# Modeling Atmospheric Mercury Deposition to the Great Lakes: Updated Analysis

Final Report for work conducted with FY2013 funding from the *Great Lakes Restoration Initiative* 

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## 1. Introduction

Mercury contamination is an ongoing concern in the Great Lakes region, with public health and wildlife toxicology ramifications (Bhavsar et al., 2010; Cohen et al., 2007; Evers et al., 2011; Gandhi et al., 2014; Wiener et al., 2012), and atmospheric deposition is likely the largest contemporary loading pathway (Jeremiason et al., 2009; Mason and Sullivan, 1997; Rolfhus et al., 2003; Sullivan and Mason, 1998). The HYSPLIT-Hg atmospheric fate and transport model has been previously used to estimate the amount and source-attribution of mercury to the Great Lakes and their watersheds (Great Lakes Basin) for 1996 (Cohen et al., 2004) and 1999 (Cohen et al., 2007) arising from anthropogenic sources in the United States and Canada. In this analysis, we use an extended version of the model to estimate 2005 deposition arising from global anthropogenic and natural sources.

The sources, transport, and fate of atmospheric mercury encompass a wide array of phenomena, some of which are relatively poorly understood (Driscoll et al., 2013). In addition to HYSPLIT-Hg, there are numerous other fate and transport models that attempt to synthesize knowledge about these phenomena to create a comprehensive simulation of atmospheric mercury, including CAM-Chem/Hg (Lei et al., 2013; Lei et al., 2014), CMAQ (Bash et al., 2014; Bieser et al., 2014; Bullock and Brehme, 2002; Grant et al., 2014; Holloway et al., 2012; Lin et al., 2012), CTM-Hg (Lohman et al., 2008; Seigneur and Lohman, 2008; Seigneur et al., 2004), ECHMERIT (De Simone et al., 2014; Jung et al., 2009), GEOS-Chem (Amos et al., 2012; Chen et al., 2014; Cheng et al., 2013; Holmes et al., 2010a; Kikuchi et al., 2013; Song et al., 2015; Zhang et al., 2012b), GRAHM (Dastoor and Larocque, 2004; Durnford et al., 2010; Kos et al., 2013), MSCE-Hg-Hem (Travnikov, 2005), and STEM-Hg (Pan et al., 2008; Pan et al., 2010). While there are similarities between the models, there are often differences in the emissions, atmospheric chemistry, phase partitioning, meteorological data, transport, dispersion, and deposition algorithms and parameterizations (Ariya et al., 2015; Bullock et al., 2008; Ryaboshapko et al., 2007a; Ryaboshapko et al., 2007b). Models are generally evaluated by comparison against ambient measurements of concentrations and wet deposition, and show varying skills. While results are sometimes encouragingly consistent with measurements, inconsistencies attest to the uncertainties in the models (Bieser et al., 2014; Kos et al., 2013; Lin et al., 2006; Lin et al., 2007; Pongprueksa et al., 2008; Subir et al., 2011; Subir et al., 2012; Weiss-Penzias et al., 2015a; Zhang et al., 2012a) and the measurements themselves (Gustin, 2015; Jaffe et al., 2014). A limited number of model intercomparison exercises have been carried out (e.g., (AMAP/UNEP, 2013; Bullock et al., 2008; Bullock et al., 2009; Ryaboshapko et al., 2007a; Ryaboshapko et al., 2007b; Ryaboshapko et al., 2002; Zhang et al., 2012a)) and it is sometimes found that there are significant differences in mercury concentrations and deposition estimated by different models.

This report describes work done during the 4<sup>th</sup> phase of an ongoing project, supported by FY2013 funding through the Great Lakes Restoration Initiative (GLRI). The first phase of the project was carried out with FY2010 GLRI funding (Cohen et al., 2011). In that initial work, a 2005 baseline analysis of atmospheric deposition to the Great Lakes was carried out, including source-attribution for the model-estimated deposition. The modeling results were found to be consistent with measurements of mercury wet deposition in the Great Lakes region. The 2<sup>nd</sup> phase of the project was carried out with FY2011 GLRI

funding (Cohen et al., 2013). In that FY2011 work, a detailed sensitivity analysis was carried out to examine the influences of important uncertainties in model inputs and methodologies. In the 3<sup>rd</sup> phase of the work, carried out with FY2012 GLRI funding, the consequences of potential future emissions scenarios on atmospheric mercury deposition to the Great Lakes and their watersheds were estimated (Cohen et al., 2014).

In this 4<sup>th</sup> phase of the work, the earlier analysis will be updated to reflect model improvements and new information regarding atmospheric mercury. As before, the goal of this work is to estimate the atmospheric mercury deposition – and source-attribution for this deposition – to the Great Lakes and their watersheds (Figure 1). In the initial conception for this phase of the work, it was anticipated that mercury emissions data for a year more recent than 2005 would be used to update the analysis. Unfortunately, the USEPA's National Emissions Inventory for 2008 and 2011 does not include explicit speciation of mercury emissions from coal-fired power plants. This speciation information, included in the 2005 and earlier inventories is essential for modeling. Given the limited resources available for this project, we were faced with a choice. We could either use this phase of the work to update the analysis to include numerous model improvements and corrections, or, we could attempt to generate the needed emissions speciation. We could not do both with the available resources. A decision was made to attempt the update with regard to model improvements and corrections during this phase of the work. We plan to attempt the reorientation of the analysis to a more recent year, e.g., 2011, with the added speciation work that that will entail, in a future phase of this work.



Figure 1. Great Lakes and their watersheds

As in previous reports, we will refer to three "kinds" of atmospheric mercury: (i) elemental mercury, Hg(0), also called Gaseous Elemental Mercury or GEM; (ii) soluble oxidized mercury (Hg(II)), also referred to as reactive gaseous mercury (RGM); and (iii) particulate mercury, or Hg(p). Except where noted, e.g., in the model evaluation section, results presented in this report are for total mercury (the sum of the three different forms), for simplicity and brevity's sake, even though the entire modeling analysis has been done with explicit treatment of the different mercury forms.

## 2. Emissions

Mercury emissions used as model input included the following components: anthropogenic, biomass burning, geogenic, soil/vegetation, ocean, and prompt reemissions. The anthropogenic component was subdivided into emissions of Hg(0), Hg(II), and Hg(p), as described below. Emissions from all other components were considered as Hg(0). All inventory components were ultimately assembled on a global 2.5° x 2.5° grid, equivalent to the horizontal spacing of the global meteorological data used for the modeling (described in Section 3.3 below).

Point-source anthropogenic mercury emissions for the U.S. were assembled from the USEPA 2005 National Emissions Inventory (NEI) (USEPA, 2009). For relatively minor, small, and widespread "area" sources (e.g., mobile sources) specified at the county level in the U.S., the 2002 NEI was utilized (USEPA, 2007), as it formed the predominant basis for the 2005 NEI area-source inventory. For point and area sources whose emissions were not separated into Hg(0), Hg(II), and Hg(p) in the NEI, EPA-recommended process-based "speciation" factors were utilized to estimate the emissions partitioning (USEPA, 2006). For point-source mercury emissions in Canada, Environment Canada's 2005 National Pollutant Release Inventory (NPRI) was utilized (Environment Canada). For Canadian area sources, 2000 data from Environment Canada were utilized, defined on a 100-km grid (Smith, 2008). For point- and area-source mercury emissions in Mexico, the latest detailed inventory that was available was a 1999 inventory prepared for the Commission for Environmental Cooperation (CEC) (Acosta-Ruiz and Powers, 2001). The area-source emissions were geographically apportioned to each of the 32 Mexican states based on year-2000 population. Since mercury emissions in the Canadian and Mexican inventories were not separated into different mercury forms, the EPA-recommended speciation factors noted above were utilized to estimate emissions partitioning. For anthropogenic mercury emissions in the remainder of the world, the 2005 Arctic Monitoring and Assessment Program (AMAP) global inventory of Pacyna and colleagues was used (Pacyna et al., 2010; Wilson et al., 2010). The AMAP inventory is specified on a 0.5 x 0.5 degree grid (approximately 50 km x 50 km), with total emissions of Hg(0), Hg(II), and Hg(p) for each grid cell. Temporal variations (e.g., monthly) variations were not available in the above data sources and so anthropogenic emissions were assumed constant throughout the year.

Global mercury emissions from biomass burning was assumed to be 600 Mg/yr as utilized by Lei et al (2013; 2014), consistent with the estimate by Friedli and colleagues (2009). This is slightly higher than the 200-400 Mg/yr values used in some other recent modeling analyses -- e.g., (Chen et al., 2014;

Holmes et al., 2010b; Kikuchi et al., 2013; Song et al., 2015) -- but the difference is small compared to the total global emissions of mercury (on the order of 6000 – 8000 Mg/yr, as discussed below). Global mercury emissions from geogenic processes were assumed to be 500 Mg/yr, as used by Lei et al. (2013; 2014) Kikuchi et al. (2013), Holmes et al. (2010a), and Selin et al. (2008). For soil/vegetation emissions and similar processes, the surface exchange of Hg(0) is of course bidirectional. In the HYSPLIT-Hg model simulations, emissions are specified as the gross, or one-way, upward flux, as opposed to the net, or bidirectional, upward flux. The downward component of the surface exchange is estimated as the simulation proceeds via run-time deposition modeling. Global, annual one-way mercury emissions from soil/vegetation were taken to be 1100 Mg/yr, similar to many other studies: e.g., 1100 Mg/yr was used by Selin et al (2008), 890 Mg/yr was used in the base simulation of Kikuchi et al. (2013), and an optimized emissions of 860 Mg/yr was recently estimated by Song et al. (2015). Prompt re-emissions of deposited Hg(II) were assumed to be 30% of the total Hg(II) deposition to terrestrial surfaces. In this analysis, prompt re-emissions amounted to 400 Mg/yr, consistent with the 260 – 600 Mg/yr range used in other modeling studies [e.g., (Holmes et al., 2010b; Kikuchi et al., 2013; Selin et al., 2008; Song et al., 2015)]. Taken together, the one-way Hg(0) emissions from soil/vegetation and prompt re-emissions totaled 1500 Mg/yr. As described below in the results section, gross, one-way dry deposition flux of Hg(0) to land surfaces was modeled to be 740 Mg/yr; thus, the net Hg(0) emissions from land surfaces in the model was ~760 Mg/yr. The global, annual, gross (one-way) mercury emissions from the ocean were taken to be 4300 Mg/yr. As described below, the gross, one-way deposition flux of Hg(0) to the ocean's surface was estimated to be 1700 Mg/yr. Thus, the net Hg(0) emissions flux from the ocean surface in this modeling analysis was 2600 Mg/yr, very similar to the bottom-up estimate of 2700 Mg/yr developed from flux measurements (Pirrone et al., 2010), and consistent with the range of 2000 – 3600 Mg/yr used in numerous other modeling analyses (Amos et al., 2012; Chen et al., 2014; Corbitt et al., 2011; Holmes et al., 2010a; Kikuchi et al., 2013; Selin et al., 2008; Song et al., 2015). The spatial and temporal (monthly) variations for the biomass-burning, geogenic processes, soil/vegetation, ocean, and promptreemission inventory components were adapted from the results of the Lei et al. (2014) analysis. The total emissions used in this analysis, using the net exchange of Hg(0) from surfaces, was 6400 Mg/yr. In Figure 2, the base-case emissions utilized in this study are compared with those used in several other analyses (Bergan and Rodhe, 2001; Chen et al., 2014; Corbitt et al., 2011; Holmes et al., 2010b; Kikuchi et al., 2013; Lei et al., 2013; Mason and Sheu, 2002; Pirrone et al., 2010; Selin et al., 2007; Selin et al., 2008; Shia et al., 1999; Song et al., 2015). Variations in addition to the base-case emissions, shown in this figure, will be described below. An overall map of total, global mercury emissions used in this modeling, in the base case, is shown in Figure 3.



