The Modeling of Regional-Scale Atmospheric Mercury Transport and Deposition Using RELMAP

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Modeling Regional-Scale Atmospheric Mercury Using RELMAP

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Abstract - The Regional Lagrangian Model of Air Pollution (RELMAP) is used to simulate the emission, transport and diffusion, chemical transformation, and wet and dry deposition of elemental mercury gas, divalent mercury gas and particulate mercury. Based on recent modeling advances in Europe, the RELMAP has been modified to simulate a reductionoxidation (redox) balance for mercury dissolved in cloud and rain water. This redox balance is used in the estimation of a variable precipitation scavenging ratio for elemental mercury. The result is more effective removal of elemental mercury gas by precipitation processes than is implied by its solubility in water. Wet removal of divalent mercury gas and particulate mercury is modeled using constant wet scavenging ratios. Dry deposition is estimated using deposition velocities developed from various modeling studies in the U.S. and in Europe. A mercury air emission inventory for the continental United States is used to estimate the releases of elemental mercury gas, divalent mercury gas and particulate mercury based on emission speciation estimates for the various emitter types in the inventory. Average annual concentrations and wet and dry deposition totals for these three forms of mercury have been simulated. The results of the simulation are used to estimate the quantity of mercury emitted to the air annually over the United States, and the amount that is subsequently deposited back to U.S. soils and water bodies. An analysis of the modeling results also provides some information about the areas of the country thought to have the most significant exposure from all air emissions of mercury. This analysis contributes to the understanding of the key variables, such as source location, chemical and physical form of emission, or meteorology, that lead to these outcomes.

Key Words - Mercury, Atmospheric, Modeling, Deposition, Emission

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BACKGROUND INFORMATION ON RELMAP

During the mid-1970's, SRI International developed a Lagrangian puff air pollution model called the EUropean Regional Model of Air Pollution (EURMAP) for the Federal Environment Office of the Federal Republic of Germany [1]. This regional model simulated monthly sulfur dioxide (SO₂) and sulfate (SO₄²⁻) concentrations, wet and dry deposition patterns, and generated matrices of international exchanges of sulfur for 13 countries of western and central Europe. In the late-1970's, the US EPA sponsored SRI International to adapt and apply EURMAP to eastern North America. The adapted version of this model was called the Eastern North American Model of Air Pollution (ENAMAP) [2,3].

By 1985, simple parameterizations of processes involving fine (diameters $< 2.5 \ \mu m$) and coarse (2.5 μm < diameters $< 10.0 \ \mu m$) particulate matter were incorporated into the model. This version of the model, renamed the REgional Lagrangian Model of Air Pollution (RELMAP), is capable of simulating concentrations and wet and dry deposition patterns of SO₂, SO₄² and fine and coarse particulate matter and can also generate source-receptor matrices for user defined regions. Currently, the RELMAP is operated by EPA's National Exposure Research Laboratory (NERL) on a wide variety of computing systems. The data preparation for this modeling study was performed at EPA's National Environmental Supercomputing Center and the model calculation was performed on the UNIX computing workstation network at the Atmospheric Modeling Division of NERL. A complete scientific specification of the RELMAP as used at EPA for atmospheric sulfur modeling has been developed and published [4]. The next section will discuss the modifications made to the original sulfur version of the RELMAP to enable the simulation of atmospheric mercury.

MODELING STRATEGY

General Information

Previous versions of the RELMAP have been described and evaluated [4,5]. The goal of this study was to model the emission, transport and fate of airborne mercury over the continental U.S. for the year of 1989. Our modifications to the RELMAP for atmospheric mercury simulation were heavily based on recent Lagrangian model developments in Europe [6]. The mercury version of the RELMAP was developed to handle three species of mercury: elemental vapor (Hg⁰), divalent vapor (the mercuric ion, Hg²⁺) and particulate Hg (Hg_P), and also aerosol carbon soot. Recent experimental work indicates that ozone [7] and carbon soot [8,9,10] are both important in determining the wet deposition of Hg⁰. Carbon soot, or total carbon aerosol, was included as a modeled pollutant in the mercury version of RELMAP to provide necessary information for the Hg⁰ wet deposition parameterization. Observed ozone (O₁) air concentration data were obtained from EPA's Aerometric Information Retrieval System (AIRS) data base. Thus, it was not necessary to include O₃ as an explicitly modeled pollutant. Observed O₃ air concentration data were objectively interpolated in time and space for each 3-hour time step of the model simulation to produce analyses of O₃ air concentration. Methyl mercury was not included in the mercury version of RELMAP because it is not yet known if it has a primary natural or anthropogenic source, or if it is produced in the atmosphere.

RELMAP may be run in either of two modes. In the field mode, wet deposition, dry deposition, and air concentrations are computed at user-defined time intervals. In the source-

receptor mode, RELMAP also computes the contribution of each source cell to the deposition and concentration at each receptor cell. For mercury, only the field mode of RELMAP operation was used. With over 10,000 model cells in the high-resolution receptor grid and a significant fraction of these cells also emitting mercury, the data accounting task of a sourcereceptor run for all mercury sources could not be performed.

Unless specified otherwise in the following sections, the modeling concepts and parameterizations described in the EPA users' guide [4] were preserved for the RELMAP mercury modeling study.

Physical Model Structure

RELMAP simulations were originally limited to the area bounded by 25 and 55 degrees north latitude and 60 and 105 degrees west longitude, and had a minimum spatial resolution of 1 degree in both latitude and longitude. For this study, the western limit of the RELMAP modeling domain was moved out to 130 degrees west longitude, and the modeling grid resolution was reduced to ½ degree longitude by ¼ degree latitude (approximately 40 km square) to provide high-resolution coverage over the entire continental U.S.

The original 3-layer puff structure of the RELMAP has been replaced by a 4-layer structure. The following model layer definitions were used for the RELMAP mercury simulations:

Layer 1 top - 30 to 50 meters above the surface (season-dependent) Layer 2 top - 200 meters above the surface

Layer 3 top	-	700 meters above the surface
Layer 4 top	-	700 to 1500 meters above the surface (month-dependent)

Mercury and Carbon Aerosol Emissions

Area source emissions are introduced into the model in the lowest layer. Point source emissions are introduced into model layer 2 to account for the effective stack height of the point source type in question. Effective stack height is the actual stack height plus the estimated plume rise. The layer of emission is inconsequential during the daytime when complete vertical mixing is imposed throughout the 4 layers. At night, since there is no vertical mixing, area source emissions to layer 1 are subject to dry deposition while point source emissions to layer 2 are not. Large industrial emission sources and sources with very hot stack emissions tend to have a larger plume rise, and their effective stack heights might actually be higher than the top of layer 2. However, since the layers of the pollutant puffs remain vertically aligned during advection, the only significant process effected by the layer of emission is nighttime dry deposition.

Global-scale natural emissions, recycled anthropogenic emissions and primary anthropogenic emissions from outside the continental U.S. are accounted for by superimposing a background atmospheric concentration of Hg⁰ gas of 1.6 ng/m³. This use of a constant background concentration is the same technique used by modelers in Europe [6]. The same model parameterizations used to simulate the deposition of Hg⁰ from explicit anthropogenic emissions are also used to simulate the deposition of Hg⁰ from this constant background concentration throughout the entire 3-dimensional model domain.

Total carbon air concentrations have been shown to be highly correlated with sulfur dioxide (SO₂) air concentrations from minor sources [11], and the emissions of total carbon and SO₂ from minor point sources are assumed to be correlated as well, since both pollutants result from the combustion of fossil fuel. A 35% proportionality constant for total carbon air concentrations versus SO_2 air concentrations has been estimated [11]. For this study, total carbon aerosol emissions were estimated using this 35% proportionality constant and SO_2 emissions data for minor sources obtained by the National Acidic Precipitation Assessment Program (NAPAP). Many of these SO₂ emissions data had been previously analyzed for use by the Regional Acid Deposition Model (RADM). For the portion of the RELMAP mercury model domain not covered by the RADM domain, state by state totals of SO₂ emissions were apportioned to the county level on the basis of weekday vehicle-miles-traveled data since recent air measurement studies have indicated that aerosol elemental carbon can be attributed mainly to transportation source types [12]. The county level data were then apportioned by area to the individual RELMAP grid cells. Total carbon soot was assumed to be emitted into the lowest layer of the model.

