

Development of Mercury Modeling Schemes Within CMAQ Framework: Science and Model Implementation Issues

Che-Jen Lin^{1*}, Pruek Pongprueksa¹, Thomas C. Ho¹, Hsing-wei Chu¹ and Carey Jang²

¹College of Engineering, Lamar University, Beaumont, TX 77710

²Office of Air Quality Planning & Standards, USEPA, Research Triangle Park, NC 27711

1. INTRODUCTION

Mercury (Hg) is a persistent, bioaccumulative pollutant regulated by the United States Environmental Protection Agency (EPA). The concern of mercury pollution arises from the health effects caused by mercury vapor inhalation through the contaminated air, and methylated mercury ingestion through the consumption of fresh water and marine fish. According to estimates of the global mercury budget, about 6,000 tons and 10,800 tons of mercury are currently present in the troposphere and in the water bodies on earth. Mercury is released into the atmosphere from a variety of natural and anthropogenic sources. The natural sources include volcanoes, soils, forests, lakes and open oceans, while the anthropogenic sources are mainly from combustion and waste incineration^[1].

In the atmosphere, mercury exists primarily as inorganic forms with two oxidation states: elemental Hg⁰ (Gaseous Elemental Mercury, GEM) and divalent Hg(II) (Reactive Gaseous Mercury, RGM, and Particulate Mercury, PHg). Elemental Hg has a long atmospheric lifetime (0.5-2 yrs) and can be transported over a great distance, causing mercury contamination in the remote areas. Divalent Hg, on the other hand, has a short atmospheric lifetime (several hours to days) and deposits back to the earth rapidly through dry and wet depositions due to its strong tendency to be scavenged into droplets or adsorbed onto particulate matter. The atmospheric water also facilitates the wet deposition of mercury, causing contamination of water and soils on earth. The deposited mercury can be reemitted into the atmosphere through a number of chemical and biological pathways leading to the global cycling of mercury^[2]. Currently, the background total mercury levels are 1–3 ng/m³.

Due to the concerns of mercury contamination and its adverse health effects to humans, there is a need to better understand the emission, transport, chemistry and deposition of mercury in the atmosphere. However, the diverse interactions between various mercury species and other

atmospheric pollutants are usually complex and nonlinear. Therefore, it requires sophisticated modeling tools to adequately address the fate of atmospheric mercury. In this regard, CMAQ's "one-atmosphere" modeling approach and state-of-the-science components serve as an excellent platform for comprehensive mercury simulation.

CMAQ modeling system has been modified by Bullock and Brehme to simulate the transport, transformation and deposition of atmospheric mercury^[3]. Although has not been released by CMAS, the latest CMAQ-Hg model is within V 4.3 as a research version. In the model, transformations of Hg are simulated with chemical reactions in the gaseous phase (e.g., Hg reactions with O₃, Cl₂, H₂O₂, and OH) and in the aqueous phase (e.g., Hg reactions with O₃, S(IV), HOCl/OCl⁻, HO₂, and OH) with a compound-specific speciation for divalent aqueous Hg using aqueous equilibrium. A linear sorption model is employed to describe the adsorption of dissolved divalent mercury to elemental carbon particles in cloud water. The CMAQ-Hg model simulates the partitioning of RGM between air and cloud water based on the Henry's constant of HgCl₂. Henry's equilibrium is assumed for GEM. Wet deposition rate is calculated based on precipitation information from MCIP2 and the physicochemical Hg speciation in the cloud chemistry mechanism. Dry deposition rate is calculated based on assumed dry deposition velocity and gaseous concentration for each of the three forms of Hg.

Since the development of the current version of the CMAQ-Hg model, more scientific findings have been reported in the literature. With the new scientific developments in atmospheric mercury, there is a need for further implementations in the model. The objectives of this work are (1) to evaluate the new mercury science components that we recommend to implement in the current version of CMAQ-Hg model and (2) to address the significance of these science implementations. These components are summarized as: (1) improving gaseous-phase mercury chemical mechanism in CMAQ-Hg, (2) implementing sea salt aerosol emission inventory in SMOKE

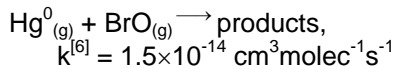
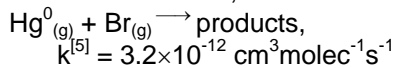
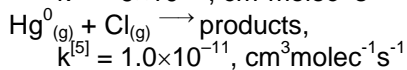
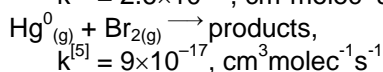
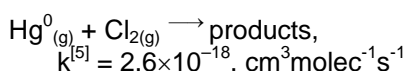
*: Corresponding author address: Che-Jen Lin, Department of Civil Engineering, Lamar University, Beaumont, TX 77710-0024. Email: Jerry.Lin@lamar.edu.

processing, (3) implementing reactive halogen activation/reaction mechanism from sea-salt aerosol in CMAH-Hg, (4) implementing new dry deposition velocity schemes for GEM and RGM in MCIP2, and (5) modifying the aqueous divalent mercury sorption algorithms in CMAQ-Hg.

