Study on the Chemical Reaction and Deposition Calculation of Mercury in the Atmosphere

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Abstract. The source-attribution of atmospheric mercury is one of the important issues for public health today. This paper discussed the assessment of chemical reaction and deposition of mercury in the atmosphere. The air quality model from the chemical reaction and atmospheric diffusion aspects simulated the mercury in the ecosystem. The deposition processes of mercury were divided into the near field and far field in the atmosphere. Two air quality models, ISTST and CAMx used for the simulation of mercury transport were introduced in this study. Details on the atmospheric diffusion and the gas-phase and aqueous-phase mercury chemistry mechanisms implemented in the model were presents in this paper. The uncertainty of simulation models such as the elemental mercury, aerosol mercury, oxidized mercury, dry deposition, and wet deposition was discussed. The results of this study will aid in the implementation of mercury transport model in the regional model.

1. Introduction
Mercury deposition is currently an important issue mainly because of the adverse health effects that it has on human. Mercury typically exists in the atmosphere in the form of Hg (0) or Hg (II) in the gas phase. Hg (II) can be methylated in water bodies, where it transforms into toxic methylmercury and can bioaccumulate within the food chain. Hg (0) is sparingly soluble and cannot be removed by wet deposition; its dry deposition velocity is also believed to be low. As a result, Hg (0) has a long atmospheric lifetime, on the order of several months, which is mainly determined by its oxidation to Hg (II). On the other hand, Hg (II) is quite soluble; wet and dry deposition processes consequently remove it rapidly. A third form of mercury, particulate mercury (Hg (p)), is mostly present in the fine fraction of particulate matter (PM_{2.5}), although some Hg (p) may be present in coarse PM [1].
Since the atmospheric mercury is such an important issue nowadays, it is necessary to find a suitable tool to simulate its transport in the environment. This paper presents the current knowledge of mercury deposition and chemical reaction from the researchers and model developers. The discussion in this article is trying to provide the foundation and raise the concern of mercury regulation in the East Asian area.

2. Methodology for Mercury Deposition Assessment
Two models, Comprehensive Air quality Model with extensions (CAMx) and Industrial Source Complex Short Term Dispersion Model (ISCST3), were selected for studying the feasibility of mercury deposition evaluation in this paper and are briefly described below.

2.1 Near Field Model (ISCST3)
The regulatory model, ISCST3, can do calculation of mercury diffusion in the near field. Detailed description of the model is shown below.

Model Description
ISCST3 is the EPA’s regulatory model. It uses the ideas of Pasqual’s stability category rather than the boundary layer turbulence structure and scaling. It assumes a Gaussian distribution of the concentration of pollutants in the crosswind profile of vertical and horizontal directions under all stability classes. ISCST3 also contains algorithms to treat building downwash, deposition of particles, as well as area and line source releases. The major advantages of ISCST3 are its simplicity and its solid predicted results, which typically show high reproducibility for the same scenario. The amount of meteorological data required as input by ISCST3 is relatively small. Moreover, the model can be operated based on the routinely collected meteorological observation data. The disadvantage of ISCST3 is that the advance in knowledge of atmospheric boundary layer structure and estimations of turbulent dispersion processes cannot be accommodated in the model.

Diffusion Calculation
ISCST3 applies the Gaussian plume assumption to calculate the pollutant diffusion in the atmosphere. The Gaussian equation can be written as the following:

\[ C(x, y, z; H) = \frac{Q}{2\pi u\sigma_y\sigma_z} \exp\left[ -\frac{y^2}{2\sigma_y^2} \right] \left[ \exp\left( -\frac{(z-H)^2}{2\sigma_z^2} \right) + \exp\left( -\frac{(z+H)^2}{2\sigma_z^2} \right) \right] \]  (1)

Where \( C \) is the pollutant concentration; \( Q \) the emission rate; \( z \) the receptor elevation; \( u \) the mean wind velocity; \( H \) the effective stack height; \( \sigma_y \) and \( \sigma_z \) are the horizontal and vertical diffusion coefficient; \( x \) the downwind distance; and \( y \) crosswind distance from the plume centreline to the receptor.

Applicability for Mercury Assessment
ISCST3 has been used in the United States and Taiwan for a long period of time. It is reliable in the prediction of particulate concentration resulted from short-range air pollutant transport. In evaluating the mercury deposition, ISCST3 can be used in the urban or rural area within the distance shorter than 50 kilometres. Since there are too many assumptions underlying this model, it is suggested not to use ISCST3 for the long-range transport study. The atmospheric chemistry processes are also not included in this model; therefore, the chemical reaction mechanisms described in the section below have to be considered together with the ISCST3 model [2].