Ozone Concentration

Hourly O_3 concentration data were obtained from EPA's Aerometric Information Retrieval System (AIRS). Any observations of O_3 concentration below 20 ppb were treated as missing. For each RELMAP grid cell, the O_3 concentrations were computed for the two midday time steps by using the mean concentration value during two corresponding time periods (1000-1300 and 1400-1600 local time). The mean of these two midday values was used to estimate the O_3 concentration for the time steps after 1600 local time and before 1000 local time the next morning. This previous-day average was used at night since ground-level O_3 data are not valid for the levels aloft, where the wet removal of Hg⁰ was assumed to be occurring. Finally, an objective interpolation scheme was used to produce complete O_3 concentration grids for each time step, with a minimum value of 20 ppb imposed to represent an average global background value.

Lagrangian Transport and Deposition

In the RELMAP model, each pollutant puff begins with an initial mass equal to the total emission rate of all sources in the source cell multiplied by the model time-step length. Emission rates for each source cell were defined from input data and a time step of three hours was used. The initial horizontal area of each puff was set to 1200 km², instead of the standard initial size of 2500 km², in order to accommodate the finer grid resolution used for the mercury modeling study. However, the standard horizontal expansion rate of 339 km² per hour was not changed.

Although each puff is defined with four separate vertical layers, all of these layers are advected through the model cell array by the same wind velocity field. Thus, the layers of each puff always remain vertically stacked. Wind field initialization data for a National Weather Service prognostic model, the Nested Grid Model (NGM), were obtained from the NOAA Atmospheric Research Laboratory for the entire year of 1989. Wind analyses for the NGM vertical model layer near 1000 m above ground level (a.g.l.) were used to define puff advection throughout the simulation, except for the months of January, February and December, when winds for a layer near 500 m a.g.l. were used to better represent the more shallow mixed layer heights of the winter season.

Pollutant mass was removed from each puff by the processes of wet deposition, dry deposition and diffusive air exchange between the surface-based mixed layer and the free atmosphere. Observed precipitation data for the entire year of 1989 were obtained from the National Climatic Data Center and used to estimate wet deposition of all mercury species. Wet and dry deposition totals were accumulated and average surface-level concentrations were calculated on a monthly basis for every model cell, except for the cells in the far southwest and eastern corners of the model domain for which NGM-derived wind data were not available. When the mass of pollutant in a puff declined through deposition or vertical diffusion to, a prescribed minimum value, or when a puff moved out of the model grid, the puff and its pollutant load were no longer tracked. The amount of pollutant in the terminated puff was taken into account in monthly mass balance calculations so that the integrity of the model simulation was assured.

Vertical Exchange of Mass with the Free Atmosphere

Due to the long atmospheric lifetime of mercury, the RELMAP was adapted to allow a treatment of the exchange of mass between the surface-based mixed layer and the free atmosphere above. As an intuitive approximation, a pollutant depletion rate of 5 percent per 3-hour time step was chosen to represent this diffusive mass exchange. When compounded over a 24-hour period, this depletion rate removes 33.6% of an inert, non-depositing pollutant. Since all three of the modeled mercury species deposit to the surface to some degree, their

effective diffusion rate out of the top of the model is somewhat less than 33.6% per day.

MODEL PARAMETERIZATIONS

Chemical Transformation and Wet Deposition

In the mercury version of RELMAP, Hg_P and total carbon are each modeled explicitly as inert pollutant species. The RELMAP was originally developed to simulate sulfur deposition, and the algorithm for transformation of sulfur dioxide to sulfate was independent of wet deposition. For gaseous mercury, however, the situation is more complex. Since there are no gaseous chemical reactions of mercury in the atmosphere which appear to be significant [6], mercury chemistry is treated only in the aqueous medium. Hg⁰ has a very low solubility in water, while oxidized forms of mercury and particulate mercury readily find their way into the aqueous medium through dissolution and particle scavenging, respectively. Swedish measurements of large north-to-south gradients of mercury concentration in rainwater without corresponding gradients of atmospheric mercury concentration suggest the presence of physical and chemical interactions with other pollutants in the precipitation scavenging process [8]. Aqueous chemical reactions incorporated into the mercury version of RELMAP are based on research efforts in Sweden [7,10,13,14,15] and Canada [16,17].

Unlike other pollutants that have been modeled with RELMAP, mercury has wet deposition and chemical transformation processes that are interdependent. A combined transformation/wet-removal scheme is used [6]. In this scheme, the following aqueous chemical processes are modeled when and where precipitation is present.

- 1) oxidation of dissolved Hg^0 by O₃ yielding Hg^{2+}
- 2) catalytic reduction of this Hg^{2+} by ubiquitous sulfite ions
- 3) adsorption of Hg^{2+} onto carbon soot particles suspended in the aqueous medium

These three simultaneous reactions are considered in the formulation of a variable wet scavenging ratio for elemental mercury gas as follows:

$$W(Hg^{0}) = \frac{k_{1}}{k_{2}} \cdot \frac{1}{H_{Hg}} \cdot [O_{3}]_{aq} \cdot (1 + K_{3} \cdot \frac{c_{soot}}{r})$$

where,

 k_1 is the second order rate constant for the aqueous oxidation of Hg⁰ by O₃ equal to 4.7 × 10⁷ M⁻¹ s⁻¹,

 k_2 is the first order rate constant for the aqueous reduction of Hg²⁺ by sulfite ions equal to 4.0×10^{-4} s⁻¹,

 H_{Hg} is the dimensionless Henry's Law coefficient for Hg⁰ (0.18 in winter, 0.22 in spring and autumn, and 0.25 in summer as calculated from [18]),

 $[O_3]_{aq}$ is the aqueous concentration of ozone,

 K_3 is a model specific adsorption equilibrium constant (5.0 × 10⁻⁶ m⁴ g⁻¹),

 c_{soot} is the total carbon soot aqueous concentration, and

r is the assumed mean radius of soot particles $(5.0 \times 10^{-7} \text{ m})$.

$[O_3]_{aq}$ is obtained from

where H_{03} is the dimensionless Henry's Law coefficient for O₃ (0.448 in winter, 0.382 in

$$[O_3]_{aq} = \frac{[O_3]_{gas}}{H_{O3}}$$

spring and autumn, and 0.317 in summer as calculated from [19]). c_{soot} is obtained from the simulated air concentration of total carbon aerosol using a scavenging ratio of 5.0×10^5 .

The model used in [6] defined one-layer cylindrical puffs, and the Hg⁰ scavenging layer was defined as the entire vertical extent of the model. The RELMAP defines 4-layer puffs to allow special treatment of surface-layer and nocturnal inversion-layer processes. Due to the low solubility of Hg⁰ in water, it was assumed for this study that the scavenging process outlined above would only take place effectively in the cloud regime where the water droplet surface-area to volume ratio is highest, and not in falling raindrops. Thus the Hg⁰ wet scavenging process was applied only in the top two layers on RELMAP, which extends from 200 meters above the surface to the model top.

For the modeling study described in [6], the wet deposition of Hg^{2+} was treated separately from that of Hg^{0} . Obviously, any Hg^{2+} dissolved into the water droplet directly from the air could affect the reduction-oxidation balance between the total concentration of Hg^{0} and Hg^{2+} in the droplet. Since the solubility and scavenging ratio for Hg^{2+} is much larger than that for Hg^{0} , and since air concentrations of Hg^{0} are typically much larger than those of Hg^{2+} , separate treatment of Hg^{2+} wet deposition is used in the RELMAP also. Thus, as was done in [6], the catalytic reduction of Hg^{2+} is only considered as a moderating factor for the oxidation of dissolved Hg^{0} .