#### Figure 2. Comparison of mercury emissions used in this analysis with those used in other studies.

For each study, the net ocean and net terrestrial emissions are combined with the antrhopogenic emissions to show the total emissions used in the analysis. In the Kikuchi et al study (2013), several variations were presented in addition to the base case: M1 (with a new soil-emissions parameterization); M2-1 (with O3 as an atmospheric oxidant); M2-2 (same as M2-1 but with a different treatment of polar emissions). The numerous variations shown for this work are described in more detail in the text and involve variations in the rates and products of certain Hg(0) oxidation reactions, Hg(II) reduction in plumes, emissions, and the value of a particular wet deposition parameter (WETR).



#### Figure 3. Base-case atmospheric mercury emissions from all source categories.

Annual total emissions of all forms of mercury (Hg(0), Hg(II), and Hg(p)) on the 2.5° x 2.5° global grid used in this modeling. Emissions shown in this map are gross "one-way" emissions used as input to the HYSPLIT-Hg model, as opposed to net emissions, and include contributions from anthropogenic, biomass burning, soil/vegetation, re-emissions, oceanic, and geogenic sources.

## 3. Simulation Methodology

#### 3.1. HYSPLIT-Hg Model

The HYSPLIT atmospheric transport model has been developed since the early 1980's (Draxler, 1982) by Roland Draxler and colleagues at the NOAA Air Resources Laboratory (Draxler, 1997; Draxler, 1998; Stein et al., 2015). In this study, we have used the HYPSLIT-Hg model, a version of the HYSPLIT model with special features (e.g., atmospheric mercury chemistry, dynamic phase partitioning) added to simulate atmospheric mercury. Initially, HYSPLIT-Hg (and HYSPLIT) used only a Lagrangian modeling scheme and was used to estimate the atmospheric transport and deposition of mercury to the Great Lakes from anthropogenic sources in the U.S. and Canada (Cohen et al., 2004; Cohen et al., 2007) and throughout a European domain in a model intercomparison experiment (Ryaboshapko et al., 2007a; Ryaboshapko et al., 2007b). A global Eulerian (GE) capability (Draxler, 2007) was recently incorporated into HYSPLIT. With this addition, HYSPLIT can be run in a Lagrangian mode, an Eulerian mode, or combination of the two. In the combined mode, emitted pollutants are initially simulated in a Lagrangian fashion. After a user-specified pollutant age (i.e., time after emission), pollutants are transferred to a global Eulerian grid and simulated with an Eulerian methodology from then on. The mercury-related algorithms in HYSPLIT-Hg were subsequently incorporated into this enhanced multi-mode version of HYSPLIT to create the integrated Lagrangian-Eulerian atmospheric mercury model used in this study. The HYSPLIT-Hg simulations presented here were carried out with the Eulerian-only configuration. The Eulerian grid used in this work had a horizontal resolution of  $2.5^{\circ}$  x  $2.5^{\circ}$ , with a surface layer and 17 vertical levels above the surface, up to a height of ~30 km (10 hPa). Meteorological data to drive the model (e.g., wind speed and direction, precipitation, relative humidity, etc.) were based on the NCEP/NCAP Global Reanalysis dataset (NCEP-NCAR, 1948-present), converted to HYSPLIT format (NOAA-ARL, 2003-present). These data are specified every 6 hours on a grid with the same horizontal and vertical resolution and structure as the mercury fate/transport grid.

In the FY10 and FY11 GLRI mercury modeling work (Cohen *et al.*, 2011, 2013), the overall methodology used to carry out the analysis involved unit source simulations from "standard source locations". These unit source simulations were then combined with the actual emissions inventory using a spatial and chemical interpolation methodology to estimate the impact of each source in the emissions inventory on each receptor of interest. This technique produces uniquely detailed source-receptor estimates. However, it requires a great deal of computational resources. Resource constraints dictated that a less computationally intensive approach be adopted for the present analysis.

In the analysis presented here, similar to the work in in Phase 3 of this work (Cohen et al., 2014), an entire simulation for a given inventory was carried out in a combined fashion, i.e., with the entire globe's emissions simulated in one model run. The simulations used essentially the same Global Eulerian Model (GEM) methodology used in the earlier studies, except that in this case, a large combination of sources were simulated in any given run, rather than one particular unit source location. In these GEM simulations, a 2.5° x 2.5° grid was utilized, corresponding to the meteorological data grid used (see the

following section). Pollutants emitted as puffs were immediately transferred to the global Eulerian grid and their fate and transport were simulated on that grid for the remainder of the run.

The emissions inventories for each scenario were broken down to their component parts, and individual simulations were run for each inventory subsection, i.e., anthropogenic, biomass, land, re-emissions, ocean, and volcano. Further, an overall combined simulation with all emissions was conducted for each scenario, as a QA/QC check (the overall simulation should be the same as the sum of the individual component simulations for each scenario). An example of this comparison (shown also in a previous report (Cohen et al., 2014) is presented in Figure 4, for concentrations at ~30 model evaluation sites and deposition at ~100 receptors in North America. It can be seen in this figure that the combined and summed results are indeed identical, as expected. Finally, the anthropogenic emissions inventory subsection was subdivided into country-specific categories: USA, Mexico, Canada, China, India, Russia, and the rest of the world. The specific countries chosen were estimated to have the highest contributors to the Great Lakes in the FY10 and FY11 GLRI modeling work. Using these country-specific inventories, country-specific simulations for each country were carried out for each scenario. As a QA/QC check, the sum of the country-specific simulations was compared to the combined anthropogenic emissions simulation. An example – also shown in a previous report (Cohen et al., 2014) -- of this anthropogenicemissions-only comparison is shown in Figure 5 for the analogous concentration and deposition results. Again, it is seen that the combined and summed results are identical as expected.



**Result from Combined Simulation with All Emissions Together** 

Figure 4. Comparison of combined simulation with sum of simulations using inventory components



Figure 5. Comparison of combined anthropogenic emissions simulation with sum of country=specific anthropogenic emissions simulations

#### 3.2. Mercury Forms Considered in the Model

The transport, fate, and intra-conversion of four mercury forms are simulated in HYSPLIT-Hg: elemental mercury [Hg(0)], oxidized, soluble mercury [Hg(II)], particulate-phase insoluble mercury [Hg(p)], and oxidized, soluble mercury reversibly adsorbed to soot [Hg2s]. Partitioning between the vapor and droplet phases is simulated for atmospheric Hg(0) using Henry's Law. For Hg(II), vapor-droplet partitioning is simulated using Henry's Law along with a droplet-phase equilibrium calculation that estimates the ionic and molecular concentrations of relevant mercury-containing species in solution, as described below. Partitioning between dissolved Hg(II) and soot-adsorbed Hg(II) (Hg2s) is estimated using the equilibrium and rate parameters utilized by Bullock and Brehm (2002) based on the measurements of Seigneur *et al.* (1998). Particulate mercury – emitted by sources or formed as the product of chemical reactions – does not partition between phases in the model. However, particulate mercury can be enveloped as part of the insoluble core of deliquesced aerosol particles or rain droplets.

We use the differentiation among non-Hg(0) mercury forms as described above -- Hg(II), Hg2s, and Hg(p) -- as opposed to the more commonly used current classification (GOM (Gaseous Oxidized Mercury) and Hg(p)). The rationale for this choice is that we consider Hg(II) in both the gas, aqueous, and particulate phases (as Hg2s) rather than solely in the gas phase as GOM.

#### 3.3. Chemical Transformations

Gas-phase Hg(0) is converted to Hg(II) and Hg(p) by reaction with  $O_3$ ,  $OH \bullet$ ,  $H_2O_2$ , HCl, and  $Cl_2$ . As summarized by Ariya et al (2015), the product partitioning of Hg(0) oxidation among Hg(II) and Hg(p) forms varies from 0% - 100% among atmospheric Hg models. In the absence of quantitative experimental measurement information, it was assumed in the base-case of this work that 10% of the product of the gas-phase oxidation by  $O_3$ ,  $OH \bullet$ ,  $H_2O_2$  is Hg(p) and 90% is Hg(II), while 100% of product of the HCl and  $Cl_2$  oxidation reactions is Hg(II). The influence of these assumptions on the results, including a variation in which the assumed fraction as Hg(p) is changed, is discussed below. In the aqueous-phase, Hg(0) is oxidized to Hg(II) by reaction with  $O_3$ ,  $OH \bullet$ , HOCl, and  $OCl^{-1}$ , while Hg(II) is reduced to Hg(0) by photolysis of Hg(OH)<sub>2</sub> and by transformation of HgSO<sub>3</sub><sup>-1</sup>. The rate and equilibrium parameters used in the base-case model configuration are summarized in Table 1 and Table 2.

Concentrations of gas-phase and aqueous-phase reactants were estimated with a variety of procedures. For  $O_3$ ,  $SO_2$ , and soot, estimates of atmospheric concentrations from a global simulation using the Mozart2 model were used (Horowitz et al., 2003; Ryaboshapko et al., 2007b). For OH•, global model results from Lu and Khalil (1991) were interpolated to create estimated concentrations dependent on latitude, elevation, month, and time of day. For total  $H_2O_2$  and HCl concentrations, a constant typical value equivalent to a gas phase mixing ratio of 1 ppb was used (Finlayson-Pitts and Pitts, 2000; Graedel and Keene, 1995). For total reactive chlorine, a constant value equivalent to a gas-phase mixing of 100 ppt was used for the lowest 100 m in the atmosphere over the ocean at night, following the approach of Bullock and Brehme (2002), consistent with the findings of Graedel and Keene (1995).

During each model time step within each grid cell, the liquid water content of the atmosphere was estimated based on the local relative humidity and elevation (see Supplemental Material). If no liquid water existed, then only gas-phase reactions were utilized (reactions 1-5 in Table 1). If liquid water was present, then a more complex treatment was utilized. First, the gas-liquid and aqueous phase ionic equilibrium conditions were estimated satisfying the relationships shown in Table 2 and mass/ion balances using an iterative Newton-Raphson-based approach. In calculating these equilibrium conditions, a constant pH of 4.5 and a constant  $Cl^{-1}$  aqueous phase concentration of 2.5 mg/liter was utilized in the simulation, following the approach of Ryaboshapko et al. (2007a).Then, the gas-phase and aqueous-phase reactions and transformation described in Table 1 were carried out.

