



## Abstract

Atmospheric mercury is a toxic air and water pollutant that is of significant concern because of its effects on human health and ecosystems. A mechanistic representation of the atmospheric mercury cycle is developed for the state-of-the-art global climate-chemistry model, CAM-Chem (Community Atmospheric Model with Chemistry). The model simulates the emission, transport, transformation and deposition of atmospheric mercury (Hg) in three forms: elemental mercury (Hg(0)), reactive mercury (Hg(II)), and particulate mercury (PHg). Emissions of mercury include those from human, land, ocean, biomass burning and volcano related sources. Land emissions are calculated based on surface solar radiation flux and skin temperature. A simplified air-sea mercury exchange scheme is used to calculate emissions from the oceans. The chemistry mechanism includes the oxidation of Hg(0) in gaseous phase by ozone with temperature dependence, OH, H<sub>2</sub>O<sub>2</sub> and chlorine. Aqueous chemistry includes both oxidation and reduction of Hg(0). Transport and deposition of mercury species are calculated through adapting the original formulations in CAM-Chem. The CAM-Chem model with mercury is driven by present meteorology to simulate the present mercury air quality during the 1999–2001 periods. The resulting surface concentrations of total gaseous mercury (TGM) are then compared with the observations from worldwide sites. Simulated wet depositions of mercury over the continental United States are compared to the observations from 26 Mercury Deposition Network stations to test the wet deposition simulations. The evaluations of gaseous concentrations and wet deposition confirm a strong capability for the CAM-Chem mercury mechanism to simulate the atmospheric mercury cycle. The results also indicate that mercury pollution in East Asia and Southern Africa is very significant with TGM concentrations above 3.0 ng m<sup>-3</sup>. The comparison to wet deposition indicates that wet deposition patterns of mercury are more affected by the spatial variability of precipitation. The sensitivity experiments show that 22 % of total mercury deposition and 25 % of TGM concentrations in the United States are resulted from domestic anthropogenic sources, but only 9 % of to-

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tal mercury deposition and 7 % of TGM concentrations are contributed by transpacific transport. However, the contributions of domestic and transpacific sources on the western United States levels of mercury are of comparable magnitude.

## 1 Introduction

5 Mercury is a toxic pollutant, having harmful effects on human health and ecosystems. United States and many other countries have listed mercury as a major air pollutant that requires regulatory control (e.g. US Clean Air Act, 1990; EMEP, 2005). Mercury is emitted into the air in forms of elemental mercury (Hg(0)), reactive mercury (Hg(II)) and particulate mercury (PHg). Elemental mercury accounts for more than 90 % of to-  
10 tal atmospheric mercury (Schroeder and Munthe, 1998). Its atmospheric lifetime (several months) is long enough for global-scale transport. As such, mercury is a global air pollutant and it is difficult to attribute the relative importance of its local and/or remote emissions sources. Several atmospheric models such as GEOS-Chem, CMAQ, and HYPLIT have been developed and achieved successful simulations of tropospheric mercury against available observations (Bullock and Brehme, 2002; Cohen et al., 2004; Selin et al., 2007, 2008; Bullock et al., 2008, 2009). However, along with the remaining  
15 issues on emission estimates (Lin et al., 1999, 2010), recently there have raised arguments on the chemical transformation of atmospheric mercury (Calvert and Lindberg, 2005; Holmes et al., 2010; Lyman and Jaffe, 2012; Rutter et al., 2012). Therefore, it is necessary to develop mercury models that incorporate the relevant emission, transport, and deposition processes as well as represent/test different mercury mechanisms.

The main issue about atmospheric mercury chemistry relates to the oxidation mechanism. Previous atmospheric mercury models were mainly based on the oxidation of elemental mercury by ozone (O<sub>3</sub>) and hydroxyl (OH) (Bullock and Brehme, 2002; Lin  
25 et al., 2006; Selin et al., 2007, 2008). These models have achieved successful global and regional validations against the near-surface observations but have problems in reproducing the concentrations of mercury species in the upper troposphere and Antarc-

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tic summer (Sprovieri et al., 2002; Temme et al., 2003; Lin et al., 2006). Based on chemical kinetics, Calvert and Lindberg (2005) pointed out that the mercury oxidation from this mechanism in the real atmosphere might be much slower than the reported laboratory results (Hall, 1995; Sommar et al., 2001; Pal and Ariya, 2004a,b). However, aircraft-based measurements in the upper troposphere and lower stratosphere show that ozone concentrations rapidly respond to the variation in concentrations of total mercury and reactive mercury, indicating the possibility of the ozone-OH oxidation mechanism in dominating the transformation of atmospheric mercury (Lyman and Jaffe, 2011). Further experiments on more accurate rate measurements also strongly support the oxidation mechanism by ozone in the presence of secondary organic aerosols and directly refute the previous comments on the laboratory results (Rutter et al., 2012). Meanwhile the chemistry for bromine (Br) oxidation of mercury has been developed based on theoretical kinetic calculations (Goodsite et al., 2004; Holmes et al., 2006). Holmes et al. (2010) evaluated the bromine oxidation mechanism in the GEOS-Chem Hg model. As reviewed by Subir et al. (2011), our current status of knowledge on these mercury reactions reflects a lack of sufficient understanding of such mechanisms. Additional measurements and modeling studies are needed to achieve a better understanding of the atmospheric mercury life cycle.

Another major challenge for modeling mercury is to obtain a well-characterized evaluation of global emissions. The current emission inventory datasets are known to contain substantial uncertainties (Pacyna et al., 2005; Street et al., 2009). Anthropogenic sources take up a quarter of the current mercury emissions. These include coal-fired power production, metal smelting, and waste incineration (Pacyna et al., 2005; Streets et al., 2005; Mason and Sheu, 2002). All of these sources are highly variable and total source rates are not well known, causing large uncertainties in estimating their emission inventories. Natural sources include fluxes from water bodies, soil, terrestrial vegetation, volcanic eruptions, and biomass burning. The difficulty in estimating natural emissions is to represent the surface fluxes in response to meteorological and physical conditions (Poissant and Casimir, 1998; Zhang et al., 2001). The accurate estimate of

the spatial and temporal distributions of emissions from major sources is the foundation for a successful simulation of atmospheric mercury.

In addition to the major problems above, a complete atmospheric mercury model also requires consideration of heterogeneous chemistry, transport processes, wet and dry deposition processes. Recent intercomparison studies have shown that large differences in modeled results over North America are caused mainly by inconsistent treatments of the chemical and physical processes affecting Hg transport and transformation (Bullock et al., 2008, 2009). Starting from a simple atmospheric model, the NCAR Community Atmospheric Model with Chemistry (CAM-Chem) has been developed with advanced representations of dynamical, physical, and chemical processes; it serves as a powerful tool for investigating global atmospheric environment and climate interactions (Lamarque et al., 2005, 2011; Heald et al., 2008; Pfister et al., 2008). The original CAM-Chem model does not include the chemical and physical processes necessary to simulating the atmospheric and surface mercury distributions, but it provides a platform to build a reliable atmospheric mercury model.

This study is aimed at developing and incorporating into the CAM-Chem model a mercury module based on the latest available numerical representations of all processes essential to the mercury lifecycle (e.g. Subir et al., 2011; Rutter et al., 2012). The basic chemical mechanism is based on the O<sub>3</sub>-OH oxidation, but we also test the effects of Br-oxidation on surface mercury concentrations. We account for spatial and temporal variability of all three types of mercury (Hg(0), Hg(II), PHg) emitted and re-emitted from various sources over both land and oceans by modifying and incorporating two dynamic parameterization models (Liss and Slater, 1974; Zhang et al., 2001; Wängberg et al., 2001). The expanded CAM-Chem with the mercury mechanism simulates the atmospheric pathways of all forms of mercury from their source emissions to eventual deposition back to land and water surfaces through both wet and dry atmospheric processes across a wide range of spatial and temporal scales. The viability of the model, hereafter called CAM-Chem/Hg, is evaluated based on multi-year simulations driven by representative meteorological conditions from the global observational

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reanalysis. The results are compared against the best-available observations for surface mercury concentration and wet deposition, including data from the National Atmospheric Deposition Program (NADP) (Lindberg and Vermette, 1995), major networks in Europe (EMEP) and Canada (CAMNet), as well others from the published literature (Friedli et al., 2004; Kock et al., 2005). The CAM-Chem/Hg model is then used to evaluate the contributions of transpacific transport and domestic anthropogenic emissions to US mercury concentrations.

## 2 Model formulation

### 2.1 The CAM-Chem model

The CAM-Chem model used in this study is an integral part of the Community Climate System Model version 3 (CCSM3) that includes fully coupled atmospheric, land, ocean, and sea ice components (Collins et al., 2006; Lamarque et al., 2011). The gas-aerosol phase chemistry is based on the MOZART (Model of Ozone and Related Chemical Tracers) chemistry-transport model (Horowitz et al., 2003; Tie et al., 2001, 2005). It has been rigorously evaluated and widely used in the recent chemistry-climate studies (Heald et al., 2008; Lamarque et al., 2005, 2008; Murazaki and Hess, 2006; Emmons et al., 2010; Lei et al., 2012, 2013). The chemical module includes 85 gas-phase species, 12 bulk aerosol compounds, 39 photolysis and 157 gas-phase reactions. The aerosol module consider sulfate, black carbon, primary organic, secondary organic, ammonium nitrate, and sea salt (Lamarque et al., 2005, 2011). Wet deposition is modeled by the formulation of Neu and Prather, (2011). See Lamarque et al. (2011) for a more extensive description of the model.

