{-1} is assumed in the current form of CMAQ-Hg based on the value of 2.5×10^{-3} g l^{-1} previously adopted for long-range mercury transport model intercomparison (Ryaboshapko et al., 2002). The speciation of dissolved Hg^{2+} compounds in cloud water is dependent on Cl^- concentration. A top priority for future development of CMAQ is the addition of sea salt and crustal aerosol emissions.

The CMAQ-Hg model parameterization for the sorption and desorption of aqueous Hg^{2+} species to ECA suspended in cloud water is adapted from previous work by Seigneur et al. (1998). A complete description of the CMAQ-Hg treatment of Hg^{2+} sorption in the aqueous media is available in Bullock and Brehme 2002.

The CMAQ-Hg model simulates the wet deposition of Hg^0, RGM, and particulate Hg in the same manner as for all other aqueous pollutant species previously resolved in the standard CMAQ model. The cloud-water concentration of each pollutant is deposited to the surface based on the simulated rate of precipitation falling from each clouded grid volume during the cloud chemistry time splitting operation. The cloud water concentration of Hg^0 is relatively low compared to the total dissolved and sorbed Hg^{2+}, and the simulated wet deposition of Hg^0 is minor compared to that of RGM and particulate Hg.

The cloud-water concentration of RGM is calculated as the sum of the dissolved-phase concentrations of all seven Hg^{2+} species in the aqueous chemistry mechanism. The cloud-water concentration of particulate Hg is calculated as the sum of the concentrations of all sorbed Hg^{2+} species.

Dry deposition of Hg^0 is assumed to be negligible in comparison to that of RGM and particulate Hg. It may actually be a minor compensation to emission fluxes of Hg^0 from geology, vegetation and water bodies such that dry evasion of Hg^0 might well be occurring instead. The dry deposition velocity for Hg^0 is currently set to zero the CMAQ-Hg model. RGM dry deposition is known to occur very readily, especially to lush vegetation and to water surfaces. The standard CMAQ dry deposition parameterization for gaseous nitric acid is also used for RGM. Dry deposition of particulate Hg is simulated based on pre-existing deposition velocity formulations in the standard CMAQ for the two modeled particle size modes.

MODELLING ACCURACY

An inter-comparison of mercury cloud-chemistry models was organized in 2000 at the Meteorological Synthesizing Center – East (MSC-East) in Moscow, Russia, with the participation of atmospheric mercury model developers from Germany, Russia, Sweden, and the U.S. (Ryaboshapko et al., 2001). Five mercury chemistry models, including CMAQ-Hg, were compared using the same hypothetical conditions for a cloud/fog volume. The same cloud microphysical parameters (i.e., liquid water content, droplet size, temperature and pressure) and initial conditions for chemistry in air and cloud water were used by all models, including identical initial concentrations in air and cloud water for three forms of mercury, Hg^0, RGM (assumed to $HgCl_2$), and particulate Hg. The results showed considerable variation among the models in their simulated accumulation of these three forms of mercury in cloud water during the 48-hour simulation period. With the exception of one model which used a rather different overall chemical system for mercury, it was not expected at the outset of the study that there would be a large amount of variation between the simulations. However, further investigation found a number of differences between the models in the exact set of reactions they simulated and the rate constants they employed for each reaction. There was also considerable difference in the way each model treated the association of aqueous Hg^{2+} with suspended particulate matter in cloud water. Overall, the results suggested that further basic research is critically needed to reduce uncertainties in the formulation of Hg chemistry models.

This international atmospheric mercury model inter-comparison activity is continuing, and a second phase of study involving full-scale model simulations for Europe has been conducted by participants from Bulgaria, Canada, Denmark, Germany, Russia, and the U.S. (Ryaboshapko et al., 2003). In addition to comparing results between the various models, these full-scale model simulations have been compared to observations of surface-level air concentration of total gaseous mercury (TPM), RGM and particulate Hg taken at five locations during 11 days in June/July of 1995 and 14 days in November 1999 (Ryaboshapko et al., 2003). Six of the models applied were Eulerian in structure and one was Lagrangian. All models used the same mercury emission inventories for input.