2.2 Far Field Model (CAMx)

Model Description
CAMx is an Eulerian photochemical dispersion model designed for an integrated “one-atmosphere” assessment of gaseous (ozone, air toxics, and mercury) and particulate (PM$_{2.5}$ and PM$_{10}$) air pollution over different scales ranging from sub-urban to continental. It is developed to unify all of the technical features required of “state-of-the-science” air quality models into a single system that is computationally efficient, easy to use, and publicly available. The model code has a highly modular and well-documented structure which eases the insertion of new or alternate algorithms and features. The input/output file formats are based on the Urban Airshed Model and are compatible with many existing pre- and post-processing tools.

Diffusion Calculation
CAMx simulates the emission, dispersion, chemical reaction, and removal of pollutants in the troposphere by solving the continuity equation for each chemical species using a system of nested three-dimensional grids. The Eulerian continuity equation describes the time dependency of the average species concentration $C_i$ within each grid cell volume as a sum of all of the physical and chemical processes operating on that volume. This equation is expressed mathematically in terrain-following height ($z$) coordinates:

$$\frac{\partial C_i}{\partial t} = -\nabla_h \cdot V \cdot H C_i + \left[ \frac{\partial (C_i \eta)}{\partial z} - C_i \frac{\partial h}{\partial z} \left( \frac{\partial C_i}{\partial t} \right) \right] + \nabla \cdot \rho K \nabla \left( \frac{C_i \rho}{\rho} \right) + \left. \frac{\partial C_i}{\partial t} \right|_{\text{Chemistry}} + \left. \frac{\partial C_i}{\partial t} \right|_{\text{Emission}} + \left. \frac{\partial C_i}{\partial t} \right|_{\text{Removal}}$$

(2)

Where $V_h$ is the horizontal wind vector, $\eta$ is the net vertical “entrainment rate”, $h$ is the layer interface height, $\rho$ is atmospheric density, and $K$ is the turbulent exchange (or diffusion) coefficient. The first term on the right-hand side represents horizontal advection, the second term the net resolved vertical transport across an arbitrary space- and time-varying height grid, and the third term the sub-grid scale turbulent diffusion. Chemistry is treated by simultaneously solving a set of reaction equations taking into account specific chemical mechanisms. Pollutant removal includes both dry surface uptake (deposition) and wet scavenging by precipitation.

Applicability for Mercury Assessment
CAMx uses the grid model to simulate the pollutant diffusion. It has been used in the air quality assessment for ozone and aerosol. The latest version of CAMx includes the mercury chemistry as described in the next section. It has the ability to simulate the mercury diffusion in the atmospheric environment.

3. Chemical Reaction of Mercury in the Atmosphere

3.1 Mercury Chemistry

Mercury exists in the atmosphere as elemental mercury, Hg (0), and oxidized mercury, Hg (II) [3]. Hg (II) consists of inorganic (e.g., mercuric chloride, HgCl$_2$) and organic (e.g., methyl mercury, MeHg) form. It can also be present as particulate mercury (e.g., mercuric oxide, HgO, or mercury sulphide, HgS). In the global atmosphere, Hg (0) is the dominant form of mercury. Hg(II) typically accounts for a few percent of total mercury and is predominantly in the gas phase. MeHg concentrations in the atmosphere are negligible, with a factor of 10 to 30 lower than that of Hg(II), based on the analysis of precipitation samples collected by Frontier Geosciences, Inc.[4].
The gas-phase transformations of mercury include the oxidation of Hg(0) to Hg(II) by ozone (O₃), hydrogen chloride (HCl) [5], hydrogen peroxide (H₂O₂) [6], molecular chlorine (Cl₂) [7], and hydroxyl radicals (·OH) [8]:

\[
\begin{align*}
\text{Hg}(0) \ (g) + \text{O}_3 \ (g) & \rightarrow \text{Hg}(\mathrm{II}) \ (g), \ k = 3 \times 10^{-20} \ \text{cm}^3 \ \text{molec}^{-1} \ \text{s}^{-1} \ (3) \\
\text{Hg}(0) \ (g) + \text{HCl} \ (g) & \rightarrow \text{HgCl}_2 \ (g), \ k = 1 \times 10^{-19} \ \text{cm}^3 \ \text{molec}^{-1} \ \text{s}^{-1} \ (4) \\
\text{Hg}(0) \ (g) + \text{H}_2\text{O}_2 \ (g) & \rightarrow \text{Hg(OH)}_2 \ (g), \ k = 8.5 \times 10^{-19} \ \text{cm}^3 \ \text{molec}^{-1} \ \text{s}^{-1} \ (5) \\
\text{Hg}(0) \ (g) + \text{Cl}_2 \ (g) & \rightarrow \text{HgCl}_2 \ (g), \ k = 2.6 \times 10^{-18} \ \text{cm}^3 \ \text{molec}^{-1} \ \text{s}^{-1} \ (6) \\
\text{Hg}(0) \ (g) + \cdot\text{OH} \ (g) & \rightarrow \text{Hg(OH)}_2 \ (g), \ k = 8 \times 10^{-14} \ \text{cm}^3 \ \text{molec}^{-1} \ \text{s}^{-1} \ (7)
\end{align*}
\]

The reaction rate constants provided above are for temperatures in the range of 20 to 25 °C. No temperature dependence information is available.

### 3.3 Aqueous-Phase Chemistry

The aqueous-phase chemical processes of mercury include (1) the reduction of Hg(II) to Hg(0) when reacted with hydroperoxy radicals (HO₂), (2) the formation of the sulfite complexes (at low HCl concentrations) such as HgSO₃ and Hg(SO₃)²⁻, and (3) the oxidation of Hg(0) to Hg(II) by dissolved O₃, ·OH, and Cl₂. Adsorption of Hg(II) species on atmospheric particulate matter (PM) is simulated using an adsorption coefficient (K = 34 L g⁻¹) recommended by Seigneur et al. [9][10][11][12].

The relevant reactions are listed below. Note that the gas-liquid equilibrium and ionic equilibrium of the non-mercury species (e.g., SO₂, O₃) involved in the mercury aqueous-phase chemistry are not shown here, since they are identical to those in the other CAMx mechanisms.

### 3.4 Gas-liquid Equilibrium [13]

\[
\begin{align*}
\text{Hg}(0) \ (g) & \rightarrow \text{Hg}(0) \ (aq), \ K = 0.11 \ \text{M atm}^{-1} \ (8) \\
\text{HgCl}_2 \ (g) & \rightarrow \text{HgCl}_2 \ (aq), \ K = 1.4 \times 10^6 \ \text{M atm}^{-1} \ (9) \\
\text{Hg(OH)}_2 \ (g) & \rightarrow \text{Hg(OH)}_2 \ (aq), \ K = 1.2 \times 10^4 \ \text{M atm}^{-1} \ (10)
\end{align*}
\]

The Henry's Law constants listed above are for temperatures in the range of 20 to 25 °C. Temperature dependence information is available for the Henry's Law constant of Hg(0), but the validity of this information for temperatures below 0 °C is not established.

### 3.5 Aqueous-phase Equilibrium

\[
\begin{align*}
\text{HgCl}_2 \ (aq) & \rightarrow \text{Hg}^{2+} + 2\text{Cl}^- , \ K = 10^{-14} \ \text{M}^2 \ (11) \\
\text{Hg(OH)}_2 \ (aq) & \rightarrow \text{Hg}^{2+} + 2\text{OH}^- , \ K = 10^{-22} \ \text{M}^2 \ (12)
\end{align*}
\]
\[ \text{Hg}^{2+} + \text{SO}_3^{2-} \rightarrow \text{HgSO}_3, K = 2.1 \times 10^{13} \text{ M}^{-1} \]  \hspace{1cm} (13)

\[ \text{HgSO}_3 + \text{SO}_3 \rightarrow \text{Hg(SO}_3)_2, K = 1.0 \times 10^{10} \text{ M}^{-1} \]  \hspace{1cm} (14)

3.6 Adsorption of Hg (II) on PM [9]

\[ \text{Hg(II)} \text{ (aq)} \rightarrow \text{Hg(II)} \text{ (p)}, K = 34 \text{ L g}^{-1} \]  \hspace{1cm} (15)

3.7 Aqueous-phase Kinetics [15][16][17]

\[ \text{Hg(0) (aq)} + \text{O}_3 \text{ (aq)} \rightarrow \text{Hg}^{2+}, k = 4.7 \times 10^7 \text{ M}^{-1} \text{s}^{-1} \]  \hspace{1cm} (16)

\[ \text{Hg(0) (aq)} + \text{OH} \text{ (aq)} \rightarrow \text{Hg}^{2+}, k = 2 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \]  \hspace{1cm} (17)

\[ \text{HgSO}_3 \text{ (aq)} \rightarrow \text{Hg (0) (aq)}, k = 0.0106 \text{ s}^{-1} \]  \hspace{1cm} (18)