Although Hg^{2^+} is recognized as a reactive species in aqueous phase redox reactions, it is modeled in the RELMAP as an inert species similar to Hg_P and total carbon soot. Given the rapid rate at which the aqueous Hg^{2^+} reduction reaction is believed to occur in the presence of sulfite, it is possible that an interactive cloud-water chemical mechanism could produce significant conversion of scavenged Hg^{2+} to Hg^{0} , with possible release of that Hg^{0} into the gaseous medium. It is anticipated that future improvements to the RELMAP will include a more sophisticated treatment of this interacting aqueous chemistry.

Wet deposition of Hg^{2+} , Hg_P and total carbon soot in the mercury version of the RELMAP are modeled with the same scavenging ratios used in [6]. These fixed scavenging ratios were applied to all four layers of the RELMAP in the calculation of pollutant mass scavenging by precipitation.

Dry Deposition

Recent experimental data indicate that Hg⁰ vapor does not exhibit a net dry depositional flux to vegetation until the atmospheric concentration exceeds a compensation point of 10 ng/m³ or more, where emission and deposition forces are equal [20]. This compensation point is apparently dependent on the surface or vegetation type and represents a balance between emission from humic soils and dry deposition to leaf surfaces [20,21]. Since the emission of mercury from soils is accounted for by a global-scale ambient concentration and not an actual emission of Hg⁰, for consistency, there is no explicit simulation of the dry deposition of Hg⁰.

During simulated daylight hours, dry deposition velocity tables previously developed based on HNO₃ data [22,23] are used to estimate Hg^{2+} dry deposition. This use of HNO₃ data to estimate Hg^{2+} dry deposition is similar to the technique used in [6]. However, in this case, the dry deposition velocity of Hg^{2+} is allowed to vary based on surface characteristics and meteorological conditions. The dry deposition velocity tables provide season-dependent values for 11 land-use types under six different Pasquill stability categories. The indicated values for Hg²⁺ dry deposition velocity vary between 0.13 cm/s and 4.83 cm/s. For nighttime, a value of 0.3 cm/s is used for all grid cells since the RELMAP does not have the capability of applying land-use dependent dry deposition at night. Since the nighttime dry deposition is applied only to the lowest layer of the model and no vertical mixing is assumed for nighttime hours, all Hg²⁺ would be quickly depleted from the lowest model layer by larger dry deposition velocities.

In [6], a dry deposition velocity of 0.2 cm/s was used for Hg_P at all times and locations. Dry deposition of Hg_P seems to be dependent on foliar activity [24]. In the RELMAP mercury model, the daytime dry deposition velocities for Hg_P are calculated using a FORTRAN subroutine developed by the California Air Resources Board (CARB) [25]. A particle density of 2.0 g/cm³ and diameter of 0.3 μ m is assumed. A wind speed of 10 m/s is assumed for Pasquill stability category A, 5 m/s for categories B and C, 2.5 m/s for categories D and E, and 1 m/s for category F. Table 1 shows the roughness lengths (z₀) used for each land-use category and season. At night, all cells use 0.02 cm/s as the dry deposition velocity for Hg_P. A value of 0.003 cm/s has been suggested for non-vegetated land [24], but since the RELMAP can not model land-use dependent dry deposition at night, the value of 0.02 cm/s is used for these cells by necessity.

For total carbon aerosol, daytime dry deposition velocities are also calculated using the CARB subroutine. A particle density of 1.0 g/cm^3 and diameter of $1.0 \text{ }\mu\text{m}$ is assumed for these aerosol soot particles. For nighttime, a dry deposition velocity of 0.07 cm/s is used for all seasons and land-use types for total carbon aerosol.

The atmospheric mercury emission inventory used for this modeling study was developed by the EPA Office of Air Quality Planning and Standards (OAQPS) and is described in Volume II of the Mercury Study Report to Congress which is due to be submitted to the U.S. Congress by OAQPS in late 1995. Data from this inventory were used to compile estimates of the mercury emissions from 7 major stationary source types (point sources) and from a group of minor source types for which individual emission site locations were not available (area sources). The 8 emission source types resolved for input to the RELMAP mercury model were; electric-utility fossil-fueled boilers, non-utility fossil-fueled boilers, municipal solid waste combustion, medical waste incineration, chlor-alkali factories, non-ferrous metal smelting, all other point sources, and area sources. For each of the sourcespecific point source types, a base-case estimate of the mercury emission speciation profile was adopted from [6] to represent the best engineering estimate of the chemical and physical forms of the Hg emissions. Since there remains considerable uncertainty about the actual chemical and physical forms of mercury emitted and about the importance of Hg²⁺ vapor attachment to particles, an alternate emission speciation was also developed to measure the sensitivity of the RELMAP results to these uncertainties. The alternate speciation represents a complete transfer of all Hg²⁺ vapor emissions to a particle-bound form. The alternate speciation is not intended to serve as a credible alternative to the base speciation, but only as a perturbation for model sensitivity testing.

The base-case and alternate mercury emission speciation profiles for the 7 point source types are shown in Table 2. The area sources are modeled as having emissions of Hg⁰ only.

The area source data used for input to the RELMAP model simulation include estimates of the emission of mercury from latex paints, which were not included in the assessment of emissions described in Volume II of the Mercury Study Report to Congress. These latex paint emission estimates for the continental U.S. total 4 metric tons per year. The compiled nationwide patterns of Hg^0 , Hg^{2+} and Hg_P emissions from all point and area source types using the base-case emission speciation profiles are illustrated in Figures 1, 2 and 3, respectively.

Table 3 shows the results of applying the base-case emission speciation profiles to the 8 mercury emission source types resolved by the RELMAP mercury model. These emissions are for the lower 48 states only. Thus, some of the specific-source totals differ slightly from the national totals shown in Volume II of the Mercury Study Report to Congress. This analysis indicates that of the total anthropogenic emissions from the lower 48 states, 26% is from medical waste incineration, 22% is from municipal waste combustion, 22% is from electric utility boilers, 13% is from fossil fuel combustion other than that by electric utilities, 4% is from non-ferrous metal smelting, and 3% is from chlor-alkali factories. The atmospheric emissions from all other point source types represent 7% of the total anthropogenic emission in the lower 48 states, while area sources represent 3% of this total. As a whole, large-scale fossil fuel combustion represents about 35% of the total anthropogenic mercury emissions to the atmosphere in the lower 48 states. Because of differences in the behavior of the various chemical and physical forms of mercury in the atmosphere, it is important to determine their relative contributions to the total mass of mercury emitted. Table 3 indicates that, based on the base-case emission speciation profiles, about 41% of all anthropogenic mercury emitted to the air in the continental United States is in the form of Hg⁰ vapor, 41% is in the form of Hg^{2+} vapor, and 17% is emitted as Hg_{P} .

INTERPRETIVE ANALYSIS OF THE RESULTS

Mass Balances of Mercury within the Model Domain

The general mass balance of Hg^0 , Hg^{2+} and Hg_P from the RELMAP simulation using the base-case emission speciation is shown in Table 4. The mass-balance accounting for the simulation of the year 1989 shows a total of 223.8 metric tons of mercury emitted to the atmosphere from anthropogenic sources in the continental United States. The base-case simulation accounting also shows that 77.9 metric tons of these anthropogenic mercury emissions deposited to the surface within the model domain and that 0.6 metric tons remained in the air within the model domain at the end of the simulation. The balance, about 145.3 metric tons, was transported outside the model domain and conceptually became part of the global atmospheric background. This estimated annual contribution of continental U.S. anthropogenic sources to the global mercury cycle amounts to about 2% of the total global reservoir. A rough calculation of the total mass of the global atmospheric mercury reservoir based on a sea-level concentration of 1.6 ng/m³ (1.6 g/km³), a total atmospheric scale height of 9 km and a global surface area of 5.1×10^8 km² yields a figure of 7.3×10^9 g, or 7300 metric tons. The simulation mass balance also indicates that 33.0 metric tons of mercury is deposited annually within the model domain from this global atmospheric reservoir.

