Atmospheric Mercury in the Great Lakes Region

An Evaluation of the Community Multiscale Air Quality Model and Implications for Research and Policy

by

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A Master’s Thesis

submitted in partial fulfillment of the requirements for the degree of

Master of Science in Environmental Studies – Environment & Resources

at the

University of Wisconsin-Madison

under the advisement of Associate Professor Tracey Holloway
Abstract

Atmospheric mercury is a significant source for methylmercury (MeHg), a dangerous neurotoxin, associated with muscle incoordination, vision loss, and speech/throat motor problems. In order to control MeHg exposures, policy-makers need a clear understanding of the atmospheric mercury cycle to link emissions control options with health outcomes. Past research on mercury has highlighted many uncertainties in scientific understanding for the atmospheric mercury cycle, especially gas-particle partitioning, chemical processing and dry and wet deposition rates. These areas of uncertainty are heavily impacted by two factors: a lack of ambient concentration measurements for model comparison, and the high complexity of mercury chemistry.

This research evaluates the representation of mercury emissions, chemistry transport and deposition in a state-of-the-art, policy-relevant regional chemical transport model developed by the U.S. EPA: The Community Multiscale Air Quality Model (CMAQ) version 4.6. The model was run over the continental U.S. and the Great Lakes Region for the year 2003, using constrained meteorology from the Weather Research and Forecasting Model (WRF), and SMOKE-processed emissions based on the 2002 National Emissions Inventory. For the continental U.S., simulations were performed at a 36 km x 36 km horizontal resolution, and for the Great Lakes region, at a 12 km x 12 km horizontal resolution. CMAQ model results were compared with full-year continuous speciated ambient mercury concentration measurements collected at two sites in Wisconsin, one rural (Devil’s Lake) and the other urban (Milwaukee). Model wet deposition was also compared with observations from the Mercury Deposition Network (MDN) for all available sites, the only standard source of mercury measurement data.
Compared to MDN quasi-weekly measurements, CMAQ generally under-predicted total wet deposition with an average fractional bias of -47% in the Great Lakes, although error was smaller in the summer (June-August), at about -39%. Inaccuracies in precipitation account for about 50% of wet deposition error in the Great Lakes, suggesting that inaccuracies reflect model processes, not just meteorology. Model surface ambient concentrations for Hg\(^0\) agreed with measurements at the Devil’s Lake site, reflecting accurate estimations of global background concentrations, while at the Milwaukee site, Hg\(^0\) was under-estimated, suggesting an under-estimate for urban emissions. Reactive species were significantly over-predicted at both sites, by as much as a factor of 25 for RGHg and a factor of 5 for PHg. High modeled surface concentrations of both RGHg and PHg at Devil’s Lake are largely due to the over-production of reactive species from background Hg\(^0\) pools, which compose about 87% of model surface RHG concentrations; high modeled reactive mercury concentrations over Milwaukee were equally influenced by local emissions and chemical production, with 44% attributable to emissions and 66% to chemical production.

This analysis clearly demonstrates the need for more research into atmospheric mercury, particularly for dry deposition and chemical cycling. While current model assumptions suggest background Hg\(^0\) as the ultimate source for nearly all deposited mercury, the associated model processes were shown to be unrealistic. Thus model conclusions about the relative importance of local versus global emissions are not reliable. This high level of uncertainty directly impacts the design of mercury control policies. If local reactive emissions are the dominant source, local to regional emission control strategies are appropriate; if global Hg\(^0\) is the main driver for deposition, then coordinated international action is required. To reduce these uncertainties, additional measurements of dry deposition,
ambient concentrations and further laboratory studies are necessary, with results used to support model development and validation.
Acknowledgements

This work is the sum of many contributions from many people and my thanks to all the wonderful people who have helped me during my time at UW-Madison. My advisor, Prof. Tracey Holloway, offered more than just guidance and expertise during the research process, but also continuously helped focus my work where efforts would have the greatest benefit. Prof. Jamie Schauer’s help allowed this study to become something much stronger than I had imagined. Thank you both for your help and support.

This study would not exist without the field work from Prof. Schauer, and Dr. Andrew Rutter, who also provided the education that my work built upon. Dr. Scott Spak served as a phenomenal mentor and without his teaching, there is no way that any of the modeling would have been completed.

Thanks are also due to my lab group – Steve Plachinski, Dr. Meiyun Lin, Claus Moberg, Erica Bickford, and Jami Morton – for their humor and shared knowledge. My colleagues and friends at the Nelson Institute, particularly those in the CHANGE program, have invisible fingerprints throughout this research, and I would like to thank them all for many thoughtful discussions. I would also like to thank the faculty, staff and students at SAGE for their support and patience.

Finally, there is nothing that I accomplish that does not directly involve the help, support, kindness and love from my family. Craig, your support and patience are unparalleled and I cannot thank you enough. To my mother, father and sister – you are in everything I do and I am always the better for it.
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>i</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>iv</td>
</tr>
<tr>
<td>List of Tables</td>
<td>vii</td>
</tr>
<tr>
<td>List of Figures</td>
<td>viii</td>
</tr>
<tr>
<td><strong>Chapter 1 – Atmospheric Mercury: A Global Pollutant, A Regional Problem or Both?</strong></td>
<td>1</td>
</tr>
<tr>
<td>Mercury and Health</td>
<td>2</td>
</tr>
<tr>
<td>Atmospheric Mercury</td>
<td>3</td>
</tr>
<tr>
<td><strong>Emissions</strong></td>
<td>4</td>
</tr>
<tr>
<td><strong>Chemistry</strong></td>
<td>5</td>
</tr>
<tr>
<td><strong>Deposition</strong></td>
<td>6</td>
</tr>
<tr>
<td><strong>Vulnerable Populations</strong></td>
<td>7</td>
</tr>
<tr>
<td>Atmospheric Mercury Uncertainty and Policy</td>
<td>8</td>
</tr>
<tr>
<td>Research Objectives</td>
<td>9</td>
</tr>
<tr>
<td>Figures</td>
<td>11</td>
</tr>
<tr>
<td>References</td>
<td>13</td>
</tr>
<tr>
<td><strong>Chapter 2 – Modeling the Mercury Cycle</strong></td>
<td>16</td>
</tr>
<tr>
<td>Introduction</td>
<td>16</td>
</tr>
<tr>
<td>Community Multiscale Air Quality Model</td>
<td>18</td>
</tr>
<tr>
<td>Emissions Processing</td>
<td>22</td>
</tr>
<tr>
<td><strong>The 2002 National Emissions Inventory</strong></td>
<td>22</td>
</tr>
<tr>
<td><strong>The Sparse Matrix Operator Kernel Emissions Model</strong></td>
<td>25</td>
</tr>
<tr>
<td>Meteorology Processing</td>
<td>26</td>
</tr>
<tr>
<td><strong>The Weather Research and Forecasting Model</strong></td>
<td>26</td>
</tr>
<tr>
<td>Conclusions</td>
<td>32</td>
</tr>
<tr>
<td>Figures</td>
<td>33</td>
</tr>
<tr>
<td>References</td>
<td>47</td>
</tr>
<tr>
<td><strong>Chapter 3 – Model Evaluation for Atmospheric Mercury</strong></td>
<td>50</td>
</tr>
<tr>
<td>Introduction</td>
<td>50</td>
</tr>
<tr>
<td>Emissions and Meteorology Evaluation</td>
<td>52</td>
</tr>
<tr>
<td><strong>Mercury Emissions</strong></td>
<td>52</td>
</tr>
<tr>
<td><strong>Meteorology</strong></td>
<td>57</td>
</tr>
<tr>
<td>CMAQ Deposition Evaluation</td>
<td>62</td>
</tr>
<tr>
<td>CMAQ Atmospheric Concentration Evaluation</td>
<td>68</td>
</tr>
<tr>
<td><strong>Devil’s Lake</strong></td>
<td>69</td>
</tr>
<tr>
<td><strong>Milwaukee</strong></td>
<td>72</td>
</tr>
<tr>
<td>Current Areas of Uncertainty in Atmospheric Mercury Chemistry and Transport</td>
<td>74</td>
</tr>
<tr>
<td>Conclusions</td>
<td>76</td>
</tr>
<tr>
<td>Figures</td>
<td>79</td>
</tr>
<tr>
<td>References</td>
<td>119</td>
</tr>
<tr>
<td><strong>Chapter 4 – Atmospheric Mercury Modeling Results and Discussion</strong></td>
<td>124</td>
</tr>
</tbody>
</table>
# Table of Contents

- Introduction 124
- The Influence of Imported Versus Local Emissions for Mercury 125
- CMAQ Model Chemistry 130
- CMAQ Deposition and Transport 135
- Conclusions and Next Steps 138
- Figures 141
- References 167

**Chapter 5 – Implications for Atmospheric Mercury Research and Policy** 168
- Introduction 168
- U.S. Atmospheric Mercury Policy 169
- Looking Forward – Developing Mercury Policy from Science 171
- References 173
List of Tables

Chapter 2
Table 2-1 – Default initial and boundary conditions for CMAQ version 4.6, and the initial and boundary conditions used in the CMAQ run for this study

Table 2-2 – Table of mercury chemical reactions and their rates used in CMAQ version 4.6

Table 2-3 – List of data sources the EPA compiles in the NEI

Table 2-4 – List of sectors used in emissions processing with the SMOKE model

Supplemental Table 2-A – List of data sources compiled for the NARR dataset

Chapter 3
Table 3-1 – Total and daily average dry deposition to CONUS and Great Lakes domains

Table 3-2 – Total and daily average wet deposition to CONUS and Great Lakes domains

Table 3-3 – Wet deposition statistics comparing model results and observations for the CONUS domain

Table 3-4 – Ambient surface concentration statistics comparing model results and observations at the Devil’s Lake sites (rural)

Chapter 4
Table 4-1 – Chemical lifetime for Hg⁰ due to gas phase oxidation based on model chemistry

Table 4-2 – Dry deposition lifetime for various modeled species over the Great Lakes domain for comparison with RGHg dry deposition lifetime
List of Figures

Chapter 1
Figure 1-1 – Diagram of the bioaccumulation process

Figure 1-2 – Diagram of the atmospheric mercury cycle

Chapter 2
Figure 2-1 – Diagram of the model framework used in this study

Figure 2-2 – Maps of both the CONUS and Great Lakes model domains showing spatial extent and resolution

Figure 2-3 – Diagram of CMAQ model framework

Figure 2-4 – Diagram demonstrating the differences between an Eulerian and Lagrangian approach to atmospheric modeling

Figure 2-5 – Diagram of SMOKE model framework

Figure 2-6 – Diagram of WRF model framework

Supplemental Figure 2-A – Diagram showing the sigma coordinate levels

Supplemental Figure 2-B – Diagram of the grid used in to model winds (u and v vectors) and mass points

Supplemental Figure 2-C – Diagram of the NARR modeling framework

Chapter 3
Figure 3-1 – Mercury species percentage of annual total mercury emissions over the CONUS domain

Figure 3-2 – Sector percentage of annual total mercury emissions for both the Great Lakes and CONUS domains

Figure 3-3 – Comparison of model performance for temperature due to an increase in horizontal grid resolution (36 km × 36 km versus 12 km × 12 km) using NCDC observations

Figure 3-4 – Maps of total monthly precipitation for January and July comparing the 36 km × 36 km resolution and 12 km × 12 km horizontal resolution with NCDC observations
Figure 3-5 – Maps of total daily precipitation for January 15th and August 15th comparing the 36 km × 36 km horizontal resolution and 12 km × 12 km horizontal resolution with NCDC observations

Figure 3-6 – Map showing model cold bias for the month of June

Figure 3-7 – Maps showing monthly average percent fractional bias for 2-meter water vapor mixing ratio for January, April, July and October

Figure 3-8 – Maps of total dry deposition for January, April, July and October over the CONUS domain

Figure 3-9 – Mercury species percentage of annual total mercury dry deposition over the CONUS domain

Figure 3-10 – Map of MDN sites in the U.S., Canada and Mexico

Figure 3-11 – Mercury species percentage of annual total mercury wet deposition over the CONUS domain

Figure 3-12– Maps of total monthly wet deposition for January, April, July, and October comparing with MDN observations over the CONUS domain

Figure 3-13 – Graph of average percent fraction bias for wet deposition in the 36 km × 36 km horizontal resolution model run compared with MDN observations for all sites in the CONUS domain, and only those sites in the Great Lakes domain

Figure 3-14 – Scatter plots comparing model precipitation and wet deposition with observations from the MDN for January, April, July and October

Figure 3-15 – Scatter plots comparing percent fractional bias for wet deposition and precipitation for January, April, July and October

Figure 3-16 – Time series showing surface concentrations for each mercury species at Devil’s Lake (rural) for both model results and observations

Figure 3-17 – Time series for the month of July showing RGHg and PHg surface concentrations using base model results, scaled model results and observations at Devil’s Lake (rural)

Figure 3-18 – Fourteen-day running average for each mercury species at Milwaukee (urban) for both model results and observations

Chapter 4
Figure 4-1 – Maps of average monthly surface concentrations during April and July for each mercury species for the base case, case EMIS and case IMPT

Figure 4-2 – Time series comparing model results and observations for RHg surface concentration at both Devil’s Lake (rural) and Milwaukee (urban) for the base case, case EMIS and case IMPT for April and July

Figure 4-3 – Time series for April and July showing RGHg and PHg surface concentrations using case IMPT model results, scaled case IMPT model results and observations at Devil’s Lake (rural)

Figure 4-4 – Scatter plots comparing model wet deposition and MDN observations over the Great Lakes domain for April and July for the base case, case EMIS and case IMPT

Figure 4-5 – Maps of total dry deposition for April and July showing percent contribution from emitted and imported reactive species

Figure 4-6 – Maps of average monthly surface concentrations for RHg and main Hg⁰ gas phase oxidants

Figure 4-7 – Spatial correlations for mercury species and main Hg⁰ gas phase oxidants over the entire model year at each model layer

Figure 4-8 – Maps of dry deposition lifetime at the surface for Hg⁰ and RGHg in January, April, July and October

Figure 4-9 – Graph of average monthly wind direction from the model and observation at Devil’s Lake, and maps of average winds for April, May 1-15th, July and October

Supplemental Figure 4-A – Average concentration for each mercury species over the CONUS domain for July

Supplemental Figure 4-B – Average inflow at the western boundary for the Great Lakes domain for each mercury species
Chapter 1

Atmospheric Mercury: A Global Pollutant, Regional Problem or Both?

The Great Lakes are the largest surface freshwater system in the world and provide valuable resources to the over 35 million people [Government Canada and U.S. EPA, 1995], Canadian and American, living within the watershed. Yet, a dangerous form of mercury, methylmercury, has been found in fish throughout the Great Lakes region and poses a significant public health risk. Methylmercury (MeHg) is highly toxic and has a number of severe health impacts, particularly in cases of prenatal exposure. As a result, the most current data shows over 3,000 fish advisories for mercury contamination in the U.S., and over 250 in Wisconsin alone [U.S. EPA, 2009].

Mercury can enter aquatic systems through a variety of pathways, and in the U.S., deposition of atmospheric mercury is one of the most significant sources of mercury to waterbodies. Once deposited, mercury can be methylated by aquatic bacteria and move up the food chain through bioaccumulation. Awareness of this cycle prompted the United States Congress to commission a report on mercury, completed in 1997, which found mercury emissions from electricity-generating units (EGUs) to be a significant health risk, and therefore, subject to additional regulation. As a result the U.S. Environmental Protection Agency developed the Clean Air Mercury Rule (CAMR) in 2005 to regulate mercury emissions from EGUs using a cap and trade scheme. The CAMR was the first national policy dealing with atmospheric mercury emissions.

The research presented here aims to further atmospheric mercury science and to inform the development of mercury policy for the protection of public health. This study focuses on the Great Lakes Region, and Wisconsin in particular, because of high of
anthropogenic emissions, large populations and the social, economic and cultural significance attached to the health of the Lakes themselves. Wisconsin is also the first and only state to regulate atmospheric mercury emissions after passing the Wisconsin Mercury Rule in 2008, and has a strong history for atmospheric mercury science. In the 1980’s inland lakes in Wisconsin were the first indicators that atmospheric mercury deposition is a significant source of methylmercury found in fish [Fitzgerald and Watras, 1989; Rada et al., 1989; Fitzgerald and Clarkson, 1991]. In addition, we utilize measurement data collected in Southern Wisconsin, which gives this study the unique opportunity to compare model results with long-term continuous observations of atmospheric mercury concentrations.

Mercury and Health

Methylmercury is a powerful neurotoxin, especially for children. In adults, symptoms of methylmercury poisoning include tingling or ‘pins and needles’, muscle incoordination, vision loss, and speech/throat motor problems. Heart disease has also been associated with MeHg exposure, although this connection is not currently well understood [Virtanen et al., 2007; Salonen et al., 1995]. Mental retardation, deafness, ataxia, cerebral palsy, and vision loss have been found in instances of prenatal MeHg exposure, most notably in two large-scale methylmercury poisoning events – one in Minimata, Japan, and a second in Iraq. Throughout the 1950’s, methylmercury was dumped directly into Minamata Bay, an area where fishing was the dominant occupation and source of food. These already high concentrations of MeHg were then further concentrated through bioaccumulation, which caused severe health problems throughout the town’s population, including cerebral palsy, blindness, and even death. In the Iraqi case, methylmercury was used as an antifungal agent and methylmercury-treated grain caused widespread poisoning in the early 1970’s.
Methylmercury exposures at these levels are highly unlikely today, largely because of precautionary measures established as a result of both accidents. However, recent research [e.g. Grandjean et al., 1997] has connected lower levels of prenatal methylmercury exposure to developmental delays in speech, motor skills, and mental capacity with effects becoming more visible with age.

Methylmercury in Great Lakes fisheries is most often the result of inorganic mercury that is methylated by bacteria living in anoxic lakebeds. As shown in Figure 1-1, the newly formed MeHg then moves through the aquatic food chain, where it bioaccumulates. Most of the mercury entering aquatic systems is due to the deposition of mercury from the atmosphere. Atmospheric mercury is found across the globe, and thus, while the Great Lakes are vulnerable to significant atmospheric deposition due to their basin size and surface area, atmospheric mercury impacts methylmercury exposure throughout the world.

