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Scientific uncertainties in atmospheric mercury models I: Model science evaluation

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Abstract

Eulerian-based, first-principle atmospheric mercury models are a useful tool to assess the transport and deposition of mercury. However, there exist uncertainty issues caused by model assumptions/simplifications and incomplete understanding of mercury science. In this paper, we evaluate the model science commonly implemented in atmospheric mercury models. The causes of the uncertainties are assessed in terms of gas phase chemistry, aqueous phase chemistry, aqueous phase speciation, aqueous phase sorption, dry deposition, wet deposition, initial and boundary conditions, emission inventory preparation, and domain grid resolution. We also present a new dry deposition scheme for estimating the deposition velocities of GEM and RGM based on RADM formulation. From our evaluation, mercury chemistry introduces the greatest uncertainty to models due to the inconsistent kinetic data and lack of deterministic product identification in the atmosphere. Model treatments of deposition velocities and aqueous Hg(II) sorption can also lead to distinct simulation results in mercury dry and wet depositions. Although model results may agree well with limited field data of GEM concentrations and Hg(II) wet deposition, it should be recognized that model uncertainties may compensate with each other to yield favorable model performance. Future research needs to reduce model uncertainties are projected.

Keywords: Atmospheric mercury; Modeling; Chemical mechanism; Deposition; Mercury speciation; Aqueous sorption; Cloud water; Emission inventory; Initial and boundary conditions

1. Introduction

Mercury (Hg) is a persistent, bioaccumulative pollutant regulated by the United States Environmental Protection Agency (USEPA). The concern of mercury pollution arises from the health effects caused by methylated mercury ingestion through

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the consumption of fresh water and marine fish (Clarkson, 1995; USEPA, 1997). Mercury is released into the atmosphere from a variety of natural (Fitzgerald et al., 1998) and anthropogenic (Porcella et al., 1997) sources. It is recognized that anthropogenic emissions have greatly increased relative to natural sources since the onset of industrialization (Fitzgerald et al., 2005). Atmospheric mercury exists primarily as gaseous elemental mercury (GEM), reactive gaseous mercury (RGM, gaseous divalent mercury) and particulate mercury (PHg, mercury associated with atmospheric particles). GEM has a long atmospheric lifetime (0.5–2 yr), and can be transported over great distances. RGM and PHg have a much shorter lifetime and deposit back to the earth rapidly via dry and wet depositions (Schroeder and Munthe, 1998; Lin and Pehkonen, 1999; Keeler et al., 2005). Recently, the rapid deposition of gaseous mercury during the Polar sunrise raises concerns of mercury contamination in the Arctic and Antarctic Regions (Schroeder et al., 1998; Ebinghaus et al., 2002; Lindberg et al., 2002a). The background total mercury concentrations are 1–3 ng m^{-3} (Slemr et al., 2003).

Numerous modeling studies have been conducted to understand the fate of mercury in the atmosphere (e.g., Pai et al., 1997; Lin and Pehkonen, 1998b; Shia et al., 1999; Ryaboshapko et al., 2002, 2005; Bullock and Brehme, 2002; Seigneur et al., 2003, 2004). The simulation of atmospheric mercury is a challenging task, because it requires extensive treatment of multiple mercury species that exhibit distinct physical and chemical properties, and exist in multiple phases of the atmosphere. In addition, it has been demonstrated that atmospheric conditions and the presence of other pollutants can strongly affect the redox cycling of mercury (Lin and Pehkonen, 1998b). The diverse interactions between various mercury species and the atmospheric environment are complex and usually generate non-linear responses. Therefore, atmospheric mercury modeling requires careful consideration of emission, transport, chemical reactions, interfacial transfer/equilibria, cloud processes, and dry/wet depositions.

One difficulty in interpreting mercury modeling results is the uncertainty associated with the implemented model science. This is mainly caused by the different science parameterizations and the assumptions/simplifications made in the models. The uncertainties can come from multiple model components, including the preparation of emission inventories and speciation, the treatment of natural emission or so-called "re-emission" (Seigneur et al., 2004; Walcek et al., 2003; Lin et al., 2005), the chemical mechanisms in both gaseous and aqueous phases (Ryaboshapko et al., 2002), the uncertainty in the chemical kinetic constants (Van Loon et al., 2000; Gardfeldt and Jonsson, 2003; Pal and Ariya, 2004a, b; Calvert and Lindberg, 2005); the speciation of GEM oxidation products (Lin et al., 2004), and the treatment of mercury deposition schemes. These uncertainty issues require a thorough evaluation for the model improvement and future scientific implementation.

The objective of this paper is to assess the uncertainties resulting from the science components implemented in atmospheric mercury models. Earlier studies by Seigneur and coworkers have addressed the uncertainty issues in mercury emission and speciation, spatial resolution of model grids, treatment of mercury re-emission, effect of dry deposition velocity, boundary conditions, and precipitation fields (Pai et al., 1999, 2000; Seigneur et al., 2001, 2003a, 2004; Shia et al., 1999). In this effort, we will focus particularly on the uncertainty issues on chemical mechanisms, aqueous sorption, treatment of mercury dry deposition, and natural emissions. The results are presented in two companion papers. In the first paper, we evaluate the mercury science commonly implemented in first-principle, Eulerian-based atmospheric models, and present a new treatment of mercury dry deposition based on the RADM scheme. The causes for model uncertainties are discussed, and recommendations for model improvement are made based on current "state-of-the-science" of mercury. In Part II, we perform a series of sensitivity simulations to quantitatively assess the uncertainties using a modified version of CMAQ-Hg in a 36-km Continental Unites States domain.

2. Mercury model science evaluation and causes for uncertainties

2.1. Gas phase redox chemistry

The speciation, property, behavior and chemistry of atmospheric mercury chemistry have been reviewed by Lindqvist and Rodhe (1985), Schroeder et al. (1991), Schroeder and Munthe (1998), and Lin and Pehkonen (1999). Since then, a number of laboratory and theoretical studies have advanced the understanding on the transformation of mercury