As shown in Table 5, the alternate case emission speciation profiles result in a noticeably different mass balance. By assuming that all of the Hg²⁺ emitted quickly becomes

bound to existing particles, the total deposition of anthropogenic Hg to the surface is reduced by about 40%. This is primarily due to the fact that the modeled dry deposition velocity of particulate matter in the assumed size range is much smaller than the modeled dry deposition velocity for Hg²⁺ vapor. A particle diameter of 0.3 μ m was assumed to be representative of continental air masses with moderate urban influences. Less efficient wet scavenging of particulate versus gaseous Hg²⁺ also contributes to the lower total deposition using the alternate emission speciation profiles. While the assumption of total Hg²⁺ attachment to particles is only intended as a bounding exercise, the results show the importance of an accurate determination of the mass of Hg_P emitted and formed during transport.

Of the total simulated anthropogenic mercury deposited to the surface in the model domain, 80% is estimated to come from Hg^{2+} emissions, 18% from Hg_P emissions and 2% from Hg^0 emissions when the base-case emission speciation profiles are used. When the deposition of Hg^0 from the global background is considered in addition to anthropogenic sources in the lower 48 states, the species fractions become 56% Hg^{2+} , 31% Hg^0 and 13% Hg_P . The vast majority of mercury already in the global atmosphere is in the form of Hg^0 concentration. Although Hg^0 is removed from the atmosphere very slowly, the global background reservoir is large and extraction of mercury from it is significant in terms of the total deposition. It should be reiterated that dry deposition of Hg^0 vapor appears to be significant only at very high concentrations and has not been included in the RELMAP simulations. Wet deposition is the only major pathway for removal of Hg^0 from the atmosphere. This removal pathway simulated by the RELMAP involves oxidation of mercury by O₃ in an aqueous solution; thus, the Hg^0 that is extracted from the atmosphere by the

modeled precipitation process would actually be deposited primarily in the form of Hg²⁺.

Results from the RELMAP simulation show that 98% of the deposited anthropogenic mercury was emitted in the form of Hg^{2+} or Hg_P . Thus, a strong argument can be made that the combined Hg^{2+} and Hg_P component of all anthropogenic mercury emissions can be used as an indicator of eventual deposition of those emissions to the lower 48 states and surrounding areas. The emission inventory and base-case chemical/physical speciation profiles indicate that of all combined Hg^{2+} and Hg_P emissions, about 36% is from medical waste incineration, 30% is from Municipal Waste Combustion, 18% is from electric utility boilers, 11% is from combustion of fossil fuel other than by electric utilities, 1% is from Chlor-alkali factories, 1% is from non-ferrous metal smelting, and 2% is from all other sources.

Qualitative Description of Mercury Concentration Results

Annual average surface-level concentration fields for Hg^0 , Hg^{2+} , and Hg_p have been obtained from the RELMAP simulation of 1989. Figure 4 shows the annual average Hg^0 concentration at ground level from anthropogenic sources obtained by using the base-case emission speciation. It shows that anthropogenic Hg^0 concentrations remain less than 0.1 ng/m^3 over most of the investigation area. The areas where the average anthropogenic Hg^0 concentrations exceed 0.1 ng/m^3 are mostly confined to the highly industrialized locations in the eastern Midwest and the Northeast regions. Compared to the estimated average global background concentration of 1.6 ng/m^3 , this 0.1 ng/m^3 elevation of Hg^0 concentration by anthropogenic emissions is rather small.

Figure 5 shows annual average Hg²⁺ air concentrations, also using the base case

speciation. These values are significantly lower than for anthropogenic Hg⁰, and there are some new areas of maximum concentration. The higher concentration areas have values from 0.05 to just over 0.1 ng/m³ and are mostly confined to Florida, the Midwest and the Northeast urban corridor. The background atmospheric mercury loading is assumed to be completely in the elemental form, so there is no background contribution to the Hg²⁺ concentrations. In most areas, the anthropogenic component of the Hg⁰ concentrations (Figure 4) are at least 3 to 5 times higher than the Hg²⁺ concentrations (Figure 5). Since the national total of Hg²⁺ emissions are about equal to those for Hg⁰, these much lower average annual Hg²⁺ concentrations must be due to more rapid depletion from wet and dry deposition.

The RELMAP-simulated Hg⁰ and Hg²⁺ air concentrations taken together with the assumed background Hg⁰ concentration of 1.6 ng/m³ agree well with observations of vaporphase Hg air concentration in Minnesota [26], in Vermont [27] and in Wisconsin [28]. These observations showed that annual average vapor-phase Hg concentrations were near the levels found over other remote locations in the northern hemisphere, from 1.6 to 2.0 ng/m³. Measurements taken for a two-week period at three sites in Broward County, Florida, [29] show slightly elevated vapor-phase Hg air concentrations for two of those sites downwind of industrial activities. These two sites had average vapor-phase Hg air concentrations of 3.3 and 2.8 ng/m³. The RELMAP simulation results for the Fort Lauderdale area show only about a 0.2 ng/m³ elevation of the annual average vapor-phase Hg (Hg⁰ plus Hg²⁺) concentration over the 1.6 ng/m³ background value assumed. However, the measurements in Broward County did not extend for a significant portion of the year and there was no discrimination between Hg⁰ and Hg²⁺ forms. The third site for their observations had an average vapor-phase air concentration of 1.8 ng/m³, exactly what the RELMAP simulation suggests. Obviously, a more comprehensive air monitoring program is required before an evaluation of the RELMAP results for Florida can be performed.

Hg_P emissions are thought to be a small fraction of the total Hg emissions for most source types. For the base-case emission speciation, 20% is the largest particulate fraction of mercury emissions for any source type. Figure 6 indicates that the simulated annual average Hg_{P} concentrations are even lower than those for Hg^{2+} vapor. The maximum annual average values are around 50-100 pg/m³ (0.05-0.1 ng/m³) in the urban centers of the Northeast. A study in urban Detroit found instantaneous Hg_P concentrations during March of 1992 of over 1 ng/m³ and average concentrations over an 18-day period of 94 pg/m³ [30]. The RELMAP simulation suggests an annual average Hg_P concentration in the Detroit area of about 50 pg/m³. However, given the 40-km horizontal scale of the RELMAP computational grid, one can not expect the simulation to reflect these extreme local-scale measurement results. Average Hg_P concentrations of between 34 and 51 pg/m³ were measured in Broward County, Florida, at three sites from 25 August to 7 September of 1993 [29]. The RELMAP simulation results agree well with these observations around the city of Fort Lauderdale. Researchers have found annual average Hg_P air concentrations of 10.5 pg/m³ in Pellston, Michigan, 22.4 pg/m³ in South Haven, Michigan, and 21.9 pg/m³ in Ann Arbor, Michigan, from April 1993 to April 1994, and 11.2 pg/m³ in Underhill, Vermont, for the year of 1993 [30]. The RELMAP simulation results agree quite well with these observations also.

Table 6 shows a percentile analysis of the simulated concentration results from the RELMAP grid cells within the lower 48 United States. This table shows that the Hg⁰ concentrations never exceeded the assumed background level of 1.6 ng/m³ by a large relative amount. It also shows that Hg²⁺ and to a lesser degree Hg_P air concentrations were highly

elevated in only a few grid cells. There is an order of magnitude difference in the Hg^{2+} concentrations at the 90th percentile level and the maximum level, with a factor of 5 difference for Hg_{p} .

For the alternate emission speciation tests, the Hg^{2+} vapor emission fraction was redistributed to the Hg_p fraction, simulating the complete attachment of Hg^{2+} vapor to ambient particulate matter. The annual average Hg^0 and Hg_p concentration fields from this test (not shown) indicate that, as one would expect, there was no change to the Hg^0 results, but the Hg_p concentrations are increased nearly to the level of anthropogenic Hg^0 , with maximum concentrations over 100 pg/m³ (0.1 ng/m³) for the larger urban areas of Florida and the Midwest and for nearly all of the Northeast urban corridor.