In preliminary simulations using nominal literature values of the gas-phase Hg(0) oxidation reactions with OH• and O<sub>3</sub>, it was found that the lifetime of Hg(0) was unrealistically short (~0.3 years) and atmospheric concentrations of Hg(0) were unrealistically low. Model-estimated lifetimes against reactions and other processes are discussed in more detail below. When the oxidation rate constants for these two reactions were provisionally reduced by a factor of 5, realistic atmospheric concentrations of Hg(0) were obtained. We note that in the chemical mechanism used here, the primary oxidants were found to be OH• and O3 in the gas phase; other gas-phase oxidation reactions and aqueous-phase oxidation reactions were much less important. The rates of the OH• and O3 gas-phase reactions are considered to be highly uncertain. It has been argued that the rates may be dramatically less than experimentally determined and may not occur at all (Ariya et al., 2015; Calvert and Lindberg, 2005; Subir

et al., 2011). Therefore, we believe that the 1/5 scaling of these reaction rates used in this work's base case is within the range of uncertainty in the reaction rates for these two reactions.

Table 1. C	Chemical	reactions and	l rate	parameters
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#	Reaction	Rate	Units					
Gas-phase reactions								
1	Hg(0) + OH• → 0.1 Hg(p) + 0.9 Hg(II) 1.74E-14 <sup>a,b,c</sup> cm <sup>3</sup> /molec-sec							
2	$Hg(0) + O_3 \rightarrow 0.1 Hg(p) + 0.9 Hg(II)$	6.0E-21 <sup>a,b,d</sup>	cm <sup>3</sup> /molec-sec					
3	$Hg(0) + H_2O_2 \rightarrow 0.1 Hg(p) + 0.9 Hg(II)$	8.5E-19 <sup>a,e</sup>	cm <sup>3</sup> /molec-sec					
4	$Hg(0) + HCl \rightarrow HgCl_2$	1.0E-19 <sup>f</sup>	cm <sup>3</sup> /molec-sec					
5	$Hg(0) + Cl_2 \rightarrow HgCl_2$	4.0E-18 <sup>a,g</sup>	cm <sup>3</sup> /molec-sec					
Aque	ous-phase reactions and transformations							
6	$Hg(0) + OH \bullet \rightarrow Hg^{+2}$	2.0E+09 <sup>h</sup>	(molar-sec) <sup>-1</sup>					
7	$Hg(0) + O_3 \rightarrow Hg^{+2}$	4.7E+07 <sup>i</sup>	(molar-sec) <sup>-1</sup>					
8	$Hg(0) + HOCI \rightarrow Hg^{+2}$	2.09E+06 <sup>j</sup>	(molar-sec) <sup>-1</sup>					
9	$Hg(0) + OCI^{-1} \rightarrow Hg^{+2}$	1.99E+06 <sup>j</sup>	(molar-sec) <sup>-1</sup>					
10	Hg(II) ↔ Hg2s	9.00E+02 <sup>k</sup>	(g Hg2s/g soot)/g dissolved Hg(II)/liter of water)					
11	$HgSO_{3}^{-1} \rightarrow Hg(0)$	T*e <sup>((31.971*T)-12595.0)/T)  </sup>	sec <sup>-1</sup>					
12	$Hg(OH)_2 + hv \rightarrow Hg(0)$	6.00E-07 <sup>m</sup>	sec⁻¹					

<sup>a</sup> In the base case, 10% of the product of this reaction assumed to be Hg(p) and 90% Hg(II).

<sup>b</sup> The Hg(0) oxidation rate shown in this table for the base case has been scaled to 20% of its nominal literature value.

<sup>c</sup> (Sommar et al., 2001)

<sup>d</sup> (Hall, 1995)

<sup>e</sup> (Tokos et al., 1998) (upper limit for rate)

<sup>f</sup> (Seigneur et al., 1994)

<sup>g</sup> (Calhoun and Prestbo, 2001), as cited by Bullock and Brehme (2002)

<sup>h</sup> (Lin and Pehkonen, 1997)

<sup>i</sup> (Munthe, 1992)

<sup>j</sup> (Lin and Pehkonen, 1998)

<sup>k</sup> Hg2s is Hg(II) adsorbed to soot, as described in the text. Equilibrium ratio shown coupled with 1<sup>st</sup> - order time constant (60 minutes) for rate of approach to equilibrium. Follows the approach of Bullock and Brehme (2002), based on experimental results from Seigneur et al. (1998)

<sup>1</sup> (Van Loon et al., 2000) (temperature T in degrees K)

<sup>m</sup> (Bullock and Brehme, 2002; Xiao et al., 1994) Rate shown in maximum at peak insolation. Actual rate is scaled according to local ratio of insolation to peak insolation.

		1					
#	Equilibrium	Equilibrium Constant	Units				
Gas-liquid partitioning							
1	$O_3^{(aq)} \leftrightarrow O_3^{(gas)}$	0.0113 <sup>a</sup>	molar/atm				
2	$H_2O_2^{(aq)} \leftrightarrow H_2O_2^{(gas)}$	7.4E+04 <sup>a</sup>	molar/atm				
3	$Hg(0) \xrightarrow{(aq)} \leftrightarrow Hg(0) \xrightarrow{(gas)}$	0.11 <sup>b</sup>	molar/atm				
4	$Cl_2^{(aq)} \leftrightarrow Cl_2^{(gas)}$	0.076	molar/atm				
5	$OH \bullet (aq) \leftrightarrow OH \bullet (gas)$	25.0 <sup>a</sup>	molar/atm				
6	$SO_2^{(aq)} \leftrightarrow SO_2^{(gas)}$	1.23 <sup>a</sup>	molar/atm				
7	$HgCl_{2}^{(aq)} \leftrightarrow HgCl_{2}^{(gas)}$	1.4E+06 <sup>c</sup>	molar/atm				
8	$Hg(OH)_2^{(aq)} \leftrightarrow Hg(OH)_2^{(gas)}$	1.2E+04 <sup>c</sup>	molar/atm				
Aqueous-phase equilibrium relationships							
9	$SO2 \leftrightarrow HSO_3^{-1} + H^+$	0.013 <sup>a</sup>	molar				
10	$HSO_3^{-1} \leftrightarrow SO_3^{-2} + H^+$	6.6E-08 <sup>a</sup>	molar				
11	$HgCl_2 \leftrightarrow Hg^{+2} + 2 Cl^{-1}$	1.0E-14	molar <sup>2</sup>				
12	$Hg(OH)_2 \leftrightarrow Hg^{+2} + 2 OH^{-1}$	1.0E-22	molar <sup>2</sup>				
13	$Hg^{+2} + SO_3^{-2} \leftrightarrow HgSO_3$	5.0E+12	1/molar				
14	$HgSO_3 + SO_3^{-2} \leftrightarrow Hg(SO_3)_2^{-2}$	2.5E+11	1/molar				

Table 2. Gas-liquid partitioning and aqueous phase equilibrium relationships

a (Seinfeld and Pandis, 1998)

b (Clever et al., 1985)

c (Lindqvist and Rodhe, 1985)

#### 3.4. Dry and Wet Deposition

Dry deposition of different mercury forms from the first-layer cells to terrestrial surfaces is estimated using a parameterized resistance-based approach (Wesely, 1989; Wesely and Hicks, 1977). For water surfaces, the approach of Slinn and Slinn (1980) is utilized. Dry deposition of gas-phase and particle/droplet phase mercury is considered. As a first approximation, a constant back-ground atmospheric particulate surface area of  $3.5E-06 \text{ cm}^2/\text{cm}^3$  is utilized equal to the "background + local sources" value estimated by Whitby (1978). A typical particle size distribution was chosen based on Whitby (1975), as cited by Prospero et al (1983). The assumed distribution is divided into 14 particle size bins, whose mid-point particle-size diameter ranges from 0.001 - 20 microns. The details of the distribution are summarized in Figure 6. To estimate the mass and mass fraction in each bin, based on the assumed surface area distribution, it was assumed that the particles were spherical with a density of 2 g/cm3. With these assumptions, the mass loading of the entire distribution corresponds to 39 ug/m3. Approximately 90% of the mass in the assumed distribution has a diameter of less than 10 um; thus, the PM-10 concentration associated with the assumed distribution is on the order of 35 ug/m3.

When no liquid water was present – i.e., the particles were dry - Hg(0) and Hg(II) were assumed to be entirely in the gas phase, while Hg(p) and Hg2s were assumed to be entirely in the particle phase. In this case, Hg(p) and Hg2s were apportioned to the different particle size bins based on the fraction of the total surface area in each size bin. When liquid water was present, the condensed-phase concentrations of Hg(0), Hg(II), and Hg2s were estimated via thermodynamic calculations as described above. For Hg(0) and Hg(II), the total droplet phase mass was apportioned among the different size ranges based on the estimated volume fraction in each size range. With or without the presence of liquid water, Hg(p) and Hg2s were apportioned among the different size ranges based on the fraction of the total aerosol surface area in each size range.

Wet deposition was estimated based on the vertical location of a given cell relative to the cloud layer during precipitation events. If the cell was above the cloud layer, no wet deposition occurred. If the cell was within the cloud layer, the particle-phase pollutants Hg(p) and Hg2s were wet deposited at a rate governed by an estimated volume-based scavenging ratio WETR (grams Hg per m3 of precipitation / grams Hg per m3 of air). As summarized by Gatz (1976), scavenging ratios for particle-phase pollutants associated with relatively small particle sizes - like Hg(p) - are relative small, with typical values (in these units) less than 100,000. A WETR value of 40,000 was used, identical to that used for particle-phase pollutants in earlier, related HYSPLIT modeling (Cohen et al., 2004; Cohen et al., 2002). In-cloud wet deposition of Hg(0) and Hg(II) was estimated using the precipitation rate and the thermodynamically estimated aqueous-phase concentrations. For cells below a precipitating cloud layer, different approaches were used, depending on the relative humidity and the mercury form. Particle and droplet phase mercury was scavenged using a size-dependent scavenging coefficient estimated for falling drops in the range of 0.04 – 0.4 mm (Seinfeld and Pandis, 1986). For each size range, the geometric mean value of the scavenging coefficient estimated for collectors of 0.04 mm and 0.4 mm was used. Gasphase mercury was scavenged assuming thermodynamic partitioning between the gas-phase and falling droplets.



Figure 6. Particle size distribution used in this analysis.

#### 3.5. Meteorological Data

The meteorological data used in the simulations were developed from the NCEP/NCAR Global Reanalysis (NCAR/NWS, 1994...; NOAA ARL, 2003...). These data are specified on a 2.50 x 2.50 grid, with a surface layer and 17 vertical levels above the surface, up to a height of ~30 km (10 hPa). The data are specified on the 3-D grid every 6 hours. As can be seen in Figure 7 and Figure 8, the NCEP/NCAR Global Reanalysis data shows a systematic over-prediction of precipitation at Mercury Deposition Network sites in the Great Lakes region.