**Atmospheric Mercury**

In the atmosphere, mercury is identified in three forms: gaseous elemental mercury (Hg⁰), reactive gaseous mercury (RGHg), and particulate mercury (PHg). Particulate mercury is usually gaseous oxidized mercury (RGHg) attached to particulate matter. Elemental mercury can exist in particulate form, but its non-reactivity generally inhibits adsorption to aerosols. Global mercury concentration estimates in the Northern hemisphere range from 1.5 to over 3 ng/m³, averaging to about 1.7 ng/m³ [Slemr et al., 2003]. Because of fewer emission sources, the average concentration is slightly less in the Southern hemisphere.

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1 Methylmercury is readily stored in fatty animal tissues, and instead of being eliminated, concentrations increase with each trophic level.

2 For our purposes here, “reactive mercury” will refer to combined gaseous reactive mercury and particulate mercury. “Mercury” is used as an umbrella term to indicate all mercury species – elemental, gaseous reactive and particulate.
at around 1.2 ng/m$^3$ with a range from 1.0 to 1.5 ng/m$^3$ [Temme et al., 2003]. Of the global atmospheric mercury pool, about 95% is elemental, with particulate and reactive gaseous mercury making up the remaining 5% [Morel, 1998]. These three mercury species are the atmospheric pollutants that can become methylmercury, and each possesses unique chemical characteristics that control its respective influence on methylmercury production and therefore, human health.

Gaseous elemental mercury$^3$ is a stable chemical species, residing in the atmosphere for one to one and half years [Mason and Sheu, 2002], and it does not easily react with other chemical species. This long atmospheric lifetime allows Hg$^0$ to be transported across the globe, traveling between the Eastern and Western hemispheres, and these global background levels dominate mercury concentrations in the Earth’s lower atmosphere.

Reactive mercury (RHg) has different chemical characteristics and unlike Hg$^0$, it is unstable and readily combines with other atmospheric constituents or deposits to the Earth’s surface. The atmospheric lifetime of RGHg is considered to be on the order of about twenty days [Slemr et al., 1981] – a short-lived species relative to elemental mercury. The lifetime of particulate mercury is dependent on particle size, local topography and weather patterns, but is still on the order of about 5-7 days, similar to other aerosols [Lynam and Keeler, 2005].

**Emissions**

Anthropogenic mercury emissions are a large source of atmospheric mercury. Studies have consistently shown a marked increase in environmental mercury concentrations coincident with the industrial revolution [e.g. Mason and Sheu, 2002]. Coal-fired electric

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$^3$ While the inhalation of gaseous elemental mercury is extremely toxic to humans, levels in the atmosphere are too low to have any direct human health impact – the EPA’s reference concentration (RfC) is 3x10$^{-4}$ mg/m$^3$, while ambient measurements range from 1.0 x10$^{-5}$-2.0 x10$^{-5}$ mg/m$^3$. [ATSDR 1999]
utility plants are the largest contributor, followed by other coal-combustion units attached to commercial, industrial and institutional point sources, such as large processing plants, refineries and manufacturing facilities. Currently, total anthropogenic mercury emissions in the U.S. average around 110 tons per year [U.S. EPA, 2002], reflecting significant reductions in the past decade due to air quality regulations. Globally, anthropogenic emissions are estimated at about 2,000 tons per year [Lindberg et al., 2007; Pirrone et al., 1996].

In addition to anthropogenic emissions, biogenic sources are also an important part of the global mercury budget. Evasion from soil and water, along with other natural processes (e.g. volcanic eruptions, wildfires) are estimated to contribute anywhere from 880 to 3,300 tons of mercury to the global atmosphere annually, where the wide range in estimates reflects the difficulty in measuring mercury fluxes [Gustin and Lindberg, 2005]. Biogenic emissions are largely in the form of Hg$^0$ due to continuous out-gassing from the Earth’s crust and surface waters. High reduction rates in the soil for reactive gaseous mercury to elemental mercury may also increase natural emissions as well. In characterizing biogenic emissions, the effect of previously deposited anthropogenic mercury is problematic. Quantifying the relative contribution of anthropogenic ‘re-emissions’ to natural mercury sources is important since it will have implications for mercury pollution regulation and policy. In the case of re-emissions, changes in anthropogenic emissions may lead to changes of biogenic emissions. Since non-anthropogenic emissions cannot be controlled, correct estimates of controllable anthropogenic emissions are critical for shrinking the global mercury pool.

The percentage of elemental and reactive mercury is an important health issue as reactive mercury is more likely to be absorbed and methylated by bacteria than elemental mercury [Ullrich et al., 2001]. Of the total gaseous mercury emitted, in the U.S. and globally,
most is in the form of elemental mercury. For some point sources, however, reactive mercury can compose over 95% of total mercury emissions [Park et al., 2008].

*Chemistry*

The complex chemical cycling of atmospheric mercury species is not yet fully understood and is the focus of many atmospheric modeling studies. Figure 1-2 illustrates the most current knowledge of this intricate cycle as has been developed and is currently used in computational modeling of atmospheric systems. Oxidation of Hg\(^0\) to RHg is a key component in the mercury cycle and may be a significant source of reactive gaseous mercury in the atmosphere. Given the large atmospheric pool and long residence time of elemental mercury, even a slow oxidation rate for elemental mercury may yield nontrivial quantities of reactive mercury. Further, the reaction rate for elemental oxidation has been shown to increase if elemental mercury is in aqueous phase [Lin and Pehkonen, 1999], which can have implications for MeHg concentrations depending on local climate.

*Deposition*

The final atmospheric process in the mercury biogeochemical cycle is deposition. Atmospheric mercury can be either wet or dry deposited. Wet deposition requires precipitation as a medium for the transfer of atmospheric mercury to the Earth’s surface. Dry deposition occurs when mercury layers onto surfaces due to chemical and physical attraction. Dry deposition is considered an important removal process for gaseous reactive mercury, but dry deposition of Hg\(^0\) is thought to be much lower due to the species’ chemical stability. Particulate mercury can also dry deposit, but not as readily as gaseous reactive mercury. Dry deposition of Hg\(^0\) depends heavily on the type of land-cover – for instance, vegetation can take-up elemental mercury, while net dry Hg\(^0\) deposition to water bodies is thought to be
negligible due to high re-emission rates at water surfaces [Schroeder and Munthe, 1998]. The volatility of reactive mercury gives it a high sticking ratio, and current mercury science holds that it dry deposits rapidly to all surfaces. The high water solubility of reactive mercury entails a high wet deposition rate for that species, while elemental mercury is less likely to be absorbed to water droplets and thus has lower wet deposition totals.

Vulnerable Populations

A discussion of atmospheric mercury and methylmercury must also recognize the social relationships that create exposure risks. Populations relying on fishing as a major source of food (e.g. low-income or indigenous groups) can have higher methylmercury exposure levels depending on fish species consumed and frequency of fish consumption. More recently, higher-income populations have been found at risk for MeHg poisoning because of increased consumption of higher-order marine species, such as swordfish.

As an example of the complexity of the mercury cycle and its complicated interactions with human health and the environment, the case of indigenous tribes in the U.S. and Canadian Arctic are illustrative. For these populations, fish and marine species constitute the majority of their diet and nearly all of the consumed species are higher-order predators with high fat content [e.g. Burger et al., 2007]. As a result, blood methylmercury levels are above average throughout these populations, including in women of childbearing age [Fontaine et al., 2008; Walker et al., 2006; Ebinghaus et al., 2002]. Further compounding the health risk is the Arctic environment itself. During polar sunrise, large amounts of $\text{Hg}^0$ are oxidized in intense depletion events, and the newly formed RHg quickly dry deposits [Schroeder et al., 1998]. Similarly, the Great Lakes region has its own unique meteorology and geography that make atmospheric mercury a salient and important issue. The large
population around the lakes and several urban centers contribute hundreds of pounds of mercury to the atmosphere each year. Although it is not yet possible to trace MeHg in fish back to an original source, the research presented here aims to begin that discussion by further characterizing atmospheric mercury in the Great Lakes region.

**Atmospheric Mercury Uncertainty and Policy**

While the general characteristics of each mercury species are widely accepted as outlined above, the orders of magnitude difference between Hg$^0$ and RHg concentrations make exact quantification difficult. It is unclear whether ambient RHg and the resulting MeHg concentrations are driven by local emissions or the chemical production of RHg from background Hg$^0$. Total mercury wet deposition can be estimated with relative confidence due to long-term monitoring networks, but speciation, and therefore the health risk, is unclear. Dry deposition is highly uncertain for all species, largely because observational data is limited to isolated measurements. Combining these uncertainties, it remains ambiguous as to whether the largest threat to public health is from global Hg$^0$ or from local/regional emissions of RHg.$^4$ Additionally, the contribution of non-anthropogenic mercury emissions to atmospheric concentrations is also unknown and may constitute a significant mercury source [Gustin et al., 2000]. Since the rate of deposition and release is highly dependent on ambient mercury concentrations [Ericksen and Gustin, 2004], these emissions may continue to increase before reaching equilibrium and have also yet to be quantified. Biomass burning events are a particular source of mercury with high uncertainty, ranging up to $\pm$ 50% [Wiedinmyer and Friedli, 2007], and generally not included in most atmospheric mercury

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$^4$ Although beyond the scope of this study, it is worthwhile to mention that the factors influencing methylation are also unclear, complicating the development of measures to protect public health.
models because inventories are rare and highly year dependent. Thus, an accurate speciated budget for mercury is still an area of uncertainty given the difficulties in measuring the reactive species and the paucity of monitoring stations around the world. Developing a global budget and a clear description of mercury cycling in the atmosphere are necessary to better understand the impacts of atmospheric mercury on human health.

In response to these gaps in understanding, nearly all atmospheric mercury modeling studies to date have called for more measurement data to better assess theoretical model results. Dry deposition is a dominant removal process in most atmospheric mercury models, but without any data to quantify dry deposition fluxes, modeled contributions to mercury loading may be non-representative [Lin et al., 2007]. These gaps impede the development of regulations and if policies are based on incomplete, or wrong information, they may insufficiently protect human health or alternatively, needlessly increase policy costs. The necessary scope of regulation also changes depending on the dominant source for MeHg. If higher global Hg\(^0\) concentrations are the ultimate source of methylmercury, then policy must focus on international agreements to control mercury releases and measures would likely need to reflect the multiple sources of mercury pollution (e.g. municipal waste, commercial products, atmospheric emissions, etc.). If local/regional emissions of RHg drive MeHg, then the national, regional or state regulation of atmospheric emissions is key.

**Research Objectives**

Given the danger presented by mercury pollution and the state of atmospheric mercury science, the research presented in the following chapters seeks to interrogate the current theoretical formulation of the atmospheric mercury cycle. The study will focus on the Great Lakes Region because of large populations, high numbers of emission sources and its
particular vulnerability as a significant watershed. Research questions for this study aim to limit the uncertainties mentioned above. As will be explained in Chapter 2, the major research tools in atmospheric chemistry are computational models of atmospheric chemistry and transport. These models are often used to inform policy decisions, and the representation of reality built into model code must be verified for sound decision-making processes. With the objective of minimizing human health risk through effective mercury policy development, Chapters 3 and 4 will compare measurements of speciated surface mercury concentrations and total wet deposition with results to evaluate parameterization, and also use model experiments to identify dominant processes. These analyses will speak directly to the adequacy of current chemical transport models and the inclusion of multiple data sources improves interpretation of model results. Based on this evaluation, recommendations for atmospheric mercury model development and areas for further research will be proposed in Chapter 5.

From this introductory discussion, it is clear that the biogeochemical cycle for mercury is complex with important implications for human health. The interactions between the different mercury species, their relative abundance and chemical properties, and the many necessary steps leading to methylmercury exposure require further attention to prevent harm. Understanding the prevailing source of methylated mercury – whether it is the global pool of Hg\(^0\) or local emissions – is an important question for scientists and policy-makers for the protection of public health.
The increase of methylmercury concentration through bioaccumulation occurs since MeHg is readily stored in fatty tissues instead of being eliminated. Any new methylmercury entering the ecosystem is captured in the organism and remains in the food chain.
As mercury cycles through the environment, it can change chemical form and is subject to transport on global to local scales. Atmospheric mercury is emitted by both natural and anthropogenic sources, and is eventually deposited on the Earth’s surface through either wet or dry processes.
References


Chapter 2

Modeling the Mercury Cycle

To protect public health, scientists need to understand how mercury cycles through Earth’s systems. The atmosphere is of particular interest because it is the largest source of mercury to aquatic systems, where highly toxic methylmercury is created and enters human consumption streams. The atmospheric mercury cycle is complex, being composed of many parts, and complicated, as these parts are highly interrelated. Consequently, mathematical modeling is an important tool for mercury research because it can process these many different parts. Modeling atmospheric mercury requires large collections of data and scientists must translate the principle systems involved – meteorology, emissions, geography, and chemistry – into mathematical relationships. In reality, these systems are affected by numerous other processes, such as population growth, technology development, trends in energy use, and climate change, that are simplified in air quality models due to their high stochasticity and rapid change. Thus, this high complexity necessitates computational modeling, but also makes it difficult to distill the atmospheric mercury cycle into a computationally efficient form. This chapter lays out the intricate mercury modeling process used in this study with the intent to provide a foundation for the information presented in the chapters to follow.

Introduction

Three computer models, two datasets and many other sub-processes are employed in this analysis of the atmospheric mercury cycle, as shown in Figure 2-1. The model requirements for nearly any chemical species revolve around the basic relationship between meteorology and chemical properties of a given species. This relationship is built in the
chemical transport model (CTM), which takes weather and emissions data as input. These inputs are impossible to measure continuously over an entire region, and thus, this information is also generated using computer models.

In this study, the Community Multiscale Air Quality Model (CMAQ), version 4.6, was used to develop hourly mercury concentration and deposition values over the Continental U.S. (CONUS) at a horizontal resolution of 36 km x 36 km and the Great Lakes region at a horizontal resolution of 12 km x 12 km, using 15 model layers for both runs. Maps for the model regions are given in Figure 2-2. CMAQ captures the dynamic interplay of atmospheric chemical species and meteorology using many chemical and transport mechanisms. Each form of mercury is included in CMAQ chemistry, and how the model portrays their chemical and physical relationships greatly impacts model accuracy.

For CMAQ, like any air quality model, how the geography and meteorology are described greatly impacts final model results since both influence chemical species concentrations in the atmosphere. In this study, the Advanced Research Weather Forecasting Model (ARW-WRF) version 3.0, referred to here as WRF, was used to generate continuous meteorology over the study regions. WRF can assimilate observational data to re-create weather for a given time and place. In this case, the North American Regional Reanalysis (NARR) dataset was used to replicate meteorology for 2003. The NARR is developed by the National Centers for Environmental Prediction (NCEP), and combines many types of observations into one comprehensive dataset from 1979 to the present. Reanalysis – the assimilation of many types of observational data combined with interpolation techniques to provide estimates over data gaps in space and time – is commonly used for model comparison and/or initial conditions, as it is here. Mercury emissions for CMAQ were
created using the Sparse Matrix Operator Kernel Emissions Model version 2.4 (SMOKE) with the 2002 National Emissions Inventory (NEI) from the U.S. Environmental Protection Agency (EPA). SMOKE creates gridded emissions files for mercury and other chemical species. The NEI and meteorology from WRF were processed through the Meteorology Chemistry Interface Processor (MCIP), and used as inputs for SMOKE. The NEI provides information on the types of emissions from a multitude of sources (e.g. mercury from coal-fired power plants, or chlorine from paper factories), which can then be gridded over space and time according to population, climate and geography. Finally, the gridded, time-variant emissions and the WRF meteorology processed through MCIP, are put into the CMAQ model, which creates hourly concentration and deposition fields for multiple chemical species.

The many parts involved in this process each offer multiple entry points for the further study of the atmospheric mercury cycle and are described in more detail below.

Community Multiscale Air Quality Model

The chemical transport model (CTM), in this case the Community Multiscale Air Quality Model (CMAQ), is the primary model for developing a picture of atmospheric mercury. Figure 2-3 lays out the different components for the CMAQ model. The choice of CMAQ as chemical transport model was particular to this study for regulatory, geospatial and chemical reasons. CMAQ is a state-of-the-art “one-atmosphere,” Eulerian model. It calculates how much mass is coming into or out of a certain space over time, as opposed to a Lagrangian, or puff, model that tracks mass and energy as it moves through the atmosphere, and treats many chemical species simultaneously. Figure 2-4 illustrates the differences between these two types of models. CMAQ is the EPA-sponsored air quality model and is
the most widely used CTM for mercury regulatory and research purposes, highlighted in its use for the development of the only national mercury regulation to date, the Clean Air Mercury Rule. The study choice of model domain and resolution also required the use of a regional model, and CMAQ is the most common choice among regional modelers in the United States. Lastly, mercury is a new addition to nearly all atmospheric models, and CMAQ has been the model of choice for most of the atmospheric mercury research to date [e.g. Pongprueksa et al., 2008; Lin et al., 2007; Gbor et al. 2007].

Using CMAQ version 4.6 [Byun and Schere, 2006] with mercury, model chemistry was calculated every 90 seconds, and transport every 15 minutes, producing hourly output files for wet deposition, dry deposition and ambient concentration. Default boundary conditions were applied for the 36 km resolution run over the Continental U.S., and the smaller 12 km resolution run over the Great Lakes used the CONUS model output as hourly boundary conditions. Default boundary conditions used in the CONUS model run are given in Table 2-1a,b. The full 2003 annual CMAQ run was broken into four quarterly runs, re-initializing from the previous days’ concentrations every 24 hours, with 10 days of spin-up\(^1\). For both runs, CMAQ was run with a vertical resolution of 15 model layers, with the model top at about 16,000 m altitude on average, and the top of the surface layer was roughly 50 m altitude as an annual average.