This study adopts anthropogenic emissions mostly from the POET (Precursors of Ozone and their Effects in the Troposphere) database for 2000 (Granier et al., 2005; Olivier et al., 2003), including those of fossil fuel and biofuel combustion based on the EDGAR-3 inventory (Olivier et al., 2001). Biogenic emissions of isoprene and monoter-

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penes, and nitric oxide (NO) emissions from soil, are calculated online using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006) as implemented by Pfister et al. (2008). Biomass burning emissions are taken from the Global Fire Emissions Database version 2 (GFED-v2), with monthly average data available for 1997–2007 (van der Werf et al., 2006).

A simulation for the years 1998–2001 was carried out with CAM-Chem for evaluation relative to observations. The simulation is driven by meteorological fields from the NCEP/DOE AMIP II reanalysis (Kanamitsu et al., 2002), including winds, mixed-layer depths, temperature, precipitation, and convective mass fluxes. These data are available at a 6-h interval and a grid spacing of  $1.9^{\circ} \times 2.5^{\circ}$  with 26 hybrid sigma-pressure levels. The initial year 1998 is considered as a spin-up. The subsequent analyses focus mainly on the statistics for year 2000 and the average of 1999–2001 relative to the respective observations.

## 2.2 Mercury chemistry

The treatment of mercury chemistry used here considers major pathways in both gas and aqueous phases. The gas-phase reactions include the oxidation of Hg(0) to Hg(II) by OH, ozone, and chlorine (Hall, 1995; Sommar et al., 2001; Calhoun and Prestbo, 2001; Pal and Ariya, 2004; Subir et al., 2011), which represents the core mechanism for CAM-Chem/Hg model. The bromine oxidation reactions are not included in the core mercury module due to incomplete knowledge of the bromine chemistry and emissions in CAM-Chem. However, a sensitivity experiment does consider this by using the global bromine field from GEOS-Chem to test possible effects on the global mercury distribution. Table 1 lists the detailed Hg chemical reactions and their rate constants (Gbor et al., 2006; Subir et al., 2011; Rutter et al., 2012). Hg(II) gas-particle partitioning is also shown in Table 1. Hg(II) phase partitioning affects both wet and dry deposition. The partitioning of Hg(II) is assumed to be divided equally between the gas and particle phases for oxidation by ozone, OH, and Br. The oxidation products by chlorine and H<sub>2</sub>O<sub>2</sub> are all reactive mercury. For the main chemical mechanism, the gaseous re-

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actions produce reactive gaseous mercury (RGM, gaseous  $\text{Hg(II)}$  compounds) that is soluble in water (with a Henry's Law constant of  $1.4 \times 10^6 \text{ Matm}^{-1}$ ), and thus dissolves to  $\text{Hg}^{2+}$  in aqueous aerosols and clouds (Pleijel and Munthe, 1995; Schroeder and Munthe, 1998). In the aqueous phase, the reduction of  $\text{Hg}^{2+}$  into  $\text{Hg}^0$  has been shown to be important in laboratory studies (Pehkonen and Lin, 1998; Lin et al., 2003). The transformation from  $\text{Hg}^{2+}$  to  $\text{Hg}^0$  can be achieved through photochemical reactions or reactions with  $\text{SO}_3^{2-}/\text{HO}_2$ . Since the solubility of  $\text{Hg}^0$  is relatively low (with a Henry's Law constant of  $1.1 \times 10^{-1} \text{ Matm}^{-1}$ ), the oxidation of  $\text{Hg}^0$  based on the dissolution of gaseous elemental mercury may not be significant. However, the main aqueous oxidation mechanisms included in Table 1 can be important for the mercury chemical equilibrium when considering the reduction of  $\text{Hg}^{2+}$ .

## 2.3 Mercury deposition

The treatment for wet deposition of  $\text{Hg(0)}$ , RGM and PHg follows that used for all other aqueously sensitive pollutants resolved in the standard CAM-Chem. It is based on the formulation of Brasseur et al. (1998), considering the solution scavenging and incorporating the main parameterization introduced by Giorgi and Chameides (1985). The wet deposition treatment includes rainout and washout from stratiform and convective precipitation, and scavenging in convective updrafts (Liu et al., 2001). In addition, the uptake by the marine boundary layer (Hedgecock and Pirrone, 2001; Selin et al., 2007) is also regarded as a major deposition process for Hg, and is considered in the calculation of the mercury emission process. The aqueous concentration of  $\text{Hg}^0$  is low relative to the total dissolved  $\text{Hg}^{2+}$ , and thus its wet deposition is minor compared to that of  $\text{Hg(II)}$  and PHg.

The treatment for dry deposition of mercury species also follows that for other chemicals in the standard CAM-Chem. Some previous studies neglected dry deposition of  $\text{Hg(0)}$  due to the rapid reemission from the ground (Bullock et al., 2002; Selin et al., 2008). Recent studies have shown that 5 ~ 40 % of newly deposited mercury is rapidly



reemitted back to the atmosphere over non-snow land surfaces (Hintelmann et al., 2002; Amyot et al., 2004), and up to 60 % over snow surfaces (Lalonde et al., 2001; Ferrari et al., 2005). In CAM-Chem, the rapid reemission of mercury has been considered in the land emission inventory by returning 20 % of total deposited Hg(II) as Hg(0) and does not need to be compensated for by dry deposition. Therefore, we determine the dry deposition velocities of Hg(0) online in the model, based on the resistance-based parameterization of Wesely (Walmsley and Wesely, 1996; Wesely and Hicks, 2000). Dry deposition of Hg(II) and PHg is simulated with the scheme based on local surface type and turbulence (Wang et al., 1998; Wesely, 1989).

## 2.4 Mercury emissions

Here we adopt the anthropogenic mercury emissions in 2000 from the Global Emission Inventory Activity (GEIA) (Pacyna et al., 2006) as the present emission from anthropogenic sources. These sources include major industrial emitters from coal-fired power production, mining, metal smelting, and waste incineration (Streets et al., 2005; Mason and Sheu, 2002).

Land sources include emissions from soil and vegetation, plus rapid reemissions of deposited mercury. Soil and vegetation contribute about 500–1800 Mgyr<sup>-1</sup> (Lindqvist, 1991; Seigneur et al., 2001; Selin et al., 2007), while the reemissions range is 260–1500 Mgyr<sup>-1</sup> (Selin et al., 2008; Smith-Downey et al., 2010), resulting in a total estimate of 1100–3000 Mgyr<sup>-1</sup>. Land emissions depend on both soil temperature (Lindberg et al., 1995; Poissant and Casimir, 1998) and surface solar radiation (Carpi and Lindberg, 1998; Zhang et al., 2001; Gustin et al., 2002). Land mercury emissions are calculated using local temperature, solar flux, and estimated source distribution. By using the GEOS-Chem soil mercury pool, the average emission flux ( $F_1$ ) for present is distributed based on soil mercury storage (Selin et al., 2008; Smith-Downey, et al., 2010). It is then adjusted using the relationship suggested by Zhang et al. (2001) and

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Poissant and Casimir (1998):

$$F_2 = F_1 \exp[-1.1 \times 10^4 (1/T_s - 1/T_0)] \exp[1.1 \times 10^3 (R_s - R_0)]$$

where  $F_2$  is the calculated land emission flux.  $R_s$  is the surface solar radiation flux and  $T_s$  is the local surface skin temperature. The reference value is  $340 \text{ Wm}^{-2}$  for  $R_0$  and  $288 \text{ K}$  for  $T_0$ . The parameterization is subject to calibration using the multi-year average (1995–2005 monthly mean)  $R_s$  and  $T_s$  distributions from the NECP reanalysis. The  $F_1$  has been adjusted to constrain the global annual total emission of  $2900 \text{ Mg yr}^{-1}$  estimated for 2000 (Smith-Downey et al., 2010).

Ocean emissions are determined by a simplified air–sea exchange scheme that has been tested through field campaigns for good agreement with observations (Liss and Slater, 1974; Wängberg et al., 2001). We estimate monthly mean mercury flux at ocean surface through the following scheme that also removes the dependence on the mercury storage in deep oceans:

$$F = K_w(C_w - C_a/H')$$

where  $F$  is the ocean emission flux of mercury,  $H' = [\text{Hg}]_{(\text{g})}/[\text{Hg}]_{(\text{aq})}$  is the dimensionless Henry's-Law constant calculated at water temperatures ( $T_w$ ) (Clever et al., 1985),  $K_w$  is the gas transfer velocity of a species in the water–air interface based on the empirical relation of Wanninkhof (1992), and  $C_w$  and  $C_a$  are respectively the  $\text{Hg}(0)$  concentration in the mixed-layer ocean ( $\text{pg/L}$ ) and in the surface atmosphere ( $\text{ngm}^{-3}$ ).  $C_w$  is simplified by using the monthly mean concentration data (Soerensen et al., 2010), which has considered the contribution from deposition, while  $C_a$  is determined by the atmospheric model.