Description of Mercury Wet Deposition Simulation Results

Figure 7 shows the simulated wet deposition of Hg⁰ from continental U.S. anthropogenic sources during 1989 using the base emission speciation factors. Figure 8 shows the simulated annual wet deposition of Hg⁰ assuming only a non-depleting global background concentration of 1.6 ng/m³. Both of these wet deposition results are influenced by O₃ and carbon soot concentrations due to the chemical transformations modeled by the RELMAP. Emission patterns influence the primary anthropogenic Hg⁰ wet deposition pattern and it is obvious that total annual precipitation is a strong positive factor in wet deposition from the global background concentration. It is widely accepted that deposition of Hg⁰ occurs on continental and global scales, and the RELMAP simulation shows areas of significant Hg⁰ wet deposition occurring in remote areas. The base-case wet deposition results for Hg²⁺ vapor shown in Figure 9 indicate maximum deposition areas that are highly coincident to the emission source areas. There are many model cells in urban areas with wet deposition totals of Hg^{2+} vapor over 20 $\mu g/m^2$, while most of the cells in the non-urban areas have wet depositions of less than 5 $\mu g/m^2$. This indicates that Hg^{2+} vapor wet deposits more on the local scale, and not on regional or global scales and that its wet removal from the atmosphere is much more rapid than for Hg^0 . This is an expected result due to the higher water solubility of most mercuric salts compared to mercury in the elemental form. Figure 10 shows that, for the base-case emission speciation, the maximum simulated wet deposition of Hg_P is about half of that for Hg^{2+} vapor. This is partly due to differences in the total mass of Hg_P emitted compared to Hg^{2+} ; but, it is also due to the less efficient wet scavenging of Hg_P . The areas of Hg_P wet deposition are also more widespread than for Hg^{2+} due to the slower depletion of Hg_P and greater opportunity for long-range transport.

The total wet deposition of mercury emitted in all three forms is shown in Figure 11. This illustration shows significant wet deposition of mercury over most of the eastern half of the U.S. For the simulated year of 1989, nearly the entire eastern half of the nation has a wet deposition total of over 5 μ g/m² and values exceed 20 μ g/m² over much of the urban northeast U.S. In fact, the largest simulated wet deposition exceeded 100 μ g/m² in the grid cell containing New York City. We have not designed Figure 11 to highlight these extreme maximum wet deposition results because at this time such high wet deposition rates for total mercury can not be substantiated by observations. In the RELMAP simulation, the most impacted areas are being subjected to wet deposition of mercury mainly from emissions of Hg²⁺ vapor. We suspect that the RELMAP model for mercury may still be significantly incomplete, and that other chemical and/or physical transformations may occur which moderate the wet deposition of Hg²⁺ vapor and possibly Hg_P.

Measurements of mercury wet deposition at three locations in northeastern Minnesota during 1989 indicated annual wet deposition rates of 6.5 μ g/m² at Duluth, 13.5 μ g/m² at Marcell and 41.9 μ g/m² at Ely [31]. A later study measuring annual wet deposition of Hg during 1990, 1991 and 1992 at Ely, Duluth and seven other sites in Minnesota, upper Michigan and northeastern North Dakota found all annual wet deposition totals to be within the range of 3.8 to 9.7 μ g/m² [32]. Measurements at Little Rock Lake, in northern Wisconsin, of Hg in snow during February and March, 1989, and in rain from May to August, 1989, have been used to estimate annual Hg depositions in rain and snow of 4.5 and 2.3 μ g/m², respectively [26]. This suggests a total annual Hg wet deposition of 6.8 μ g/m² at Little Rock Lake. Measurements at Presque Isle, also in northern Wisconsin, from 1993 to 1994 suggested a wet deposition rate for total Hg of 5.2 μ g/m²/yr [28], somewhat less than the measurements at Little Rock Lake. The extremely heavy rainfall during the summer of 1993 in the mid-west states to the south and west of Presque Isle may be responsible for the lower wet deposition. The RELMAP simulation results for 1989 indicate 2 to 10 μ g/m² wet deposition of total Hg over most of the area represented by these studies, the major exception being the Minneapolis-Saint Paul metropolitan area where the RELMAP indicates over 20 $\mu g/m^2$.

There were also some Hg wet deposition measurement programs conducted during the early 1990's in somewhat less remote sites in Michigan and Vermont. Observations during two years of event precipitation sampling at three sites in Michigan show evidence for a north-to-south gradient in Hg wet deposition [33]. From March 1992 to March 1993, the total Hg wet deposition observed at South Haven, in southwest Michigan, was 9.45 μ g/m². At

Pellston, in the northern part of the lower peninsula of Michigan, the wet deposition was 5.79 $\mu g/m^2$. At Dexter, in southeast Michigan about 100 km west of Detroit, the wet deposition was 8.66 µg/m². From March 1993 to March 1994, wet deposition at South Haven was 12.67 $\mu g/m^2$, significantly higher than for the previous year, while measurements at Pellston and Dexter remained about constant at 5.54 and 9.11 µg/m², respectively. The higher secondyear wet deposition at South Haven has been attributed to increased precipitation rate, and measurements at Underhill, Vermont, by [27] are cited as further evidence of the importance of precipitation amount [33]. From December 1992 to December 1993, the average volumeweighted Hg concentration at Underhill (8.3 ng/L) was similar to that observed at Pellston (7.9 ng/L). However, with more precipitation during that period, the total Hg wet deposition at Underhill was 9.26 μ g/m², significantly higher than at Pellston. The RELMAP simulation for 1989 shows 5-10 μ g/m² wet deposition of total Hg at the Pellston site, which agrees well with the 1992 to 1994 observations there. At Underhill, the RELMAP simulation indicates 10-20 μ g/m² wet deposition for 1989 which is slightly larger than the observation in 1993. At the South Haven and Dexter sites, the RELMAP appears to be estimating nearly 20 μ g/m² wet deposition of total Hg for 1989 which is significantly larger than the measurements of 1992 to 1994.

The very large total Hg wet deposition values (>50 μ g/m²) from the RELMAP simulation for some of the larger urban centers in the Ohio Valley and Northeast regions can not be evaluated thoroughly due to a lack of long-term precipitation event sampling at those locations. Precipitation event sampling was performed from 19 August to 7 September of 1993 at 4 sites in Broward County, Florida, in and around the city of Fort Lauderdale [29]. During the 20-day sampling period, total Hg mean concentrations in precipitation were 35, 57, 40 and 46 ng/L at the 4 sites. Given the average annual precipitation of 150 cm per year typical of that area, the resulting annual wet deposition estimates at these 4 sites are 52.5, 85.5, 60 and 69 μ g/m². Since most of the annual rainfall in Broward County occurs in warm tropical conditions of the March to October wet season, this extrapolation from 20 days during the wet season to an annual estimate may be considered reasonable. However, additional urban measurement studies will certainly be required to allow any credible evaluation of RELMAP wet deposition results in heavily populated, industrialized areas.

Figure 12 shows the wet deposition of total mercury from the alternate emission speciation and offers some measure of the sensitivity of the RELMAP simulation results to the emission speciation estimates used. This figure shows basically the same large-scale pattern as for the base-case emissions, but in general the amount of wet deposition is increased. Since the wet scavenging ratio for Hg_P is less than one-third of that for Hg²⁺, we would expect the wet deposition to be reduced when using the alternate emission speciation profiles which reallocate all Hg²⁺ vapor emissions to the Hg_P form. This unexpected increase is the result of an interaction of the wet deposition processes with those for dry deposition. The alternate emission speciation profiles result in greatly reduced dry deposition compared to the base-case speciation. This results in much slower depletion of mercury by dry deposition and provides a greater opportunity for wet deposition to occur.

