

MODELING STUDY OF REACTIVE GASEOUS MERCURY IN THE URBAN AIR

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ABSTRACT

Chemical speciation and concentrations of reactive gaseous mercury (RGM) in the urban atmospheric boundary layer (ABL) have been modeled using a photochemical box model. Measurements for gaseous elemental mercury (GEM) and trace gases were carried out in Seoul (37.6°N, 127°E), Korea, during a one-year period from March 2001 to February 2002. Model simulations suggested that the most dominant sink of elemental mercury (Hg(0)) was the reaction with O₃, which in turn significantly contributed to the formation of mercury oxide (HgO). The dominant RGM species in the urban ABL are likely to be HgO and Hg(HO)₂.

1. INTRODUCTION

Chemical speciation of Hg is an essential step toward the evaluation of its geochemical cycle leading to emission, transport, chemical transformation, and deposition across various environmental compartments on the earth. The divalent mercury (Hg(II)) fraction of total gaseous mercury (TGM) is typically termed as RGM. Studies of concentration and chemical speciation of the RGM in air have attracted a great deal of attention due to recent advances in

analytical techniques for RGM components [1-3]. We attempted to model the chemical speciation and concentrations of individual RGM species in the urban ABL.

2. OBSERVATIONAL DATA

This study is based on the measurements of gaseous elemental mercury (Hg(0),GEM) and a number of important environmental parameters (several atmospheric trace gases and relevant meteorological parameters) made at the sampling site during the time period of Mar 2002 - Feb 2003. The measurement site is located in the Yang Jae district of Seoul (37.6°N, 127°E). GEM concentrations were routinely measured using an on-line automatic analytical system [4]. They were measured by transporting outdoor air via 2 m long sampling train made of Teflon tube into the analytical system. We used relevant environmental data collected from nearby environmental monitoring stations. These stations recorded both meteorological parameters, criteria pollutants as well as trace gases (O₃, NO_x, CO, CH₄, non-methane hydrocarbon (NMHC), H₂O₂, and SO₂).

3. MODEL DESCRIPTIONS

A photochemical box model (PCBM) was employed to estimate RGM concentrations in the ABL. We added the chemistry of halogen and mercury species to our previous PCBM. The revised PCBM of a HO_x/NO_x/CH₄/NMHC/Hg(0)/halogen system was chemically constrained to 1 hr averaged values of observed O₃, H₂O₂, NO, NO₂, CO, SO₂, GEM, and NMHC. The revised PCBM used a mass balance approach to calculate the concentrations of RGM and halogen compounds. The time rate of RGM concentration (and halogen compounds) change in the ABL (C_g) change can be expressed as follows:

$$\frac{d[C_g]}{dt} = P_g - L_g C_g + \frac{F_g}{h} - \frac{V_d C_g}{h} - Lk_t ([C_g] - [C_{g,eq}]) \quad (1)$$

where P_g and L_g are the chemical production rate and loss frequency, respectively; F_g is the

emission flux of the gas; h is the boundary layer height; V_d is the deposition velocity; L is the dimensionless liquid water content; k_t is the transfer coefficient; and $C_{g,eq}$ is gas phase concentration in equilibrium with aqueous phase. The chemical reactions of mercury compounds considered in the PCBM includes 24 gas phase reactions, 7 gas/liquid equilibrium reactions, 13 aqueous phase reactions, and 13 aqueous equilibrium reactions.