As can also be seen in Figure 8, for other MDN sites, the correlation between measured and modeled precipitation is not very satisfactory (it is less than zero) but the average is very consistent (e.g., the slope of the best fit line has a slope of ~1.0). Given the relatively coarse grid of the global data (2.5 degrees, or roughly 250 km), it would not be expected that the modeled and measured precipitation would be overly consistent. Therefore, the degree of consistency found, while not perfect, is somewhat unexpected. It is noted that there is some uncertainty in the "measured" precipitation at the MDN sites. The precipitation at the sites is reported in two ways: (a) based on a precipitation gauge at the site and (b) based on the amount of precipitation collected in the sample. Ideally, the two measures of precipitation would be identical, but they are sometimes different.

These two measures of precipitation are shown in Figure 7, and it is seen that in some cases, the sample-precipitation value is closer to the modeled value than the rain-gauge measured precipitation. A comparison of rain-gauge vs. sample-measured precipitation at all MDN sites with 2005 data is shown in Figure 9. It is seen that there are non-trivial differences between the two at many of the sites, suggesting that the precipitation measurements are somewhat uncertain.



Figure 7. Comparison of measured and modeled precipitation at MDN sites in the Great Lakes region



Total 2005 Precipitation Measured with Rain Gauge (m/yr)





Figure 9. Comparison of precipitation measured by rain gauges at MDN sites with that in the NCEP-NCAR Global Reanalysis meteorological dataset

#### 3.6. Model Spin-up

In previous phases of this work, increasingly long spin-up times have been used. In the present work, we have increased the spin-up time further to increase the accuracy of the simulation. In doing this, we've been able to take advantage of increased computational resources. In the work presented in this phase, 5 year spin-up periods have been used, to prepare the model for the 2005 analysis. Thus, the total simulation time used was 72 months (60 months spin-up + 12 months for the actual 2005 simulation).

In Figure 10, some illustrative results are presented, showing the typical differences that are associated with these changes in spin-up times. The results shown are for one particular model configuration, and just for ocean emissions, and are based on the total, 2005 model-estimated mercury deposition to selected receptors, using different spin-up times. It can be seen that by increasing the spin-up time from 24 months to 36 months (equivalent to increasing the total simulation time from 36 to 48 months), there is approximately a 3% increase in the estimated deposition.

The reason that the deposition increases with increased spin-up is that the atmosphere needs to be "filled up" with a realistic amount of mercury before the simulation can be regarded as being representative of the real-world situation. Increasing the spin-up another 12 months adds another 1%, for a total of a 4% increase from the 24-month spin-up case. Increasing the spin-up period yet another 12 months, to 5 years (i.e., a total simulation time of 60 + 12 = 72 months) raises the simulation results only a very small additional amount.

It can be seen that a point of diminishing returns is gradually reached. For this work, we have used the 60-month spin-up, i.e., the highest results shown in the figure below. The differences introduced by this increased spin-up are not expected to be dramatic -- they should only be on the order of a few percent. Nevertheless, it was deemed worth the computational investment to configure the simulations in this manner.



Figure 10. Illustrative example of some differences in 2005 simulation results using spin-up times of 24, 36, 48, and 60 months.

## 4. Model Changes and Improvements

A number of changes and improvements were made to the HYSPLIT-Hg model during this study, and several of the most important and/or most relevant changes will be briefly noted here.

#### 4.1. Deposition Tracking for Different Terrestrial and Ocean Surfaces

Wet and dry deposition to each of the 20 land-use classifications considered in the HYSPLIT-Hg model (e.g., ocean, agricultural, mixed forest, desert, etc.) is now tracked individually. A new output file is written from each model run with these data, and a new post-processing program has been created to provide useful, abbreviated summaries of these data. One important reason for adding this feature was to be able to estimate the net surface exchange from specific surface types, e.g., the ocean. Using the ocean as an example, the model is given (i.e., as input) the gross (or one-way) mercury emissions flux upwards from the ocean. The new output gives the gross downwards mercury deposition flux to the ocean. From these data, the net ocean mercury flux can be determined. Since some models only consider this net ocean flux, the ability to determine its value in the HYSPLIT-Hg simulations is needed in order to compare its results with these other models. The same type of net-flux calculation is also now possible for other types of surfaces, e.g., reemissions and other emissions from soil/vegetation.

#### 4.2. Model Spin-Up Time

As discussed in above, the spin-up time in the current analysis was increased significantly to a total of 60 months. While this has significantly increased the computational resources required to carry out the analysis, it has improved the accuracy of the simulation.

#### 4.3. Conversion of Output to Standard Temperature and Pressure

Added to feature to the model so that it now converts specialized-receptor-output air concentrations during run-time to the standard temperature and pressure corresponding to the mercury measurements used for model evaluation. Previously, this conversion required a very significant post-processing effort. With the current approach, the model results are "evaluation-ready", i.e., can be directly compared to measurement data.

#### 4.4. Fixed problem with Spurious Puffs in Eulerian Simulations

In earlier work, a known "bug" in the model was associated with the emissions of mercury into the Eulerian computation grid. With this "bug", a computation puff was first introduced, and then quickly transferred to the Eulerian grid. However, during the first hour of the puff's life, i.e., before it was transferred at the end of 1 hour, it could contribute concentration and deposition of mercury to receptors. The Eulerian emissions were set at the centroid of grid squares. If a particular receptor (e.g., a Mercury Deposition Network site with wet deposition measurements) happened to be near the

centroid, a small but potentially significant spurious "burst" of mercury deposition or concentration could be contributed to the site by the initial puff. We did see evidence that this was affecting the calculation in a few situations. To fix the problem, we changed the model so that mercury emissions were emitted directly into the Eulerian grid cells, bypassing the nascent puff stage. This made essentially no difference for most of the model results, but with the correction, we were able to use a few more model evaluation sites that "unluckily" had been very close to the grid centroids and were affected by this issue.

#### 4.5. Model Evaluation Methodology

The methodology used to evaluate the modeling results has been significantly improved. In the past, annual average values were used for comparison regardless of the time period that the sampling actually corresponded to. So, for example, if sampling was only carried out for the equivalent of 2 months at a given site, the two-month sampling average was compared with the 12-month average model result. In the new approach taken here, all model results were output on an hourly basis. Then, the model evaluation comparison was made on only the hours for which measurements were made during 2005. In some cases, where the site collected measurements for essentially the entire year, the new approach made little difference. But for many of the sites, where more sporadic sampling was carried out during 2005, the comparison was now able to be made on a much more accurate and representative basis. In carrying out this new type of analysis, the HYSPLIT "DATEM" data format was utilized { http://www.arl.noaa.gov/DATEM.php }. This had a number of advantages, including allowing a number of specialized data analysis programs in the HYSPLIT modeling suite to be used that required DATEM format inputs.

#### 4.6. Process-Specific Analysis

To investigate process-specific lifetimes, e.g., for specific chemical reactions or deposition processes, a feature was added to the model that allows one or more of the fate processes to be turned off and on in any given simulation. So, to study a specific chemical reaction, it could be turned out in isolation, i.e., with all other reactions, as well as all deposition processes, disabled in the model. Using this approach, process-specific simulations were carried out, as discussed in Section 5 below.

#### 4.7. Thickness of lowest layer

An algorithmic error was found in the specification of the thickness of the lowest model layer in the 3dimensional global Eulerian grid. This error was fixed, and all of the simulations presented here reflect the corrected code. The error correction did not make a dramatic difference in the results, but just about every aspect of the simulation was affected to some degree by the correction.

### 4.8. Box Model Created

A box-model version of the HYSPLIT-Hg model was created to further investigate specific processes. Results of this analysis are not presented in this report, but the box model was used to verify that the chemical transformation and deposition algorithms in HYSPLIT-Hg were working as intended.

### 5. Model-Estimated Lifetimes for Specific Processes

A special set of simulations was carried out to investigate specific processes and process combinations. In these simulations, the entire three-dimensional domain was initially filled with a constant mixing ratio (1 ng / kg of air) of a particular form of mercury, i.e., Hg(0), Hg(II), or Hg(p). During the subsequent simulation, no additional mercury was added to the system. In any given simulation, one or more chemical transformation and/or deposition process was turned on, while others were disabled. These process-specific simulations were carried out for two years, and the decrease in mass of the starting mercury form was tracked throughout. The results of these simulations are summarized in Figure 2 for Hg(0) and Figure 3 for Hg(II) and Hg(p).

The approximate lifetimes reported are based on the hour-by-hour decreases in mass over the two-year simulation. Assuming a first order removal process, governed by dm/dt = -km, hourly values of k were estimated from the change in mass (dm/dt) and the mass in the system (m). The instantaneous 1/e atmospheric lifetime  $\tau$  is equivalent to the instantaneous value of 1/k. Values of the median, 25<sup>th</sup> and  $75^{\text{th}}$  percentile, average, and the mass-weighted average of hourly  $\tau$  estimates are shown, as well as the average over the first week of the simulation. In addition, the figures show the lifetimes estimated from a linear regression of ln(m) vs. time over the 2-year simulation. As can be seen from the figures, the different estimation methodologies result in different, approximate lifetime estimates for a given process. The differences arise from numerous factors, including the fact that the processes are not spatially or temporally uniform. Further, the mass distribution of mercury is changed – affecting the efficiency of removal processes - as the simulation proceeds. This is particularly important for the estimation of deposition processes. For example, only material in the surface layer is removed during dry deposition, and the surface layer mass is therefore depleted at a relatively fast rate at the beginning of the simulation. Once the initial surface layer material is depleted, the rate of dry deposition depends more on the rate of dispersion from layers aloft to the surface layer. From this perspective, the 1<sup>st</sup>-week average values may be the most relevant for wet and dry deposition processes. However, particularly for wet deposition, the variability of precipitation means that any given week will not necessarily be representative of the long-term average. Based on the above discussion, the atmospheric lifetimes presented in Figures 2 and 3 should be regarded as rough estimates.

In Figure 2 it can be seen that if the OH and O3 rates are specified at 100% of their potential values, the modeled lifetime for Hg(0) due to oxidation is on the order of 0.3 year (3-4 months). Because this was much shorter than the ~8-14 month lifetime for Hg(0) found in other studies (e.g., Lamborg et al., 2002; Selin et al., 2007), we specified the rates of these reactions to be 20% of the potential value in our base case, as discussed above, and considered variations of 10% and 33% in a sensitivity analysis. The oxidation lifetime of Hg(0) considering all oxidation reactions considered in the model is ~1 year in the base case, with the OH• and O<sub>3</sub> reactions scaled to 20%. For the comparable 10% and 33% scaling variations, the Hg(0) lifetime against all oxidation reactions in the model is ~1.5 and ~0.7 years, respectively. The lifetime of Hg(0) with respect to dry deposition – with all chemical transformation processes turned off – is ~3 years. We note that this lifetime is for the case where Hg(0) is distributed at a constant mixing ratio throughout the three-dimensional model domain. The average lifetime with

respect to dry deposition for Hg(0) in the lower levels of the atmosphere would be significantly less. The comparable lifetime of Hg(0) with respect to wet deposition is extremely long (~100 years) owing to the minimal solubility of Hg(0) in water.