The percentile analysis of the wet deposition simulation results in Table 7 shows that, for the base-case emission speciation, 50 percent of the land area of the continental U.S. has an annual wet deposition of total mercury of more than about 3.4 μ g/m², and 10 percent of the area has more than 16 μ g/m². However, due to rapid wet deposition of Hg²⁺ and Hg_P there are select areas where wet deposition may be significantly higher. For the area of the

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U.S. east of 90 degrees west longitude, the 50th and 90th percentile levels for simulated annual total mercury wet deposition are about 12 μ g/m² and 25 μ g/m², respectively.

Qualitative Description of Mercury Dry Deposition Results

As indicated previously, the RELMAP mercury model assumes that Hg^0 is not effectively dry deposited. The percentile analysis of the simulated dry deposition using the base-case emission speciation profiles shown in Table 8 indicates the strong local dry deposition of Hg^{2+} vapor as parameterized in the RELMAP mercury model. There is considerable uncertainty regarding the dry deposition velocity of Hg^{2+} and we have little confidence in the extremely high local depositions indicated from the simulation.

Figure 13 shows the simulated annual dry deposition patterns for Hg^{2+} using the base emission speciation. Dry deposition of Hg^{2+} appears to occur primarily on the local scale, within one or two grid cells (40 to 80 km) from the source, much like the Hg^{2+} wet deposition. The magnitude of the dry deposition of Hg^{2+} is similar to that for wet deposition, with urban areas showing values in excess of 20 µg/m². As was the case for wet deposition, dry deposition of Hg^{2+} vapor in heavily populated urban centers is relatively high, exceeding 100 µg/m² in the model grid cell containing New York City. Again, it must be stressed that dry deposition of Hg^{2+} vapor is not well understood. We have used nitric acid vapor as a surrogate for Hg^{2+} vapor. The authors have been unable to find observations of Hg^{2+} dry deposition to compare with the RELMAP simulation results. Dry deposition rates for vaporphase Hg have been estimated from vertical eddy flux calculations at a single site, but these calculations estimate the combined effects of both Hg^{0} and Hg^{2+} vapors [21]. The relatively high solubility and reactivity of Hg^{2+} compounds suggest that dry deposition of total vaporphase Hg may be strongly driven by the Hg^{2+} component.

Figure 14 shows the simulated annual dry deposition totals for Hg_p using the base emission speciation. For this regional-scale modeling study, the dry deposition velocity estimates for Hg_p were made based on the assumption that the particulate mass was concentrated around a 0.3 µm diameter size. The patterns show less intense local dry deposition of Hg_p than for Hg^{2+} , but the dry deposition still appears to occur primarily within a few hundred km of the source areas. This slower dry deposition combined with relatively smaller quantities of Hg_p emission results in maximum dry deposition values for Hg_p of only around 0.5 µg/m². In urban areas where larger particle sizes are more prevalent, these estimates of Hg_p dry deposition are probably too low. However, the RELMAP could treat only one particle size and could not separately model large-particle deposition on the urban scale.

Figures 15 and 16 show the simulated annual dry deposition for total mercury in all forms using the base-case and alternate emission speciations, respectively. A comparison of these figures clearly demonstrates the sensitivity of the modeling results to changes in the emission speciation profiles. Dry deposition is not a major pathway for removal of the atmospheric mercury burden when the alternate emission speciation profiles are employed. This result indicates that dry deposition is much less important when greater transfer of Hg²⁻ to Hg_P is occurring through enhanced particle adsorption or condensation. Thus, it is very important that our understanding of the physical transformations of Hg in the atmosphere be complete and accurate.

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DISCUSSION OF IMPORTANT MODELING UNCERTAINTIES

Transport

The RELMAP model top is defined to be the maximum vertical extent of the convectively driven mixed layer. Monthly values defined from mixed-layer-height climatology are rough estimates of a meteorological phenomenon that may not exist in many situations. Even when a surface-based mixed layer is well defined, pollutants that persist in the atmosphere for long periods of time are certain to mix to some degree into the free troposphere above the mixed-layer top. Extremely persistent compounds such as chlorofluorocarbons (CFCs) are even known to diffuse into the stratosphere. Elemental mercury deposits relatively slowly through precipitation processes due to its low water solubility, and its dry deposition appears to be minimal since it is in vapor form under normal atmospheric conditions. Thus, the diffusion of elemental mercury into the atmosphere above the mixed layer is certainly an important transport pathway.

Since the RELMAP only simulates the flux of pollutant through the top of the mixed layer due to turbulence and not that due to large-scale vertical motions, the use of horizontally divergent or convergent wind fields to define the motion of the pollutant puffs can sometimes result in unrealistic instantaneous concentration fields. Horizontally convergent winds will tend to concentrate puffs at the point of convergence, resulting in artificially high modeled concentrations when the effects of the puffs are summed together. Ordinarily, horizontal convergence in the surface-based mixed layer would push the mixed-layer top higher into the atmosphere. This higher mixed-layer top would compensate for the greater pollutant mass

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loading per unit area from the converging puffs. The RELMAP, with its monthly definition of the mixed layer height, was not designed to provide instantaneous realizations of pollutant concentration fields. Rather, it was designed for seasonal and annual simulations where the effects of convergent and divergent wind fields can balance one another on the whole. Nonetheless, there is some uncertainty as to whether this balance occurs for all situations.

Aqueous Chemistry

The aqueous reduction-oxidation chemistry mechanism in the mercury version of the RELMAP was applied only to the Hg⁰ dissolved from the air into water droplets. Where significant concentrations of Hg²⁺ from emissions exist in air, this Hg²⁺ could also be dissolved into the water droplet and inhibit the scavenging of Hg⁰. The RELMAP results described above indicate that Hg²⁺ air concentrations are certainly lower than those for Hg⁰ at the length scales of the RELMAP grid cells; however, the magnitude of the effect of ambient Hg²⁺ air concentrations on the wet scavenging of Hg⁰ is not yet well understood.

Another source of modeling uncertainty in aqueous chemistry relates to the fact that the aqueous chemical mechanisms in the RELMAP are invoked only when and where precipitation is known to have occurred. Precipitation fields are mostly defined over land areas where precipitation observations are routinely available. Significant wet transformation and removal of mercury may occur over oceanic areas were precipitation observations are not available. It is also possible that significant aqueous chemistry is occurring in nonprecipitating clouds throughout the entire model domain. Since the RELMAP vertical domain covers only the surface-based mixed layer and vertical wind shear is small when the mixed-layer is well defined, under ideal conditions of strong vertical mixing, horizontal diffusion is probably handled adequately. When the surface-based mixed layer is not well defined, vertical gradients in the speed and/or direction of the wind may be present which can not be represented by the motion of individual Lagrangian puffs whose layers remain vertically stacked. There are two techniques that might be used to represent vertical wind shear in the RELMAP: puff splitting and wind-shear-dependent puff expansion. Puff splitting is computationally expensive due to the large number of puffs that result from the process, and wind-shear-dependent puff expansion does not resolve the direction of the shear. The most complete solution to the problem of vertical wind shear is the use of an Eulerian reference frame for numerical modeling.

Boundary Fluxes of Pollutants

Due to the fact that the RELMAP simulates atmospheric pollutant loading as the combined effect of a population of discrete Lagrangian puffs originating from inside the horizontal domain, natural and recycled anthropogenic mercury emissions from the oceans and land surfaces and fresh anthropogenic emissions from outside the model domain could not be explicitly modeled. Instead, a background Hg⁰ air concentration of 1.6 ng/m³ was used to represent these sources of mercury to the atmosphere. Simulated puffs of oceanic and terrestrial mercury emissions could be generated from all model grid cells, but their effects

would be artificially concentrated in the eastern sections of the model domain due to the prevailing west-to-east wind flow over the continental United States. The puffs that would impact the western areas would primarily be those originating from farther west in the model domain, while the eastern areas would be impacted by puffs from all parts of the model domain. Puffs arriving from outside the model domain can not be simulated by the RELMAP. The use of an Eulerian-type model structure would allow a more realistic definition of these lower and lateral boundary fluxes of mercury.