Biomass burning emissions are specified as monthly means from the IPCC estimate of biomass burned and the IMAGE projection of managed forests for a typical year. The approach and emission factors as a function of vegetation types are adopted from Streets et al. (2009).

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Volcanic emissions of mercury are based on those of sulfur in the GEIA inventory. The method uses a typical ratio of Hg relative to SO<sub>2</sub> volcanic emissions to estimate mercury emissions. A similar method has been used in the previous studies (Ferrara et al., 2000; Nriagu et al., 2003; Pyle and Mather, 2003). Here we adopt a Hg/SO<sub>2</sub> ratio of  $1.5 \times 10^{-6}$  for all volcanic eruptions (Aiuppa et al., 2007; Witt et al., 2008).

## 2.5 Global Budget

Figure 1 summarizes the partition of global mercury emissions in 2000 among different sources. It shows that the oceans are the largest contributor, followed by natural land emissions and the human-related emissions. However, the oceanic flux per unit area is small as the total emissions are distributed over 72 % of the Earth's surface. In contrast, the average emission flux over land is 3.5 times larger than the flux over ocean, when counting the natural, anthropogenic, and biomass burning emissions together.

Our estimate of global total emissions from all sources is about 9680 Mgyr<sup>-1</sup>. This falls in the middle between the values of 6200 and 11 200 Mgyr<sup>-1</sup> used in the GEOS-Chem model (Selin et al., 2007, 2008). However, our estimate for the ocean emissions is notably larger than the previously published values (3400 versus 2600±300 Mgyr<sup>-1</sup>). This reflects our inclusion of emissions from the mixed-layer ocean storage and the rapid reemissions from deposited mercury.

Dry and wet depositions of mercury are calculated separately in CAM-Chem/Hg, in contrast to the net removal rate considered in some studies (Bullock et al., 2002). In the Earth's surface, total estimated deposition is around 8800 Mgyr<sup>-1</sup>, in which dry deposition accounts for 70 %. About 55 % of the total deposition occurs over the ocean and 45 % over the land. Over land, total deposition is 1800 Mgyr<sup>-1</sup> for Hg(II), 1600 Mgyr<sup>-1</sup> for Hg(0), and 600 Mgyr<sup>-1</sup> for PHg. The oceans are a net sink for atmospheric mercury, taking up approximate 2000 Mgyr<sup>-1</sup>, balancing a portion of the human-related and volcanic sources.

The CAM-Chem/Hg model calculates a total mercury lifetime of 0.69 yr in the atmosphere against deposition, as deposition is the only sink for total mercury in the model.

Our derived lifetime of mercury agrees well with the estimated lifetime of 0.5 to 0.79 yr determined in the GEOS-Chem model studies (Selin et al., 2007, 2008). Previous studies had estimated the lifetime at 1.0 to 1.7 yr (Bergan et al., 1999; Shia et al., 1999; Seigneur et al., 2001; Lamborg et al., 2002). The shorter lifetime in the more recent studies may result from the modeling approaches where the processes of deposition and reemission are treated separately.

### 3 Global mercury distribution

#### 3.1 CAM-Chem/Hg results

Figure 2 shows the annual mean surface air concentrations of total gaseous mercury (TGM) averaged over the 1999–2001 time period as simulated by the CAM-Chem/Hg model using the present emission. The TGM is taken as the sum of gaseous Hg(0) and gaseous Hg(II). The major characteristic is that the mercury concentrations are greatest over land and coastal regions. The most-polluted area occurs in Asia, where strong surface TGM concentrations are derived along the continent boundaries. In particular, the concentrations across the Middle East, India, China, and Japan are above  $3 \text{ ng m}^{-3}$ . The second most-polluted area is southern Africa, where high mercury emissions result from the intensive development of mercury-related industries, especially mining. Mining in Australia also results in heavy mercury deposition along the southeast coast. These areas of heavy mercury pollution are identified with high human-related emissions over land (Nelson, 2007). In contrast, the Antarctic pollution is low because of little human-related emissions. On the other hand, the high concentrations along Chile and the eastern coast of the South Pacific are associated with large natural emissions from the oceans that are accelerated by warm sea surface temperatures in those locations. The high concentrations over the eastern coast of the South Atlantic are likely caused by transport of inland pollutants from South Africa under the prevailing easterly to northeasterly winds near the surface.

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The derived CAM-Chem/Hg model results share a general similarity with previous modeling studies. For example, the interhemispheric total integrated concentration in the Northern Hemisphere relative to that in the Southern Hemisphere, the TGM concentration ratios, for surface air were estimated to range between 1.2 and 1.8 (Lamborg et al., 2002), without considering the heavy polluted East Asia. The CAM-Chem/Hg model derived value is 1.68. The spatial pattern of TGM in our study also compares well with that from the GEOS-Chem model over the globe (Selin et al., 2007, 2008). In particular, the concentrations over land are very close between the GEOS-Chem and CAM-Chem/Hg models, while their differences (around  $0.2 \text{ ng m}^{-3}$ ) over oceans are largest in the Arctic. This disagreement may partially result from the use of different driving meteorological conditions that are important to mercury reactions and transport.

Table 2 compares the modeled 1999–2001 mean surface TGM concentrations with measurements at 19 nonurban land sites worldwide with varying periods (time average) between 1995 and 2007 (Selin et al., 2007). The model captures the general spatial pattern of global mercury air pollution. The TGM concentrations match the range of observations at 14 out of the total 19 sites, where model biases are smaller than  $0.3 \text{ ng m}^{-3}$ . Larger positive biases ( $2.8 \text{ ng m}^{-3}$ ) occur at the Cape Point site in South Africa, where mining industry development dominates the regional mercury emissions, accounting for a quarter of the total global anthropogenic emissions (Pacyna et al., 2006). The latest measurements indicate that the TGM concentration at the Cape point site is up to  $1.51 \text{ ng m}^{-3}$ , with its variability similar to that over the tropical Atlantic (Witt et al., 2010). Our analyses and studies by Witt et al. (2010) show that the prevailing strong westerly winds in near surface layers bring cleaner marine air rather than inland polluted air to the Cape Point, effectively diluting mercury pollutions. The coarse resolution CAM-Chem/Hg model has the limited capability to simulate this westerly wind to lead to large positive biases at Cape Point. The inaccurate representation of emissions might also contribute to the biases. On the other hand, the model tends to underestimate the TGM concentrations at 4 Asian sites (Chongqing, Beijing, Tokyo, and Seoul) likely because the emissions there have likely continued to increase after year 2000.

The model biases at these sites are less than 20 % relative to the observations (Sakata and Marumoto, 2002; Kim et al., 2006; Wang et al., 2007; Yang et al., 2008).

Figure 3 illustrates the CAM-Chem/Hg model simulated zonally- and annually-averaged surface air TGM concentration variations for 1999–2001 compared to observations at various locations worldwide, including land stations (Ebinghaus et al., 2002; Baker et al., 2002; Sakata and Marumoto, 2002; Kellerhals et al., 2003; Weiss-Penzias et al., 2003; Environmental Canada, 2003; Han et al., 2004; EMEP, 2005; Kim et al., 2006; Wang et al., 2007; Liu et al., 2007; Yang et al., 2008) and ocean cruises (Selin et al., 2007; Temme et al., 2003; Laurier et al., 2003; Lamborg et al., 1999). Note that these measurements are not necessarily representative of zonally- and annually-averaged conditions, but are used to depict the available variations with latitude. All of the land station data and the corresponding CAM-Chem/Hg model values listed in Table 2 are also shown in Fig. 3. In general, the model captures the major TGM characteristic variation with latitude, following the variation of mercury emission sources. In particular, two peak values occur in the northern and southern middle latitudes that correspond to the intensive sources from industrial and mining activities. Due to the relatively even distribution of mercury emissions from oceans, the variations of zonally averaged TGM concentrations tend to be associated with the amount of land fraction as a function of latitude.

In comparison, the GEOS-Chem model simulates a range between 1.25 and 1.75 for zonal mean surface air TGM concentrations (Selin et al., 2007) with latitude. The CAM-Chem/Hg model values are larger than this at lower and middle latitudes, but smaller at high latitudes. As explained by Selin et al. (2007), the Arctic concentrations may be overestimated by the GEOS-Chem model due to missing halogen chemistry. The larger CAM-Chem/Hg model values in the northern middle latitudes are mainly attributed to high surface concentrations over East Asia as confirmed from the observations. In contrast, the results for the southern middle latitudes may be overestimated by the CAM-Chem/Hg model due to uncertainties in the southern African emissions and meteorology (e.g. Cape Point site in Table 2).