For the chemical transport solver, this study used Carbon Bond Five (CB05) lumped gas phase chemistry [Yarwood et al., 2005], the AERO4 aerosol mechanism [Binkowski and Roselle, 2003], the global mass-conserving Yamartino advection scheme, and the

\(^1\) Thus, the first quarter run lasted from December 21\(^{st}\), 2002 to March 2003, quarter two included the last ten days of March 2003 through to the end of June 2003, quarter three included the last ten days of June 2003 to the end of September 2003, and the final fourth quarter ran from September 20\(^{th}\), 2003 to the end of December 2003. For each quarter, the ten day spin-up was thrown out and not used for analysis.
Asymmetrical Convective Model with mercury (ACM2), which controls cloud formation, vertical diffusion, and eddy diffusion. These elements will be discussed below as is pertinent to atmospheric mercury chemistry in CMAQ. This version of CMAQ builds on CMAQ-Hg [Bullock and Brehme, 2002] with a few modifications in gaseous chemistry and aerosol treatment described in the mercury notes for CMAQ v.4.6 (available at http://www.cmascenter.org/help/model_docs/cmaq/4.6/MERCURY_NOTES.txt).

Developing an effective CTM requires recognition of the complexity of the atmosphere and computational limitations. CB05 manages these two factors by ‘lumping’ chemical species: species are grouped and reacted according to their bond structure instead of by the actual molecule type [Gery et al., 1989]. This greatly reduces the number of computations needed for each calculated time step. CB05 with mercury\(^2\) includes 56 chemical species (52 core species and 4 mercury species) and is an update of the earlier Carbon Bond 4 (CBIV) gas phase mechanism. CB05 serves a dual purpose in that it is the only gas phase chemistry module in CMAQ to include mercury chemistry, and it was also developed for the regional scale [Gery et al., 1989], which suits study focus on the Great Lakes area. The core mechanism uses 156 gas phase reactions, with the mercury reactions from CMAQ-Hg adding another 4 gas phase reactions. Additionally, aqueous chemistry is significant for mercury, as studies have shown that aqueous phase reactions are important for elemental mercury oxidation in the atmosphere [Munthe and McElroy, 1992; Lin and Pehkonen, 1997; Lin and Pehkonen, 1998; Pehkonen and Lin, 1998]. Thus, the CB05 mechanism with mercury has an additional 6 aqueous reactions and 7 sorption/de-sorption reactions. Table 2-2 lists all reactions and equilibria for mercury in CMAQ version 4.6.

\(^2\) CB05 can be used without mercury as well.
The ultimate fate for atmospheric mercury is deposition to the Earth’s surface through either dry or wet deposition, both of which are modeled in CMAQ for mercury. Dry deposition is calculated according to the formula

\[ F_{\text{dry}} = V_d \times C_s \quad \text{[Lin et al., 2006]} \]

where \( F_{\text{dry}} \) is the dry deposition flux based on the deposition velocity, \( V_d \), and the concentration of the chemical species, \( C_s \). Dry deposition velocity is calculated in MCIP, the meteorology preprocessor. In MCIP version 3.4 used here, the M3DRY scheme [Pleim et al., 1999] explicitly models both elemental mercury (Hg\(^0\)) and reactive gaseous mercury (RGHg) dry deposition, and is calculated based on the amount of vegetation cover, vegetation type and stomatal resistance. The inclusion of dry deposition for Hg\(^0\) is a recent update to MCIP, added only with version 3.1, and is based on observational data reported in Lin et al. [2006]. Particulate mercury (PHg) dry deposition is governed by the aerosol scheme, in this case AERO4, not through the M3DRY scheme. For particulates, dry deposition is a function of particle size (see Binkowski and Shankar [1995] for full description), and in CMAQ, PHg is modeled in either the Aitken or accumulation mode; there are no modeled coarse mercury particulates\(^3\).

In CMAQ, mercury is wet deposited in the same manner as all other species with aqueous chemistry. Mercury wet deposition depends on cloud water concentration, \( m^{\text{cld}} \), the lifetime of the cloud, \( \tau_{\text{cld}} \), and the precipitation rate, \( P_r \). Cloud water concentration depends on the species’ scavenging coefficient, which is in turn determined by Henry’s Law

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\(^3\) Aitken mode particles, also called i-mode particles, have aerodynamic diameters less than or equal to 0.1 \( \mu m \), and the aerodynamic diameter of accumulation particles, j-mode particulates, is between 0.1 \( \mu m \) and 2.5 \( \mu m \). Coarse particulates have an aerodynamic diameter greater than 2.5 \( \mu m \).
equilibria\(^4\) (see equations H1 and H2 in Table 2-2), washout time, and cloud properties such as cloud depth, density, water content and temperature. Wet deposition for an aqueous species \(i\), \(w_{dep_i}\), is calculated using

\[
w_{dep_i} = \int_0^{t_{eq}} m_i c\cld P_r dt
\]

[Byun and Schere, 2006].

For particulates, including particulate mercury, wet deposition depends on the particle size. Accumulation and coarse mode particles are assumed to be completely absorbed into the cloud or precipitation (depending on model layer), and the amount wet deposited is then dependent on concentration and cloud properties. For Aitken mode particles, wet deposition differs slightly, in that absorption is a function of time\(^5\). As mentioned earlier, mercury is only modeled in the accumulation and Aitken modes, the model does not include any course particulates for mercury.

Emissions Processing

The 2002 National Emissions Inventory

Like all Eulerian chemical transport models, CMAQ requires gridded emissions data. In this study this information was developed using an emissions model (discussed in the next section) and input data from the 2002 NEI from the U.S. EPA. The emissions inventory files are developed using data from multiple databases and are identified in two groups – criteria air pollutants (CAPs) and hazardous air pollutants (HAPs). Qualitatively, criteria air pollutants are defined as those chemical species judged unhealthy above a set standard, i.e. there is an identified concentration below which the species poses no risk to human health

\(^4\) The scavenging coefficient requires the effective Henry’s Law coefficient, H*, calculated based on the true Henry’s coefficient of the pollutant, its acid dissociation constant and the pH of the cloud.

\(^5\) Thus, any modeled precipitation will deposit all accumulation mode PHg, but Aitken mode PHg may remain in the atmosphere if the cloud lifetime is not sufficiently long enough.
(primary standards) or to the environment (secondary standards), or are chemical precursors to such species. Hazardous air pollutants are defined as those chemical species known or suspected to be carcinogenic or have acceptable risk level\(^6\). Mercury is considered a hazardous pollutant.

The emissions inventory contains the annual emissions for sources across all fifty states, the District of Columbia, Puerto Rico, the Virgin Islands and the territories of federally recognized American Indian nations. The national emissions inventory is a composite of inventories for different source categories: point, nonpoint, mobile, and biogenic. In some cases these are divided even further, for example, nonpoint emission sources include nonroad vehicles (e.g. tractors, ATVs), aircraft, locomotive and marine vehicles, and agriculture. All of the inventories are, however, distributed in a similar fashion – the inventory lists basic information on the geographic location of the source (e.g. for point sources the exact latitude and longitude, or for area sources the state and county), its source classification (e.g. coal-fired power plant, dry cleaning facility, residential wood stoves, etc.), and the total annual emissions for the pollutants relevant to that source. The inventory was prepared using a variety of information sources given in Table 2-3 including direct measurements, models, state/local/tribal databases, and others. The 2002 NEI is not truly ‘raw data’; it is model output compiled into a manageable form. More details on how these inventories were created and compiled for each source category can be found at [http://www.epa.gov/ttn/chief/net/2002 inventory.html](http://www.epa.gov/ttn/chief/net/2002 inventory.html).

\(^6\) Legal definitions of these terms set by the EPA, which differ slightly from the above modeling definitions, identify 6 specific criteria air pollutants and 188 specific hazardous air pollutants.
Beyond the inventories themselves, the 2002 NEI includes a wealth of data required to make the emissions usable for modeling, including the temporal, spatial and chemical properties of the emissions, emissions parameters specific to point, mobile and biogenic, and a few other general parameters. The NEI temporal profile of emissions varies with each source, and this information is used to calculate hourly emissions files from the annual emissions given in the inventory. This is accomplished through the use of pre-determined diurnal, weekly and monthly temporal profiles that are then cross-referenced to different sources – for example there is a temporal profile specific to coal-fired power plants of different ages and type, and another for medical incineration. Spatial information is manipulated in a similar fashion: NEI spatial surrogates map annual emissions onto a specific grid, and restrict those emissions activities to particular grid cell locations and percentage of total grid-cell area. For biogenic sources, information about leaf area index, biomass, emissions fluxes and seasonal variation is also available through the NEI.

All of the NEI data is dependent on the grid resolution and projection chosen by the user, thus requiring that meteorology be created to coincide with the grid and projection provided by the NEI or that the user manipulate the NEI data to fit the desired grid. The chemical speciation data contains cross-referencing information and a speciation profile that separate combined inventory pollutant emissions into the model species required by the specified CTM. As an example, the NEI reports total organic carbon emissions, and the pre-determined speciation profile breaks down that larger category into other species (e.g. ethane, methane, toluene, etc.) based on emission source. This information primarily targets unspeciated organic carbon emissions; most other chemical species are simply given a “breakdown” of 100% into the original species.
Lastly, ancillary information from the NEI describes the specific locations used for area source emissions, look-up tables for information on country, state, county, and source category, a list of sources to exclude for certain chemical species, and a list of output species. 

*The Sparse Matrix Operator Kernel Emissions Model*

CAP and HAP emissions were processed for both study domains through the Sparse Matrix Operator Kernel Emissions Model (SMOKE) version 2.4 using the 2003 meteorology from WRF described below, and the 2002 NEI, the most recent year available. Although some changes would be expected in emissions from 2002 to 2003, these have not been quantified, and further, adding an emissions growth factor would bring in additional sources of error.

SMOKE creates gridded, weather-dependent emissions by reading in the raw emissions inventory data, allocating the emissions in space and time, converting reported species to the chemical classes used in the model chemistry and creating combined output with all the relevant information, as depicted in Figure 2-5. All the emissions from each sector are combined into a single hourly emissions file. Point source emissions must be assigned to the correct vertical model layer depending on stack height, emissions temperature, and other factors. Only point and biogenic sectors use meteorology data to determine emissions. Biogenic mercury sources and biomass burning were not included as they were not available at the time. Canadian point emissions were modeled only for mercury and CAPs, since non-Hg HAP point emissions were not publicly available. Annual averages were used as the basis for U.S. point emissions inventories because hourly or daily Continuous Emissions Monitoring (CEM) data is not available for mercury species. More
information about the 2002 NEI and the emissions sectors used for this modeling study is
given in Table 2-4.

For this study, the grids used to create the meteorology varied slightly from those
used in the published NEI data, and thus required that new spatial references, or surrogates,
be made. This was achieved using a spatial allocator program developed for SMOKE, the
Multimedia Integrated Modeling System (MIMS) Spatial Allocator from the University of
North Carolina.

**Meteorology Processing**

*The Weather Research and Forecasting Model*

For this study, meteorology was generated using WRF-ARW version 3 for 2003. The
Advanced Research WRF modeling system is presented in Figure 2-6 and is composed of
two main subsystems: the WRF Pre-Processing System (WPS) and the WRF-ARW model.
Both subsystems have multiple options available to the user to specify the spatial domain,
physics mechanisms, dynamics, etc. The ARW solver is the dynamical core containing both
the dynamics and physics packages and the heart of the whole system.

The ARW solver is a nonhydrostatic⁷ Eulerian model. The solver uses the sigma
vertical coordinate, which is mass-based and follows surface terrain, with the model top set at
10,000 Pa. [Supplemental Figure 2-A] The horizontal grid uses an Arakawa C-grid
staggering scheme, which helps to minimize error and supports higher grid resolution.
[Supplemental Figure 2-B] Other features include a 3ʳᵈ-order Runge-Kutta time-step

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⁷ WRF does not use hydrostatic equilibrium where the pressure gradient force is assumed equal and opposite to gravity. This assumption is based on a ‘shallow’ atmosphere – where the horizontal scale is much larger than the vertical scale. By using a nonhydrostatic approximation, on the other hand, one can assume a ‘deep’ atmosphere and solve for vertical momentum. Thus, model resolution is not limited in the vertical and smaller scale processes may be included.
integration\textsuperscript{8}, high-order advection scheme\textsuperscript{9}, complete Coriolis terms and possible two-way nesting. There are multiple physics options available for land-surface interactions (including boundary layer and sea surface physics), model microphysics, longwave and shortwave radiation, cloud parameterization and diffusion. Lastly, within the ARW-WRF solver, the incorporation of real data is done through four-dimensional data assimilation (FDDA) or “nudging.” WRF meteorology has four possible nudging fields – the u and v horizontal wind components, specific humidity and temperature – and can be used throughout the entire vertical profile or used only above the planetary boundary layer (PBL).

North American Regional Reanalysis data (NARR) was used to nudge the WRF-ARW meteorology model throughout the entire model. The NARR data consists of raw observations from many sources [Supplemental Table 2-A] that are (re)analyzed using three models: the Eta atmospheric model, a data assimilation system (R-CDAS), and the Noah land-surface model [Rogers et al., 1995; Eta updates particular to NARR noted by Mesinger et al., 2005]. These models smooth inconsistencies inherent in data collection, (e.g., discrete data points in space and time, data collection interruption, etc.) and combine multiple observations across the entire domain into a uniform output. Raw observational data is first fed into the data assimilation system where it is interpolated across the grid and adjusted to best fit all data using a regional optimum interpolation (ROI) process [DiMego et al., 1992]. From this interpolation, the atmospheric model Eta makes a simple forward calculation of the meteorological conditions three hours later, which then serves as new initial conditions. This “first guess” is corrected against available observations, optimized using ROI and then

\textsuperscript{8} The 3\textsuperscript{rd} order Runge-Kutta Scheme is a numerical approximation method using three differentiation steps with the time-step midpoint to arrive at the next point.

\textsuperscript{9} Advection is calculated using a Taylor series approximation, where additional orders of magnitude correspond with higher levels of convergence.
integrated to the next time step. [Supplemental Figure 2-C] The NARR data output from this process is given in GriB\(^1\) format in three-hour increments, and includes some derived categories, such as surface wind stress. Multiple studies have shown that the final NARR dataset agrees well with observations, and is reliable in its larger synoptic structures and variability [Mesinger et al., 2004; Bukovsky and Karoly, 2006].

Nudging with the NARR data was used for all possible variables – u and v wind vectors, temperature and moisture – throughout the vertical profile, including the PBL, as supported by Stauffer et al. [1991], and Otte [2008]. The data assimilation scheme used is a point-by-point analysis, iteratively comparing WPS-processed NARR input across space every three hours, technically giving a three-dimensional assimilation. The method for nudging, given by Skamarock et al. [2008] is

\[
\frac{\partial \theta}{\partial t} = F(\theta) + G_\theta W_\theta (\hat{\theta}_0 - \theta) \tag{Eq. 1}
\]

where \(F(\theta)\) is the modeled result, \(G_\theta\) is the nudging coefficient, and \(W_\theta\) is a function to determine nudging influence in space and time (e.g. turned on or off in the boundary layer) for \(\hat{\theta}_0\) the input data forcing the model output. The nudging coefficient is defined by the user before processing and serves to control for the level of confidence in the nudging input data. Typical values for \(G_\theta\) are on the order of \(10^{-4}\) s\(^{-1}\). Larger values of \(G_\theta\) can overcorrect model calculations causing mass and momentum balance errors, as well as hampering model creation of larger-scale structures (e.g. front lines). If \(G_\theta\) is too small, model errors are allowed to propagate more easily. In this study, all assimilated variables (u and v winds,

\(^1\)GriB stands for gridded binary and it is a format for compressing large quantities of spatially referenced data. There are two GriB formats, first edition (GriB1) and second edition (GriB2).
temperature and moisture) were given nudging coefficients of $3.0 \times 10^{-4}$, following Otte [2008], Seaman [2000] and others.

Meteorology for 2003 was simulated using a two-way nest, using quarterly runs with one month of spin-up. The smaller Great Lakes grid was nested in the larger Continental U.S. (CONUS) domain. The coarser CONUS grid was used for lateral boundary conditions on the finer Great Lakes grid, and the values on the finer grid replace the coarse grid values where the two overlap. Default boundary conditions were used for the larger 36 km × 36 km domain. [Table 2-1] Vertical resolution was set at 30 model layers, concentrated in the lower atmosphere, for both domains, using the eta variable described earlier and WRF default terrestrial data.

The Pleim-Xiu land-surface model was developed with the specific needs of air quality modeling in mind [Xiu and Pleim, 2001], and thus was the LSM used in this study. Land-surface models (LSM) simulate surface fluxes for moisture and heat, which influence ground-level temperature and moisture, and PBL height [McPherson, 2007; Jacobson, 1998]. To make surface moisture flux parameterizations as accurate as possible, the Pleim-Xiu model indirectly uses the NARR data for nudging soil moisture, where discrepancies between modeled and observed values for related parameters – surface temperature and relative humidity – are used to correct temperature and moisture for both surface and deep soil. [Pleim and Xiu, 2000]

The Pleim-Xiu LSM is used in conjunction with the Asymmetric Convective Model version 2 (ACM2) to describe the PBL. ACM2 uses a stability-dependent definition of boundary layer height, the Blackadar boundary layer mixing description, and a combined
local-nonlocal closure scheme for eddy diffusion. By including nonlocal diffusion, ACM2 can account for eddy effects above the grid-cell scale. (Eddy diffusion has been assumed to effect only subgrid processes.) The Blackadar scheme [Pleim, 2006] describes convective mixing as originating at the surface layer and includes flow from each upper layer back to the surface. The ACM2 boundary layer height calculation improves upon past models by using a different equation during unstable atmospheric conditions.

The microphysics scheme chosen for this simulation is the WRF Single-Moment 6-Class (WSM6) [Hong and Lim, 2006]. In meteorology models, the microphysics scheme controls cloud particulates and precipitation drops throughout the atmosphere. The WSM6 includes six water species, and has been shown to result in better precipitation prediction as species velocity can be more precisely simulated.