4. RESULTS AND DISCUSSION

4.1 Temporal distribution of GEM

In the spring (Mar-May), moderately low $Hg(0)$ concentrations were observed, whereas high $Hg(0)$ concentrations occurred quite frequently in the winter (Dec-Feb). $Hg(0)$ concentrations measured in the summer (Jun-Aug) were similar to those seen in the fall (Sep-Nov). Relatively lower $Hg(0)$ levels in the spring are likely to be affected by the enhanced photochemical reactivity (or oxidants). Diurnal variations of $Hg(0)$ during each season of the observational period are shown in Fig. 1. In the winter, there were distinct concentration

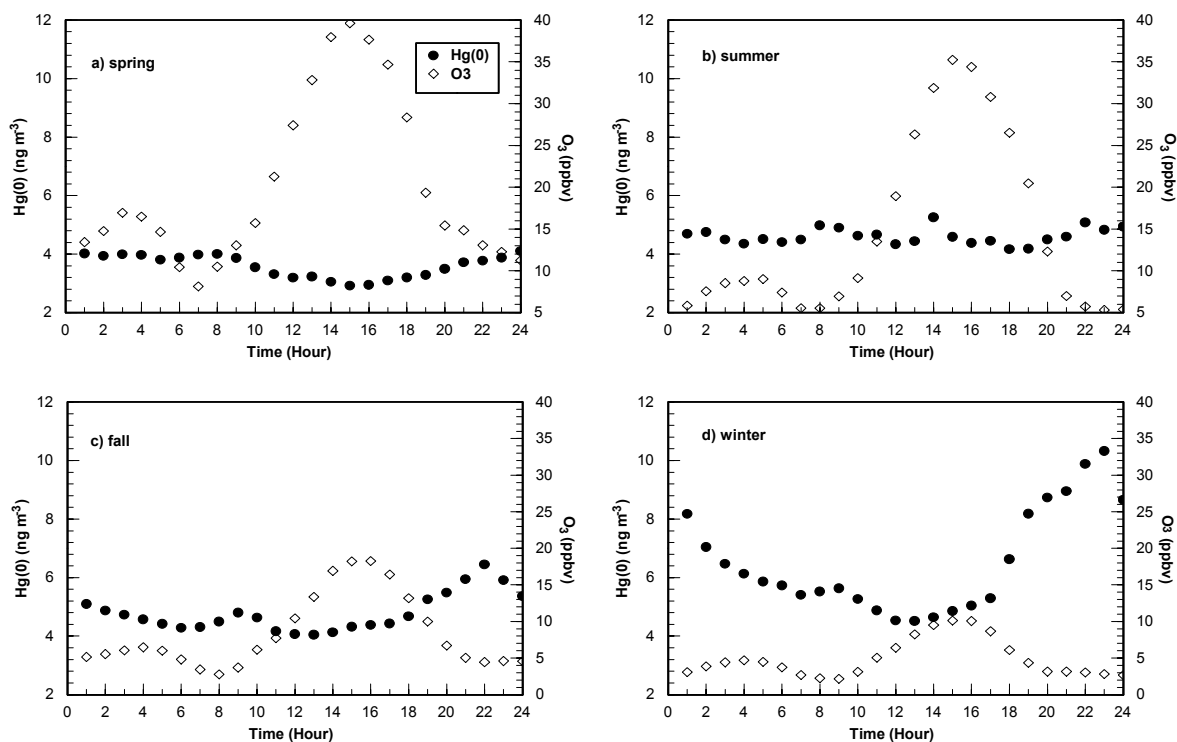


Figure 1. Diurnal variation of GEM and ozone during each season

differences in Hg(0) between day and night. In contrast, the differences were not so significant during other seasons.

4. 2 Composition and diurnal variation of RGM species

The dominant RGM species in the urban air are expected to be HgO and Hg(HO)₂ with the model estimated range of 0.5×10^4 to 1.1×10^4 molecules cm⁻³ (i.e., 1.8 to 3.7 pg m⁻³) and of 0.2×10^4 to 3.5×10^4 molecules cm⁻³ (i.e., 0.7 to 12 pg m⁻³), respectively. The relatively high RGM concentrations estimated in the spring and summer were likely due to the strong photochemical reactivity which was indicated by high oxidants levels. The results of our model simulations clearly pointed out the significance of H₂O₂ in the urban air for the RGM formation, especially in the summer. The diurnal variations of RGM species in the CBL