The lifetime of Hg(II) with respect to reduction (~0.4 year) is controlled by S(IV) processes in the model (Figure 3). Wet and dry deposition processes are effective removal processes for Hg(II) with lifetimes on the order of 0.1 year. For Hg(p), wet deposition lifetimes are also on the order 0.1 year, and somewhat dependent on the value of WETR used, as would be expected. Hg(p) dry deposition is slower, characterized by a lifetime on the order of 0.7 year.









## 6. Model Configurations Used in this Analysis

In addition to the base-case atmospheric chemistry and emissions configuration described above (configuration "1A"), several additional simulations with different configurations were carried out to investigate the impact of differing assumptions on model results. These are summarized in Table 1.

In all of the "1" variations (1A-1E), the base-case oxidation rate parameters were used, i.e., the gasphase Hg(0) oxidation reactions by OH• and O<sub>3</sub> were scaled by 20%. In all of the "2" variations (2A-2D), the gas-phase Hg(0) oxidation reactions by OH• and O<sub>3</sub> were scaled by 33%. In all of the "3" variations (3A-3B), the gas-phase Hg(0) oxidation reactions by OH• and O<sub>3</sub> were scaled by 10%.

In configuration 1B, the Hg(p) fraction in the products of the OH•,  $O_{3,}$  and  $H_2O_2$  gas-phase oxidation reactions was assumed to be 0%, i.e., 100% of the products were assumed to be Hg(II). In 1C, the Hg(p) fraction was assumed to be 25%, and, the scavenging ratio WETR for wet deposition of Hg(p) and Hg2s was raised to 80,000 [(g Hg / m<sup>3</sup> precipitation) / (g Hg / m<sup>3</sup> air)].

In configurations 2A and 3A, the scaling of the gas-phase Hg(0) oxidation reactions by OH• and  $O_3$  were changed to 33% and 10%, respectively, from the base case value of 20%. In these configurations the net oceanic and land-based emissions of Hg(0) were adjusted as shown in Table 1.

In configurations 1D and 1E, it was assumed that 50% and 75%, respectively, of anthropogenic emissions of Hg(II) were reduced promptly to Hg(O) immediately after release. The prompt reduction of emitted Hg(II) in plume has been hypothesized by some to be more consistent with observations (e.g., Kos et al., 2013; Zhang et al., 2012b). In configurations 2B and 2C, these same plume reduction assumptions were combined with the 33% oxidation scaling assumption of configuration 2A. In configuration 2D and 3B, the base-case emissions were used with the 33% and 10% oxidation scaling assumption, respectively.

Table 1 also shows a few model evaluation metrics for each configuration, e.g., the average bias in the model-estimated Great Lakes region Hg(0) atmospheric concentration and mercury wet deposition. The model evaluation methodology and additional results are provided in Section 7 (beginning on page 33, below). We note here that the "bias" is defined by the following:

 $bias = \frac{average modeled value - average measured value}{average measured value}$ 

Table 1	. Model	configurations
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	Model Configuration <sup>a</sup>										
	1A	1B	1C	2A	3A	1D	1E	2B	2C	2D	3B
Brief description	Base- base	Oxid particle 0%	Oxid particle 25%, WETR 80K	Oxid 33%, adjust- ed ocean- land emit	Oxid 10%. Adjust- ed ocean- land emit	Plume reduc- tion 50%	Plume reduc- tion 75%	Oxid 33%, Plume reduc- tion 50%	Oxid 33%, Plume reduc- tion 70%	Oxid 33%, base emit	Oxid 10%, base emit
Oxidation scaling <sup>b</sup>	20%	20%	20%	33%	10%	20%	20%	33%	33%	33%	10%
Particle fraction <sup>c</sup>	10%	0%	25%	10%	10%	10%	10%	10%	10%	10%	10%
WETR parameter <sup>d</sup>	40	40	80	40	40	40	40	40	40	40	40
Plume reduction of Hg(II)	0%	0%	0%	0%	0%	50%	75%	50%	75%	0%	0%
Net ocean Hg(0) emit (Mg/yr)	2600	2600	2600	3600	1300	2600	2600	3600	3600	2600	2600
Net land- vegetation emit <sup>e</sup> (Mg/yr)	350	350	350	900	175	350	350	900	900	350	350
Total emit using net Hg(0) exchange (Mg/yr) <sup>f</sup>	6400	6400	6300	8000	4800	6400	6300	8000	8000	6400	6400
GL Hg(0) bias <sup>g</sup>	1.6%	2.5%	-0.2%	-0.4%	2.3%	5.4%	7.3%	2.4%	3.7%	-23%	35%
GL MDN bias <sup>g</sup>	-10%	-14%	-10%	6.5%	-25%	-20%	-25%	-3.4%	-8.3%	-9%	-11%
(Emissions – Deposition) / Emissions <sup>g</sup>	2.2%	2.0%	2.8%	2.4%	2.3%	2.2%	2.2%	2.4%	2.4%	2.4%	2.2%

a. Numbers in bold font represent the base case model "input" values; italics represent variations of these values. b. Scaling of the OH• and  $O_3$  gas-phase Hg(0) oxidation reaction rates relative to nominal literature values.

c. Fraction of the products of the OH•,  $O_3$ , and  $H_2O_2$  gas-phase Hg(0) oxidation reactions that are assumed to be Hg(p). The remainder of the products of these reactions are assumed to be Hg(II).

d. The WETR parameter affects the in-cloud wet deposition of Hg(p) and Hg2s.

e. Not including prompt re-emissions

f. Rounded to the nearest 100 Mg/yr

g. Summary values from model evaluation results.

## 7. Model Evaluation

### 7.1. Atmospheric mercury measurement data used for model evaluation

Atmospheric mercury measurement data for 2005 was utilized to evaluate the model results, with particular emphasis on measurement sites in the Great Lakes region. Atmospheric mercury concentration measurements used for model evaluation are summarized in Table 3 and shown in Figure 13. Measured mercury wet deposition fluxes and ambient concentrations were compared with HYSPLIT-Hg model output at the sites also shown in Figure 13. Measured wet deposition of total mercury in North America was obtained from the Mercury Deposition Network (MDN) (National Atmospheric Deposition Program, 2012). A total of 86 MDN sites were operating at the start of 2005 and were still operating at the end of 2005. Of these 86 sites, 32 were in the Great Lakes region, 17 were in the Gulf of Mexico region, and 37 were elsewhere in North America (Figure 13).

Given the relatively coarse computational grid used in this work (2.5° x 2.5°), it is not expected that any grid-average model result will match the measurements at any given measurement location. This is the normal case with essentially any comparable modeling study. The impact of sub-grid-scale phenomena such as the impacts of "local" sources on a given site will not be captured by the coarse Eulerian computational grid. With this important limitation and caveat in mind, we will nevertheless carry out detailed comparisons of measurements with grid-averaged model results in the sections below. In future phases of this work, we hope to be able to employ a finer grid and/or utilize other methodologies to better capture fate/transport phenomena on a more highly resolved scale. This will allow a better evaluation of the modeling results.



#### Figure 13. Measurement sites with 2005 data used for model evaluation.

Sites with atmospheric mercury concentration data shown as larger white circles with 3-character site abbreviation, described in Table **3**. Mercury Deposition Network (MDN) sites with wet deposition measurements shown as smaller colored symbols, Classification of MDN sites into Great Lakes (GL) or other regional categories was made on State and Provincial basis, i.e., if site was in State or Province adjacent to one or more GL, it was classified as a GL site.

#### 7.2. Comparison of Modeled vs. Measured Mercury Wet Deposition

Before showing the comparison of modeled vs. measured wet deposition of mercury, we first show a comparison of modeled vs. measured precipitation. Precipitation measurement data at the 86 sites are compared in Figure 14 with the gridded precipitation data in the NCEP/NCAR meteorological model output data used to drive the HYSPLIT-Hg model in this analysis. Due primarily to the coarseness of the model output grid (2.50 x 2.50), but also to both model and measurement uncertainties, an exact match is not expected. Precipitation at a specific location within a grid cell would not generally be the same as the grid cell average, even if both the model and measurements were "perfect". In comparing HYSPLIT-Hg model output with measured mercury wet deposition, the modeled flux at measurement locations was multiplied by the ratio of measured to modeled precipitation, in a post-processing procedure. It is recognized that the impact of the precipitation "errors" in the meteorological datasets will introduce complex, non-linear deviations in the simulations. So, using the measured/modeled precipitation ratio at any given site is an approximation. Given this limitation, however, we would not expect an exact agreement between modeled and measured mercury wet deposition, even if both were "perfect".



measured: MDN rain gauge precipitation (m/yr)

Figure 14. Measured vs. modeled 2005 precipitation.

Figure 15 shows a comparison of modeled vs. measured 2005 mercury wet deposition at the 86 MDN sites for which essentially complete data were available for 2005. The comparison is differentiated among sites in the Eastern Great Lakes region, the Western/Central Great Lakes region, the Gulf of Mexico region, and all other MDN sites. The overall agreement seems very reasonable in the Great Lakes

regions and other regions, aside from a tendency for the model to underestimate mercury wet deposition in the Gulf of Mexico region. We have focused our efforts on the Great Lakes region, and it is beyond the scope of this work to examine the Gulf of Mexico region in depth. Model underestimates of mercury wet deposition in the Gulf of Mexico region has been found in other modeling studies (e.g., Amos et al., 2012; Bullock et al., 2009; Holmes et al., 2010a; Lin et al., 2012; Selin et al., 2007; Zhang et al., 2012b), and may be due to an inaccurate characterization of deep convective thunderstorm scavenging of mercury.



Measured Mercury Wet Deposition (µg/m<sup>2</sup>-yr)

Figure 15. Comparison of modeled vs. measured mercury wet deposition for the base case.

How does the model performance with respect to wet deposition estimation change in the different model configurations considered? Figure 16 shows comparable plots of modeled vs. measured values for each configuration. Observations that can be drawn from this figure include the following:

- Changing the fraction of gas-phase oxidized Hg(0) assumed to be Hg(p), along with increasing the efficiency by which Hg(p) is removed by precipitation, has a noticeable effect (1A vs. 1C). However, simply changing the Hg(p) product fraction does not have a dramatic effect (1A vs. 1B)
- The basic 33% and 10% oxidation rate scaling configurations (2A, 3A) show some differences with the base-case 20% configuration (1A), but primarily when the emissions are adjusted to make Hg(0) concentrations realistic. That is, increasing the oxidation rate results in higher wet

deposition (2A vs. 1A), while decreasing the oxidation rate results in lower wet deposition (3A vs. 1A), in these cases where the emissions are adjusted to make the Hg(0) concentrations realistic. However, in comparable comparisons in which the emissions are *not* adjusted (2D vs. 1A, and 3B vs. 1A), there is little change in wet deposition.

• The plume reduction configurations result in slightly lower wet deposition model estimates, i.e., 1D vs. 1A, and 1E vs. 1A for the base 20% oxidation scaling, and 2B vs. 2A and 2C vs. 2A for the 33% oxidation scaling case.