In WRF, the amount of solar energy passing through the atmosphere can be calculated for both longwave and shortwave radiation, and in this case, the Rapid Radiative Transfer Model (RRTM) was used for longwave radiation with the Goddard shortwave radiation scheme [Chou and Suarez, 1999]. The RRTM uses stored radiation absorption coefficients depending on temperature and pressure for a given model layer, and interpolates to give a continuous representation of the atmosphere’s absorption profile [Mlawer et al., 1997]. This improves over earlier models where changes in absorption coefficients were not smoothed, resulting in discontinuities between model layers. The Goddard shortwave radiation scheme, while not as computationally efficient as other available schemes (e.g. Dudhia), performs well, and is better suited to the regional scale. This scheme groups radiation into spectral bands to lessen computational effort, while maintaining a high level of
sophistication in its incorporation of scattering and the ozone profile, both of which greatly impact the degree of shortwave absorption. [Chou, 1992]

The new Kain-Fritsch model was chosen for cumulus parameterization [Kain, 2004]. It includes shallow (non-precipitating) convective clouds, an improved scheme for simulating downdrafts, and a stricter handling of entrainment (mixing between cloud and non-cloud air masses). This last update has noticeably improved precipitation rates since lenient entrainment rates resulted in widespread light precipitation patterns that did not occur in actual weather systems.

For this study, simple second-order diffusion was used along model levels. The PBL model, ACM2, handles vertical diffusion. Along similar lines, the diffusion rates were calculated using only horizontal winds with the two-dimensional Smagorinsky definition [Smagorinsky, 1963], with ACM2 calculating vertical diffusion rates. An explicit sixth-order numerical diffusion scheme was used in addition to cancel out grid-scale noise in wind fields – particularly valuable when calculating lake breeze effects.

The WRF meteorology output was then processed using the Meteorology Chemistry-Interface Processor (MCIP) version 3.4, which translates model output into form that the emissions and chemical transport models can use. MCIP manipulates the base grid depending on user-specifications – in this case, removing three grid cells around the perimeter, and interpolating the 30 vertical model layers from WRF to 14 layers for CMAQ. The new vertical resolution uses the same terrain-following technique as in the eta variable, which concentrates model layers near the Earth’s surface to better resolve the PBL. Most of the remaining meteorological variables are simply passed through, although MCIP does calculate radiation fields and dry deposition velocities. As shall be explored further in the next chapter,
the dry deposition velocity for mercury species is highly uncertain, and model treatment of dry deposition velocities is an area of significant research interest.

Conclusions

The highly complex nature of the atmospheric mercury cycle requires close attention to the choice of model configuration. By using the best available input data and the most up-to-date mercury modeling science, the framework described above provides a strong foundation for the analysis presented in Chapters 3 and 4. To protect public health, science must present the most accurate picture of atmospheric mercury possible and through the choices given above, this study strives to further atmospheric mercury science.
Figure 2-1 – Model Overview

Chemical Transport Model (CMAQ v 4.6)

Meteorology
- Observed Meteorology Data (NARR)
- Meteorology Model (WRF-ARW v 3)
- Meteorology Pre-processor (MCIP v 3.4)
- Continuous Gridded Meteorology

Emissions
- Emissions Inventory Data (2002 NEI)
- Continuous Gridded Emissions
- Emissions Model (SMOKE v 2.4)

Dry Deposition
Ambient Concentration
Wet Deposition
Maps show a) the 36 km × 36 km horizontal resolution over the Continental U.S. (CONUS domain) and b) the 12 km × 12 km horizontal resolution over the Great Lakes (Great Lakes domain)
Figure 2-3 – CMAQ Model Overview
Figures show a) the Eulerian model and b) Lagrangian model conceptions of space.
Table 2-1 a) – Default Initial and Boundary Conditions in CMAQ v 4.6

<table>
<thead>
<tr>
<th>Species</th>
<th>Sigma (σ) layer range**</th>
<th>1.00-0.98</th>
<th>0.98-0.93</th>
<th>0.93-0.84</th>
<th>0.84-0.60</th>
<th>0.60-0.30</th>
<th>0.30-0.00</th>
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<tbody>
<tr>
<td>Hg (ppm)</td>
<td>1.780 × 10^{-7}</td>
<td>1.770 × 10^{-7}</td>
<td>1.760 × 10^{-7}</td>
<td>1.750 × 10^{-7}</td>
<td>1.740 × 10^{-7}</td>
<td>1.730 × 10^{-7}</td>
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</tr>
<tr>
<td>RGHg (ppm)</td>
<td>2.000 × 10^{-9}</td>
<td>3.000 × 10^{-9}</td>
<td>4.000 × 10^{-9}</td>
<td>5.000 × 10^{-9}</td>
<td>6.000 × 10^{-9}</td>
<td>7.000 × 10^{-9}</td>
<td></td>
</tr>
<tr>
<td>PHg* (µg/m³)</td>
<td>1.080 × 10^{-5}</td>
<td>1.026 × 10^{-5}</td>
<td>9.718 × 10^{-6}</td>
<td>7.558 × 10^{-6}</td>
<td>4.859 × 10^{-6}</td>
<td>1.620 × 10^{-6}</td>
<td></td>
</tr>
</tbody>
</table>

*Only j-mode (accumulation mode) particulate mercury is modeled in boundary conditions.

**See Figure 2-A for an explanation of sigma layers

Table 2-1 b) – Initial and Boundary Conditions for Model Runs

<table>
<thead>
<tr>
<th>Model Run</th>
<th>Initial Conditions</th>
<th>Boundary Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>36 km × 36 km resolution over Continental U.S.</td>
<td>Defaults for CMAQ 4.6 (see Table 4a)</td>
<td>Defaults for CMAQ 4.6 (see Table 4a)</td>
</tr>
<tr>
<td>12 km × 12 km resolution over Great Lakes region</td>
<td>Defaults for CMAQ 4.6 (see Table 4a)</td>
<td>36 km × 36 km resolution over Continental U.S. output</td>
</tr>
<tr>
<td>Chemical Equation</td>
<td>Rate</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td><strong>Gas-phase reactions for Hg</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RG1</td>
<td>$\text{Hg}_2^0(g) + \text{O}_3(g) \rightarrow \frac{1}{2}\text{PHg} + \frac{1}{2}\text{RGHg}$</td>
<td>$2.11 \times 10^{-18} \text{cm}^3\text{molecules}^{-1}s^{-1}$</td>
</tr>
<tr>
<td>RG2</td>
<td>$\text{Hg}_2^0(g) + \text{Cl}_2(g) \rightarrow \text{RGHg}$</td>
<td>$2.6 \times 10^{-18} \text{cm}^3\text{molecules}^{-1}s^{-1}$</td>
</tr>
<tr>
<td>RG3</td>
<td>$\text{Hg}_2^0(g) + \text{H}_2\text{O}_2(g) \rightarrow \text{RGHg}$</td>
<td>$8.5 \times 10^{-19} \text{cm}^3\text{molecules}^{-1}s^{-1}$</td>
</tr>
<tr>
<td>RG4</td>
<td>$\text{Hg}_2^0(g) + \text{OH}_2^{-}(g) \rightarrow \frac{1}{2}\text{PHg} + \frac{1}{2}\text{RGHg}$</td>
<td>$7.7 \times 10^{-14} \text{cm}^3\text{molecules}^{-1}s^{-1}$</td>
</tr>
<tr>
<td><strong>Aqueous-phase reactions for Hg</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RA1</td>
<td>$\text{Hg}_2^0(aq) + \text{O}_3(aq) \rightarrow \text{HgO(aq)}$</td>
<td>$4.7 \times 10^{7} M^{-1}s^{-1}$</td>
</tr>
<tr>
<td>RA2</td>
<td>$\text{HgSO}_4^2(aq) \rightarrow \text{Hg}_2^0(aq) + \text{products}$</td>
<td>$T \exp\left(\frac{31.971T - 12595}{T} \right) s^{-1}$</td>
</tr>
<tr>
<td>RA3</td>
<td>$\text{Hg(OH)}_2(aq) + \text{hv} \rightarrow \text{Hg}_2^0(aq) + \text{products}$</td>
<td>$6.0 \times 10^{-7} * \text{cos(solar zenith angle)} s^{-1}$</td>
</tr>
<tr>
<td>RA4</td>
<td>$\text{Hg}_2^0(aq) + \text{OH}^{-}(aq) \rightarrow \text{Hg}_2^{2+}(aq)$</td>
<td>$2.0 \times 10^{9} M^{-1}s^{-1}$</td>
</tr>
<tr>
<td>RA5</td>
<td>$\text{Hg}_2^{2+}(aq) + \text{HO}_2(aq) \rightarrow \text{Hg}_2^0(aq) + \text{products}$</td>
<td>$1.1 \times 10^{4} M^{-1}s^{-1}$</td>
</tr>
<tr>
<td>RA6</td>
<td>$\text{Hg}_2^{2+}(aq) + \text{HCl}_2(aq) \rightarrow \text{Hg}_2^{2+}(aq) + \text{products}$</td>
<td>$2.09 \times 10^{6} M^{-1}s^{-1}$</td>
</tr>
<tr>
<td>RA7</td>
<td>$\text{Hg}_2^0(aq) + \text{OCl}^{-}(aq) \rightarrow \text{Hg}_2^{2+}(aq) + \text{products}$</td>
<td>$1.99 \times 10^{6} M^{-1}s^{-1}$</td>
</tr>
<tr>
<td><strong>Aqueous-phase equilibria for Hg</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E1</td>
<td>$\text{Hg}_2^{2+} + \text{SO}_3^{-2} \Leftrightarrow \text{HgSO}_3$</td>
<td>$2.0 \times 10^{-13} M$</td>
</tr>
<tr>
<td>E2</td>
<td>$\text{HgSO}_3 + \text{SO}_3^{-2} \Leftrightarrow \text{Hg(SO}_3)^2^{-2}$</td>
<td>$4.0 \times 10^{-12} M$</td>
</tr>
<tr>
<td>E3</td>
<td>$\text{Hg}_2^{2+} + 2\text{Cl}^{-} \Leftrightarrow \text{HgCl}_2$</td>
<td>$1.0 \times 10^{-14} M^2$</td>
</tr>
<tr>
<td>E4</td>
<td>$\text{Hg}_2^{2+} + \text{OH}^{-} \Leftrightarrow \text{HgOH}^+$</td>
<td>$2.51 \times 10^{-11} M$</td>
</tr>
<tr>
<td>E5</td>
<td>$\text{HgOH}^+ + \text{OH}^{-} \Leftrightarrow \text{Hg(OH)}_2$</td>
<td>$6.31 \times 10^{-12} M$</td>
</tr>
<tr>
<td>E6</td>
<td>$\text{HgOH}^+ + \text{Cl}^{-} \Leftrightarrow \text{HgOHCl}$</td>
<td>$3.72 \times 10^{-8} M$</td>
</tr>
<tr>
<td><strong>Henry’s Law Constants for Hg</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H1</td>
<td>$\text{Hg}_2^0(g) \Leftrightarrow \text{Hg}_2^0(aq)$</td>
<td>$1.11 \times 10^{-1} M \text{ atm}^{-1}$</td>
</tr>
<tr>
<td>H2</td>
<td>$\text{HgCl}_2(g) \Leftrightarrow \text{HgSO}_2(aq)$</td>
<td>$1.41 \times 10^6 M \text{ atm}^{-1}$</td>
</tr>
<tr>
<td><strong>Sorption/Desorption rates for Hg</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>$\text{HgCl}_2(aq) \Leftrightarrow \text{HgCl}_2(\text{ sorbed})$</td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>$\text{HgSO}_3(aq) \Leftrightarrow \text{HgSO}_3(\text{ sorbed})$</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>$\text{Hg(OH)}_2(aq) \Leftrightarrow \text{Hg(OH)}_2(\text{ sorbed})$</td>
<td></td>
</tr>
<tr>
<td>S4</td>
<td>$\text{Hg(SO}_3)^2^{-2}(aq) \Leftrightarrow \text{Hg(SO}_3)^2^{-2}(\text{ sorbed})$</td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td>$\text{Hg(OH)}_2(aq) \Leftrightarrow \text{Hg(OH)}_2(\text{ sorbed})$</td>
<td></td>
</tr>
<tr>
<td>S6</td>
<td>$\text{HgOHCl}_2(aq) \Leftrightarrow \text{HgOHCl}_2(\text{ sorbed})$</td>
<td></td>
</tr>
<tr>
<td>S7</td>
<td>$\text{Hg}_2^{2+}(aq) \Leftrightarrow \text{Hg}_2^{2+}(\text{ sorbed})$</td>
<td></td>
</tr>
</tbody>
</table>

All RGHg species sorb/desorb at same time rate based on an adsorption coefficient of $900 \text{l g}^{-1}$ (original of $925 \text{l g}^{-1}$ from Seigneur et al. 1998) and e-folding time of $3600 \text{s}$
<table>
<thead>
<tr>
<th>Source Category</th>
<th>Data Sources for CAPs</th>
<th>Data Sources for HAPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point – Electric Generating Units</td>
<td>EPA’s Emission Tracking System (ETS); Continuous Emissions Monitoring Data (CEM); Department of Energy fuel use information</td>
<td>EPA’s Maximum Achievable Control Technology (MACT); Toxic Release Inventory (TRI); State and local data</td>
</tr>
<tr>
<td>Point – Other Stationary Sources</td>
<td>Local and state data</td>
<td>EPA’s Maximum Achievable Control Technology (MACT); Toxic Release Inventory (TRI); State and local data</td>
</tr>
<tr>
<td>On-road Mobile</td>
<td>Federal Highway Administration (FHWA); EPA MOBILE Model</td>
<td>EPA Office of Transportation and Air Quality (OTAQ) estimates</td>
</tr>
<tr>
<td>Non-road Mobile</td>
<td>EPA NONROAD Model</td>
<td>EPA Office of Transportation and Air Quality (OTAQ) estimates</td>
</tr>
<tr>
<td>Stationary Area</td>
<td>Local and state data; EPA estimates</td>
<td>EPA emission factors and activity data</td>
</tr>
</tbody>
</table>
Figure 2-5 – SMOKE Model Overview
Table 2-4 – Emissions Sectors Modeled with SMOKE

<table>
<thead>
<tr>
<th>Emission Sector</th>
<th>Source</th>
<th>Chemical Species Included</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CAPs**</td>
</tr>
<tr>
<td>Area</td>
<td>Non-point</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Air traffic, locomotives, and marine vessels</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Non-road vehicles</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Canadian area</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Agriculture</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Fugitive dust</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Biogenic</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Area Fires</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Point IPM*</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Point Non-IPM</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Canadian point</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Point Fires</td>
<td></td>
</tr>
<tr>
<td>Mobile</td>
<td>On-road vehicles</td>
<td>✓</td>
</tr>
</tbody>
</table>

*The Integrated Planning Method (IPM) identifies all emissions sources that contribute to national electricity grids. This category is dominated by emissions from coal-fired electric generating units.

**These categories denote the relevant CAPs and HAPs for each sector. For example, the only chemical species modeled for agricultural emissions is ammonia (NH₃).
WPS comprises three programs: ungrib, geogrid and metgrid. Ungrib can be considered an extraction and translation step, which manipulates the gridded meteorology data into WPS/WRF readable form. The program geogrid builds the model space, and metgrid translates the “ungribbed” meteorology onto that described space. In the WRF-ARW system, there are two main programs, real and the ARW solver. The program real vertically interpolates the metgrid output called for by the WRF solver, which is the dynamical core of the entire system, containing the physics and dynamic mechanisms.
Supplemental Figure 2-A – Sigma (σ) Coordinate Levels
Supplemental Figure 2-B – Staggered Grid Arakawa C
Supplemental Table 2-A – Meteorology NARR inputs

<table>
<thead>
<tr>
<th>Dataset</th>
<th>Observation Method</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Satellite radiances(^1)</td>
<td>NOAA TVOS-1B</td>
</tr>
<tr>
<td></td>
<td>Rawinsondes(^2); dropsondes(^3); aircraft</td>
<td>NCEP GTS</td>
</tr>
<tr>
<td></td>
<td>Ship and buoy measurements</td>
<td>COAD</td>
</tr>
<tr>
<td></td>
<td>Rawinsondes; dropsondes; pibals; aircraft</td>
<td>NCEP GTS</td>
</tr>
<tr>
<td></td>
<td>Rawinsondes; dropsondes</td>
<td>NCEP GTS</td>
</tr>
<tr>
<td>Moisture</td>
<td>Satellite radiances</td>
<td>NOAA NESDIS TOVS-1B</td>
</tr>
<tr>
<td></td>
<td>Rawinsondes; dropsondes</td>
<td>NCEP GTS</td>
</tr>
<tr>
<td>Precipitation</td>
<td>Merged satellite and rain gauges</td>
<td>CMAP</td>
</tr>
<tr>
<td></td>
<td>Rain gauges (CONUS)</td>
<td>NCDC (daily); CPC (daily); HPD (hourly)</td>
</tr>
<tr>
<td>Surface Measurements (temperature, moisture, pressure, etc.)</td>
<td>Climatological Stations</td>
<td>NCAR MDL; NCEP GTS</td>
</tr>
<tr>
<td>Sea/Lake Ice</td>
<td>Ship and buoy measurements</td>
<td>GLERL; CIS</td>
</tr>
<tr>
<td>Sea Surface Temperature</td>
<td>Ship and buoy measurements</td>
<td>COADS; GLERL</td>
</tr>
<tr>
<td>Cloud Drift Winds</td>
<td>Satellite</td>
<td>NCEP</td>
</tr>
<tr>
<td>Snow Cover/Depth (initialization)</td>
<td>Satellite; Surface synoptic reports</td>
<td>NOAA GEOS; U.S. Air Force</td>
</tr>
<tr>
<td>Tropical Cyclones</td>
<td>Historical cyclone locations</td>
<td>LLNL</td>
</tr>
</tbody>
</table>

\(^1\) Radiances are measurements of the amount of light passing through or reaching a certain area.
\(^2\) Rawinsondes are meteorological measurement devices often found on weather balloons, which transmit data to a fixed receiver on the ground.
\(^3\) Dropsondes are meteorological measurement devices dropped from airplanes that gather information to be relayed back to a fixed receiver on the ground.
Supplemental Figure 2-C – NARR System Overview [Mesinger et al., 2005]
References


Chapter 3

Model Evaluation for Atmospheric Mercury

The atmospheric mercury cycle and anthropogenic influence has been the subject of scientific study since at least the 1970’s [Weiss et al., 1971]. Since then, research has continued to reveal many complex connections in the mercury biogeochemical cycle. With the introduction of sophisticated measurement technology and new computer modeling tools, the frontiers of atmospheric mercury science are further advanced as researchers uncover new information. However, this is not to say that all is known for atmospheric mercury; the complexity of the mercury cycle, and the large differences between the mercury species slow research efforts. While the overarching properties for mercury, such as relative global concentrations, major sources and sinks, and general chemical processes, have been identified, there are many critical aspects of the atmospheric mercury cycle that remain unclear, and it is these uncertainties that can stymie efforts to develop effective mercury policy for public health.