The air concentrations of Hg^0 assumed to be present at the lateral boundaries of the Eulerian models and super-imposed across the model domain of the Lagrangian model were a strong factor in each model's simulated total gaseous mercury (TGM) air concentration pattern over Europe, and each simulation of this species agreed quite well with observations in a statistical sense. However, for the RGM fraction of TGM, it was found that the models were only able to match observations of air concentration within a factor of 4 on average, and the difference was found to exceed an order of magnitude for some individual samples. The agreement between models and measurements for TPM was generally within a factor of 2, and most of the models were able to reproduce observed peaks in TPM air concentration at the proper time, if not at the proper amplitude. Ryaboshapko et al. (2003) concluded that the models had shown some skill in reproducing general TGM conditions, but our knowledge of the physico-chemical processes of RGM is still incomplete and sufficiently accurate parameterizations for this species have not yet been incorporated into the models.

A third phase of the MSC-East model inter-comparison study is now in the final stages of completion where simulations of monthly wet deposition flux are being compared to observations at nine locations in Europe. These results are not yet available for publication, but a comparison of simulated weekly wet deposition flux to observations at eleven sites in the U.S. has been conducted by the U.S. EPA using the same full-scale model it later applied for the European study (Bullock and Brehme, 2002). In the earlier study, the Community Multi-scale Air Quality (CMAQ) model was used to

Figures 2 and 3 show comparisons of simulated weekly Hg wet deposition versus observations from the Mercury Deposition Network (MDN) taken during the Spring and Summer test periods, respectively.

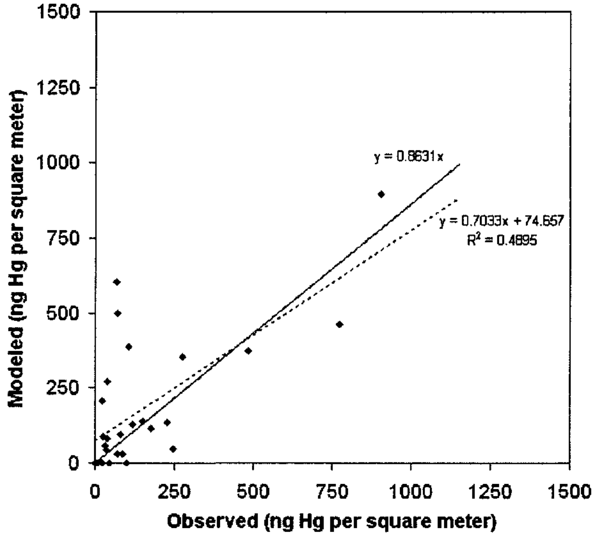

Figure 2. Scatter of the CMAQ – simulated versus MDN-observed weekly wet deposition flux of total mercury for the period 4 April to 2 May 1995.

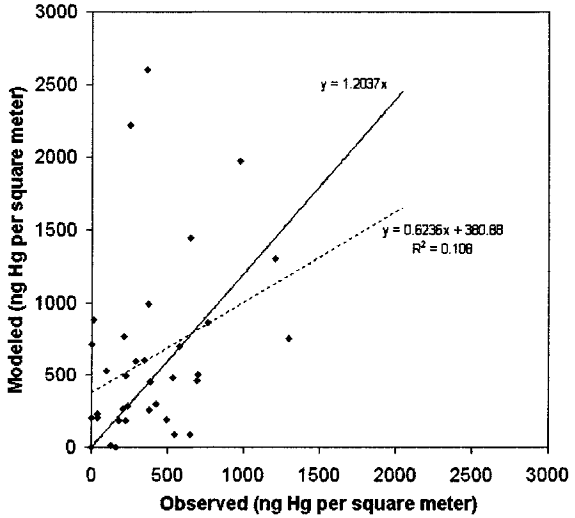

Figure 3. Scatter plot of the CMAQ-simulated versus MDN-observed weekly wet deposition flux of total mercury for the period 20 June to 18 July 1995.

simulate mercury for two 4-week periods in 1995 over the central and eastern U.S. and adjacent parts of southern Canada.