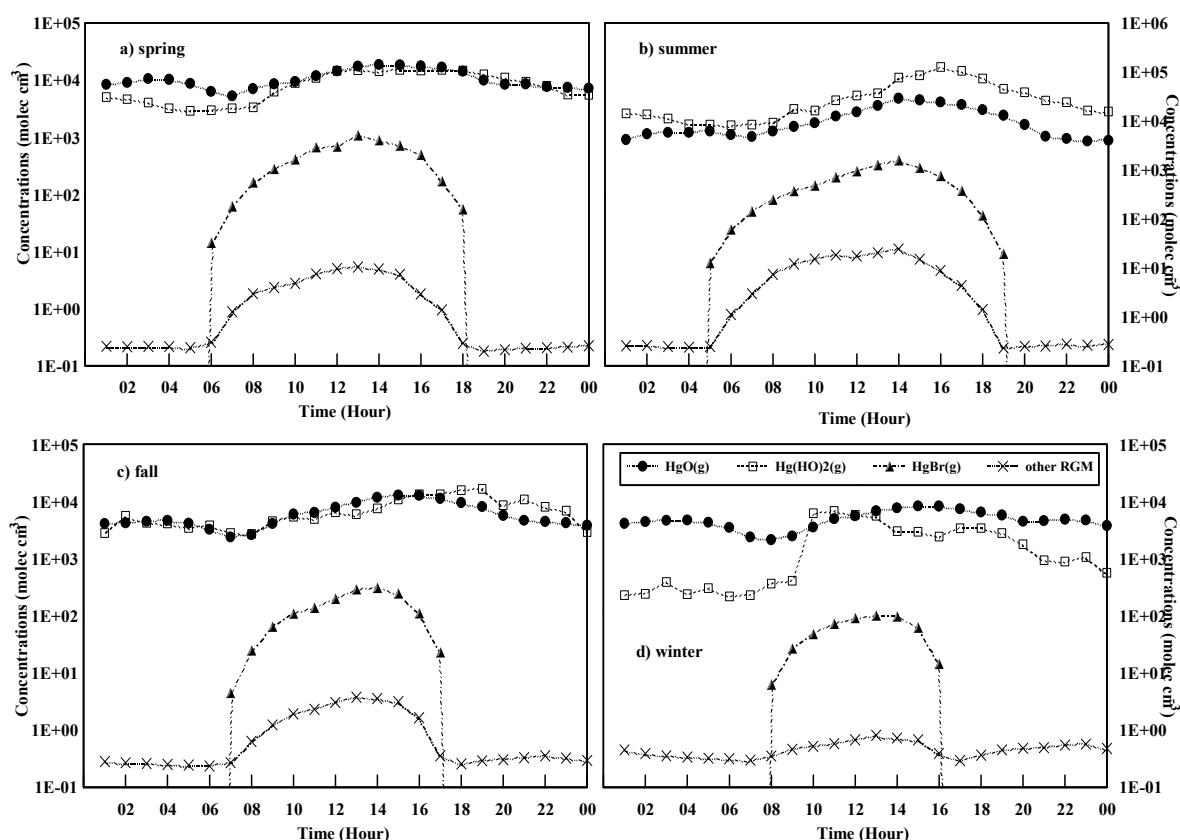


Figure 2. Diurnal variation of RGM during each season

during each season are shown in Fig. 2. Most RGM species (HgO, Hg(HO)₂, and HgBr) consistently showed daytime maxima and nocturnal minima. The presence of small peaks was typically observed a few hours before sunrise in the diurnal variation of HgO during all

four seasons, while that of $\text{Hg}(\text{HO})_2$ in the fall. These peaks for HgO appear to be influenced by the diurnal pattern of ozone. The pattern for $\text{Hg}(\text{HO})_2$ also appears to be affected by that of H_2O_2 . For HgBr and other RGM, concentration levels rapidly rose after sunrise and then dropped after sunset in line with the daytime source patterns of the corresponding oxidants (mainly halogen species). HgBr_2 represented the dominant species of other RGM chemical speciation.