Introduction

In atmospheric chemistry, developing a clear picture of any chemical cycle requires ascertaining atmospheric concentrations, transport, emissions sources and removal processes. Multiple research groups have measured global atmospheric concentrations [e.g. Slemr et al., 2008; Temme et al., 2003]. Current estimates place total mercury\(^1\) concentrations in the Northern Hemisphere in the range of 1.5 to over 3 ng/m\(^3\), averaging to about 1.7 ng/m\(^3\) [Slemr et al., 2003]. The average concentration is slightly less in the Southern Hemisphere at

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\(^1\) Throughout this study the term “total mercury” refers to all mercury species, and “reactive mercury” encompasses both particulate and reactive gaseous mercury.
around 1.2 ng/m$^3$ with a range from 1.0 to 1.5 ng/m$^3$ [Temme et al., 2003] due to fewer emission sources and atmospheric residence times too short to allow north-south hemispheric mercury transport. Determining mercury sources and sinks is much harder to discover and requires the distinction between mercury species because each has substantially different chemical properties that govern its cycling in the environment.

Mathematical models of atmospheric systems and measurement data both contribute to atmospheric chemistry research, including mercury. Laboratory experiments yield information about possible atmospheric processes but cannot replicate the highly dynamic and complex interactions of the atmosphere and biosphere – a task better approximated by computer models. Measurement studies are constrained by the number of variables that can be varied at any given time. For atmospheric chemistry, there are thousands of different compounds interacting in the environment, and to test each of these relationships would require infinite time and resources. Modelers use measurements as the factual foundation and validation of their results and in turn, the model output may inform the design of new field experiments. By simplifying some of the major processes, chemical transport models allow scientists to test variables in turn, and provide a well-constrained environment for experimentation. However, the same assumptions that allow models to function efficiently can also mask compensating errors and limit how models can be used.

The current state of atmospheric mercury science is a prime example of the strong interdependence of these two methodologies. Compared to other health-relevant atmospheric species, mercury science suffers from a dearth of measurements due to cost and complicated chemistry. Further, because of the high complexity in the atmospheric mercury cycle and the small concentrations of highly reactive species, theoretical understanding is slow to advance
testing the myriad of chemical and physical processes that make up the mercury cycle demands many hours for computing and careful analysis. As many studies have argued [e.g. Lindberg et al., 2007; Lin et al., 2007; Lin and Pehkonen 1999], more mercury measurements are imperative for continued research. The work presented here further underscores this point, offering recommendations for mercury model updates, and highlighting specific areas that merit further study.

Emissions and Meteorology Evaluation

The evaluation of chemical transport models using measured data is fundamental to gaining scientific knowledge of any atmospheric species. Yet, this is not the only area of the modeling process that requires verification. Assessing uncertainty and error in the CMAQ input is critical to the interpretation of CMAQ output, and understanding the current skill of the model in simulating mercury processes. These inputs include emissions information, topographical maps, climate data, and human behaviors, and require many models to develop a robust understanding of atmospheric chemistry.

Mercury Emissions

In the U.S., total anthropogenic mercury emissions are known with relative confidence due to governmental monitoring efforts such as the Toxic Release Inventory (TRI), although there remain some questions about mercury speciation [Lin et al., 2006]. In the rest of the world, however, questions about fuels, emissions control technologies, and even the number and location of sources [Seigneur et al., 2001] make anthropogenic emissions difficult to quantify. Non-anthropogenic mercury emissions are also highly uncertain with current global estimates ranging from 800 to 3000 Megagrams/acre [Gustin et al. 2008]. In comparison, anthropogenic mercury emissions are estimated at about 2000 to
2400 Megagrams/acre globally [Paeyna et al., 2006]. Studies have shown that non-anthropogenic emissions contribute a significant amount of gaseous elemental mercury to the atmosphere, which can then be oxidized and deposited as reactive mercury [e.g. Xin and Gustin, 2007]. These non-anthropogenic emissions from soils, water surfaces and vegetation are due, in part, to mercury originally deposited from anthropogenic sources, i.e. a bidirectionality of mercury fluxes from most terrestrial surfaces that acts as a large confounding factor for assessing natural emissions and possible sinks. Lastly, biomass burning is another large source of mercury [Biswa et al., 2007; Friedli et al., 2003], but is difficult to model and uncertainty ranges to nearly ±50% [Wiedinmyer and Friedli, 2007].

This study uses the 2002 National Emissions Inventory (NEI) with the Sparse Matrix Operator Kernel Emissions (SMOKE) model as outlined in the previous chapter. At the time the study began, it was the most up-to-date inventory of U.S. emissions, and includes important Canadian and Mexican sources as well. Additionally the NEI is used for all government mercury modeling, and by using the same modeling format, the work presented is highly relevant to policy decisions. An in-depth evaluation of the 2002 NEI for mercury is beyond the scope of this study\(^2\), but the following serves to characterize the emissions input and provide a first-order assessment.

Total annual mercury emissions over the entire modeled CONUS domain amount to just under 120 tons. This emissions total is comprised of roughly 72.5 tons of Hg\(^0\), 37.1 tons RGHg, and 10.1 tons PHg\(^3\). Figure 3-1 shows the relative contribution of each species to total annual emissions over the Continental U.S. (CONUS) domain. Modeled mercury emissions

\(^2\) For a more information on the 2002 NEI for mercury see the EPA documentation at www.epa.gov/ttn/chief/net/2002inventory.html.

\(^3\) Unlike in CMAQ, particulate mercury emissions are not divided into size classes. Modeled PHg is emitted only in Aitken mode (i-mode). See Chapter 2 for discussion of particle modes.
show a high percentage of reactive species, making up about 40% of total annual emissions over the U.S. Breaking the processed NEI emissions into sectors, as shown in Figure 3-2, the largest percentage of emissions on a national scale, comes from point sources not defined as electric-generating units (EGUs). This category includes a wide variety of sources, including hazardous waste incineration, hospital incineration, industrial facilities, etc. The emissions from the single category of power utilities is greater than any of these individual groups at the national scale, and thus, remains the single largest contributor to mercury emissions that can be defined and regulated.

In the Great Lakes region, EGUs are the largest source of mercury, producing 26.7 tons per year, compared to non-electricity-generating point sources producing 18.8 tons of mercury annually. Most EGUs emit 0.1-10 grams of mercury per hour across the Great Lakes Region. However, a few EGUs do reach hourly emission levels above 20 grams. Additionally, the outlying emitters in the electric utilities sector are clustered in western Pennsylvania, where local coal is high in mercury [Toole-O'Neil et al., 1999]. Further, the Great Lakes region hosts about 50% of the largest U.S. coal-fired EGUs, which explains why the Great Lakes show higher EGU emissions compared to the national average. Thus, controlling the electric sector is imperative for reducing mercury emissions in the Great Lakes region.

The highest total emissions are centered around clusters of coal-fired power plants along the Ohio River and western Pennsylvania, as well as over larger cities. Total mercury emissions from EGUs in the Great Lakes average to about 0.4 g/hr, but multiple utilities have mercury emissions greater than 80 g/hr. Non-EGU sources in the Great Lakes have a wide range of hourly mercury emissions, some measuring on the range of micrograms per hour,
while others reach over 40 g/hr. The majority of non-EGU total mercury emissions are on the order of 0.1 g/hr to less than 10 mg/hour. Area and mobile mercury emissions are several orders of magnitude smaller. Along major roadways, mobile mercury emissions are less than 1 mg/hr, and rarely higher than 10 mg/hr in urban centers. Mercury emissions for area sources are more variable: outside urban areas, emissions range from less than 1 mg/hr to about 6 mg/hr, but can reach over 200 mg/hr in larger cities. There are also a number of spatial patterns that are likely due to differences in data collection/organizational methods, although local and regional regulations may also be a factor.

Emissions show little absolute variation from month to month, but examining total monthly emissions as percent of total annual mercury emissions shows higher mercury emissions in cooler months from area sources. Assessing each major emissions sector for seasonal trends, the total mercury emissions from point sources are generally stable throughout the year, while mobile sources are highest in the summer months and area sources show highest emissions in winter (December, January, and February). The winter peak in area sources is due to residential coal, gas or oil boilers used for heat and energy in the winter, as has been found in other U.S. regions with similar climate (e.g. NESCAUM 2005), and higher “vacation” traffic in summer leads to higher emissions. The stability of the point source emissions is most likely an artifact of employing annual total inventories, which are temporally distributed based on source type characteristics including the number of households served, efficiency and output capacity for EGUs, or facility size, and seasonality of demand for an industrial facility.

Species distributions across sources show total monthly emissions Hg$^0$ dominating U.S. mercury emissions at 57.6% of total annual emissions on average compared to RGHg at
29.5% and PHg at 12.9%. [Figure 3-1] For electric utilities, PHg constitutes 25% of total monthly emissions throughout the annual cycle on average, and the remaining mercury is split between Hg\(^0\) and RGHg. The relative amount of RGHg and Hg\(^0\) varies widely for individual EGU\(s\), as the model apportions mercury species based on source attributes. For EGU\(s\) in the Ohio River Valley and Pennsylvanian Appalachians, RGHg comprises the largest percentage of mercury emissions at about 65-70%, while Hg\(^0\) dominates the remaining EGU mercury emissions at similar percentages. On average, non-EGU point source emissions are composed of 10-30% RGHg, 50-70% Hg\(^0\), and 10-20% PHg. Noticeably, non-EGU\(s\) in Illinois emit a higher percentage of RGHg, reaching up to 50%, when compared to other states.

Mobile emissions in the U.S. Great Lakes Region are emitted as Hg\(^0\), with less than 1% emitted in reactive forms. Overall, U.S. area source emissions, including landfills, residential emissions, etc., emit about 60% of mercury in the form of Hg\(^0\), with the remaining 40% split between the reactive species. Illinois shows a slightly different pattern, with 80% of total monthly emissions in the elemental form, which is likely an artifact of data collection and aggregation methods, as mentioned earlier. Canadian mobile and area emissions were combined in the 2002 NEI, and together these sources reach hourly emissions levels of around 25 mg/hr in the cities and on average are comprised of 15% PHg, 45% RGHg, and 40% Hg\(^0\), which gives higher RGHg emissions than in the U.S. These differences are likely reflective of data methodology as opposed to significant differences in emissions between the U.S. and Canada.

Emissions for Devil’s Lake and Milwaukee are very different, as expected since Devil’s Lake is a rural site, while Milwaukee is an industrial urban center. The urban
emissions in Milwaukee are governed by a few EGUs with average annual emissions of 5-17 grams per day, peaking in the winter. There are some non-EGU point sources within a 120 kilometer radius. However, the highest daily total emissions from these sources are 80% less than the lowest EGU emissions. In the grid cell containing the Milwaukee site, the highest daily total emissions reach 0.77 grams in the winter, with summer emissions at about 0.48 grams per day\textsuperscript{4}. In comparison, Devil’s Lake has only one EGU within a 100 kilometer radius of the measurement site, which emits an average of 7 grams of mercury a day and the closest non-EGU point source is about 100 kilometers to the northwest and emits an average of 23 grams of mercury a day. Area and mobile emissions are much lower, with the highest sources within a 120 km radius reaching no more than .6 grams per day as an annual average. Daily emissions in Devil’s Lake peak in the winter at 6.6 milligrams per day, and are lowest in the summer at about 4.5 milligrams per day.

In sum, mercury emissions in the Great Lakes region are shaped by EGU sources, with highest emissions in the winter due to residential heating needs. Speciation profiles for the largest sources vary, although reactive mercury (RGHg and PHg) constitutes a high percentage (\geq 60\%) of mercury emissions along the Ohio River Valley and in western Pennsylvania. Mobile and area sources are more diffuse with considerably lower emissions, mostly in the form of Hg\textsuperscript{0}.

\textit{Meteorology}

\textsuperscript{4} The grid cell containing the actual latitude and longitude of the Milwaukee measurement site was modeled as lake. These issues of resolution are expected when considering shore sites. To accommodate this difference the grid cell immediately to the west was also examined and showed similar emissions totals with the highest daily total emissions at 0.84 grams in the winter, and maximums of 0.51 grams in the summer. The small difference in emissions is expected since point emissions, which drive mercury emissions, are based on the actual latitude and longitude of the source.
In addition to emissions, meteorology also plays an important role in chemical transport modeling. Meteorology models are the most developed tools of all the models used in this study. Computational models for climate have existed since the 1950’s and have been continuously refined. Confining our assessment to meteorological modeling for the purposes of air quality models, there are a few areas of uncertainty that can impact results. However, it must be stressed that these uncertainties in meteorology modeling are still significantly less than those associated with mercury emissions and chemistry modeling.

Maintaining the end goal of best capturing atmospheric mercury processes, the meteorology evaluation presented below focuses on precipitation and temperature. Accurate precipitation is required to replicate wet deposition fields, and temperature is important for a number of chemical processes, including gas to particle partitioning of reactive mercury. Modeled meteorology from WRF was evaluated against observational data from the National Climatic Data Center (NCDC) as well as against processed North American Regional Reanalysis (NARR) data.

The NCDC reports actual precipitation and surface temperature at hundreds of sites across the U.S. and thus was used to complement the NARR dataset evaluation. The NARR provides data on water-vapor mixing ratios and air temperature at 2-meters over both domains. However, the water-vapor mixing ratio is only one of many variables used in precipitation calculations. Thus, while the NARR data comparison is spatially and temporally comprehensive, it does not provide a sufficient investigation of model precipitation performance.

Comparisons with the NCDC data include monthly total precipitation and monthly average temperatures as well as daily temperature and precipitation for a few episodes at both
resolutions. The NARR was not used in its raw format, as it is described in Chapter 2, but was drawn from WRF/MCIP output. WRF retains the original NARR input for 2-meter air temperature and water vapor mixing ratio at 3-hour intervals and then uses linear interpolation to derive the intermediate values [Gilliam et al., 2007]. The processed NARR data was compared with the WRF model output only at the time steps retaining the original NARR values, and only for the 12 km resolution run over the Great Lakes.

Bias and percent fractional bias (%FB) were used as performance measures for both the NCDC and NARR datasets,

\[ \text{Bias} = \frac{1}{n} \sum_{i=1}^{n} (M_i - O_i) \]
\[ \% \text{FB} = 100 \times \frac{2}{n} \sum_{i=1}^{n} \left( \frac{M_i - O_i}{M_i + O_i} \right) \]

where \( M \) is the model output, \( O \) is the observed value and \( n \) is the number of model-observation pairs. Bias is in the same units as the observed and modeled process (e.g. millimeters for precipitation), and is not bounded. Negative bias indicates model under-prediction, and positive bias indicates model over-prediction. Percent fractional bias is a unitless measure, equally weights positive and negative biases, and is bounded at +200% and -200%, representing “infinite” over/under-prediction. Values of ±67% are equivalent to over/under-prediction by a factor of two. These measures will be used throughout this study.

Based on the NCDC data, model performance for monthly average temperature over the Great Lakes Region did not improve significantly with the increase in horizontal resolution from 36 km × 36 km to 12 km × 12 km. As shown in Figure 3-3, at a 12 km resolution, modeled average monthly temperature fields were consistently within two degrees Celsius of NCDC measure temperatures, and was rarely underestimated. The model had
trouble capturing temperature in central Indiana and Ohio throughout the year, possibly due to errors in lake temperature that will be discussed below.

For comparison with the NCDC precipitation data, model monthly total precipitation, $P_{tot}$, was calculated using

$$P_{tot} = \sum_{i=1}^{t} (Rn_i + Rc_i)$$

where $Rn$ is hourly nonconvective precipitation, $Rc$ is hourly convective precipitation, and $t$ is the number of hours for a given month. Percent fractional bias for monthly total precipitation was calculated using the NCDC precipitation data and monthly WRF model totals, and is listed in Table 3-1. Modeled monthly total precipitation was not as well captured, with variable performance throughout both domains. At the 36 km resolution, precipitation was over-predicted during the summer months (June, July August) along the Gulf Coast, particularly in Southern Florida, but did well throughout the rest of the domain. The increase in resolution, again, did not significantly improve model results for monthly total precipitation, which is demonstrated in Figure 3-4. Lastly a few randomly selected episodes were compared against model results using the NCDC dataset Global Summary of the Day, and are shown in Figure 3-5. While the daily observations are not spread as densely throughout the domain as the monthly comparisons, they do provide insight to development of fronts and other episodic weather patterns. At both resolutions, the model performed best in winter, spring and late fall, and was less capable during the summer and early fall.

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5 WRF treats convective precipitation and nonconvective precipitation separately in the model; their sum represents total precipitation reaching the ground.
Comparison with the processed NARR data revealed further patterns. Bias and percent fractional bias (%FB) were calculated at every available NARR timestep for both 2-meter air temperature and water vapor mixing ratio. WRF exhibited a noticeable cold bias for surface temperatures over the Great Lakes waterbodies from April through September, demonstrated in Figure 3-6. However, the %FB for surface temperature over the lakes for this time period never dipped below -10%, demonstrating good prediction. Water vapor mixing ratios also showed good agreement. Figure 3-7 illustrates model behavior and shows that during the winter and late fall, model humidity was too high over the lakes, but too low in the spring and summer. Over land, humidity was consistently under-predicted for April through June, while the remainder of the year showed close agreement over land with low fractional bias in both the positive and negative direction. Fractional bias in the water vapor mixing ratio grows stronger throughout each separately modeled quarter. This error propagation is highly likely with long-running times for climate models. Still, these errors are acceptable and rarely exceed ±7.5% over land or ±30% over the lakes.