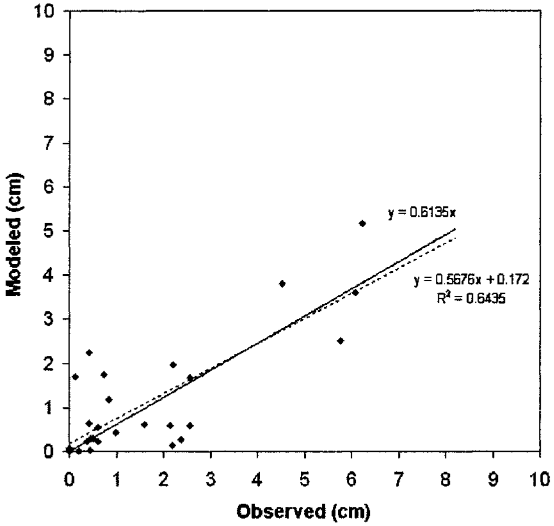

Figure 4. Scatter plot of the MM5-simulated versus MDN-observed weekly precipitation amount the period 4 April to 2 May 1995.

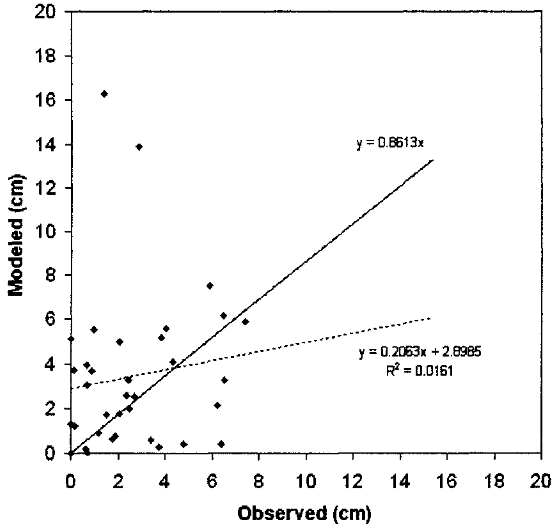

Figure 5. Scatter plot of the MM5-simulated versus MDN-observed weekly precipitation amount for the period 20 June to 18 July 1995.

The results in Figure 2 differ slightly from the Spring-period results published in Bullock and Brehme (2002) and show a slight increase in model accuracy due to correction of a slight error in the results analysis. Figure 2 indicates moderate model skill, but Figure 3 shows rather poor model performance.

Figures 4 and 5 show comparisons of simulated versus observed weekly precipitation amount during the Spring and Summer periods, respectively.

Precipitation rate and all other meteorological variables for CMAQ simulations are derived from previous applications of the MM5 meteorological model.

Figure 5 shows that the precipitation inputs for the CMAQ atmospheric mercury simulation of the Summer period were highly inaccurate. Obviously, the accuracy of CMAQ simulations of the wet deposition of Hg is dependent on an accurate definition of precipitation.

Comprehensive evaluation of this or any other atmospheric mercury model is currently not feasible due to a lack of measurements of the dry deposition flux of mercury. Without a confident definition of the true atmospheric deposition flux of Hg by both wet and dry processes, we cannot determine with confidence that any model is an accurate reflection of real atmospheric processes. A model could be simulating the wet deposition flux in the correct amount only because it has grossly over-represented the dry flux and has therefore left too little pollutant in air to be wet deposited. Likewise, it could be simulating too much wet deposition because the dry deposition flux was under-represented and the simulated air concentrations are too high. Air concentration measurements for each of the pertinent mercury species could certainly help to constrain this problem. However, we have no reason to believe that mercury contamination of aquatic ecosystems is due only to the wet deposition of atmospheric mercury.

Until we can assess model performance regarding the *total* atmospheric deposition of mercury, we gain insight into only a fraction of the problem, and we cannot know the size of that fraction.

SUMMARY

Atmospheric simulation models are being used widely to inform governmental policy makers about current scientific indications regarding the most effective mercury emission control options to reduce atmospheric deposition. Unfortunately, these models do not always agree as to the sources responsible for the deposition observed in particular areas. This disagreement between models does not appear to come only from differences in the sets of chemical and physical reactions of mercury they simulate. Uncertainty regarding actual air concentrations of Hg^0, RGM and particulate Hg at high altitudes and over remote locations requires continental-scale modelers to adopt boundary air concentration values that are based either on lower-resolution global-scale models or on very sparse observational data. Uncertainty about exchanges of mercury between the atmosphere and the various surfaces beneath it requires still more assumptions to be made. Obviously, these types of assumptions provide ample opportunity for model simulations to differ. The current lack of measurement data to support comprehensive model evaluation will certainly need to be addressed if we are to know which models, with all of their attendant assumptions, are the most accurate reflections of reality.

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. 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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PART-IV:

HUMAN EXPOSURE