Chemical and Physical Forms of Mercury Air Emissions

The RELMAP modeling results show that 98% of the total mercury deposition to the surface is from emissions of Hg^{2+} and Hg_{P} . Obviously, an accurate model of atmospheric mercury deposition requires an accurate determination of the chemical and physical forms of all air emissions of mercury. The current estimates for these chemical and physical speciations are based on measurements of hot materials inside exhaust stacks and estimates of the various effects of cooling and dilution of those exhaust materials after they are released to the atmosphere. If these estimates of the cooling and dilution effects are inaccurate, then an accurate model simulation is not possible.

SUMMARY

At this time there is significant uncertainty regarding the chemical and physical forms of mercury air emissions and their chemical and physical transformations in the atmosphere.

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This modeling study has relied heavily on the assumptions of a previous Lagragian modeling study in Europe regarding emission speciation estimates and chemical and physical pathways for atmospheric mercury deposition [6]. The modeling results from this previous study were compared to measurements of Hg^0 and Hg_p air concentration and wet deposition in northern Europe, showing that the simulation agreed with measurements to within a factor of 2 in most cases. While the climate of northern Europe may be quite different from that of many locations in North America, it is assumed that the predominant chemical and physical mechanisms for mercury transport, transformation and deposition should be the same for both regions.

This modeling study of atmospheric mercury emission, transport and deposition indicates that nearly all areas of the continental United States are subject to atmospheric deposition of mercury from current anthropogenic activities and that wet deposition of mercury from the global atmospheric reservoir is a significant part of the total deposition. The results from the RELMAP simulation of atmospheric mercury agree with actual measurements of air concentration and deposition within a factor of 2 in nearly all cases. The RELMAP annual wet deposition estimates of 50 to 100 μ g/m² in some of the more highly industrialized areas of the United States are quite significant and worthy of concern, but there are very few measurements with which one can evaluate these results. The RELMAP simulation results also indicate that the importance of dry versus wet deposition processes may be dependent on the fraction of mercury that becomes bound to particles before deposition. Very few direct measurements of the dry deposition of gaseous and particulate Hg have been made to date. Vertical concentration gradients and eddy flux correlations have been used to estimate the dry flux of total gaseous Hg, but no discrimination has been made between Hg⁰

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and Hg²⁺ forms.

Many of the measurement studies performed up until recent years are now suspected of having been subject to laboratory contamination upon analysis of their samples. It is only recently that, by employing ultra-clean laboratory techniques, mercury measurement studies have been able to accurately assess atmospheric concentrations and deposition quantities of mercury in near-background conditions. Even now, it is very difficult to obtain an accurate assessment of the chemical forms of mercury in typical ambient air samples. The RELMAP air concentration results seem quite plausible, with the vast majority of atmospheric mercury estimated to be in the Hg⁰ form, but the individual air concentrations of Hg⁰, Hg²⁺ and Hg_p can not be simulated with much confidence until a more complete understanding is established of all pertinent chemical and physical processes in the atmosphere.

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Land-Use Category	Roughness Length (meters)				
	Autumn-Winter	Spring-Summer			
Urban	0.5 .	0.5			
Agricultural	0.15	0.05			
Range	0.12	0.1			
Deciduous Forest	0.5	0.5			
Coniferous Forest	0.5	0.5			
Mixed Forest/Wetland	0.4	0.4			
Water	10 ⁻⁶	10-6			
Barren Land	0.1	0.1			
Non-forested Wetland	0.2	0.2			
Mixed Agricultural/Range	0.135	0.075			
Rocky Open Areas	0.1	0.1			

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Table 1. Roughness Lengths Used in the Dry Deposition Velocity Calculations

	Base Speciation (%)			Alternate Speciation (%)		
Point Source Type	Hg ⁰	Hg ²⁺	Hg _p	Hg ⁰	Hg ²⁺	Hg _p
Electric Utility Boilers	50	30	20	50	0	50
Non-utility Fossil Fuel Combustion	50	30	20	50	0	50
Municipal Waste Combustion	20	60	20	20	0	80
Medical Waste Incineration	20	60	20	20	0	80
Non-ferrous Metal Smelting	85	10	5	85	0	15
Chlor-alkali Factories	70	30	0	70	0	30
Other Point Sources	80	10	· 10	80	0	20

Table 2. Emission Speciation Profiles for the Point Source Types Defined

Source Type	Hg ⁰	Hg ²⁺	Hg _{part}	Total Hg
Medical Waste Incineration	11.7	35.1	11.7	58.6
Municipal Waste Combustion	10.0	29.9	10.0	49.8
Electric Utility Boilers	24.3	14.6	9.7	48.5
Non-Utility Fossil Fuel	14.3	8.6	5.7	28.5
Non-Ferrous Smelting	7.4	0.9	0.4	8.7
Chlor-alkali Factories	4.6	1.9	0.0	6.5
Other Point Sources	13.0	1.6	1.6	16.2
Area Sources	6.9	0.0	0.0	6.9
Total	92.0	92.6	39.1	223.8

Table 3. Mercury Emissions Inventory Totaled by Source Type Using Base-Case EmissionSpeciation Profiles (metric tons per year)

Table 4. Modeled Mercury Mass Budget in Metric Tons for 1989

Using the Base-Case Emission Speciation Profiles

(all figures rounded to the nearest tenth of a metric ton)

Source/Fate	Hg⁰	. Hg ²⁺	Hg _{part}	Total Hg
Total U.S. anthropogenic emissions	92.0	92.6	39.1	223.8
Mass advected from model domain	90.4	29.9	25.0	145.3
Dry deposited anthropogenic emissions	0.0	39.0	0.6	39.6
Wet deposited anthropogenic emissions	1.2	23.6	13.4	38.3
Remaining in air at end of simulation	0.4	0.1	0.1	0.6
Total deposited anthropogenic emissions	1.2	62.6	14.1	77.9
Deposition from background Hg ⁰	33.0	0.0	0.0	33.0
Mercury deposited from all sources	34.2	62.6	14.1	111.0

Table 5. Modeled Mercury Mass Budget in Metric Tons for 1989

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Using the Alternate Emission Speciation Profiles

(All figures rounded to the nearest tenth of a metric ton)

Source/Fate	Hg ⁰	Hg ²⁺	Hg _{part}	Total Hg
Total U.S. anthropogenic emissions	92.0	0.0	131.7	223.8
Mass advected from model domain	90.4	0.0	84.5	174.9
Dry deposited anthropogenic emissions	0.0	0.0	2.1	2.1
Wet deposited anthropogenic emissions	1.2	0.0	44.9	46.1
Remaining in air at end of simulation	0.4	0.0	0.2	0.6
Total deposited anthropogenic emissions	1.2	. 0.0	47.0	48.2
Deposition from background Hg ⁰	33.0	0.0	0.0	33.0
Mercury deposited from all sources	34.2	0.0	47.0	81.3

Variable	Min	10th	50th	90th	Max
FULL AREA					
Hg ⁰ concentration (ng/m ³)	1.602	1.606	1.619	1.681	1.899
Hg ²⁺ concentration (pg/m ³)	0.265	0.804	. 3.368	14.72	149.1
Hg _p concentration (pg/m ³)	0.391	1.426	5.183	19.18	99.33
Total (ng/m ³)	1.603	1.608	1.627	1.715	2.114
EAST OF 90°W					
Hg ⁰ concentration (ng/m ³)	1.615	1.638	1.665	1.705	1.899
Hg ²⁺ concentration (pg/m ³)	1.486	4.745	9.966	25.25	149.1
Hg _p concentration (pg/m ³)	4.058	8.815	14.88	28.01	99.33
Total (ng/m ³)	1.622	1.655	1.691	1.755	2.114
WEST OF 90 W					
Hg ⁰ concentration (ng/m ³)	1.602	1.605	1.612	1.636	1.818
Hg ²⁺ concentration (pg/m ³)	0.265	0.687	1.909	6.303	29.80
Hg _p concentration (pg/m ³)	0.391	1.243	3.327	8.565	28.73
Total (ng/m ³)	1.603	1.607	1.618	1.651	1.860