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Figure 4 compares the CAM-Chem/Hg modeled Hg(0) vertical distribution with that measured in the ACE-Asia aircraft campaign during April–May 2001 over Ontario, Japan (Friedli et al., 2004). The measurements show a decrease in the mixing ratio from  $2 \text{ ng m}^{-3}$  near the surface to  $1.25 \text{ ng m}^{-3}$  at 2.5 km, a relatively small change from 2.5 to 6.5 km, and a sharper decrease to  $0.6 \text{ ng m}^{-3}$  at 7.5 km. The model result is close to observations within the boundary layer below 1.5 km and at 7.5 km. However, large discrepancies exist in middle layers between 2 and 7 km, where the model simulates a monotonically rapid reduction to a constant value of  $0.55 \text{ ng m}^{-3}$  above 4.5 km. The observed enrichment in the middle layers may result from an occasional pollution influence (Friedli et al., 2004), or the enhanced high-altitude recycling of Hg(II) by photolysis (Selin et al., 2007). At present, the CAM-Chem/Hg model only considers the photochemical reduction of Hg(II) in the aqueous phase, which is mostly confined to the lower troposphere. This may partially explain the model underestimation. Figure 5 compares the CAM-Chem/Hg modeled and observed seasonal variations of surface TGM concentrations at two coastal monitoring sites, Mace Head, Ireland and Zingst, Germany (see the location information in Table 2). These two sites have made continuous measurements, with well characterized accuracy and precision. The monthly means are averaged in 1998–2004 for the observations (Kock et al., 2005) and in 1999–2001 for the model result. Both sites were observed to have TGM levels higher in winter than summer. This seasonality is captured by the CAM-Chem/Hg model. At Zingst, the model result is closely comparable with the observations during February–August, but approximately 10 % ( $0.2 \text{ ng m}^{-3}$ ) lower for the other months. Model underestimations of a similar magnitude occur at Mace Head throughout the year. Note that air pollution at coastal sites in midlatitudes can be strongly affected by land or sea breezes. In summer, warmer land than ocean temperatures causes prevailing winds toward inland. As such, measurements at coastal sites may be affected more by oceanic than inland mercury levels. The winter conditions generally reverse. This effect is challenging to simulate, especially using a relatively coarse resolution model like CAM-Chem that cannot accurately represent local circulation patterns. On the other hand, the wet



deposition measurements suggest that the removal of atmospheric mercury is high in summer at most non-coastal sites over the contiguous US (NADP, 2008). That would be a reason to understand this pattern. At this time, it is not known whether the above disagreements are caused by differences in local source emissions or meteorological conditions.

## 3.2 Results by adding bromine oxidation

In order to test how the bromine oxidation reactions affect the mercury distributions, we add the bromine chemical reactions in both gas and aqueous phases (as shown in Table 1) in addition to the ozone-OH oxidation mechanism. The experiment is implemented by directly using the monthly averaged Br concentrations from the GEOS-Chem mercury model. The evaluation of GEOS-Chem simulations of Br chemicals shows well agreement with available aircraft observations (Parrella et al., 2012). The annual mean Br mixing ratio from GEOS-Chem peaks in higher latitude ocean regions but is generally low over land. The seasonality shows high levels during March–May and September–November. Similar to CAM-Chem/Hg simulation, the modified model is driven by NCEP reanalysis meteorology and runs for two year during 1999–2000. The first year run is considered as a model spin-up, and the second year (year 2000) data is used to compare with CAM-Chem/Hg simulation in 2000.

Figure 6 shows the change in TGM concentration on surface layer resulted from introducing bromine reactions. Generally, adding bromine chemistry appears to have little impact on overall TGM spatial and temporal patterns with less than  $0.2 \text{ ng m}^{-3}$  decrease found in most areas across the globe. The additional bromine reactions will accelerate the transformation of Hg(0) to RGM, the major part of which will stay in TGM. We also notice that regions with large emission and precipitation tend to have larger TGM reduction. This is because bromine chemistry transforms more Hg(0) into RGM, which subsequently enhances the wet deposition of Hg(II), leading to the reduced TGM concentration. Theoretically, bromine may be possible to increase the TGM in some places where the reduction reactions become more significant (more RGM is reduced

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to Hg(0), leading to less wet deposition loss from the atmosphere). However, it is not shown in this experiment.

Overall, including the bromine chemistry does not significantly affect the TGM pattern, but it may affect the gaseous mercury partitioning between the elemental mercury and reactive gaseous mercury. Due to the difficulty in monitoring gaseous Hg(II), our knowledge on Hg(0)/Hg(II) partitioning is limited and needs further investigation (NADP 2008). In the following sections, we continue analyses of the CAM-Chem/Hg simulated results without considering the possible effects of bromine chemistry.

## 4 US Mercury wet deposition

Wet deposition is mainly determined by the distribution of precipitation amount and air pollutant concentration. Previous regional modeling studies suggested that mercury wet deposition over the US also depended on the mercury emissions used (Bullock et al., 2002; Gbor et al., 2005). Table 3 compares the modeled annually-averaged wet depositions for total mercury with the measurements at 26 monitoring sites of the Mercury Deposition Network (MDN) within the US National Atmospheric Deposition Program (NADP). The model values are averaged over 1999–2001, while observations are given as the means of all measurements during the most closely matching data periods. The results show that the CAM-Chem/Hg simulation is realistic at 18 of the 26 sites, where differences from observations are within  $\pm 20\%$ . However, at some coastal sites (FL11, WA18), model biases are as large as  $6\text{ }\mu\text{g m}^{-2}$ . These differences are likely caused by errors in simulating precipitation near the coast by the CAM-Chem model with its coarse resolution. In addition, relative biases are larger at some sites (e.g. CA72) with low wet depositions. The differences in data periods may partially explain the model-observation discrepancies.

Figure 7 illustrates the geographic distribution of wet deposition for annually-averaged total mercury for 1999–2001 over the US as derived by the CAM-Chem/Hg model. The spatial pattern of mercury wet deposition follows more closely to that of

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precipitation (Liang et al., 2004) than of the atmospheric mercury concentration. In general, the largest wet deposition occurs in the eastern US, where the peaks correspond to the maximum annual precipitation centers over the Southeast, and locate on the southwest flank of the TGM concentration maxima. This is because the TGM concentration has much smaller spatial variations than precipitation. The secondary peaks of annual total mercury wet depositions are simulated over the Northwest, where precipitation prevails during cold seasons.

Figure 8 presents the scatter diagrams comparing modeled monthly total mercury wet deposition during 1999–2001 at the four MDN sites with continuous records, representing the Southeast (FL11), eastern coast (NC42), Midwest (WI08), and Southwest (TX21). The temporal correlation coefficients between modeled and measured depositions are reasonably high, suggesting that the CAM-Chem/Hg model largely captures observational variations at each site. The best result is obtained in the Midwest, where the correlation reaches 0.67. The result is also good for the Southeast and fair for the Southwest, with a respective correlation of 0.45 and 0.32, but relatively poor for the east coast with a low correlation of 0.19.

## 5 Domestic versus transpacific contributions to US mercury air quality

The transpacific transport is the primary process for bringing Asian pollutants to the US. Various ground-level observation analyses, field campaigns, and model simulations have been conducted to investigate the current pathways and characteristics of transpacific transport, as well as their influence on US air quality (e.g. Jacob et al., 1999; Wilkening et al., 2000; Yienger et al., 2000; Jaeglé et al., 2003; Hudman et al., 2004; Parrish et al., 2004; Bertschi and Jaffe, 2005; Heald et al., 2006; Wuebbles et al., 2007; Lin et al., 2008). Previous sections have shown that the mercury pollution in East Asia is severe in the world. Therefore, analysis of the contributions from transpacific transport on US mercury air quality is worth investigating.

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Two sensitivity experiments are conducted to examine the domestic versus international contributions to US mercury concentrations. The first sensitivity experiment (EXP1) assumes no anthropogenic emissions over the United States and uses the current model settings elsewhere. The second sensitivity experiment (EXP2) assumes no anthropogenic emissions over Asia and keeps the current settings elsewhere. Simulations of global mercury concentrations in the previous section are used as the control run (CtrRun) to present the practical mercury effects on air quality.

Figure 9 shows the CAM-Chem simulated TGM concentrations (from CtrRun) on latitude-pressure cross sections over the northern Pacific Ocean between 80° E and 80° W. The cross sections are provided from 20° N to 60° N in the north hemisphere with an interval of 5°. High concentration of TGM occurs on the longitude from 100° E to 130° E, which indicates the strong emissions from East Asia. The red rectangle lies over mountains (Rockies, Sierras, etc.) indicating the higher surface altitude. Due to the blocking effect of terrain, surface mercury concentration from the east to the region near 120° W shows a decreasing trend. The loss of mercury suggests a possible deposition on the western US. The changes in low-level concentrations on these cross sections also suggested that the transpacific transport of mercury is strong between 30° N and 55° N.

Surface TGM concentrations are directly affected by transpacific transport. The top plots in Fig. 10 show the contributions to TGM concentrations from domestic (CtrRun-EXP1 (TGM)) and transpacific transported (CtrRun-EXP2 (TGM)) anthropogenic sources respectively. Domestic anthropogenic emissions contribute 0.2 to 0.9 ngm<sup>-3</sup> to the total surface TGM over the western US and 0.2–1.1 ngm<sup>-3</sup> over the eastern US. Contributions from transpacific transport mainly focus on the western US with a magnitude of 0.16–0.32 ngm<sup>-3</sup>. However, the contributions to the eastern US are below 0.16 ngm<sup>-3</sup>. This pattern follows the expected effect of transpacific transport on ozone (Lin et al., 2008). Relatively, domestic anthropogenic emissions are the dominant anthropogenic sources, contributing around 25 % of total gaseous mercury concentrations on a national basis.