Linking the biases in surface air temperature and humidity, it is appropriate that the strong under-prediction in model temperature over the lakes would lead to an under-prediction in model water vapor mixing ratios. Lower temperatures should cause any water vapor to condense out of the air. This difference in water content and temperature over the lakes is important to bear in mind when interpreting modeled mercury wet deposition over the lakes. Reviewing the NARR and NCDC data comparison together leads to the conclusion

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6 The NARR is available at 3-hour intervals.
7 The water vapor mixing ratio gives the amount of liquid water mass to dry air in a unit volume of air. While it is not used in direct calculations for chemistry, it serves as a proxy for precipitation fields.
that WRF precipitation is moderately under-predicted throughout the year (annual average %FB of -2.7% compared to NARR), and temperature is well captured.

The choice of WRF v 3.0 for meteorology takes advantage of the most up-to-date climate science and performs well over the Great Lakes based on this analysis. Temperature is well captured, with an average annual percent fraction bias of less than 0.2%. Comparisons for water vapor mixing ratio, used as a proxy for precipitation fields, show some model under-prediction, but again the percent fractional bias is very low, in this case with an annual average of less than -2.5%, and larger under-prediction in the summer. These meteorology fields are important for various calculations in a chemical transport model, most notably in the wet deposition. Given this evaluation for WRF, it is likely that wet deposition will also be slightly under-predicted.

CMAQ Deposition Evaluation

Total mercury wet deposition is the most tested aspect of the mercury cycle. Uncertainty in modeled precipitation and aqueous chemistry are the most significant problems for wet deposition since general atmospheric wet deposition processes – i.e. in-cloud scavenging and below-cloud washout – are well understood [e.g. Levine and Schwartz, 1982]. However, mercury wet deposition is imperfect insofar as aqueous mercury chemistry uncertainty confounds in-cloud scavenging. Incomplete modeling of cloud microphysics\(^8\) and meteorological inaccuracies are usually the largest source of error in wet deposition values. Dry deposition on the other hand, is highly uncertain and many studies have identified these rates as a priority for atmospheric mercury study. A few measurements exist for dry deposition [e.g. Sakata et al., 2008; Lyman et al., 2007], but none with significant spatial

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\(^8\) For example, using the CMAQ operator splitting technique described in Byun and Ching [1999].
variability. Model errors for dry deposition are therefore difficult to diagnose, and will not be
evaluated; general dry deposition trends, however, will be reported and discussed.

Dry deposition over the U.S. is highest over forested areas in the north, and generally
higher on the East Coast of the U.S. Some increase in dry deposition near general emission
sources is evident, with a number of grid cells with extremely high dry deposition, as shown
in Figure 3-8. Mercury dry deposition is composed of RGHg and Hg$^0$, presented in Figure 3-9,
with RGHg contributing an average of 53% of total annual mercury deposition to land in the
CONUS domain, compared to 43% for Hg$^0$. PHg dry deposition is very small with a
maximum contribution of 0.4% to total annual dry deposition. Dry deposition to water bodies
is nearly 100% in the form of RGHg since Hg$^0$ is not water-soluble. Table 3-1 shows that
total dry deposition for both domains is highest in the winter; however, there are spatial
differences in seasonal peaks. For example, in the southwest, dry deposition is highest in the
June, compared to maximums in January for the northern areas of the domain. As mentioned
above, it is not possible to evaluate these processes, but it is nonetheless worthwhile to
mention general dry deposition trends.

Nearly all atmospheric mercury modeling studies to date have compared with the
Mercury Deposition Network (MDN) [e.g. Pongprueksa et al. 2007, Gbor et al. 2007],
maintained by the National Atmospheric Deposition Program (NADP) since 1996. The MDN
reports total wet deposition as the integral over about a week$^9$ for over 85 sites across the
U.S. and Canada shown in Figure 3-10 [NADP, 2009]. The MDN uses a modified Aerochem
Metrics model 301 collector to gather precipitation, and samples are then analyzed using cold

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$^9$ Actual sampling periods may vary.
vapor atomic fluorescence spectroscopy (CVAFS) that does not distinguish between mercury species [Vermette et al. 1995].

Annual totals for wet deposition over the continental U.S. at 36 km horizontal resolution (heretofore referred to as the CONUS domain) agree well with other modeling studies [e.g. Selin et al., 2008]. Annual wet deposition averages 5.925 g/km² over the domain, with higher deposition on the East Coast, particularly in the South where annual totals reached over 15 g/km². Given the low deposition velocity for Hg⁰ set in the model, reactive species were expected to dominate wet deposition, which is clearly shown in Figure 3-11. Table 3-2 shows monthly total wet deposition and average daily wet deposition over the entire domain for each study region, both of which peak in August.

Monthly totals from the Mercury Deposition Network (MDN) were compared to model results at both the 36 km and 12 km resolution. CMAQ wet deposition values were summed for the grid cell containing each MDN site according to the MDN start and end times rounded down to the nearest hour. Monthly totals were based on the ending date of the MDN measurement, such that the month of the end date was the month the MDN total was counted towards. Where data was missing or invalid for 50% or more of the reported sampling periods for a given MDN monitor, the site was not counted towards monthly totals. MDN reports of zero wet deposition were included.

As shown in Figure 3-12, CMAQ reproduces the order of magnitude for monthly total deposition throughout the entire year compared to the MDN over the CONUS domain. Table 3-3 gives performance statistics for modeled total monthly wet deposition on the CONUS
domain using bias, percent fractional bias and the Pearson product moment correlation coefficient,\textsuperscript{10} referred to throughout as $r^2$, where

$$r^2 = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sqrt{\sum (x - \bar{x})^2 \sum (y - \bar{y})^2}}$$

for each MDN monthly total deposition, $x$, and corresponding modeled wet deposition, $y$. Analysis indicates that CMAQ does particularly well in February, October and November, with percent fractional bias less between 5% and -5%. While the maps show reasonable agreement throughout the year, performance statistics reveal that model performance is poorer than initially apparent, and under-prediction is more significant. R-squared values in Table 3-3 are near zero for all modeled months, excepting June, July, August and September, and fractional bias is negative for most months. The better agreement in the summer is also notable since summer wet deposition is often the standard for atmospheric mercury modeling evaluation, and better agreement for these months, very small r-squared values the remainder of the year, suggests that model development has been influenced by these comparisons.

Overall model performance at the 36 km resolution decreases when only the 31 Great Lakes MDN sites are considered, particularly over Wisconsin, Indiana and Ohio, Figure 3-13 demonstrates that the change in model performance is less pronounced in the Great Lakes’ warm season, the late summer and fall, which is surprising. The Great Lakes normally experiences more convective precipitation during this time, which is hard to model at horizontal resolutions less than about 10 km [Morris et al., 2005], and thus it would be expected that model deposition performance would also suffer. One possible explanation is that since fractional bias is a relative measure, the increase in average deposition monthly

\textsuperscript{10} R-squared values indicate the proportion of the variance in independent variable $y$ attributable to the variance in dependent variable $x$ and ranges from -1.0 to 1.0.
totals in the summer allows more absolute deviation from observed values without greatly changing the FB.

There is improvement in monthly total deposition performance at the higher 12 km resolution (heretofore referred to as the Great Lakes domain). While the percent fractional bias for monthly total deposition at the 12 km resolution is within 15% only in February and August, monthly model results are consistently better throughout the year. Only one month, January, has a percent fractional bias over ±60%, compared to 5 months at the 36 km resolution. The strong bias in January, at both resolutions, is most likely due to the small number of MDN observations – there were only 55 valid measurements for January compared to an average of 109 measurements for the rest of the year. The results for monthly total mercury wet deposition support the choice of the Great Lakes model domain; the higher uniformity of results suggests that the chosen region describes an area with similar meteorology and atmospheric chemistry.

Comparison of weekly\textsuperscript{11} MDN observations with CMAQ mercury wet deposition over the Great Lakes domain shows a larger monthly fractional bias (poorer model performance) than for monthly total deposition across sites in the winter and early spring. This is explained by a few extreme under-/over-predictions in CMAQ that have a more pronounced impact when averaged by sample interval. In the late spring, summer and fall modeled weekly deposition is as accurate as total monthly deposition, which demonstrates the model’s ability to capture wet deposition in warmer months, when deposition is at its highest.

\textsuperscript{11} As stated earlier, mercury wet deposition is usually reported at integrated weekly intervals, although sampling periods presented here range from less than a day to over two weeks. “Weekly” is intended to identify a single sampling period, which may actually be longer or shorter than a week. CMAQ results are always compared as integrals using identical start and end times.
By definition wet deposition occurs only with precipitation, and model precipitation can be an important source of error in wet deposition fields. This is particularly true for mercury. As stated above, reactive mercury species are responsible for over 98% of modeled wet deposition and below-cloud scavenging results in rapid depletion. If modeled precipitation frequency and intensity are inaccurate, while still showing good agreement with wet deposition reports, then either model deposition velocities or ambient concentrations are incorrect (assuming wet deposition measurements are correct). The meteorology model evaluation showed that WRF precipitation was lower than NCDC and NARR observations, but it is also necessary to compare against MDN reported precipitation to maintain consistency, account for differences in measurement techniques, and provide the best picture of wet deposition model results.

Scatter plots in Figure 3-14a,b show weekly precipitation and wet deposition for observed versus modeled results. R-squared values for wet deposition range between 0.3 and 0.7 for all months except December, indicating that CMAQ can explain between 30% and 70% of the variation in mercury wet deposition. Precipitation accuracy limited model performance for wet deposition, as evidenced by model versus observed $r^2$ values ranging from 0.4 to 0.9. Figure 3-15 shows precipitation versus wet deposition percent fractional bias averaged for each site. The r-squared values can be interpreted as the percent in wet deposition error that can be traced to precipitation error.

Mercury wet deposition sensitivity to precipitation fields has been shown in many other modeling studies [e.g. Bullock et al., 2009; Lin et al., 2007], but other sources of error, including deposition velocity, and atmospheric concentration, are also important. Using only MDN observations, CMAQ estimates total monthly wet deposition of mercury with lower
precision that for other atmospheric species [e.g. Davis and Swall, 2006; Civerolo et al., 2007; Morris et al., 2005], but the general tendency of CMAQ v.4.6 to under-estimate mercury wet deposition presented here is in agreement with other studies [e.g. Lin et al., 2007; Gbor et al. 2006]. In sum, the under-prediction for monthly total deposition at both the 36 km resolution and 12 km resolution are mediated by a demonstrated under-prediction in precipitation. CMAQ evaluation against weekly mercury wet deposition totals shows under-prediction for every month except December, although changes in model performance (as indicated by percent fractional bias) from monthly to weekly deposition totals are not significant. Comparing error in precipitation with error in wet deposition shows that although precipitation is a source of some wet deposition error, there is significant unexplained error. Precipitation in error is likely the source of about 30% of wet deposition error as a yearly average, leaving the majority of wet deposition error unexplained. The close coupling of precipitation patterns and wet deposition is to be expected by definition, and examining ambient concentration data in the next section will further elucidate other factors affecting mercury wet deposition.

CMAQ Model Evaluation for Atmospheric Concentration

Currently, there is no network for measuring ambient mercury concentrations, and any existing measurements are discrete endeavors, usually supported by individual scientists or research groups. These few measurements are invaluable because, unlike the MDN, the majority report mercury species, which is necessary for assessing mercury chemical cycling.

Speciated atmospheric mercury concentration measurements were taken at two sites in Wisconsin, Devil’s Lake (43.43° N, 89.68° W) and Milwaukee (43.12° N, 87.88° W). The measurements were collected for just under a full year (Devil’s Lake from mid-April 2003 to
mid-March 2004, and Milwaukee from the end of June 2004 to mid-May 2005). Samples were taken every two hours using a Tekran ambient mercury analyzer [Landis et al., 2002; Lynam and Keeler, 2002; Lu et al., 1998]; measurement methods are described in Manolopoulos et al. [2007]. The Devil’s Lake site is in a rural area dominated by agriculture, and is collocated with a MDN sampler. The Milwaukee site is an urban setting on the shore of Lake Michigan, and while there was no MDN monitor collocated at the site, there is an MDN monitor in Milwaukee, which falls into the same model grid cell (for both resolutions) as the ambient concentration sampler. There are atmospheric mercury sources near each of the sites, and with a number of emission sources included in the NEI. Ambient concentrations were extracted from both the CONUS and Great Lakes domains from the grid cell containing the measurement locations at the lowest vertical layer. CMAQ model runs were for January 2003-December 2003, and thus overlap with most of the measurements taken at the Devil’s Lake site. Lastly, fourteen-day running averages were compared for 2003 model data and Milwaukee ambient measurements from 2004 to examine CMAQ’s ability to capture general mercury trends in urban settings.

Differences in model concentration between the 36 km resolution and 12 km resolution were slight, and did not significantly improve results. Reactive mercury concentrations tended to be slightly higher at the finer resolution at the Devil’s Lake site, but not significantly so. The slightly lower concentrations at the coarser resolution are likely due to dilution effects, and have been discussed elsewhere [e.g. Lin et al., 2006; Pai et al., 2000]. Given the minimal change between the two runs, only results from the 12 km simulation over the Great Lakes domain will be presented here.

_Devil’s Lake_
As is typical of remote sites, the concentrations of all mercury species at Devil’s Lake were low, although the measurements do show a number of spikes throughout the year attributable to plumes from point sources [Rutter et al., 2008]. Observed gaseous elemental mercury averaged about 1.6 ng/m$^3$ over the entire measurement period (April 2003 – March 2004), agreeing with published measurements of Hg$^0$ global background levels in the Northern hemisphere [e.g. Slemr et al., 2003]. Reactive species were also low, with observed averages of 5.3 pg/m$^3$ for RGHg, 9.8 pg/m$^3$ for PHg and 15.1 pg/m$^3$ for total reactive mercury (RHg)$^{12}$ over the entire period. Seasonal trends for the Devil’s Lake measurements show the highest monthly average concentration for all species in the spring, and the lowest for elemental and particulate mercury occurring in August. After peaking in the spring, reactive gaseous mercury concentrations remained below 5 pg/m$^3$ for the rest of the year. Particulate mercury sustained higher concentrations through the winter, nearly reaching springtime levels in January and February.

CMAQ annual averages for reactive species are much higher than observed, with RGHg at 19.9 pg/m$^3$, PHg at 27.9 pg/m$^3$, and RHg at 47.9 pg/m$^3$. Figure 3-16 shows concentration time series for each species at Devil’s Lake and Table 3-4 lists monthly and annual statistics for both observed and modeled concentrations; both clearly show significant model over-prediction at the site. Elemental gaseous mercury has a modeled annual surface concentration of 1.5 ng/m$^3$, which agrees well with the observed average, reflecting known global background levels used in model boundary and initial conditions. Seasonal trends in modeled mercury concentrations show a smoother curve throughout the year with reactive

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$^{12}$ Total reactive mercury and reactive mercury refer to combined particulate and reactive mercury values.
species reaching a slight maximum in monthly average concentration during the summer. Modeled Hg\textsuperscript{0} average concentration decreases in July, and peaks in October.

Closer inspection of the observed concentrations underscores CMAQ’s over-prediction for reactive species. Percent fractional bias is within ±10% for Hg\textsuperscript{0} July through December, and is never more than ±25%. The reactive species, on the other hand have a much larger deviation, averaging over 100% fractional bias for the period. That percent fractional bias for reactive mercury is highest in August at over 150% further highlights the observed minimum in summer concentration compared to the modeled near maximum at the same time. From mid-April through to early May, however, the model RGHg concentration matches observed quite well, as shown in Figure 15, with a %FB of 40.0% from April 10\textsuperscript{th} to May 20\textsuperscript{th}. The magnitude of model concentrations remain at this high level for the rest of the year, however, and indicates that the model is not capturing actual atmospheric processes. This springtime behavior will be further examined in Chapter 4. Removing concentration spikes\textsuperscript{13} greater than 2 standard deviations from the observed monthly mean does improve %FB for reactive gaseous mercury for the remainder of the year, but not significantly. Percent fractional bias for Hg\textsuperscript{0} and PHg are essentially unchanged.

Scaling model concentrations to the observed order of magnitude, however, does show that the model reproduces the diurnal cycles for reactive species quite well for most months, as shown in Figure 13-17. During the period from April 10\textsuperscript{th} to May 20\textsuperscript{th}, diurnal variation for modeled PHg is similar to observed values if model results are reduced by a factor of 2.5. In this case, percent fractional bias lowers to 16.6%. Concentrations for each

\textsuperscript{13} Since CMAQ was run without explicit plume modeling, and emissions were based on annual data, it is reasonable to expect that these spikes are too finely resolved to be found in the model.
species are not uniformly over-predicted such that one scaling factor gives a better fit throughout the year, but factors can be calculated roughly by month. In July, model agreement for reactive species is significantly increased by reducing model concentrations of RGHg by a factor of 25, and reducing PHg surface concentrations by a factor of 5. Similarly, a factor of 5 reduction in modeled RGHg concentrations and a factor of 4 reduction in PHg gives much better model agreement in for October.

At Devil’s Lake, CMAQ is able to replicate Hg\(^0\) concentrations, but substantially over-predicts both reactive species. Diurnal cycling in the model closely resembles observed trends, however, and indicates that even though concentrations are too high, the model is tracking some chemical cycling correctly. To better constrain the possible sources of error, the next section analyzes concentration measurements taken at the Milwaukee site. This urban site has a much different emissions profile and the evaluation that follows lays the foundation for more detailed analyses of the two sites presented in Chapter 4.