2. PROPOSED IMPLEMENTATIONS

2.1 Gaseous-phase Chemical Mechanism

The current version of CMAQ-Hg does not consider the more recent chemical mechanisms for Hg reactions with reactive halogens. These reactions may play an important role for mercury deposition in marine boundary layer, in coastal areas, and near anthropogenic halogen emission sources. Recent modeling study using conditions representing typical marine boundary layer has suggested that the lifetime of elemental mercury in summertime is around 10 days^[4]. This is much shorter than the generally accepted 0.5 – 2 years atmospheric lifetime of mercury, indicating the potential forcing of mercury deposition by halogen chemistry. These reactions include:



In addition, a recent study on Hg⁰-O₃ kinetics reveals that the rate constant is significantly greater than previously implemented value (7.5 × 10⁻¹⁹ vs. 3 × 10⁻²⁰ cm³molec⁻¹s⁻¹)^[7]. To illustrate the potential impact of these reactions on Hg⁰ oxidation, which is the primary driving force for mercury deposition, we computed the oxidation rates contributed by various oxidants under three typical atmospheric scenarios. Table 1 shows the typical concentrations of the oxidants under considerations. With the concentrations in Table 1, the resulted pseudo-first-order oxidation rates of Hg⁰ are shown in Figure 1. As seen, O₃ becomes a dominant GEM oxidant in the gaseous phase in all scenarios when the new Hg⁰-O₃ kinetics is implemented. Also, oxidations by Cl and Br atoms are important in the Marine Boundary Layer (MBL). By implementing the new gaseous-phase chemical mechanism, mercury simulation in CMAQ should better represent the chemistry of

mercury cycle under various atmospheric conditions. We also recommend testing the impact of changing the Hg⁰-O₃ reaction kinetics on mercury deposition in the model.

Table 1. Typical concentrations of Hg⁰ oxidants in various scenarios

Oxidants	Typical Location			Remark
	Urban	Remote Area	MBL	
O ₃ ⁽⁸⁾ (ppbV)	150	30	30	Daytime
O ₃ ⁽⁸⁾ (molecules cm ⁻³)	3.69 × 10 ¹²	7.38 × 10 ¹¹	7.38 × 10 ¹¹	Daytime
OH ⁽⁹⁾ (molecules cm ⁻³)	5 × 10 ⁶	5 × 10 ⁵	1 × 10 ⁶	Daytime
H ₂ O ₂ ^{(10), (11)} (molecules cm ⁻³)	4.92 × 10 ¹⁰	2.46 × 10 ¹⁰	2.46 × 10 ¹⁰	Daytime
Cl ₂ ^{(12), (13)} (molecules cm ⁻³)	3.69 × 10 ⁸	0	1.23 × 10 ⁹	Nighttime
Cl ^{(5), (12)} (molecules cm ⁻³)	1 × 10 ⁴	0	5 × 10 ⁴	Daytime
Br ₂ ⁽¹⁴⁾ (molecules cm ⁻³)	0	0	2.46 × 10 ⁷	Nighttime
Br ⁽¹⁴⁾ (molecules cm ⁻³)	0	0	1 × 10 ⁵	Daytime
BrO ^{(14), (15), (16)} (molecules cm ⁻³)	0	0	5 × 10 ⁶	Daytime

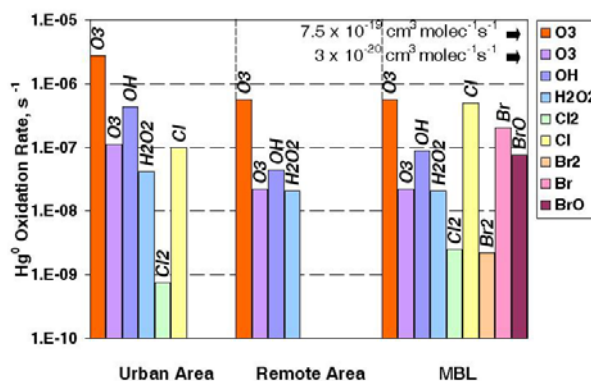


Figure 1. Comparison of Hg⁰ oxidation rates in the scenarios shown in Table 1

2.2 Sea-salt Aerosol Generation

Sea-salt aerosol is the most important source for reactive halogen species in the marine boundary layer. Since reactive halogens play an important role in oxidizing GEM and sea surface cover 71 % of the earth, the inclusion of sea-salt aerosol is critical to simulate the global deposition of mercury. In addition, divalent aqueous mercury can be greatly stabilized in sea salt aerosol due to the strong complex formation with halogen ions, which in turn enhances the deposition of divalent mercury. To realistically represent the concentrations of reactive halogens in coastal areas, marine boundary layer, and remote regions, we recommend including sea salt aerosol

generation in SMOKE processing. The size-dependent generation of sea salt aerosol has been parameterized by Monahan using wind speed at sea surface^[17]. This parameterization can be built into SMOKE framework to provide sea salt aerosol emission inventory above sea surface.