The two plots on the bottom of Fig. 10 show the contributions to total annual mercury deposition (dry and wet) by domestic (CtrRun-EXP1 (Deposition)) versus transpacific transported (CtrRun-EXP2 (Deposition)) anthropogenic emissions. Domestic anthropogenic emissions contribute 6–12  $\mu\text{g m}^{-2}$  to the total surface TGM deposition over the eastern and generally below 7  $\mu\text{g m}^{-2}$  over the western United States. The highest contributions are over the Midwest. The domestic anthropogenic emissions contribute on average 22 % to total deposition in the United States, but near 50 % in the industrial regions. This result is consistent with previous modeling studies by Seigner et al. (2004) and Selin et al. (2008). Contributions from transpacific transport to total mercury deposition in the US are 1–4  $\mu\text{g m}^{-2}$  over the western, but below 2  $\mu\text{g m}^{-2}$  over the eastern United States. The pattern is consistent with the contributions to TGM concentrations. In addition, it is noted that the contributions from domestic anthropogenic emissions to total mercury deposition on the western United States is of comparable magnitude to that from transpacific transport of East Asian mercury sources, but is still one to 3 times larger.

## 6 Summary and conclusion

A tropospheric mercury chemistry module has been developed and incorporated into the CAM-Chem model to represent the processes affecting atmospheric mercury and its deposition over the globe. It includes the chemistry, emission, deposition, and transport processes for elemental, reactive, and particulate forms of mercury. The chemistry considers the oxidation of elemental mercury by ozone with temperature dependence, the oxidation by OH, hydrogen peroxide and chlorine in gaseous phase, as well as the aqueous reduction and oxidation on mercury species. The transport and deposition of mercury are determined using the approaches used for other chemicals in the CAM-Chem model. Mercury emissions are included based on published estimates for human-related, volcano eruption, and biomass burning sources, as well as the dynamic parameterizations for natural sources, including air–sea exchanges from global

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oceans and land surfaces (soil, vegetation), and reemissions depending on the temperature, solar radiation and soil storage. The total emissions of mercury at the present climate condition is estimated to be  $9600 \text{ Mg yr}^{-1}$  over the globe, of which 2200, 2900, 3400, 600, and  $500 \text{ Mg yr}^{-1}$  are from respectively anthropogenic, land, ocean, biomass burning and volcano sources. The atmospheric lifetime of mercury against deposition is approximately 0.69 yr in the absence of recycling from surface reemissions. In our model, the dynamic schemes for land and ocean emissions are simplified from the previous dynamic models for point source emission, and then calibrated by the latest estimate on present global natural emissions based on observations. This solution not only considers the physical processes associated with natural emissions, but also includes the latest knowledge on it. Compared with the original approaches, both simplified schemes also save substantial amounts of computational time. Although our approach appears to provide a good approximation of current knowledge on the reemission process, uncertainties such as the influence from meteorology factors other than temperature and solar radiation and the role of vegetation coverage remain that require further analysis.

The CAM-Chem/Hg model has been evaluated relative to the available measurements worldwide using meteorological conditions driven from the NCEP observational reanalysis. The evaluation includes both surface air TGM concentrations and annual total mercury wet depositions. They are compared with observations from 19 land sites distributed evenly over the globe along with 3 ocean cruise tracks for evaluating concentrations, and with 26 US monitoring sites for evaluating the wet deposition. For both quantities, the model captures the major characteristics of their geographic distributions and seasonal variations. As a result of these many analyses, we conclude that the CAM-Chem/Hg is a reasonable and reliable modeling tool to study the physical and chemical processes governing the emission, transport, transformation and deposition of atmospheric mercury. At the same time, we recognize that the model needs further improvement. In particular, improvements are needed to reduce the large underestimations of wet depositions near the coastal regions and of the concentrations in the

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middle atmospheric layers. The underestimation may be associated with two potential issues. One issue is our poor understanding of the Hg(0)/Hg(II) redox chemistry including gaseous, aqueous and heterogeneous reactions, which could have an important effect on deposition patterns. The other issue is the wet deposition scheme, which may need to be modified to better account for mercury attachment on other aerosols or for electrostatic adherence on droplets. Any laboratory and/or field experiments to improve our understanding on these two issues would greatly enhance model performances.

In order to address the current debate on mercury chemistry mechanism, we also incorporate the bromine mechanism into the CAM-Chem/Hg in the combination to ozone-OH-oxidation mechanism. By using external bromine concentration data, a sensitivity experiment was set to test the possible impact of bromine reactions on mercury concentration distribution. The result shows that the effect of extra bromine reactions on TGM concentration is relatively small, but the effect on Hg(0)/Hg(II) partitioning is significant although how partitioning occurs in the real atmosphere is still subject to further investigation. Reference to several latest studies, we conclude that ozone-OH oxidation is still a reasonable mechanism for capturing the mercury pollution for models.

The sensitivity study on effects of domestic emissions versus transpacific transport of anthropogenic mercury emissions on the concentrations of mercury compounds in the United States shows that, on a national basis, around 22 % of total mercury deposition in the United States results from domestic anthropogenic sources, and only 9 % are contributed by transpacific transport. However, the contributions to deposition on the western United States are of comparable magnitude, with around 50 % from domestic sources and around 20 % from transpacific sources. Domestic anthropogenic emissions are the dominant anthropogenic sources that contribute around 25 % of total gaseous mercury concentrations on a national basis. The averaged percentage contribution to TGM concentrations from transpacific transport is only 7 %. These analyses provide improved understanding of the present US mercury concentrations and deposition, and the relationship between Asian and US mercury pollution. Another important issue is how the US mercury concentrations and this Asia-US relationship will



likely to change in the coming decades. A comprehensive understanding through further research on this issue would help policy-makers in considering effective strategies for mercury pollution.

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**Table 1.** Reactions rate and Hg(II) gas-particle partitioning in CAM-Chem/Hg model.

Reactions	Rate constant	Reference
<b>Gaseous Reactions</b>		
	Unit: $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$	
$\text{Hg}_{(\text{g})}^0 + \text{O}_{3(\text{g})} \rightarrow 0.5 \text{PHg} + 0.5 \text{RGM}^{\text{a}}$	$2.11 \times 10^{-18} \exp(-1256.5T^{-1})$	Gbor et al. (2006); Rutter et al. (2012)
$\text{Hg}_{(\text{g})}^0 + \text{H}_2\text{O}_{2(\text{g})} \rightarrow \text{RGM}$	$8.5 \times 10^{-19}$	USEPA (1997)
$\text{Hg}_{(\text{g})}^0 + \text{Cl}_{2(\text{g})} \rightarrow \text{RGM}$	$2.6 \times 10^{-18}$	Gbor et al. (2006)
$\text{Hg}_{(\text{g})}^0 + \text{OH}_{(\text{g})} \rightarrow 0.5 \text{PHg} + 0.5 \text{RGM}^{\text{a}}$	$9.0 \times 10^{-14}$	Subir et al. (2011)
<b>Additional Bromine reactions</b>		
$\text{Hg}_{(\text{g})}^0 + \text{Br}_{(\text{g})} \rightarrow \text{HgBr}_{(\text{g})}$	$1.5 \times 10^{-32} (T/298)^{-1.86}$	Donohoue et al. (2006)
$\text{HgBr}_{(\text{g})} + \text{Br}_{(\text{g})} \rightarrow \text{RGM}$	$2.5 \times 10^{-10} (T/298)^{-0.57}$	Goodsite et al. (2004)
$\text{HgBr}_{(\text{g})} + \text{OH}_{(\text{g})} \rightarrow 0.5 \text{PHg} + 0.5 \text{RGM}^{\text{a}}$	$2.5 \times 10^{-10} (T/298)^{-0.57}$	Goodsite et al. (2004)
$\text{HgBr}_{(\text{g})} \rightarrow \text{Hg}_{(\text{g})}^0 + \text{Br}_{(\text{g})}$	$3.9 \times 10^9 \exp(-8357T^{-1}) (T/298)^{-0.57}$	Holmes et al. (2010)
$\text{HgBr}_{(\text{g})} + \text{Br}_{(\text{g})} \rightarrow \text{Hg}_{(\text{g})}^0 + \text{Br}_{(\text{g})}$	$3.9 \times 10^{-11}$	Balabanov et al. (2005)
<b>Aqueous Reactions</b>		
	Unit: $\text{m}^{-1} \text{s}^{-1}$	
$\text{Hg}_{(\text{aq})}^0 + \text{O}_{3(\text{aq})} \rightarrow \text{Hg}_{(\text{aq})}^{2+} + \text{products}$	$4.7 \times 10^7$	Munthe (1992)
$\text{HgSO}_3 \rightarrow \text{Hg}_{(\text{aq})}^0 + \text{products}$	$T \exp(31.971 - 12595T^{-1})$	Van Loon et al. (2000)
$\text{Hg}_{(\text{aq})}^{2+} + \text{HO}_{2(\text{aq})} \rightarrow \text{Hg}_{(\text{aq})}^0 + \text{products}$	$1.1 \times 10^4$	Pehkonen and Lin (1998)
$\text{Hg}(\text{OH})_{2(\text{aq})} + h\nu \rightarrow \text{Hg}_{(\text{aq})}^0 + \text{products}$	$6.0 \times 10^{-7}$	Xiao et al. (1994)
$\text{Hg}_{(\text{aq})}^0 + \text{OH}_{(\text{aq})} \rightarrow \text{Hg}_{(\text{aq})}^+ + \text{products}$	$2.4 \times 10^{10}$	Lin and Pehkonen (1997)
$\text{Hg}_{(\text{aq})}^+ + \text{OH}_{(\text{aq})} \rightarrow \text{Hg}_{(\text{aq})}^{2+} + \text{products}$	0.1	Gardfeldt et al. (2001)
$\text{Hg}_{(\text{aq})}^0 + \text{HOCl}_{(\text{aq})} \rightarrow \text{Hg}_{(\text{aq})}^{2+} + \text{products}$	$2.09 \times 10^6$	Lin and Pehkonen (1998)
$\text{Hg}_{(\text{aq})}^0 + \text{OCI}_{(\text{aq})}^- \rightarrow \text{Hg}_{(\text{aq})}^{2+} + \text{products}$	$1.99 \times 10^6$	Lin and Pehkonen (1998)
<b>Additional Bromine reactions</b>		
$\text{Hg}_{(\text{aq})}^+ + \text{Br}_{2(\text{aq})} \rightarrow \text{Hg}_{(\text{aq})}^{2+} + \text{products}$	0.2	Wang and Pehkonen (2004)
$\text{Hg}_{(\text{aq})}^+ + \text{HOBr}_{(\text{aq})} \rightarrow \text{Hg}_{(\text{aq})}^{2+} + \text{products}$	0.28	Wang and Pehkonen (2004)
$\text{Hg}_{(\text{aq})}^+ + \text{OBr}_{(\text{aq})}^- \rightarrow \text{Hg}_{(\text{aq})}^{2+} + \text{products}$	0.27	Wang and Pehkonen (2004)