**Milwaukee**

Concentration measurements from the Milwaukee site were compared to model output based on daily and 14-day averages. Average daily concentrations were only calculated if at least 6 measurements were available\(^{14}\) for a given day, and a 14-day running average was used only if 50% of more of each 14-day period had valid measurements\(^{15}\). Model results were compared across years since monthly meteorology and emissions are

\(^{14}\) Recall that ambient concentration measurements were taken every two hours, so our methods require at least a 50% valid sample rate for measurements to be included in daily averages.

\(^{15}\) Since the measurements were taken every two hours, the threshold number of measurements required was 50% of total possible observations (168 possible samples over 14 days).
relatively stable from year-to-year\textsuperscript{16} and the model run and the atmospheric concentration measurements are not separated by a large time gap\textsuperscript{17}.

As expected, measured concentrations of all mercury species were higher at the Milwaukee site than at Devil’s Lake. The average over the entire measurement period (April 2003-March 2004) for Hg\textsuperscript{0} concentration was 2.3 ng/m\textsuperscript{3}, 9.9 pg/m\textsuperscript{3} for PHg, 7.8 pg/m\textsuperscript{3} for RGHg, and 17.6 pg/m\textsuperscript{3} for RHg. From the running averages, elemental mercury concentrations peak in November and April, and reactive gaseous mercury shows a slight bimodal pattern. RGHg has maximums in September and April, with concentrations bottoming in December through January. PHg concentrations are highest in February and lower through the summer. The CMAQ Hg\textsuperscript{0} concentration average over the 2003 model year is low (1.5 ng/m\textsuperscript{3}), showing almost no change from the Devil’s Lake site. Reactive species are again over-predicted (37.8 pg/m\textsuperscript{3} RGHg, 35.7 pg/m\textsuperscript{3} PHg and 73.5 pg/m\textsuperscript{3} RHg). All mercury species reach maximum monthly concentration in September and decline sharply in October. For the 14-day running averages shown in Figure 3-18, CMAQ’s over-prediction for the reactive species and under-prediction of Hg\textsuperscript{0} are clear. Further, the seasonal cycle – PHg increasing through the winter with a drop in RGHg – is visible in the measured concentrations, but not in the model.

The clearest conclusion drawn from comparisons with these measurements is that CMAQ mercury speciation needs to be investigated thoroughly. The extreme over-prediction


\textsuperscript{17} There were no significant policy changes for gaseous mercury emissions between January 2003, the start of the CMAQ model run, and March 2005, the end of the Milwaukee measurement period. The final Clean Air Mercury Rule (CAMR) was proposed by the EPA in May of 2005, but would not have gone into effect until 2010, and was later vacated before being enacted. The CAMR and other policy options relevant to this research will be discussed in Chapter 5.
in Devil’s Lake, and strong evidence of the same in Milwaukee raises a number of questions about model process. As will be examined further in Chapter 4, some initial possibilities include chemical mechanism, and removal processes. At both the Milwaukee and Devil’s Lake sites, there is an increase in PHg in the winter coincident with a decrease in RGHg. As explained in Rutter et al. [2008] this is due to less particle to gas partitioning of reactive mercury because of lower ambient temperatures. This relationship is currently missing from CMAQ chemistry and would improve modeled winter concentration for reactive mercury species. In remote areas, the global background concentration of elemental mercury functions well as ambient surface concentration measurements show. However, the model does not show the observed higher variability in the urban Hg$^0$ concentration, although some of this variability that can be related to plume activity, which was not modeled explicitly in this study. Lastly, the springtime increases in reactive mercury concentrations, particularly at the rural site, are not picked up in the model, nor are summertime minimums. This may indicate other important chemical relationships not yet incorporated into the CMAQ model.

**Current Areas of Uncertainty in Atmospheric Mercury Chemistry and Transport**

In atmospheric chemistry modeling, there are two main sources of error: model simplifications, and uncertain science used in the model. Atmospheric mercury is subject to both. Model limitations were previously discussed in Chapter 2 and the following section will discuss areas of uncertainty in mercury science.

Dry deposition and chemical cycling among mercury species are the largest areas of uncertainty in the atmospheric mercury cycle. While dry deposition rates are not known to a high degree of accuracy, it is widely held that those of reactive mercury species much higher than those for Hg$^0$ [Lin et al., 2006]. Measured estimates for RGHg dry deposition rates
range from 0.1 [Rea et al., 2000] to as high as 7.6 cm/s [Poissant et al., 2004] depending on the surface roughness and moisture content of the air. Hg$^0$ dry deposition, on the other hand, is thought to be about an order of magnitude smaller than RGHg, usually measuring a few hundredths of a cm/s [Seigneur et al., 2004], and for this reason, many earlier mercury modeling studies did not even include Hg$^0$ dry deposition [e.g. Bergan and Rodhe, 2001; Bullock and Brehme, 2002]. The dry deposition velocity of PHg, like all aerosols, depends on particle size and mass. Field measurements have largely found PHg as particulate matter with an aerodynamic diameter around 1 µm (e.g. Wang et al. 2006). Particles of this size are normally given a dry deposition velocity between 0.1 and 1.0 cm/s [Zhang et al., 2001]. Measurements of dry deposition for Hg$^0$ and RGHg also show a diurnal cycle, peaking in the afternoon and decreasing at night, and a seasonal cycle reaching a maximum in the summer [Lindberg et al., 2002]. While atmospheric models seek to incorporate the most up-to-date laboratory findings, it is impossible to evaluate dry deposition performance without field observations, and in the case of atmospheric mercury, none exist at sufficient temporal and spatial scales; only a few isolated measurement studies exist for mercury dry deposition [e.g. Sakata et al., 2008; Lyman et al., 2007].

The most current understanding of mercury deposition indicates a strong dependence on the oxidation of Hg$^0$. Research shows that Hg$^0$ has a low dry deposition rate and low water solubility [e.g. Engle et al., 1997]. Building on the assumption that RGHg and PHg concentrations are low (>5%) and have short atmospheric lifetimes, a large fraction of wet deposited mercury must be due to the atmospheric transformation of Hg$^0$ to reactive mercury (RHg). Thus, two central goals for atmospheric mercury research are understanding mercury species cycling and mercury residence times. Most studies have maintained the assumption
of low RHg concentrations and short lifetimes based on the evidence of ambient
collection measurements, and focused on the investigation of atmospheric mercury
chemistry. The species of Hg\(^0\) oxidant depend on availability and photochemical activity, and
uncertainties in distribution and reaction rates make modeling mercury chemistry difficult
since incorrect atmospheric concentrations confound deposition totals. In gaseous phase
redox chemistry, the oxidation of gaseous Hg\(^0\) is thought to be largely controlled by O\(_3\),
OH\(^-\), H\(_2\)O\(_2\) and reactive halogens (e.g. Br, BrO, and Cl), along with other oxidizing species
to a lesser degree [Ariya et al., 2002]. Research shows that aqueous chemistry is also an
important driver for oxidizing Hg\(^0\). In this case O\(_3\), OH\(^-\), and compounds of chlorine and
bromine are the oxidants proposed to date [Pan et al., 2008; Bullock and Brehme 2002; Lin et
al., 1999]. Aqueous reduction of RGHg is highly uncertain and depends on the specific
species of mercury (e.g. HgCl\(_2\), HgBr\(_2\), HgBr\(_\), etc.). Reaction rates exist in the literature for
aqueous mercury species only as controlled by S\(^{4+}\), HO\(_2\), and photolysis [Lin et al., 2006].
RGHg reduction by HO\(_2\), however, has been questioned by Gardfeldt and Jonsson [2003],
who claim that this reaction does not occur naturally.

Conclusions

The combination of extreme over-prediction for reactive mercury concentrations and
under-prediction of RGHg and PHg dominated wet deposition at Devil’s Lake questions to
what degree CMAQ currently simulates actual atmospheric and chemical processes.
Evaluations of the WRF-ARW meteorology showed acceptable agreement at a larger, scale,
but precipitation was found to be a significant source of error as study focus narrowed to
individual MDN sites, including Devil’s Lake. Emissions remain uncertain and a full
evaluation is beyond the scope of this work; however, modeled mercury did use the most up-to-date emissions inventory and agreed well with other published studies. As mentioned earlier, the lack of measurement data has long stymied atmospheric mercury researchers, and the results presented thus far provide ample opportunity for discovery, but still suffer the risks associated with small sample size.

Wet deposition is uncertain for all species and given this state of uncertainty, it is possible that wet deposition rates, via aqueous chemistry, have been allocated to each mercury species to agree with MDN observations. Since the MDN is the only widely available measurement data available for mercury, these measurements have had a strong influence on model development, and possibly causing model processes to be tuned to total wet deposition.

While both ambient concentrations and deposition data are extremely important for continued research, without speciated wet deposition measurements, the two datasets remain slightly disconnected. Also, the paucity of MDN sites on the west coast gives rise to the possibility that atmospheric mercury research has been ‘tuned’ to the mercury deposition patterns found on the east coast, and the limited spatial and temporal variability of most concentration measurements further obscured geographic trends. While the information gathered from the MDN and any other atmospheric mercury measurements is necessarily improving scientific understanding of the mercury cycle, coordinated efforts to build on already existing technology are excellent next steps for mercury research.

The larger conclusion drawn from this evaluation is that mercury modeling does well when considered from a broad perspective. Each model captured the order of magnitude and CMAQ wet deposition did well against monthly totals. Yet in all cases, model performance
degrades at finer temporal scales, although this is not unexpected. In response, Chapter 4 will thoroughly examine the relationships surrounding ambient concentration and wet deposition for both measurements and model results with the intention of expanding current air quality models for mercury.
Figure 3-1 – Percent of Annual Emissions
Percent of annual emissions for a) Hg\(^0\), b) RGHg and c) PHg.
Figure 3-2 – Percentage of annual emissions for each source sector at both resolutions

a

b

LEGEND:
- EGUs
- Non-EGU Point Sources
- Mobile Sources
- Area Sources
Figure 3-3 – Grid Resolution Comparison

CMAQ output with NCDC observations (small circles) for average monthly temperature at a) 36 km resolution and b) 12 km resolution for July 2003.
Figure 3-4 – Model Performance for Precipitation
Total monthly precipitation for CMAQ and NCDC observations (small circles) for a) January at 36 km resolution, b) January at 12 km resolution, c) July at 36 km resolution and d) July at 12 km resolution.
Figure 3-5 – Resolution Comparison and Evaluation for Episodes
CMAQ total daily precipitation compared to daily total precipitation from NCDC Global Summary of the Day data for a) January 15th at 36 km resolution, a) January 15th at 12 km resolution, a) August 15th at 36 km resolution, and a) August 15th at 12 km resolution.
Figure 3-6 – Cold Bias for June

Bias calculated using CMAQ output compared with NARR data at three-hour intervals, averaged over the month of June.
Figure 3-7 – Fractional Bias for 2-m water mixing ratio
Fractional bias calculated using CMAQ water results and NARR fields at 3-hour intervals averaged over each month.
Figure 3-8 – Monthly Total Dry Deposition

(a) Graph 1

(b) Graph 2

Legend:

- Red: 12,000 ng/m²
- Orange: 10,000 ng/m²
- Yellow: 9,000 ng/m²
- Green: 8,000 ng/m²
- Blue: 5,000 ng/m²
- Purple: 2,000 ng/m²
- Pink: 1,000 ng/m²
- Brown: 100 ng/m²
- Black: 0 ng/m²

(ng/m²)
Total dry deposition for a) January, b) April, c) July and d) October, 2003.
Figure 3-9 – Percent Species Contribution to Annual Dry Deposition
Percent of total annual dry deposition for a) Hg$^0$, b) RGHg and c) PHg. Note the different scale for c) PHg.
Table 3-1 – Dry Deposition

<table>
<thead>
<tr>
<th>Month</th>
<th>CONUS Domain</th>
<th>Great Lakes Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Dry Deposition (kg)</td>
<td>Average Daily Dry Deposition (ng/m²)</td>
</tr>
<tr>
<td>Jan</td>
<td>3,474</td>
<td>1.765</td>
</tr>
<tr>
<td>Feb</td>
<td>3,196</td>
<td>1.798</td>
</tr>
<tr>
<td>Mar</td>
<td>3,364</td>
<td>1.709</td>
</tr>
<tr>
<td>Apr</td>
<td>3,104</td>
<td>1.630</td>
</tr>
<tr>
<td>May</td>
<td>2,982</td>
<td>1.515</td>
</tr>
<tr>
<td>Jun</td>
<td>2,776</td>
<td>1.458</td>
</tr>
<tr>
<td>Jul</td>
<td>2,784</td>
<td>1.415</td>
</tr>
<tr>
<td>Aug</td>
<td>2,460</td>
<td>1.250</td>
</tr>
<tr>
<td>Sep</td>
<td>2,289</td>
<td>1.202</td>
</tr>
<tr>
<td>Oct</td>
<td>2,435</td>
<td>1.237</td>
</tr>
<tr>
<td>Nov</td>
<td>2,800</td>
<td>1.470</td>
</tr>
<tr>
<td>Dec</td>
<td>3,125</td>
<td>1.588</td>
</tr>
<tr>
<td>Annual</td>
<td>34,790</td>
<td>1.503</td>
</tr>
</tbody>
</table>
Figure 3-10 – Map of MDN Sites

National Atmospheric Deposition Program
Mercury Deposition Network

- Active
- Inactive
Figure 3-11 – Percentage of Annual Wet Deposition

(a) Percentage of Annual Wet Deposition

(b) RGHg, PHg (%)
Percent of total annual wet deposition for a) Hg\textsuperscript{0}, b) RGHg, and c) PHg. Note the different scale for a) Hg\textsuperscript{0}.
Table 3-2 – Wet Deposition Statistics

<table>
<thead>
<tr>
<th>Month</th>
<th>CONUS Domain</th>
<th>Great Lakes Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Wet Deposition (kg)</td>
<td>Average Daily Wet Deposition (ng/m²)</td>
</tr>
<tr>
<td>Jan</td>
<td>805</td>
<td>9.813</td>
</tr>
<tr>
<td>Feb</td>
<td>676</td>
<td>9.131</td>
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<td>Mar</td>
<td>884</td>
<td>10.78</td>
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<td>Apr</td>
<td>959</td>
<td>12.08</td>
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<tr>
<td>May</td>
<td>1,247</td>
<td>15.21</td>
</tr>
<tr>
<td>Jun</td>
<td>1,511</td>
<td>19.05</td>
</tr>
<tr>
<td>Jul</td>
<td>1,822</td>
<td>22.22</td>
</tr>
<tr>
<td>Aug</td>
<td>1,927</td>
<td>23.50</td>
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<tr>
<td>Sep</td>
<td>1,755</td>
<td>22.11</td>
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<tr>
<td>Oct</td>
<td>1,638</td>
<td>19.97</td>
</tr>
<tr>
<td>Nov</td>
<td>1,285</td>
<td>16.20</td>
</tr>
<tr>
<td>Dec</td>
<td>1,164</td>
<td>14.20</td>
</tr>
<tr>
<td>Annual</td>
<td>15,675</td>
<td>16.19</td>
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</table>
Figure 3-12 – Wet Deposition over the CONUS domain
Monthly total deposition at 36 km horizontal resolution for a) January, b) April, c) July and d) October.
Table 3-3 – Wet Deposition Statistics for CONUS domain

<table>
<thead>
<tr>
<th>Month</th>
<th>MDN Average (ng/m²)</th>
<th>CMAQ Average (ng/m²)</th>
<th>Bias (ng/m²)</th>
<th>Fractional Bias (%)</th>
<th>$r^2$ Precipitation</th>
<th>$r^2$ Deposition</th>
</tr>
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<tbody>
<tr>
<td>Jan</td>
<td>287.80</td>
<td>211.87</td>
<td>-96.23</td>
<td>-52.96</td>
<td>0.020</td>
<td>0.414</td>
</tr>
<tr>
<td>Feb</td>
<td>395.38</td>
<td>460.94</td>
<td>83.57</td>
<td>-4.01</td>
<td>0.854</td>
<td>0.751</td>
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<tr>
<td>Mar</td>
<td>772.59</td>
<td>579.09</td>
<td>-169.28</td>
<td>-41.60</td>
<td>0.807</td>
<td>0.550</td>
</tr>
<tr>
<td>Apr</td>
<td>716.93</td>
<td>622.58</td>
<td>-86.01</td>
<td>-12.26</td>
<td>0.498</td>
<td>0.239</td>
</tr>
<tr>
<td>May</td>
<td>831.00</td>
<td>981.44</td>
<td>243.68</td>
<td>16.63</td>
<td>0.337</td>
<td>0.458</td>
</tr>
<tr>
<td>Jun</td>
<td>1395.50</td>
<td>1011.20</td>
<td>-373.46</td>
<td>-31.20</td>
<td>0.103</td>
<td>0.021</td>
</tr>
<tr>
<td>Jul</td>
<td>1165.89</td>
<td>1048.62</td>
<td>10.70</td>
<td>-8.53</td>
<td>0.388</td>
<td>0.392</td>
</tr>
<tr>
<td>Aug</td>
<td>1358.00</td>
<td>920.33</td>
<td>-286.30</td>
<td>-29.09</td>
<td>0.011</td>
<td>0.000</td>
</tr>
<tr>
<td>Sep</td>
<td>739.08</td>
<td>583.50</td>
<td>-51.97</td>
<td>-22.90</td>
<td>0.502</td>
<td>0.091</td>
</tr>
<tr>
<td>Oct</td>
<td>623.39</td>
<td>585.26</td>
<td>26.12</td>
<td>-3.9</td>
<td>0.470</td>
<td>0.169</td>
</tr>
<tr>
<td>Nov</td>
<td>456.42</td>
<td>592.79</td>
<td>147.62</td>
<td>36.53</td>
<td>0.003</td>
<td>0.002</td>
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<tr>
<td>Dec</td>
<td>512.18</td>
<td>632.08</td>
<td>90.08</td>
<td>10.10</td>
<td>0.205</td>
<td>0.035</td>
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</table>
Figure 3-13 – Fractional bias at 36 km horizontal resolution

Percent fractional bias for all MDN sites compared with percent fractional bias for only the 31 Great Lakes sites using output from the 36 km resolution CMAQ run over the CONUS domain.
Figure 14a – Modeled vs Observed Precipitation