Figure 16. Comparison of modeled vs. measured mercury wet deposition for all model configurations.
A statistical summary of the comparison of each of the model configurations with measured values, broken down by different regions, is presented in Table 2. Overall, it can be seen that there is a tendency for the model to under-predict (-8% to -38%) mercury wet deposition in the Western/Central Great Lakes region, but a tendency to over-predict (-3% to +42%) in the Eastern Great Lakes region. Overall, the model tends to show a moderate under-prediction (-25% to +7%) for the Great Lakes region as a whole, in most configurations. As noted above, the model shows a significant under-prediction of mercury wet deposition in the Gulf of Mexico, and a moderate under-prediction in other regions. Overall, the model shows a tendency to moderately under-predict mercury wet deposition at the 86 sites with data for 2005. In future work, we will examine the influence of different wet deposition parameterizations and algorithms, as well as a increased spatial resolution, on the relative accuracy of the model's mercury wet deposition estimations.

			Model Configuration										
		ue	1A	1B	1C	2A	3A	1D	1E	2B	2C	2D	3B
		Measured valu	Base- base	Oxid particle 0%	Oxid particle 25%, WETR 80K	Oxid 33%, adjust- ed ocean- land emit	Oxid 10%. Adjust- ed ocean- land emit	Plume reduc- tion 50%	Plume reduc- tion 75%	Oxid 33%, Plume reduc- tion 50%	Oxid 33%, Plume reduc- tion 70%	Oxid 33%, base emit	Oxid 10%, base emit
Great Lakes	Avg	7.9	7.1	6.8	8.7	8.4	5.9	6.3	5.9	7.6	7.3	7.2	7.0
	Bias <sup>a</sup>		-10%	-14%	10%	7%	-25%	-20%	-25%	-3%	-8%	-9%	-11%
	$RMSE^{b}$		2.7	2.7	3.0	3.0	3.0	2.6	2.8	2.5	2.4	2.6	2.7
Western GL	Avg	8.2	6.1	5.9	7.5	7.3	5.1	5.4	5.1	6.6	6.2	6.2	6.0
	Bias		-25%	-28%	-8%	-11%	-38%	-33%	-38%	-20%	-24%	-24%	-26%
	RMSE		2.9	3.2	2.5	2.6	3.6	3.1	3.3	2.4	2.5	2.9	3.0
Eastern GL	Avg	7.5	8.8	8.4	10.6	10.4	7.3	7.8	7.4	9.4	9.0	8.8	8.6
	Bias		17%	12%	42%	39%	-3%	5%	-1%	26%	20%	18%	15%
	RMSE		2.1	1.8	3.7	3.5	1.4	1.5	1.5	2.7	2.4	2.1	2.0
MOD	Avg	13.6	5.9	5.6	6.8	7.3	4.6	5.6	5.5	7.0	6.9	6.1	5.7
	Bias		-57%	-59%	-50%	-46%	-67%	-59%	-60%	-48%	-49%	-56%	-58%
	RMSE		8.8	9.1	8.1	7.6	10.0	9.0	9.0	7.7	7.8	8.7	9.0
Other	Avg	7.1	5.8	5.4	7.2	7.0	4.5	5.6	5.5	6.8	6.7	5.8	5.7
	Bias		-19%	-24%	2%	-1%	-36%	-22%	-23%	-4%	-5%	-18%	-20%
	RMSE		3.2	3.3	3.5	3.3	3.7	3.4	3.5	3.4	3.4	3.2	3.3
AII	Avg	8.7	6.3	5.9	7.7	7.6	5.1	5.9	5.6	7.2	7.0	6.4	6.2
	Bias		-28%	-32%	-12%	-12%	-42%	-33%	-35%	-17%	-20%	-27%	-29%
	RMSE		4.7	4.9	4.6	4.4	5.4	4.8	4.9	4.3	4.4	4.7	4.8

Table 2. Statistical summary of model vs. measured 2005 wet deposition comparisons.

a. Bias = (modeled – measured) / measured; negative numbers shown in red text; positive bias shown in green text.

b. RMSE = Root Mean Square Error

### 7.3. Comparison of Modeled vs. Measured Atmospheric Mercury Concentrations

## 7.3.1. Introduction and Overview of Comparisons

There are limited ambient mercury concentration monitoring data available for 2005, but we were able to obtain 2005 data for Hg(0), Hg(II), and/or Hg(p) at the sites summarized in Table **3** (below) and Figure 13 (page 34, above). For several of the sites, relatively complete data were available for the entire year for Hg(0) or Total Gaseous Mercury (TGM). For seven sites, only Hg(0) or TGM measurements were available during 2005. For the seven sites with Hg(II) and/or Hg(p) measurements, the fraction of the year covered by measurements was relatively low – from as low as 4% to as high as 37%. Each of the datasets had a particular sample averaging period, i.e., 1, 2, 3, or 24 hours, as shown in Table **3**.

				2005 M	Data	
Site <sup>a</sup>	Lat	Long	Elevation (m.a.s.l.)	Hg forms measured <sup>b</sup>	Fraction of year covered <sup>c</sup>	Averaging period (hours) <sup>c</sup>
Egbert, ON (EGB) <sup>d</sup>	44.23	-79.78	251	TGM	95%	1
Burnt Island, ON (BRI) <sup>d</sup>	45.81	-82.95	75	TGM	98%	1
Point Petre, ON (PPT) <sup>d</sup>	43.84	-77.15	75	TGM	97%	1
Stockton, NY (STK) <sup>e</sup>	42.27	-79.38	500	TGM, Hg(II)	12%, 7%	24
Potsdam, NY (PTD) <sup>e</sup>	44.75	-75.00	100	TGM, Hg(II)	19%, 16%	24
St. Anicet, QU (STA) <sup>d</sup>	45.12	-74.28	49	TGM	96%	1
Underhill, VT (UND) <sup>f</sup>	44.53	-72.87	399	Hg(0), Hg(II), Hg(p)	36%, 37%, 8%	2
Kejimkujik, NS (KEJ) <sup>d</sup>	44.43	-65.20	127	TGM	93%	1
Bratts Lake, SK (BTL) <sup>d</sup>	50.20	-104.71	577	TGM	93%	1
Mt Bachelor, OR (MBO) <sup>g</sup>	43.98	-121.69	2700	Hg(0), Hg(II), Hg(p)	22%	1, 3, 3
Desert Research Institute, NV (DRI) <sup>h</sup>	39.57	-119.80	1509	Hg(0), Hg(II), Hg(p)	35%	2
Paradise, NV (PAR) <sup>i</sup>	41.50	-117.50	1388	Hg(0), Hg(II), Hg(p)	5%	2
Gibbs Ranch, NV (GBR) <sup>i</sup>	41.55	-115.21	1806	Hg(0), Hg(II), Hg(p)	4%	2
Alert, NU (ALT) <sup>d</sup>	82.50	-62.33	210	TGM	93%	1

Table 3. 2005 Ambient concentration measurements used for model evaluation.

<sup>a</sup> 3-letter abbreviation in parentheses used in Figure 13

<sup>b</sup> TGM = Total Gaseous Mercury

<sup>c</sup> Values are given individually for each mercury form measured if significant differences among measured forms

<sup>d</sup> (Cole et al., 2014; Cole et al., 2013; Temme et al., 2007)

<sup>e</sup> (Han et al., 2007; Han et al., 2005; Han et al., 2004)

<sup>f</sup> (Zhang et al., 2012a)

<sup>g</sup> (Swartzendruber et al., 2006)

<sup>h</sup> (Peterson et al., 2009)

<sup>i</sup> (Lyman and Gustin, 2008)

In order to compare the model predictions against any particular dataset, the model results were assembled with a matching averaging period, in order to make the "fairest" comparison. In other words, for example, hourly-average measurement data were compared against hourly-average model results, while 24-hour average measurements were compared against 24-hour average modeling data. And of course, the comparisons were made only for the times that the measurements were made during the year at any given site. Further, as measurements are routinely reported at Standard Temperature and Pressure (STP) (0 deg C, and 1 atm), the modeling results were converted to the same STP so that the comparisons could be made. There are a large number of comparisons – 14 sites, with up to 3 different mercury forms measured, compared to the results of the base case plus 10 alternative model configurations. We will attempt to show the comparisons in a variety of ways in this section of the report.

We begin with Figure 17, which simply shows the average measured and modeled concentrations at each of the sites with 2005 data used in this model evaluation process. In this figure, we have shown all of the data on the same scale. It can be seen that the concentrations of the non-Hg(0) mercury forms are generally much smaller than Hg(0). Note that we will present many detailed figures and data below that show the non-Hg(0) forms more clearly.



Figure 17. Overall comparison of measured vs. modeled average atmospheric mercury concentrations for the model Base Case (1A)

In Figure 18 through Figure 20, these same data are shown with different scales, *and with the sites labeled*. We will not generally label the sites in the comparison plots that follow, but, these initial labeled figures should allow the reader to find any particular site on a plot, by referring back to these initial "orientation" plots. Note that for some of the sites, data for different "levels" are shown. For example, in Figure 18, Hg(0) model results for Reno at model level 2 ("Reno-2") and model level 3 ("Reno-3") are shown. Data for different levels are also shown for the Mt. Bachelor site, and for the Underhill site. The reason that different model output level results are shown for these sites is that the sites are located in somewhat complex terrain, and there is some degree of uncertainty as to which output model level should be most reasonably compared to the measurements.

In all of the comparisons shown, we have compared Hg(II) model output concentrations with the "Reactive Gaseous Mercury" (RGM) or "Gaseous Oxidized Mercury" (GOM) measurements reported. We have not included the model-output Hg2s concentrations in these Hg(II) comparisons, as it is unclear *where* in the measurement system Hg2s would register. Likewise, for Hg(p) comparisons, we have used the model output Hg(p) – including material on all particle sizes – to compare against the measured Hg(p) values. The measurements of Hg(p) are usually for relatively small particles only, i.e., particles ~2.5 microns and smaller. We have not included the modeled Hg2s concentrations in the Hg(p) comparisons. For a few sites, both Hg(II) and Hg(p) were measured simultaneously (e.g., Mt. Bachelor and Reno-DRI). In these cases, we have carried out a comparison of the total non-elemental mercury measured [i.e., the sum of Hg(II) and Hg(p)] against the total non-elemental mercury modeled. In this "non-Hg(0)" comparison, we have included modeled concentrations of Hg2s, along with Hg(II) and Hg(p).



Figure 18. Comparison for the Base Case (1A) for Hg(0) concentrations, with selected sites labeled.



Figure 19. Comparison for the Base Case (1A) for Hg(0) concentrations, with the remainder of sites labeled.



Figure 20. Comparison for the Base Case (1A) for non-Hg(0) concentrations, with all sites labeled.

