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Atmospheric Environment 39 (2005) 749–761

ATMOSPHERIC ENVIRONMENT

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Modeling study of reactive gaseous mercury in the urban air

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Received 30 April 2004; received in revised form 12 September 2004; accepted 20 September 2004

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 the relevant trace gases were carried out in Seoul (37.6°N, 127°E), Korea, during a one-year period from March 2001 to February 2002. A moderately strong inverse correlation between GEM (Hg(0)) and ozone was observed in the spring. In addition, it was also observed that there were distinct GEM concentration differences between day and night, especially in the winter. Model simulations suggested that the most dominant sink of elemental mercury (Hg(0)) was the reaction with O_3, which in turn contributed significantly to the formation of mercury oxide (HgO). The dominant RGM species in the urban ABL are likely to be HgO and $Hg(HO)_2$. Seasonally averaged concentrations of HgO and $Hg(HO)_2$ are estimated to range from 0.5×10^4 to 1.1×10^4 and 0.2×10^4 to 3.5×10^4 molecules cm^{-3}, respectively. According to our model simulations, most RGM species are expected to exhibit relatively enhanced concentrations during the daytime compared to the nighttime.

Keywords: Gaseous elemental mercury; Reactive gaseous mercury; Urban; Photochemical box model; Halogen

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. In general, atmospheric mercury consists of three different chemical/physical forms such as gaseous elemental mercury (GEM, Hg(0)), divalent mercury (Hg(II)), and particulate mercury. Out of those three terms, the former two can be used to represent the total gaseous mercury (TGM). The Hg(II) fraction of TGM is hence typically termed as reactive gaseous mercury (RGM). In recent years, studies of concentration and chemical speciation of the RGM in air have attracted a great deal of attention due to considerable advances in analytical techniques for RGM components (Stratton et al., 2001; Sprovieri et al., 2003).

RGM concentration levels were estimated to be typically less than about 5% (e.g., 10–200 pg m^{-3}) of TGM in the continental boundary layer (CBL) (Stratton et al., 2001; Munthe et al., 2003). In contrast, much lower RGM levels (e.g., 0.2–30 pg m^{-3}) were observed in the marine boundary layer (MBL), with a diurnal cycle characterized by a midday maximum (Sprovieri et al.,

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doi:10.1016/j.atmosenv.2004.09.071

2003). The chemical speciation of RGM is generally assumed to consist of $HgCl_2$, HgO, $Hg(HO)_2$ and/or other mercury halides. Daytime oxidation by the major oxidants (O_3, OH, H_2O_2, etc.) is thus likely to play a significant role in the diurnal cycle of RGM.

In recent years, a rapid decrease in background Hg(0) concentrations has been observed in the Artic spring (Schroeder et al., 1998) as well as in the Antarctic spring (Ebinghaus et al., 2002). During these mercury depletion events (MDEs) significantly increased levels of RGM (and particulate mercury) were measured in the high latitudes (Lindberg et al., 2001). In general, Hg(0) is believed to be relatively inert with a strong volatility under most atmospheric conditions. Thus, Hg(0) is not easily oxidized to less volatile forms by the major oxidants (O_3, OH, etc.) so that its residence time is estimated in the range of 1–2 years (Lindqvist and Rodhe, 1985). The major oxidation pathways of atmospheric Hg(0) have been considered to be the gas or aqueous-phase oxidation with ozone; the latter is known to take place in fog and cloud droplets (Pleijel and Munthe, 1995) and to an extent in deliquesced aerosol particles (Pirrone et al., 2000). The importance of the OH radical in Hg(0) oxidation has also been suggested by Lin and Pehkonen (1997). A recent kinetic study for their reaction indicated that it could be more important than that with O_3 (Sommar et al., 2001). However, Bauer et al. (2003) suggested that there is no evidence for such a reaction. Calvert and Lindberg (2003) reported that the ozone and gaseous Hg(0) depletion in high latitudes are likely to be related to halogen chemistry. However, correlation between these species in mid-latitude is still uncertain. In addition, knowledge of atmospheric mercury speciation is critical to modeling its fate. To our knowledge, no attempts have been made to model the chemical speciation and concentrations of individual RGM species in the urban atmospheric boundary layer (ABL).

In this paper, we present the oxidation chemistry of gaseous mercury using both gas and aqueous-phase oxidation mechanisms in the urban ABL. To this end, we first report the observational data sets of mercury and trace gases obtained from field measurements. Secondly, we present the detailed descriptions of our approach and model used for the analyses of the concentration levels of individual RGM species. Thirdly, the environmental significance of atmospheric mercury oxidation mechanisms is explored under urban conditions. Finally, we attempted to account for the factors governing the temporal variations of RGM in the ABL and to quantify the RGM budget.

2. Observational data

This study is based on the measurements of GEM and a number of important environmental parameters made at the sampling site during the time period of March 2002–February 2003. The measurement site is located in the Yang Jae district of Seoul (37.6°N, 127°E) (see Fig. 1). The site, a densely populated residential area, is about 2 km south of the Han Nam Bridge, which traverses the central part of the Han River in metropolitan Seoul. GEM concentrations were routinely measured using an on-line automatic analytical system. They were measured by transporting outdoor air via 2 m long sampling train made of Teflon tube into the analytical system. The detailed information concerning the measurement method, including detection limit, precision, and accuracy, has been discussed in Kim and Kim (2001). To interpret the physicochemical implications of GEM distribution, we used relevant environmental data collected from a nearby environmental monitoring station. This station constantly records both meteorological parameters (wind speed, wind direction, air temperature, and relative humidity (RH)), criteria pollutants as well as trace gases (O_3, NO_x, CO, CH_4, non-methane hydrocarbon (NMHC), and SO_2). Atmospheric hydrogen peroxide (H_2O_2) has also been measured on a nearby sampling site (the campus of Korea University in Seoul) since January 2002. Ambient air was pulled through a glass coil, where gaseous hydroperoxide was extracted onto aqueous solution. Then the hydroperoxide species was separated in a HPLC column and quantified by fluorescence signals produced by post-column derivatization utilizing enzyme. The detection limit of hydrogen peroxide was 15 pptv. The precision and uncertainty of the experiments overall was better than 6% and 8%, respectively (manuscript in preparation).

3. Model descriptions

3.1. Approach

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, which was employed to calculate the concentrations of major oxidants, OH, NO_3, etc. (Shon et al., 2004). The chemical mechanisms employed in the previous PCBM are summarized in Shon et al. Detailed descriptions on the halogen chemistry used in this study were introduced previously by Shon and Kim (2002), and those on the mercury chemistry are discussed in Section 3.2. The revised PCBM of a $HO_x/NO_x/CH_4$/NMHC/Hg(0)/halogen system was chemically constrained to one-hour averaged values of observed O_3, H_2O_2, NO, NO_2, CO, SO_2, GEM, and NMHC. Constrained NMHC concentrations were estimated from total NMHC concentrations using a fraction of the NMHC contribution taken from Blake et al. (1996) and Choi et al. (2003).