<sup>a</sup> The partitioning is expected to depend on temperature, aerosol load, and aerosol composition (Lin et al., 2006; Rutter and Schauer, 2007). Future work will link Hg(II) partitioning to environment conditions, while here we assume 50/50 partitioning of Hg(II) as widely used in recent studies (Holmes et al., 2010).

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**Table 2.** CAM-Chem/Hg simulated 1999–2001 annual mean total mercury concentrations compared with measurements with varying periods at available land sites worldwide.

Site	Observations Period	Reference	Concentration (ngm <sup>-3</sup> )	CAM-Chem/Hg (ngm <sup>-3</sup> )
Alert, Canada (82° N, 62° W)	1995–2002	Environmental Canada (2007)	1.55	1.43
Esther, Canada (52° N, 110° W)	1997–1999	Kellerhals et al. (2003)	1.69	1.15
Zeppelin, Norway (79° N, 12° E)	2000–2004	EMEP (2005)	1.55	1.51
Pallas, Finland (67° N, 24° E)	1998–2002	EMEP (2005)	1.34	1.57
Lista, Norway (58° N, 6° E)	2000–2003	EMEP (2005)	1.68	1.63
Råö, Sweden (57° N, 11° E)	2001	EMEP (2005)	1.66	1.67
Rörvik, Sweden (57° N, 25° E)	2001–2002	EMEP (2005)	1.66	1.70
Zingst, Germany (54° N, 12° E)	2000	EMEP (2005)	1.56	1.84
Mace Head, Ireland (54° N, 10° W)	1995–2001	Ebinghaus et al. (2002)	1.75	1.79
Langenbrügge, Germany (52° N, 10° E)	2002	EMEP (2005)	1.70	1.84
Cheeka Peak, Washington, United States (48° N, 125° W)	2001–2002	Weiss-Penzias et al. (2003)	1.56	1.61
Detrit, United States (43° N, 84° W)	2003	Liu et al. (2007)	2.2	1.9
Chongqing, China (29° N, 106° E)	2006–2007	Yang et al. (2008)	6.7	4.9
Beijing, China (40° N, 116° E)	2005	Wang et al. (2006)	4.9	3.9
Tokyo, Japan (35° N, 135° E)	2000–2001	Sakata and Marumoto (2002)	2.80	2.54
New York, United States (42° N, 73° W)	2000–2003	Han et al. (2004)	2.3	1.93
Seoul, Korea (36° N, 128° E)	2003	Kim et al. (2009)	5.0	4.7
Cape Point, South Africa (34° S, 19° E)	1998–2002	Baker et al. (2002) and Witt et al., (2010)	1.37	4.1
Neumayer, Antarctica (70° S, 8° W)	2000	Ebinghaus et al. (2002)	1.06	1.26

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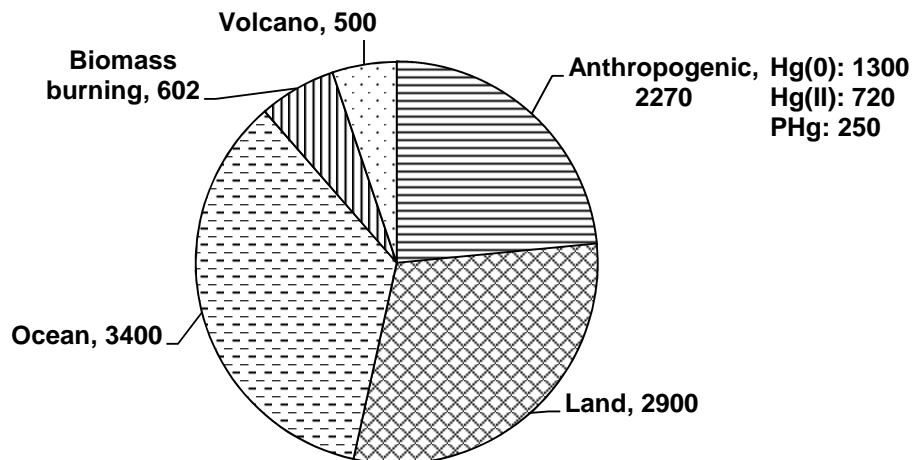
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**Table 3.** CAM-Chem/Hg modeled annual total mercury wet depositions as compared with measurements at the selected monitoring sites of the NADP MDN.

Site	Location (Lat, Lon)	Observation years	NADP ( $\mu\text{g m}^{-3}$ )	Model (1999–2001) ( $\mu\text{g m}^{-3}$ )
A (FL11)	(25.39° N, 80.68° W)	1998–2002	17.9	11.9
B(GA09)	(30.74° N, 82.13° W)	1998–2002	12.3	12.5
C(GA40)	(33.93° N, 85.05° W)	2001–2003	17.7	18.2
D(SC19)	(33.81° N, 80.78° W)	1998–2002	12.7	15.9
E(NC42)	(35.74° N, 76.51° W)	1998–2002	11.2	13.1
F(VA28)	(38.52° N, 78.43° W)	2003–2005	13.2	14.7
G(PA47)	(39.99° N, 76.38° W)	2003–2005	11.6	14.3
H(NY20)	(43.97° N, 74.22° W)	2000–2002	9.1	12.1
I(ME98)	(44.38° N, 68.26° W)	1998–2002	7.2	10.3
J(IN20)	(40.84° N, 85.46° W)	2001–2003	12.2	12.3
K(WI22)	(43.07° N, 87.88° W)	2003–2005	10.1	10.8
L(WI08)	(46.75° N, 91.61° W)	1998–2002	7.7	9.2
M(MN23)	(46.25° N, 94.50° W)	1998–2002	7.3	6.7
N(IL11)	(40.05° N, 88.37° W)	1999–2002	9.3	10.1
O(KY10)	(37.13° N, 86.15° W)	2003–2005	11.7	15.7
P(AL03)	(32.90° N, 87.25° W)	2001–2003	13.6	14.2
Q(LA28)	(30.50° N, 90.38° W)	1999–2002	15.8	13.3
R(TX21)	(32.38° N, 94.71° W)	1998–2002	12.3	11.4
S(NM10)	(33.06° N, 107.29° W)	1998–2002	4.1	4.7
T(OK99)	(35.75° N, 94.67° W)	2003–2005	13.7	10.5
U(CO97)	(40.54° N, 106.68° W)	1999–2002	6.8	5.7
V(MT05)	(48.51° N, 114.00° W)	2004–2006	5.7	5.9
W(WA18)	(47.68° N, 122.26° W)	1998–2002	6.2	10.4
X(OR10)	(44.21° N, 122.25° W)	2003–2005	7.8	8.6
Y(CA72)	(37.43° N, 122.06° W)	2000–2002	3.6	6.7
Z(CA97)	(39.82° N, 123.24° W)	1998–2002	3.2	3.8

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**Fig. 1.** Estimated global total mercury emissions ( $\text{Mgyr}^{-1}$ ) from different sources in 2000.