#### 7.3.2. Model Output Elevation and Averaging Time Considerations

During all of the simulations carried out for this analysis, the HYSPLIT-Hg model was configured to provide output at 6 different concentration levels: 100, 500, 1000, 2000, 3000, and 4000 meters above ground level. Since "level 1" is defined in the model as the ground level, and is used to track deposition, the 6 levels above the surface are numbered 2-7, i.e., the 100m level is level-2, and 500m level is level-3, etc. During the Eulerian-only simulations used in this analysis, the first several 3-dimensional Eulerian grid layers were approximately the following: 0-400, 400-1100, 1100-2700, and 2700-3800 meters above ground level. Thus, while the model concentrations would generally be different from one Eulerian layer to another at a given location, the concentrations are assumed to be uniform within a given Eulerian layer at a given location. Due to variations in the vertical variation of atmospheric pressure, the thickness and heights of the Eulerian model levels did vary somewhat over time and space. So, the Eulerian levels were not "constant" at these average values. No interpolation was done for the vertical concentration estimates. So, the 100m output concentration level (L2) was essentially always determined by the concentration in the lowest Eulerian level (0m - ~400m). Both the 500m and 1000m output concentration levels (L3 and L4) were generally (but not always) determined by the 2<sup>nd</sup> Eulerian level (~400m - ~1100m). Because of this, the L3 and L4 output concentrations were essentially the same. The 2000m output level (L5) was almost always determined by the 3<sup>rd</sup> Eulerian level (~1100m - ~2700m), and the 3000m output level (L6) was almost always determined by the 4<sup>th</sup> Eulerian level (~2700m -~3800m). The 4000m output level (L7) was almost always determined by the 5<sup>th</sup> Eulerian level, beginning at a height of ~3800m above ground level.

The coarseness of the 3-dimensional Eulerian model grid leads to limited accuracy in the vertical resolution of simulation results, especially in areas of relatively complex terrain. In areas where the surface is relatively flat, the Eulerian model layers are easily interpreted. For most monitoring sites, this is the case, and the most relevant output concentration model layer is L2, determined by the 1<sup>st</sup> Eulerian model layer. However, in areas where there are mountains and other complex terrain features, the interpretation of the Eulerian model levels is more difficult.

Consider, for example, the Eulerian grid square containing the Underhill monitoring site. The Underhill monitoring site is located at ~400m above sea level, on the side of a mountain. The "height" of the surface of the Eulerian grid square containing Underhill is ~335m above sea level. This can be regarded as the average terrain height over the entire grid cell. Relative to this cell "floor", the Underhill site is only ~65m above the "Eulerian model surface". So, for the Underhill site, what model output concentration level should be used to compare with measurements? The best answer might be the lowest layer (L2), defined by the 1<sup>st</sup> Eulerian layer, although the possible relevance of L3 cannot be ruled out.

The Mt. Bachelor Observatory (MBO) site is a second case where the site is located in complex terrain. MBO is located at ~2700m above sea level, near the top of a Mt. Bachelor in Oregon. The "height" of the surface of the Eulerian grid square containing MBO is ~600m above sea level. This can be regarded as the average terrain height over the entire grid cell. Relative to this cell "floor", the MBO site is only ~2100m above the "Eulerian model surface". However, while the site is located near a peak, the terrain at the base of the peak and in the surrounding region is at an elevation of ~1000m, within ~50 of the site. So, relative to the surrounding terrain, the MBO site is at an elevation of roughly 1700m above ground level. So, for the MBO site, what model output concentration level should be used to compare with measurements? The possible answers range from L4 (1000m), to L5 (2000m), to L6 (3000m).

The third case considered in which complex terrain may play a role is the Reno Desert Research Institute site. The Reno-DRI site is located at ~1509m above sea level. The "height" of the surface of the Eulerian grid square containing MBO is ~1360m above sea level. This can be regarded as the average terrain height over the entire grid cell. Relative to this cell "floor", the MBO site is only ~150m above the "Eulerian model surface". The Reno-DRI site is ~5 km north of downtown Reno, Nevada, located in a somewhat hilly region, is about 165m above the level of the city. Therefore, the most relevant model output concentration level data will likely be L2 (100m) or L3 (500m).

Another feature that can be seen in some of the data presented in this section is the presentation of more than one averaging-time dataset for certain comparisons. This was done for some of the datasets with almost complete sampling coverage over 2005. For those datasets, two different comparisons were made: (a) one with the native sampling averaging time compared against model results with the same averaging time (e.g., 1 hour), and (b) one with a 24-hr averaging time, compared against 24-hr averaged model results. For the 24-hr averages, only days where all 24 hours of data were available were used. In most cases, this only resulted in the exclusion of a few days of data. For the annual average results, the native vs. 24-hr averages were therefore very similar. Differences can be seen, however, in the distribution of concentrations, shown later in this section.

# 7.3.3. Summary Comparisons of Average Concentrations Against Simulation Results Using Different Model Configurations

In Figure 21, we show the annual average measured Hg(0) concentrations (large, open circles) compared against simulation results using different model configurations. The "red square" symbols show the base case (1A) and the other symbols represent the other 10 configurations. Several observations can be made.

First, the extreme cases 2D and 3B, in which the chemistry was altered but the base-case emissions were used, generally show the expected tendencies. Case 2D, using a faster oxidation rate for Hg(0), but base-case emissions, shows a significant under-prediction of Hg(0) for most sites, as would be expected. Similarly, for case 3B, with slower Hg(0) oxidation kinetics, shows a significant over-prediction of Hg(0) for most sites, as would be expected.

Second, it is notable that the results for all of the other model configurations – i.e., except for the extreme cases discussed immediately above -- are relatively similar, generally falling with 100 pg/m3 (0.1 ng/m3) of one another. For Reno, the Level 3 model results are closer to the measured values than the surface Level 2, suggesting perhaps that the site is influenced by air above the "surface layer". For Mt. Bachelor, the model results for Level 5 are closer to the measured values than lower levels (3,4), a result expected in light of the discussion above. For the Underhill site, there is not a dramatic difference

between the Level 2 and Level 3-4 model results, but the higher level results are slightly closer to the measured values. This suggests that the Underhill site also is influenced by air above the "surface layer".

For the sites in the Great Lakes region, the model results are encouragingly close to the measured concentrations. For sites outside of the Great Lakes region, the results are more mixed. For the Stockton, Potsdam, Paradise, and Gibbs Ranch sites, the coverage of data during 2005 was relatively limited, with less than 10-20% of the year represented by measurements. In these situations, the influence of sub-grid plume impacts may have been relatively large. Over the course of a year, if measurements were made continuously, one might expect the influence of sub-grid plume impacts to balance out, somewhat. But when measurements are made on a more sporadic basis, the influence may be much more significant.



Figure 21. Annual average measured Hg(0) concentrations compared with simulation results using different model configurations.

Figure 22and Figure 23 show comparable modeled vs. measurement comparisons for Hg(II), Hg(p), and total non-Hg(0), for all model configurations. The data plotted in the two figures are identical. However, the concentration scale in Figure 22 is linear while the concentration scale in Figure 23 is logarithmic. It can be seen from these figures that the model tends to show higher than measured concentrations of Hg(II), Hg(p), and total non-Hg(0). In some cases the difference is relatively small, and in some cases more significant. Before discussing the possible reasons for these model-vs.-measurement differences, it can be seen that the different model configurations generally give relatively similar results at any given site. The one exception to this is configuration 1B, which assumes that no Hg(p) during gas-phase Hg(0)

oxidation. In that configuration, the model-estimated Hg(p) concentrations tend to be significantly lower than the other configurations.

First, we note that this same type of discrepancy has been found in other modeling studies. For example, Zhang et al. (2012b) found that a nested-grid version of the GEOS-Chem model overestimated Hg(II) and Hg(p) by a factor of 4 and 2, respectively, unless it was assumed that a significant fraction (~75%) of Hg(II) emitted by coal-fired power plants was immediately reduced to Hg(0) in the downwind plume. With the assumed plume reduction of emitted Hg(II), the model overestimated Hg(II) and Hg(p) by ~40%. In another example, "reactive mercury", defined as the sum of Hg(II) and Hg(p), was overestimated by a factor of 2.5 relative to measurements (Weiss-Penzias et al., 2015b). A summary of model vs. measured concentrations of Hg(II) and Hg(p) in the Great Lakes region showed that models generally overestimated measurements by a factor of 2 to 10 (Zhang et al., 2012a). In a related study, large model overestimates of Hg(II) and Hg(p) were also found (Kos et al., 2013). There are a number of possible reasons for the tendency of the model-estimated concentrations to be greater than the reported measurements.

First, the measurement of Hg(p) is somewhat uncertain. In a comparison of Hg(p) measured with manual (filter) and automated (Tekran) methods, Talbot and colleagues (2011) found that manually-measured concentrations 21% higher than automated concentrations, on average. Further, they found that as much as 85% or more of the data showed a difference of greater than 25%. Further, the measurements of Hg(p) are generally limited to Hg(p) on particles less than about 2.5 microns in diameter. The reported measurements are more accurately called "Fine Particulate Mercury", rather than "Total Particulate Mercury". In the modeling results, we are showing the estimates for total particulate mercury. Therefore, one would expect the modeled Hg(p) to be somewhat higher than the reported measurements of Hg(p). There are very limited data on the size distribution of Hg(p). In a related study investigating aerosol mercury at a marine and a coastal site, significant mercury was often found in coarse aerosol size fractions (Feddersen et al., 2012). In some cases, the majority of Hg(p) appeared to exist on particles larger than 2.5 microns in size, although this was not always found. Keeler et al. (1995) found that, on average, about 88% of Hg(p) was associated with particles less than 2.5 microns in measurements in Detroit, but this varied from 60% - 100%, depending on conditions.

For Hg(II), new experimental evidence is emerging that suggests that the commonly used measurements of "Gaseous Oxidized Mercury" (GOM) [also sometimes called "Reactive Gaseous Mercury" (RGM)] using coated denuders may be underestimates of the true concentration in the atmosphere. For example, Lyman et al. (2010) found that atmospheric ozone reduced the efficiency and retention of GOM capture on KCl-coated denuders. Denuders exposed to ozone lost from 29-55% of loaded HgCl<sub>2</sub> and HgBr<sub>2</sub>. Collection efficiency of denuders decreased by 12-30% for denuders exposed to 50 ppb of O<sub>3</sub>. There are other examples and hypothesized explanations of this potential measurement bias (Ariya et al., 2015; Gustin, 2015; Jaffe et al., 2014; Kos et al., 2013; Weiss-Penzias et al., 2015b).

From the discussion above, it is seen that (a) other models have found comparable discrepancies between measured and modeled Hg(II) and Hg(p), and (b) this discrepancy may at least in part be due to the measurements being biased low.



Figure 22. Annual average measured Hg(II), Hg(p), and total non-Hg(0) concentrations compared with simulation results using different model configurations (linear scale).



Figure 23. Annual average measured Hg(II), Hg(p), and total non-Hg(0) concentrations compared with simulation results using different model configurations (logarithmic scale).