 Table 6. Percentile Analysis of RELMAP Simulated Concentration Results

for the Continental U. S. Using the Base-Case Emissions Speciation

Table 7. Percentile Analysis of RELMAP Simulated Wet Deposition

for the Continental	U.S.	Using	the	Base-Case	Emissions	Speciation

Variable	Min	10th	50th	90th	Max
FULL AREA					
Hg^0 wet dep. ($\mu g/m^2/yr$)	0.022	0.590	2.143	6.306	10.66
Hg^{2+} wet dep. ($\mu g/m^2/yr$)	0.002	0.087	0.749	6.217	125.1
Hg _p wet dep. ($\mu g/m^2/yr$)	0.001	0.067	0.502	3.618	37.72
Total Hg (µg/m²/yr)	0.025	0.792	3.365	15.85	173.5
EAST OF 90°W					
Hg^0 wet dep. ($\mu g/m^2/yr$)	0.540	3.099	5.382	7.406	10.66
Hg^{2+} wet dep. ($\mu g/m^2/yr$)	0.242	1.837	4.269	12.40	125.1
Hg_P wet dep. ($\mu g/m^2/yr$)	0.191	1.252	2.607	6.482	37.72
Total Hg (µg/m²/yr)	0.979	6.846	12.40	25.42	173.5
WEST OF 90°W					
Hg^0 wet dep. ($\mu g/m^2/yr$)	0.022	0.512	1.337	3.995	7.854
Hg^{2+} wet dep. ($\mu g/m^2/yr$)	0.002	0.067	0.313	1.767	13.93
Hg_{P} wet dep. ($\mu g/m^{2}/yr$)	0.001	0.050	0.253	1.146	6.550
Total Hg (µg/m²/yr)	0.025	0.686	1.993	6.936	23.87

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Table 8. Percentile Analysis of RELMAP Simulated Dry Deposition

for	the	Continental	U.	S.	Using	the	Base-Case	Emission	Speciation
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Variable	Min	10th	50th	90th	Max
FULL AREA					
Hg^{2+} dry dep. ($\mu g/m^2/yr$)	0.113	0.412	1.641	8.500	153.5
$Hg_{P} dry dep. (\mu g/m^{2}/yr)$	0.002	0.010	0.035	0.130	0.749
Total Hg (µg/m²/yr)	0.117	0.425	1.669	8.629	154.2
EAST OF 90°W					
Hg^{2+} dry dep. (µg/m ² /yr)	0.434	2.649	6.263	15.53	153.5
$Hg_{P} dry dep. (\mu g/m^{2}/yr)$	0.017	0.049	0.104	0.189	0.749
Total Hg (µg/m²/yr)	0.451	2.699	6.373	15.73	154.2
WEST OF 90°W					
Hg^{2+} dry dep. (µg/m ² /yr)	0.113	0.342	0.923	3.614	29.85
$Hg_P dry dep. (\mu g/m^2/yr)$	0.002	0.009	0.024	0.063	0.236
Total Hg (µg/m²/yr)	0.117	0.352	0.948	3.679	30.03

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Legends for figures

Fig. 1. Estimated elemental mercury vapor emissions from all anthropogenic sources in the continental United States in kilograms per year resolved to the RELMAP horizontal grid.

Fig. 2. Estimated divalent mercury vapor emissions from all anthropogenic sources in the continental United States in kilograms per year resolved to the RELMAP horizontal grid.

Fig. 3. Estimated particulate mercury vapor emissions from all anthropogenic sources in the continental United States in kilograms per year resolved to the RELMAP horizontal grid.

Fig. 4. Annual average elemental mercury vapor air concentration from continental U. S. emissions as simulated by the RELMAP using the base-case emission speciation estimates. Concentrations are in units of nanograms per cubic meter (ng/m^3) . The assumed global background elemental mercury concentration of 1.6 ng/m³ is not included.

Fig. 5. Annual average divalent mercury vapor air concentration from continental U. S. emissions as simulated by the RELMAP using the base-case emission speciation estimates. Concentrations are in units of nanograms per cubic meter (ng/m³).

Fig. 6. Annual average particulate mercury air concentration from continental U. S. emissions as simulated by the RELMAP using the base-case emission speciation estimates. Concentrations are in units of nanograms per cubic meter (ng/m^3) .

Legends for figures (continued)

Fig. 7. Annual total wet deposition of elemental mercury vapor from continental U. S. emissions as simulated by the RELMAP using the base-case emission speciation estimates. Depositions are in units of micrograms per square meter (μ g/m²).

Fig. 8. Annual total wet deposition of elemental mercury vapor from the global background air concentration of 1.6 nanograms per cubic meter (ng/m^3) as simulated by the RELMAP. Depositions are in units of micrograms per square meter $(\mu g/m^2)$.

Fig. 9. Annual total wet deposition of divalent mercury vapor from continental U. S. emissions as simulated by the RELMAP using the base-case emission speciation estimates. Depositions are in units of micrograms per square meter ($\mu g/m^2$).

Fig. 10. Annual total wet deposition of particulate mercury from continental U. S. emissions as simulated by the RELMAP using the base-case emission speciation estimates. Depositions are in units of micrograms per square meter (μ g/m²).

Fig. 11. Annual total wet deposition of all forms of mercury from continental U. S. emissions and from the global background concentration as simulated by the RELMAP using the base-case emission speciation estimates. Depositions are in units of micrograms per square meter (μ g/m²).

Fig. 12. Annual total wet deposition of all forms of mercury from continental U. S. emissions and from the global background concentration as simulated by the RELMAP using the alternate emission speciation estimates. Depositions are in units of micrograms per square meter (μ g/m²).

Fig. 13. Annual total dry deposition of divalent mercury vapor from continental U. S. emissions as simulated by the RELMAP using the base-case emission speciation estimates. Depositions are in units of micrograms per square meter ($\mu g/m^2$).

Fig. 14. Annual total dry deposition of particulate mercury from continental U. S. emissions as simulated by the RELMAP using the base-case emission speciation estimates. Depositions are in units of micrograms per square meter ($\mu g/m^2$).

Fig. 15. Annual total dry deposition of all forms of mercury from continental U. S. emissions as simulated by the RELMAP using the base-case emission speciation estimates. Depositions are in units of micrograms per square meter ($\mu g/m^2$).

Fig. 16. Annual total dry deposition of all forms of mercury from continental U. S. emissions as simulated by the RELMAP using the alternate emission speciation estimates. Depositions are in units of micrograms per square meter ($\mu g/m^2$).



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Fig. 4





Fig. 6.





Fig. 8



Fig.9

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Fig 10



Fig 11





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16. ABSTRACT

The Regional Lagrangian Model of Air Pollution (RELMAP) is used to simulate the emission, transport and diffusion, chemical transformation, and wet and dry deposition of elemental mercury gas, divalent mercury gas and particulate mercury. Based on recent modeling advances in Europe, the RELMAP has been modified to simulate a reduction-oxidation (redox) balance for mercury dissolved in cloud and This redox balance is used in the estimation of a variable rain water. precipitation scavenging ratio for elemental mercury. Wet removal of divalent mercury gas and particulate mercury is modeled using constant wet scavenging ratios. Dry deposition is estimated using deposition velocities developed from various modeling studies in the U.S. and in Europe. A mercury air emission inventory for the continental United States is used to estimate the releases of elemental mercury gas, divalent mercury gas and particulate mercury based on emission speciation estimates for the various emitter types in the inventory. Average annual concentrations and wet and dry deposition totals for these three forms of mercury have been simulated. The results of the simulation are used to estimate the quantity of mercury emitted to the air annually over the United States and the amount that is subsequently deposited back to U.S. soils and water bodies. An analysis of the modeling results also provides some information about the areas of the country thought to have the most significant exposure from all air emissions of mercury. This analysis contributes to the understanding of the key variables, such as source location, chemical and physical form of emission, or meteorology,

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