4.3 Budgets of RGM and $\text{Hg}(0)$

In the case of $\text{Hg}(0)$, the chemical reaction of $\text{Hg}(0)$ with ozone is the predominant sink of $\text{Hg}(0)$, constituting $\geq 70\%$ of total sink. The chemical reactions of $\text{Hg}(0)$ with OH and H_2O_2

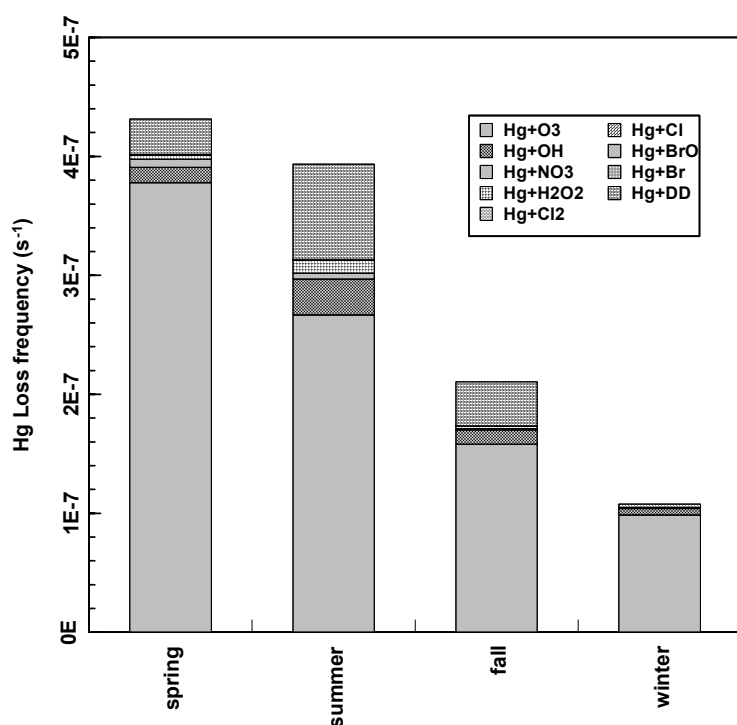


Figure 3. Loss frequencies of $\text{Hg}(0)$ during each season

and its dry deposition are less important photochemical sinks (see Fig. 3). On average, the dry deposition of $\text{Hg}(0)$ constitutes less than 15% of the total sink. When averaged over 24 hrs, the reaction of $\text{Hg}(0)$ with O_3 is the most important source of HgO , followed by its reaction with OH . The production rate of HgO in the

summer was equal to that in the spring due to the significant contribution of OH in the summer, although its production from ozone was low in the summer. The reaction of $\text{Hg}(0)$ with ozone can constitute $\geq 85\%$ of the total source. For the sink of HgO , it was seen that aerosol scavenging was an important removal process due to its high solubility.

5. CONCLUSIONS

The dominant RGM species in the urban air are expected to be HgO and Hg(HO)₂. Relatively high RGM concentrations occurred in the spring and summer possibly due to the stronger photochemical reactivity. The results of our study indicated the significance of H₂O₂ in the urban air for the RGM formation, especially in the summer. Most RGM species (HgO, Hg(HO)₂, and HgBr) exhibited daytime maxima and nocturnal minima. For the mercury halides production, the reaction of Hg(0) with Br can be more important than other halogen species (Cl₂, Br₂, and Cl) due to the combinations of the relatively fast reaction rates at relatively high concentrations. For Hg(0) sink, the chemical reaction of Hg(0) with O₃ is a predominant sink, followed by OH, dry deposition, and H₂O₂ in the order of its sink strength. The major source of HgO may be considered as the chemical reaction with O₃. For the sink of HgO, aerosol scavenging was an important removal process because of high solubility.

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