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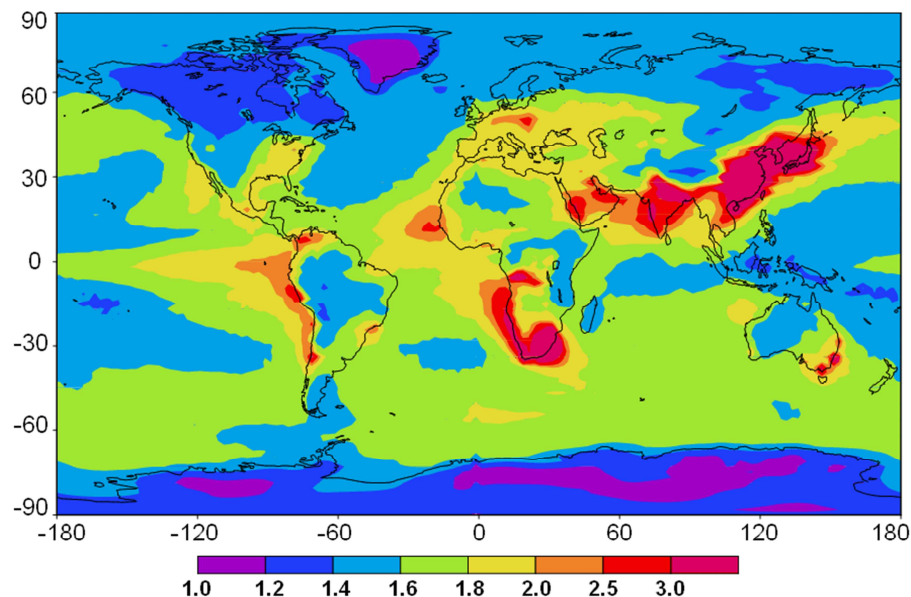
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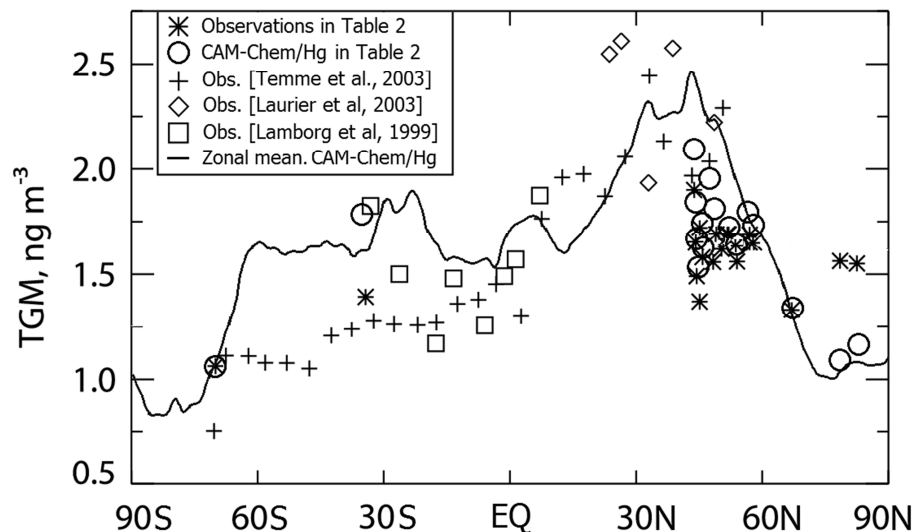
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**Fig. 2.** Annual mean surface TGM concentrations ( $\text{ngm}^{-3}$ ) averaged in 1999–2001 derived by the CAM-Chem/Hg model.

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**Fig. 3.** Variation of TGM surface concentrations with latitude. Zonally averaged and annual mean CAM-Chem/Hg model results (curve) are compared to observations (symbols) from previous studies. The observations on Land-based stations and corresponding CAM-Chem/Hg values are from table 2. Reported measurements over the oceans are from Temme et al. (2003), Laurier et al. (2003) and Lamborg et al. (1999).

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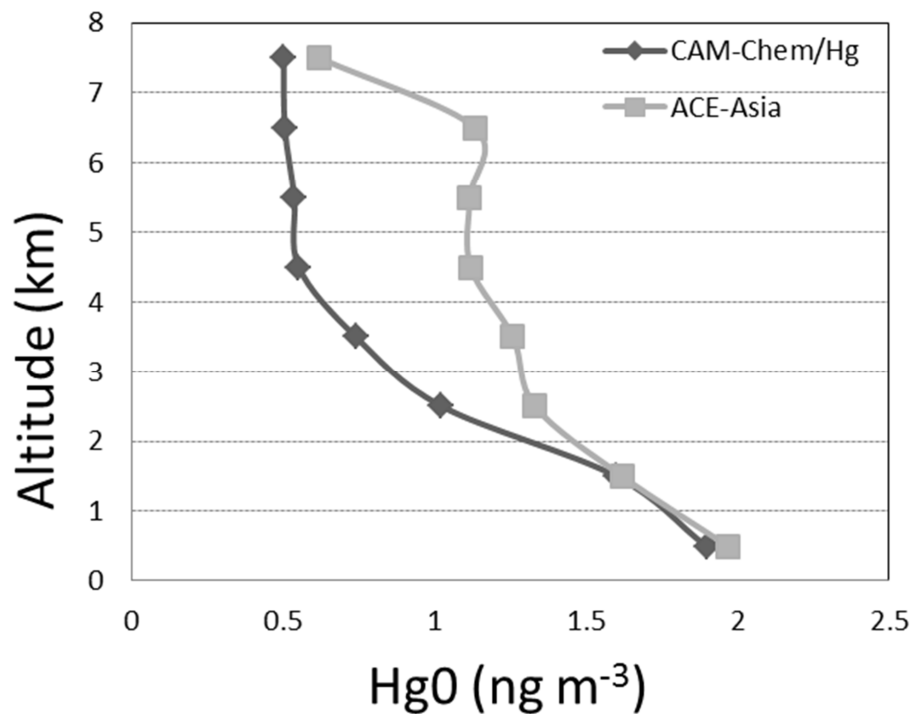
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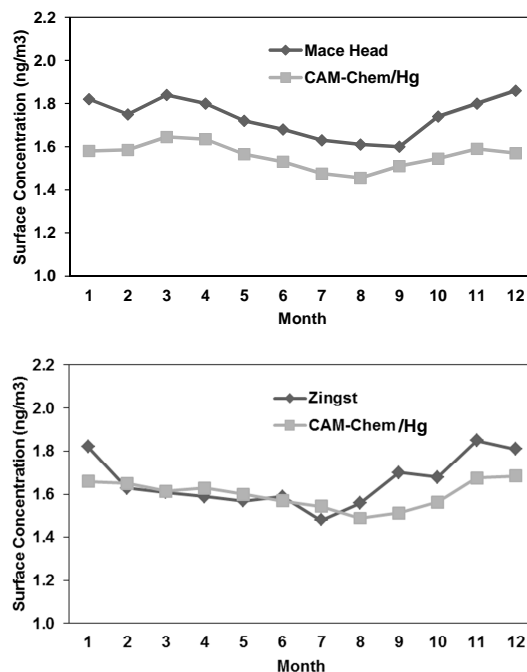




**Fig. 4.** Vertical profile of Hg(0) mixing ratios over southern Japan. Observations are from the ACE-Asia aircraft campaign during April–May 2001. The CAM-Chem/Hg result is averaged during the same period and over the same area.

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**Fig. 5.** Seasonal variations of surface atmospheric TGM concentrations ( $\text{ngm}^{-3}$ ) at coastal stations: Mace Head, Ireland and Zingst, Germany. Shown are monthly means averaged in 1998–2004 for observations and 1999–2001 for the CAM-Chem/Hg.

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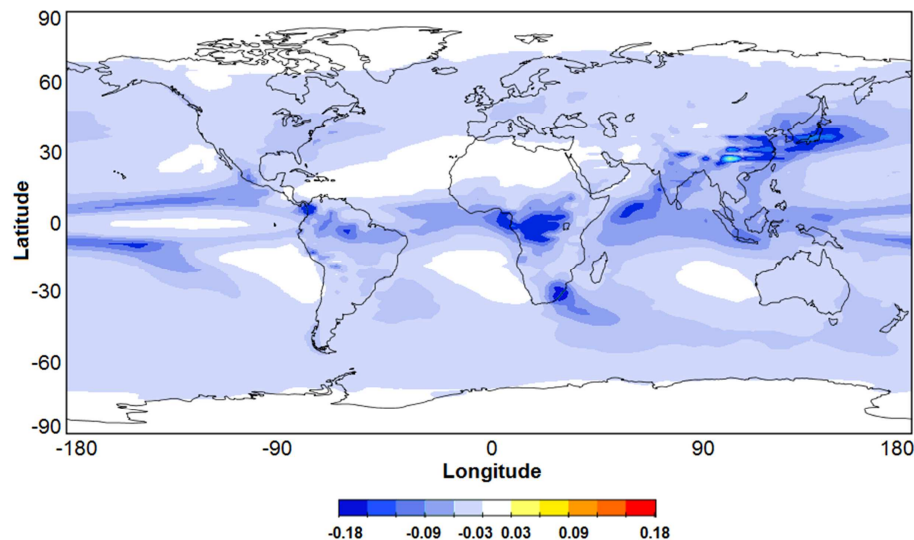
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**Fig. 6.** Change in TGM concentration ( $\text{ngm}^{-3}$ ) on surface layer by introducing bromine chemistry.