# 7.3.4. Statistical Distribution of Measured and Modeled Concentrations Using Different Model Configurations

In this section, we present a more detailed look at the comparisons between measured and modeled atmospheric mercury concentrations by showing "box and whisker plots" of the measured and modeled concentrations data side by side. Figure 24 shows a set of these comparisons for the base case (1A). In each plot, the first element in each data pair is the measured distribution, and the 2<sup>nd</sup> element in the modeled distribution. As is the common practice with these plots, the 25<sup>th</sup>, 50<sup>th</sup>, and 75<sup>th</sup> percentiles in the data are shown by the rectangle. The minimum and maximum in the data are shown by the "error bars" or whiskers. The averages of the data are also shown with red circles and are connected for each data comparison pair by a red line. Comparable sets of plots are shown for each of the other 10 alternative model configurations in Figure 25 through Figure 34.



2005\_ox20\_pf10\_W40K

Figure 24. The distributions of measured and modeled concentrations for the base case configuration 1A.

#### 2005\_ox20\_pf00\_W40K



Gibbs Ranch measured max of 23600 pg/m3 not shown on Hg(0) plot, with chosen scale. Mt Bachelor measured Hg(II) maximum of 600 pg/m3 not shown on Hg(II) plot, with chosen scale.

the bachelor measured right maximum of 000 pg/m5 hot shown on right plot, with chosen scale.

Figure 25. The distributions of measured and modeled concentrations for configuration 1B.

#### 2005\_ox20\_pf25\_W80K



Figure 26. The distributions of measured and modeled concentrations for configuration 1C.

#### 2005\_ox33\_pf10\_W40K



Figure 27. The distributions of measured and modeled concentrations for configuration 2A.

#### 2005\_ox10\_pf10\_W40K



Figure 28. The distributions of measured and modeled concentrations for configuration 3A.

#### 2005\_ox20\_pf10\_W40K\_Hgred50



Figure 29. The distributions of measured and modeled concentrations for configuration 1D.

#### 2005\_ox20\_pf10\_W40K\_Hgred75



Figure 30. The distributions of measured and modeled concentrations for configuration 1E.

#### 2005\_ox33\_pf10\_W40K\_Hgred50



Figure 31. The distributions of measured and modeled concentrations for configuration 2B.

#### 2005\_ox33\_pf10\_W40K\_Hgred75



Figure 32. The distributions of measured and modeled concentrations for configuration 2C.





Figure 33. The distributions of measured and modeled concentrations for configuration 2D.



2005\_ox10\_pf10\_W40K\_base\_emit

Figure 34. The distributions of measured and modeled concentrations for configuration 3B.

# 8. Simulation Results

# 8.1. Global Mercury Budget

Figure 35 shows a summary of the 2005 emissions and deposition fluxes for the base case (1A). The total mercury emissions – using the net emissions of Hg(0) from soil/vegetation and the ocean – was ~6400 Mg/yr, while the total, comparable deposition was ~6200 Mg/yr. Note that more significant figures are shown in this figure than are justified by the accuracy of the estimates, in order to preserve the values for future calculations without introducing unnecessary round-off error. The slight (~3%) imbalance between emissions and deposition may reflect one or more of the following situations:

- The emissions and deposition for any given year will not usually balance out exactly, even if the global system is at "steady state", as both are governed by numerous stochastic processes.
- Like all mercury models, there are numerous uncertainties in characterization of emissions and deposition.
- Emissions during 2005 may have been increased relative to previous years.

Overall, the net flux of Hg(0) from terrestrial surfaces – not including anthropogenic, biomass burning, and geogenic sources – is estimated to be ~760 Mg/yr during 2005, i.e., there was a net upward flux of elemental mercury from terrestrial surfaces. For the ocean, the comparable, model-estimated net Hg(0)flux during 2005 is ~2600 Mg/yr. As shown in Figure 2 above (page 11), these net flux results are reasonably consistent with many other mercury modeling analyses.

In Figure 36 through Figure 45, the comparable mass balance results for other model configurations are shown. In all configurations, the terrestrial and oceanic surfaces are net emitters of Hg(0). Also, in all configurations, there is a small (~2-3%) imbalance in global emissions and deposition.



Figure 35. Global mercury budget for base case (1A).



Figure 36. Global mercury budget for model configuration 1B.



Figure 37. Global mercury budget for model configuration 1C.



Figure 38. Global mercury budget for model configuration 2A.



Figure 39. Global mercury budget for model configuration 3A.



Figure 40. Global mercury budget for model configuration 1D.



Figure 41. Global mercury budget for model configuration 1E.



Figure 42. Global mercury budget for model configuration 2B.



Figure 43. Global mercury budget for model configuration 2C.



Figure 44. Global mercury budget for model configuration 2D.



Figure 45. Global mercury budget for model configuration 3B.

#### 8.2. Source Attribution for Great Lakes Mercury Deposition

Figure 46 shows the deposition attributed to different source types – anthropogenic, geogenic, biomass burning, prompt reemission, land/vegetation, and the ocean – to each of the Great Lakes. The values shown are for deposition directly to the lakes. Estimates for deposition to each lake's watershed were also made, but are not shown here. The figure also shows estimates for an area-weighted average over the all five of the Great Lakes. In each panel of the figure, estimates are shown for the base case as well as the 10 alternative model configurations considered.

The same data are shown in Figure 47 but expressed as fractions of the total estimated deposition to each lake. In Figure 48 and Figure 49, comparable plots are shown that include country-specific estimates of the anthropogenic contributions to each of the Great Lakes from the United States, Canada, Mexico, China, Russia, India, and all other countries. Due to resource and time limitations, not all of the model configurations could be included in this more detailed source-attribution analysis. However 8 out of the 11 total configurations studied could be included.

Several observations can be made regarding these results.

- First, as was found with the model evaluation analysis, differences among the base case and the various alternative configurations were generally not very dramatic.
- In most cases, the smallest deposition fluxes were estimated by configurations with either slow oxidation kinetics (3A) or the default oxidation kinetics with significant plume Hg(II) reduction (1D, 1E). The reduction in deposition in these cases tended to be on the order of 10-20% less than the base case.
- In contrast, configurations with fast oxidation kinetics (2A, 2B, and 2C) -- with emissions adjusted so that realistic Hg(0) concentrations would be generated generally produced deposition on the order of 10-20% higher than the base-case. It is also noted that configuration 3B (with slow kinetics but unadjusted emissions) also produced comparable high deposition estimates, but we remind the reader that this configuration (along with 2D) is considered to be less likely because it did not generate realistic Hg(0) concentrations.
- Direct anthropogenic emissions tended to have the highest impact on Lake Erie (~35-57% of total estimated deposition) and the lowest impact on Lake Superior (~22-28%), with intermediate impacts on the other lakes.
- United States anthropogenic sources directly contributed on the order of ~10-25% of 2005 deposition to the Great Lakes basin, on average, using different simulation methodologies. The importance of US contributions to individual lakes varied from ~20-45% (Lake Erie) to ~6-12% (Lake Superior).
- China was generally the country with the 2<sup>nd</sup> highest anthropogenic contribution, behind the United States, contributing on the order of ~5-8% of 2005 deposition to the Great Lakes basin, on average, using different simulation methodologies. The importance of Chinese anthropogenic emissions contributions to individual lakes was much more uniform than that for the U.S., as expected, given their relative remoteness.

- Canada's direct anthropogenic sources were estimated to contribute on the order of ~2% of the total model estimated deposition to the Great Lakes during 2005. India, Mexico, and Russia were all estimated to contribute on the order of ~0.5–1% of the total 2005 deposition.
- The total direct anthropogenic contribution from all "other" countries in the world during 2005 was on the order of ~4-6% of the total model-estimated deposition.
- The remainder of the deposition came from oceanic natural emissions and re-emissions of previously deposited mercury (~32-38%), terrestrial natural emissions and re-emissions (16-24%), biomass burning (~5-6%) and geogenic emissions (~6-7%).

These overall source-attribution results are similar to the findings of other source-attribution studies. Examples include the following.

- The GEOS-Chem model was used to develop source-attribution estimates for North America as a whole i.e., all of Mexico, the United States, and Canada -- for 2005-2011 (Chen et al., 2014). Results showed that 9% of North American deposition could be attributed North American anthropogenic emissions, while 27% and 64% of North American deposition could be attributed to other anthropogenic emissions from other regions and "natural" emissions, respectively. Natural emissions in this analysis included emissions and re-emissions from all oceanic and terrestrial emissions pathways other than direct anthropogenic emissions. As discussed above, these "natural" pathways include re-emissions of mercury from previously deposited anthropogenic emissions.
- In a related analysis (Zhang et al., 2012b) 12-21% of 2008-2009 mercury deposition to the contiguous U.S. was attributed to North American anthropogenic sources, but 22-39% of deposition in the Ohio River valley region was attributed to North American anthropogenic sources.
- In another GEOS-Chem-based analysis (Selin and Jacob, 2008), 20% of contiguous U.S. mercury deposition for 2004-2005 was attributed to North American anthropogenic sources, but as much as 50-60% of the deposition in the industrial Midwest and Northeast was attributed to these sources.
- Simulations with the CAM-Chem-Hg model (Lei et al., 2013) found that 22% of total 1999-2001 mercury deposition in the United States could be attributed to U.S. anthropogenic emissions, while in industrial regions, ~50% of the deposition was due to these domestic emissions.
- The CMAQ model (with GEOS-Chem boundary conditions) was used to estimate sourceattribution for 2005 mercury deposition to 6 regions within the U.S. (Lin et al., 2012). Results showed that 25% of deposition in the East Central and 29% of deposition in the Northeast U.S. could be attributed to U.S. anthropogenic emissions, while the overall average over the Continental U.S. (CONUS) was 11%.

- CMAQ model simulations with boundary conditions generated by the Mozart global model (Grant et al., 2014) found that U.S. fossil-fueled power plants contributed significantly more to Lake Erie than to other Great Lakes, with contributions ranging up to ~50% in portions of the lake during some seasons. Contributions to mercury deposition from Chinese anthropogenic emissions varied from ~1-10% over the Great Lakes basin, with the largest relative impacts on Lake Superior.
- In a measurement-based study, Keeler et al (2006) found that approximately 70% of the wet deposition of mercury could be attributed to local and regional sources in Eastern Ohio (in the vicinity of Lake Erie).



Figure 46. Model estimated atmospheric mercury deposition to the Great Lakes arising from different source types during 2005.



Figure 47. Fraction of model estimated atmospheric mercury deposition to the Great Lakes arising from different source types during 2005.



Figure 48. Model estimated atmospheric mercury deposition to the Great Lakes arising from different source types during 2005, including selected country-specific anthropogenic contributions.





100% 90% 80% Model Estimated Mercury Deposition Flux (ug/m2-yr) 70% 60% 50% 40% 30% 20% Lake Michigan 10% 0% oxid oxid 33%, plume particle adj reduction 25%, WETR ocean/land 50% (1D) oxid 33%, plume reduction 50% (2B) oxid 33%, plume reduction 75% (2C) oxid 33%, base emit (2D) plume reduction 75% (1E) base (1A) 80K (1C) emit (2A)





Figure 49. Fractions of model estimated atmospheric mercury deposition to the Great Lakes arising from different source types during 2005, including selected country-specific anthropogenic contributions.
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