\[ \text{Hg (II) (aq)} + \text{HO}_2 \text{ (aq)} \rightarrow \text{Hg (0) (aq)}, k = 1.7 \times 10^4 \text{ M}^{-1} \text{s}^{-1} \]  \hspace{1cm} (19)

\[ \text{Hg (0) (aq)} + \text{HOCl (aq)} \rightarrow \text{Hg}^{2+}, k = 2.09 \times 106 \text{ M}^{-1} \text{s}^{-1} \]  \hspace{1cm} (20)

\[ \text{Hg (0) (aq)} + \text{OCl}^{-} \rightarrow \text{Hg}^{2+}, k = 1.99 \times 106 \text{ M}^{-1} \text{s}^{-1} \]  \hspace{1cm} (21)

In the last two reactions listed above, HOCl and OCl\(^-\) originate from the dissolution and subsequent dissociation of molecular chlorine (Cl\(_2\)). Note that Hg(II) (aq) refers to all divalent Hg species in solution, which are governed by the following equation:

\[ \text{Hg}^{2+} + \text{HgCl}_2 \text{ (aq)} + \rightarrow \text{Hg(OH)}_2 \text{ (aq)} + \text{HgSO}_3 + \text{Hg (SO}_3)_2^{2-} \]  \hspace{1cm} (22)

The rate constants listed for the aqueous-phase kinetics are for temperatures in the range of 20 to 25ºC. Temperature dependence information is available for the HgSO\(_3\) reduction reaction.

4. Implementation Approach

4.1 Implementation Study in CAMx

The implementation study of mercury transformation pathways in CAMx is based on the assumption that the concentrations of mercury species are much lower than that of the species they react. The concentrations of the non-mercury species can be assumed to be constant during the mercury chemistry calculations and analytical solutions are available for both the gas-phase and aqueous-phase conversions. The mercury chemistry requires the concentrations of the following non-mercury species: O\(_3\), H\(_2\)O\(_2\), OH, SO\(_2\), HO\(_2\), Cl\(_2\), HCl, and atmospheric particulate matter (PM). The concentrations of most of these species are available from CAMx. However, Cl\(_2\) and HCl are not explicitly simulated because the emission data required to simulate these species are generally inadequate or unavailable. Thus, we specify typical vertical concentration profiles of HCl and Cl\(_2\). The Cl\(_2\) concentrations are set to be non-zero over oceans and zero elsewhere. Moreover, the daytime Cl\(_2\) concentrations are lower than nighttime values to account for the fact that Cl\(_2\) is photolyzed during the day. The zenith angle is used for the determination of night/day.

4.2 Implementation Study with other Air Quality Models

The Atmospheric Mercury Model Inter-comparisons project has perform the comparison among the performance of different model for mercury deposition. This project includes the EMEP mercury
model inter-comparison; local deposition comparison: HYSPLIT-Hg vs. ISC (Gaussian Plume); and the comparison of utility contributions to the Great Lakes: HYSPLIT-Hg vs. CMAQ-Hg. The scope includes three stages: (1) the comparison of chemical schemes for a cloud environment; (2) air concentrations in short term episodes; and (3) long-term deposition and source-receptor budgets. Table 1 is the names and institution participated in the research program.

Table 1. Implementation study of mercury deposition with other air quality models

| Model Acronym | Model Name and Institution |
|---------------|----------------------------|
| CAM           | Chemistry of Atmos. Mercury model, Environmental Institute, Sweden |
| MCM           | Mercury Chemistry Model, Atmos. & Environmental Research, USA |
| CMAQ          | Community Multi-Scale Air Quality model, US EPA |
| ADOM          | Acid Deposition and Oxidants Model, GKSS Research Center, Germany |
| MSCE-HM       | MSC-E heavy metal regional model, EMEP MSC-E |
| GRAHM         | Global/Regional Atmospheric Heavy Metal model, Environment Canada |
| EMAP          | Eulerian Model for Air Pollution, Bulgarian Meteo-service |
| DEHM          | Danish Eulerian Hemispheric Model, National Environmental Institute |
| HYSPLIT       | Hybrid Single Particle Lagrangian Integrated Trajectory model, US NOAA |
| MSCE-HM-Hem   | MSC-E heavy metal hemispheric model, EMEP MSC-E |

Conclusion

The simulation technique of mercury deposition in the atmospheric environment was discussed in this paper. The studies from other researchers were reviewed here and two models for short range and long range were discussed in this paper. The results of simulation capability for CAMx model were also presents in this article for further research of mercury transport in East Asian area.

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