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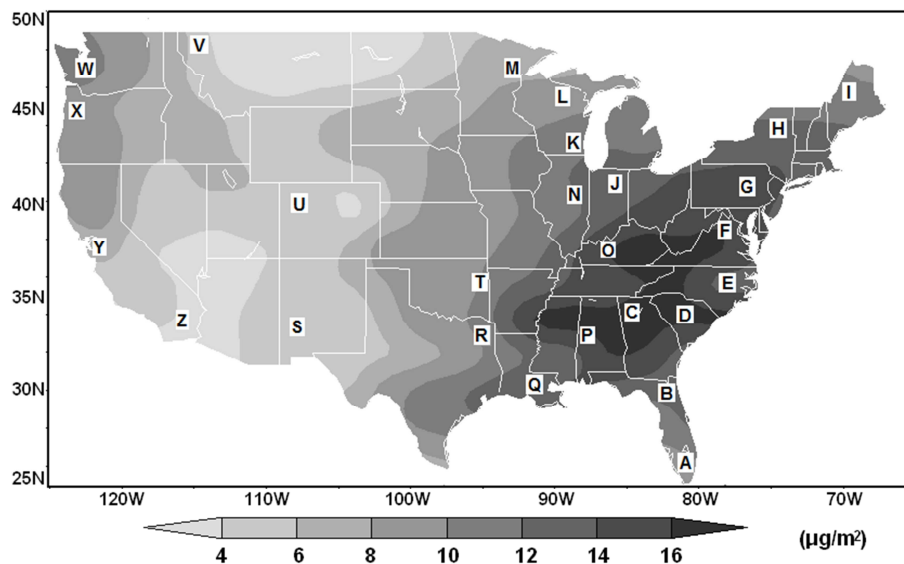
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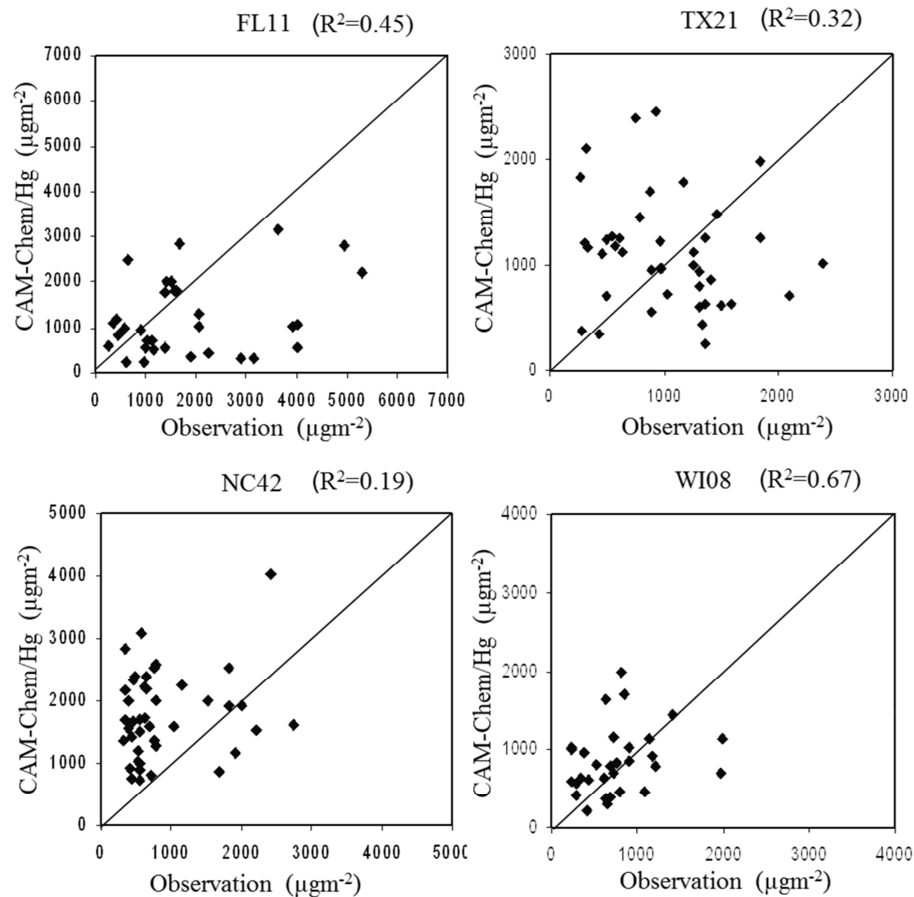
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**Fig. 7.** Annual total mercury wet deposition ( $\mu\text{g m}^{-2}$ ) averaged during 1999–2001 as simulated by the CAM-Chem/Hg. Letters represent the MDN monitoring sites in Table 3.

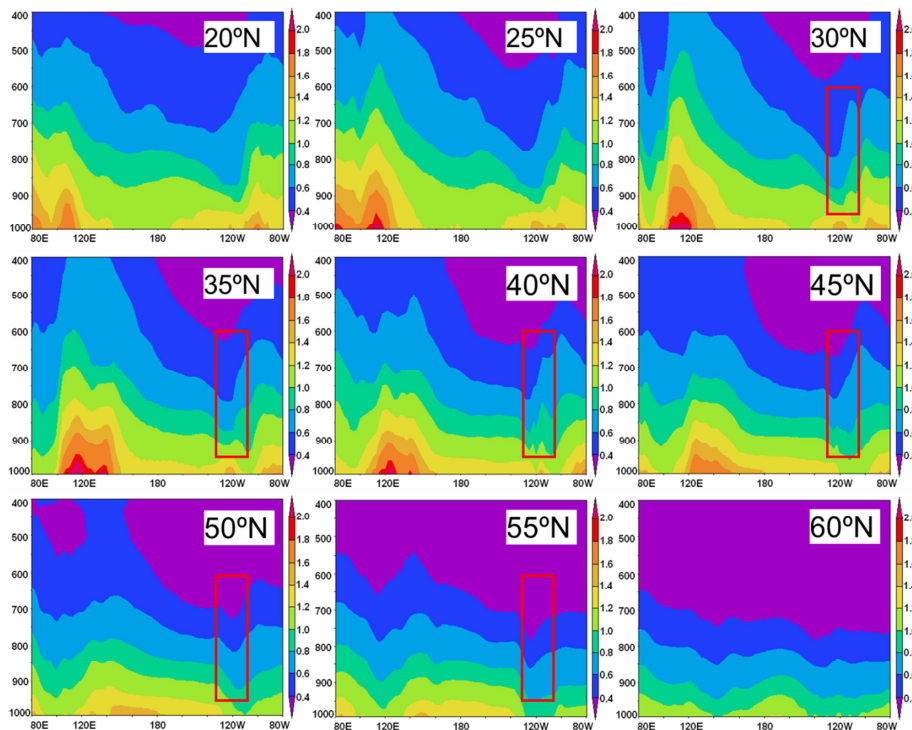


**Fig. 8.** Scatter diagrams comparing modeled and measured monthly total mercury wet deposition during 1999–2001 at four MDN sites. Temporal correlation coefficients squared are also listed for each site.



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**Fig. 9.** Latitude-pressure cross section for CAM-Chem/Hg simulated TGM concentrations. The red rectangle shows where the deposition may happen.

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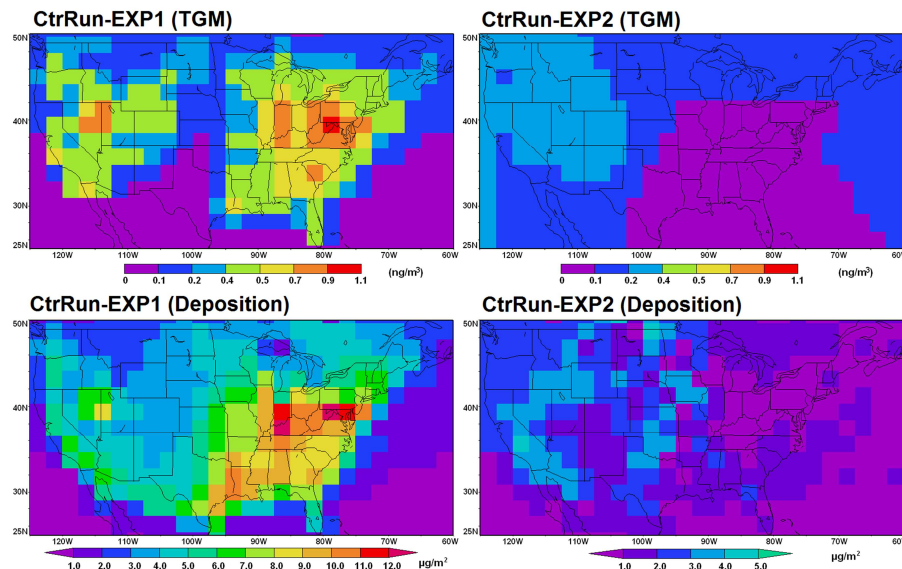
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**Fig. 10.** Sensitivity experiments for domestic versus transpacific contributions to annual mean atmospheric concentration and deposition of US mercury. CtrRun-Exp1 (TGM): Contributions of domestic anthropogenic emissions of mercury on TGM concentrations. CtrRun-Exp2 (TGM): Contributions of transpacific anthropogenic emissions of mercury on TGM concentrations. CtrRun-Exp1 (Deposition): Contributions of domestic anthropogenic emissions of mercury on deposition of total mercury. CtrRun-Exp2 (Deposition): Contributions of transpacific anthropogenic emissions of mercury on deposition of total mercury.

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