2.3 Reactive Halogen Activation Chemistry

With the emission inventory of sea salt aerosol, the concentration of reactive halogen species can be simulated using a reactive halogen activation chemical mechanism. Reactive halogens can be generated from sea-salt aerosol through acid displacement reactions, oxidation of halides by photochemical oxidants, reactions of chlorine nitrate and bromine nitrates, and even from autocatalytic mechanisms. Several chemical mechanisms of halogen activation from sea-salt aerosol have been developed^[14, 18, 19] for polluted and remote (clean) marine boundary layers, these mechanisms can be employed to provide the temporally resolved concentrations of important GEM oxidants such as Cl, Br, BrO, and HOCl. We recommend incorporating the reactive halogen activation chemistry in CMAQ-Hg for the simulation of mercury-halogen interactions. Although this additional module may increase the computational cost, it is of prime importance to simulate these species for assessing the fate of mercury in the marine boundary layer and in coastal areas.

2.4 Implementation of Dry Deposition Scheme of GEM and RGM

At present, the CMAQ-Hg implements dry deposition velocity for reactive gaseous mercury (RGM) and particulate mercury (PHg). In the treatment of dry deposition, the dry deposition velocity of HNO₃ (ranging from 0.5 – 8 cm/s⁻¹ in summer depending on the aerodynamic and boundary layer resistance, from MCIP2 output) is used for the dry deposition of RGM; and the dry deposition velocities of aerosol in Aitken and Accumulation modes are used for the dry deposition of PHg. The reported dry deposition velocity of RGM usually ranges from 0.5 – 2.0 cm/s^[4], therefore the currently implemented dry deposition velocity may be over-estimating.

Furthermore, the current CMAQ version has no dry deposition scheme for GEM. Dry deposition of GEM may contribute significantly to the total deposition of mercury because of the relatively high concentration of GEM compared to RGM. The dry deposition velocity of GEM estimated from flux and concentration measurements ranges from 0.05 – 0.2 cm/s. Even though the dry deposition

velocities of GEM are much lower than those of RGM, the dry deposition flux (the product of concentration multiply by deposition velocity) of GEM and RGM are comparable due to the predominant concentrations of GEM over RGM.

To better simulate total mercury deposition in CMAQ-Hg, we propose to implement the dry deposition velocities for both GEM and RGM in MCIP2:

$$V_d = (r_a + r_b + r_c)^{-1}$$

Where r_a (aerodynamic resistance) will be estimated from turbulent transport, r_b (quasi-laminar resistance) will be estimated from mercury diffusivities^[20], and r_c (surface resistance) will be estimated from the Henry's constants of GEM and RGM, respectively.

2.5 Modification of Aqueous Hg(II) Sorption Algorithm

The current CMAQ-Hg model simulation for the adsorption of aqueous Hg²⁺ species to Elemental Carbon Aerosol (ECA) suspended in cloud water is adapted from a sorption study using atmospheric particulate matter (APM) as the sorbent^[3]. In CMAQ-Hg, the ECA is assumed to be 5 % of the total APM in cloud water. The adsorption is treated as bi-directional non-equilibrium kinetics using a linear aqueous-phase adsorption isotherm for deriving the adsorption (k_s) and desorption (k_D) rate constants:

$$k_s = \frac{[Hg_S^{2+}]_{aq}}{\bar{t}^* ([Hg_S^{2+}]_{aq} + [Hg_D^{2+}]_{aq})}$$

$$k_D = \frac{[Hg_D^{2+}]_{aq}}{\bar{t}^* ([Hg_S^{2+}]_{aq} + [Hg_D^{2+}]_{aq})}$$

Where \bar{t}^* is the time constant (3600 s as the time step) for sorption equilibrium, $[Hg_D^{2+}]_{aq}$ is the dissolved aqueous concentration of Hg(II), and $[Hg_S^{2+}]_{aq}$ is the adsorbed aqueous concentration of Hg(II). This kinetic treatment may not be optimal since the total Hg(II) available in cloud water is not conserved in the non-equilibrium sorption treatment. Furthermore, the kinetic relationship of sorption and desorption does not include the concentration gradient between the adsorbed and bulk species, which is the fundamental driving force of sorption phenomena.

Since the APM concentration in cloud water is usually small (in the order of magnitude of a few mg/L or lower), and the particles size is usually

very small, we recommend directly employing the sorption equilibrium to characterize the quantity of Hg(II) adsorbed onto the ECA particles. This will resolve the mass conservation issues and greatly improve the efficiency of the code in the sorption treatment, i.e.,

$$[Hg_D^{2+}]_{total} = (1 + k_{ECA}[ECA])[Hg_D^{2+}]_{aq}$$

Where k_{ECA} is the sorption equilibrium constant, $[ECA]$ is the concentration of ECA in cloud water and $[Hg_D^{2+}]_{total}$ is the total Hg(II) concentration in bulk and particulate phase in cloud water. We also propose to investigate the impact of the changed sorption algorithm in the wet deposition of mercury in CMAQ-Hg.

3. ACKNOWLEDGEMENT

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