**Figure 14a1**
January Precipitation (mm)

$y = 0.8191x + 1.2773$

$R^2 = 0.2745$

**Figure 14a2**
April Precipitation (mm)

$y = 0.5792x + 1.1607$

$R^2 = 0.6374$

Weekly precipitation totals from the MDN plotted against weekly precipitation from CMAQ output for a1) January, a2) April, a3) July and a4) October.
Figure 14b – Modeled vs Observed Wet Deposition

**b1**

January Wet Deposition (ng/m²)

\[ y = 0.5002x - 0.7973 \]

\[ R^2 = 0.3979 \]

**b2**

April Wet Deposition (ng/m²)

\[ y = 0.4484x + 59.287 \]

\[ R^2 = 0.3702 \]
Weekly wet deposition totals from the MDN plotted against weekly precipitation from CMAQ output for b1) January, b2) April, b3) July and b4) October.
Figure 3-15 – Precipitation vs Wet Deposition Fractional Bias

(a) January Fractional Bias

(b) April Fractional Bias
Monthly average fractional bias for precipitation and wet deposition at each MDN site using CMAQ output and MDN reported data.
Figure 3-16 – Surface Concentration Times Series at Devil’s Lake
Surface concentration comparison for observations and model results at Devil’s Lake for a) Hg$^0$, b) RGHg and c) PHg.
Table 3-4 – Statistics for Modeled versus Observed Surface Mercury Concentrations at Devil’s Lake

<table>
<thead>
<tr>
<th>Month</th>
<th>Hg⁰ Bias (ng/m³)</th>
<th>Fractional Bias (%)</th>
<th>RGHg Bias (ng/m³)</th>
<th>Fractional Bias (%)</th>
<th>PHg Bias (ng/m³)</th>
<th>Fractional Bias (%)</th>
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</thead>
<tbody>
<tr>
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<td>25.27</td>
<td>22.69</td>
<td>102.27</td>
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<td>May</td>
<td>-0.28</td>
<td>-16.37</td>
<td>14.61</td>
<td>85.76</td>
<td>14.28</td>
<td>58.08</td>
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<td>-0.27</td>
<td>-15.07</td>
<td>24.09</td>
<td>155.05</td>
<td>23.67</td>
<td>123.27</td>
</tr>
<tr>
<td>Jul</td>
<td>-0.04</td>
<td>-1.41</td>
<td>23.78</td>
<td>167.83</td>
<td>25.27</td>
<td>123.53</td>
</tr>
<tr>
<td>Aug</td>
<td>0.13</td>
<td>-9.94</td>
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<td>194.32</td>
<td>23.45</td>
<td>136.62</td>
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<td>0.08</td>
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<td>23.10</td>
<td>159.97</td>
<td>30.40</td>
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<tr>
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<td>3.52</td>
<td>15.96</td>
<td>126.24</td>
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<td>177.04</td>
<td>17.14</td>
<td>101.17</td>
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<table>
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<th>RHg Bias (ng/m³)</th>
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<td>May</td>
<td>29.13</td>
<td>69.97</td>
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<td>Jun</td>
<td>48.31</td>
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<td>Jul</td>
<td>50.33</td>
<td>148.44</td>
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<tr>
<td>Aug</td>
<td>50.99</td>
<td>188.52</td>
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<tr>
<td>Sep</td>
<td>54.75</td>
<td>152.03</td>
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<tr>
<td>Oct</td>
<td>36.79</td>
<td>122.04</td>
</tr>
<tr>
<td>Nov</td>
<td>24.98</td>
<td>154.41</td>
</tr>
<tr>
<td>Dec</td>
<td>33.57</td>
<td>154.26</td>
</tr>
<tr>
<td>Month</td>
<td>Hg$^n$</td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>--------</td>
<td>------------------</td>
</tr>
<tr>
<td></td>
<td>Observed Average (ng/m$^3$)</td>
<td>CMAQ Average (ng/m$^3$)</td>
</tr>
<tr>
<td>Apr</td>
<td>1.88</td>
<td>1.49</td>
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<td>May</td>
<td>1.79</td>
<td>1.50</td>
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<tr>
<td>Jun</td>
<td>1.78</td>
<td>1.50</td>
</tr>
<tr>
<td>Jul</td>
<td>1.52</td>
<td>1.46</td>
</tr>
<tr>
<td>Aug</td>
<td>1.38</td>
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<td>1.51</td>
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<table>
<thead>
<tr>
<th>Month</th>
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<th></th>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed Average (ng/m$^3$)</td>
<td>CMAQ Average (ng/m$^3$)</td>
<td>Observed Average (ng/m$^3$)</td>
<td>CMAQ Average (ng/m$^3$)</td>
<td></td>
</tr>
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<td>Apr</td>
<td>10.78</td>
<td>31.91</td>
<td>30.63</td>
<td>52.01</td>
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<td>10.48</td>
<td>31.10</td>
<td>17.08</td>
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<td>6.21</td>
<td>52.56</td>
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<tr>
<td>Sep</td>
<td>6.96</td>
<td>35.84</td>
<td>10.12</td>
<td>60.91</td>
<td></td>
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<td>7.11</td>
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<td>11.07</td>
<td>47.35</td>
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<td>Nov</td>
<td>6.48</td>
<td>19.27</td>
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<td>30.51</td>
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<td>Dec</td>
<td>9.40</td>
<td>26.46</td>
<td>11.03</td>
<td>42.31</td>
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</table>
Figure 3-17 – Uniform Scaling of Model Concentration Output

$\text{pg/m}^3$
Comparison of $a_{1,2}$ surface RGHg concentrations reduced by a factor of 25 (94%) compared with ambient measurements and $b_{1,2}$ surface PHg concentrations reduced by a factor of 5 (80%) compared with ambient measurements.
Figure 3-18 – Fourteen-day Running Average for Observed and Modeled Surface Concentrations at Milwaukee

\[ \text{ng/m}^3 \]
Fourteen-day running average of surface concentration compared for observations and model results at Devil’s Lake for a) Hg⁰, b) RGHg and c) PHg.
References


Chapter 4

Atmospheric Mercury Modeling Results and Discussion

As mentioned in previous chapters, modeling atmospheric mercury is not a simple task, and numerous uncertainties in atmospheric mercury chemistry and transport make model results difficult to interpret. The goal of this chapter is to begin to diagnose model error for further model development and advancement of atmospheric mercury science.

Chapter 3 showed that the Community Multiscale Air Quality Model (CMAQ) under-predicts total mercury wet deposition, while over-predicting surface concentrations for reactive species. There are numerous explanations for this model behavior, including model emissions, chemistry, transport and removal processes for sources of error. To investigate model behavior, two additional runs using modified boundary conditions were compared to the base case CMAQ run described in Chapter 2. Both of these model experiments will be discussed throughout this chapter and analyzed to diagnose model error.

Introduction

Chapter 3 clearly showed that the model over-predicted surface concentrations of reactive species at both the Devil’s Lake and Milwaukee sites. This suggests that RHg emissions are too high, background RHg in the model is too high, chemical production of RHg from Hg$_0$ is too fast, RHg removal is too slow or some combination of these. The complex interactions between mercury species require careful consideration since errors in any of these processes can be compensated by errors in other systems. Building on the model evaluation presented in Chapter 3, this chapter intends to diagnose how these model processes may lead to surface over-prediction while still reporting accurate total wet deposition.
To investigate possible sources of error, CMAQ was run with zero mercury concentrations at the domain boundaries\(^1\) for April and July with 10 days spin-up over the Great Lakes. Boundary inflow data was created from the 36 km resolution model run over the Continental U.S. with mercury species set to zero and all other species unaltered. The results from this run, referred to as Case EMIS, model the effect of local mercury emissions alone. Case EMIS output was then subtracted from the base case results to show the influence of imported mercury alone, referred to here as Case IMPT; once transported into the domain, these imported concentrations are subject to the same chemical and removal processes as local emissions.

**Influence of Imported Versus Local Emissions for Mercury**

The Case EMIS and Case IMPT scenarios described above were done for the months of April and July. These two months were chosen based on the 2003 base case run. In April, CMAQ performance for surface concentrations and wet deposition was better than any other month – RHg concentrations showed 57% fractional bias, and wet deposition totals for the domain had a fraction bias of -32%. July showed performance typical of the rest of the year with wet deposition estimates showing an average -42% fractional bias over the Great Lakes domain, and high RHg surface concentrations at an average 136% fractional bias for Devil’s Lake. Further, July also showed higher total deposition and higher concentrations of oxidants that can transform Hg\(^0\) to RHg in the atmosphere. Lastly, many atmospheric mercury modeling studies focus on July [e.g Pongprueska et al., 2008; Gbor et al., 2007, Bullock and

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\(^1\) Runs were also done with zero mercury boundary conditions and zero mercury initial conditions. This run showed no significant difference from the zero boundary conditions runs and is not discussed. Lin et al. 2008 found similar results for RHg initial conditions.
Brehme, 2002], and results presented here can be assessed in the context of other modeling research.

As mentioned in Chapter 1 and elsewhere, the global background concentration of Hg\(^0\) is much larger than reactive species concentrations, and this Hg\(^0\) pool accounts for over 95% of ambient total mercury concentrations. Figure 4-1 shows the average monthly surface concentrations for the base case (imported and locally emitted mercury) and the amount due to boundary inflow and area emissions for April and July. Looking at just the base case concentrations, there is little absolute change in Hg\(^0\) concentrations, although the western edge of the Great Lakes domain for July shows lower Hg\(^0\) surface concentrations. This is may be due to lower Hg\(^0\) concentrations in the southwestern U.S., which serves as a large source of Hg\(^0\) into the Great Lakes region, [Supplemental Figure 4-A] or higher production of RHg, and consequent deposition, because of higher oxidant concentrations. Investigation of the average Hg\(^0\) entering the Great Lakes domain along the western border does show a decrease in July [Supplemental Figure 4-B], but a concurrent increase in oxidant concentrations (summer O\(_3\), \(\cdot\)OH, and H\(_2\)O\(_2\)) throughout the domain prevents any strong conclusions. Other patterns for surface concentrations in the base case show an increase, about a factor of 1.3, in average surface RGHg concentrations form April to July. These changes are paralleled by an increase of a factor of 1.4 in the surface RGHg concentration in the Case IMPT, suggesting that the increase in RGHg surface concentration between April and July is due to increased Hg\(^0\) oxidation. This hypothesis is also supported by an increase in the concentration of mercury-relevant oxidants (O\(_3\), \(\cdot\)OH, H\(_2\)O\(_2\)) between two months, and a decrease in the average contribution of local emissions – in April the domain average contribution of RGHg local emissions to surface concentrations is 26%, while in July local
emissions contribute 21%. For PHg there is a decrease in the surface concentration as a domain average of a factor of 0.95 April to July. This decrease is likely due to changes in local emissions, and not imported mercury because PHg concentrations in Case EMIS decrease more significantly from April to July (factor of 0.81), than in Case IMPT (factor of 0.97). Additionally, 13% of PHg surface concentrations are attributable to local emissions April, compared to 11% in July – further evidence that the average decrease in PHg surface concentrations in from April to July is due to changes in emissions. In sum, RGHg surface concentrations increase on average from April to July due to changes associated with imported mercury, while PHg surface concentrations decrease on average from April to July due to changes in emissions.

Looking further at the relative influence of local emissions and imported concentrations, it is unsurprising that modeling only locally emitted mercury (Case EMIS) results in drastically reduced Hg$_0$ concentrations – showing average reductions by a factor of 66 in April and 88 in July compared to the base case. This underscores yet again the dominance of imported Hg$_0$ for ambient total mercury concentrations as mentioned throughout this study. Reductions in PHg and RGHg surface concentrations in Case EMIS are significant. As a domain average, RGHg is reduced by a factor of 7 in April and 9 in July, while PHg shows reductions of a factor of 11 in April and 16 in July. The average percent contribution of RGHg and PHg emissions to surface concentrations is much larger than for Hg$_0$, but is still considerably smaller than the contribution from imported mercury. All mercury species show a decrease in the contribution of emissions from April to July. For Hg$_0$, this is likely due to a decrease in emissions, while for RGHg and PHg, this probably due to the increase in available oxidants, which transform Hg$_0$ to both species.
In contrast to the large reductions in surface concentration with Case EMIS, the background-only case, Case IMPT, shows smaller changes in surface concentrations. For both test months, Hg\(^0\) maintains values similar to those seen in the base case run, while RGHg and PHg are only marginally reduced, even when local emissions are entirely omitted. Thus, overall, ambient concentrations in April and July show almost identical values between Case IMPT and the base case.

At Devil’s Lake and Milwaukee, the strong influence of imported mercury on modeled surface concentrations for reactive mercury species is equally clear, shown in Figure 4-2a. At Devil’s Lake, Case EMIS shows RHg values closer to observed values in July, which was consistently over-predicted in the base case. In April, Case EMIS underpredicts reactive species at Devil’s Lake, which is expected considering that modeled surface concentrations were similar to measurements in the base case. The better agreement in July with Case EMIS is limited to order of magnitude, however. In Milwaukee, neither Case EMIS nor Case IMPT capture the magnitude of observed surface RHg concentrations, and modeled surface concentrations are equally influenced by emissions and imported concentrations. This may imply that both emissions and RHg concentrations due to imported mercury are too high over Milwaukee in the model, but since the comparison is across different years, it is unclear.

In comparison with the scaled July concentrations for Devil’s Lake from Chapter 3, Case EMIS does not capture general diurnal cycling of RGHg and PHg concentrations. Case IMPT, however, does capture Devil’s Lake diurnal cycles in July, similar to Chapter 3, shown in Figure 4-3 Using the same scaling, with a factor of 25 reduction for RGHg and a factor of 5 reduction for PHg, percent fractional bias is -1.5% for RGHg and -8.5% for PHg.
That this diurnal trend is evident in Case IMPT and not Case EMIS suggests that CMAQ may be capturing some part of the cycle for producing RGHg and PHg from background Hg$^0$, albeit at much higher levels than in reality.

Although the Case EMIS surface concentrations were of the same magnitude as observations, wet deposition over the Great Lakes is appreciably reduced for both July and April without background mercury, illustrated in Figure 4-4. Changes to Case IMPT wet deposition, however, are very small. Weekly wet deposition fractional bias for the base case is -24% in April and -46% in July, while Case IMPT shows a fractional bias of -31% and -50%, and Case EMIS fraction bias is -119% and -170% for those respective months. Recalling from Chapter 3 that CMAQ wet deposition is composed of over 90% RHg, comparison of the two cases shows that imported reactive species are also the main source of wet deposited mercury. Similar analysis for dry deposition shows that imported RHg constitutes 62.3% of total dry deposition in April and 67.3% in July as a domain average and is mapped over the Great Lakes in Figure 4-5.

In light of the Case EMIS and Case IMPT results, it is clear that mercury inflow at the boundaries is driving surface concentrations, and wet and dry deposition for all species. Thus, the surface concentration over-prediction in conjunction with slight wet deposition under-prediction in CMAQ indicates errors in boundary values, model chemistry and/or deposition rates. Of these possible errors, model chemistry and deposition are areas of high uncertainty, and are also very sensitive to model parameterization. The order of magnitude difference between RHg and Hg$^0$ concentrations allows small changes in reaction rates and chemical cycling to have a pronounced impact on RHg concentrations throughout the atmosphere. Likewise, the large difference in wet and dry deposition rates for RHg and Hg$^0$
makes mercury modeling sensitive to removal processes. Further, these processes are interdependent and incorrect concentrations will lead to incorrect removal and vice versa. To clarify what processes are the main sources of model error, the next two sections will focus on model chemistry, transport and deposition.

**CMAQ Model Chemistry**

As described in Chapter 2, CMAQ includes both gas phase and aqueous phase mercury chemistry. Gas phase chemistry is limited to the oxidation of Hg\(^0\) to RGHg and PHg, while aqueous chemistry both oxidizes Hg\(^0\) and reduces reactive species. [See Chapter 2, Figure 2-6] The above discussion of Case IMPT and Case EMIS showed that imported mercury is the main source of surface concentrations. So, to diagnose model over-prediction for surface RHg concentrations, investigation will focus on the various model processes that link imported mercury to RHg. If a strong connection can be demonstrated between oxidizing species and RHg concentrations, then over-prediction can be explained as a result of higher reaction rates than actually occur in the atmosphere. This section will examine the chemical processes for RHg and their likelihood for error.

In the CB05 chemistry mechanism used in CMAQ v4.6, gaseous Hg\(^0\) is oxidized by four gas phase species – O\(_3\), Cl\(_2\), 'OH and H\(_2\)O\(_2\). Atmospheric modeling studies have shown that oxidation by O\(_3\) or 'OH is the dominant chemical production pathway for RHg, depending on the choice of reaction rate [Lin et al., 2006; Lin and Tao, 2003]. Using the second-order reaction rates given in Chapter 2 [see Figure 2-6, reactions RG1-RG4], \(k\), and average monthly oxidant concentrations, \([X]\), Hg\(^0\) lifetimes, \(\tau\), were calculated for gas-phase reaction, using
\[ \tau = \frac{1}{k[X]} \]

Since these lifetimes assume that oxidant concentrations are 100% gas phase, these calculations reflect an upper bound for oxidation in gas phase. In model calculations, some percentage of these concentrations are actually in aqueous phase, which has different chemistry [see Chapter 2, Figure 2-6, reaction RA1-RA7], but model output does not indicate phase for each species.

Calculations show that oxidation by gaseous O\(_3\) occurs at the shortest timescale, on an average of 4.5 days. [Table 4-1] Hg\(^0\) oxidation by \(^{\cdot}\)OH and H\(_2\)O\(_2\) occur more slowly, on timescales of roughly 100 days and a year, respectively. Oxidation by Cl\(_2\) is orders of magnitude greater than those for O\(_3\), \(^{\cdot}\)OH and H\(_2\)O\(_2\), on the order of millions of years, largely due to very small concentrations of Cl\(_2\). The important of O\(_3\) and \(^{\cdot}\)OH oxidation is expected based on a review of the literature [e.g. Lin et al., 2007; Lin and Tao; 2003] and the summer peak in surface concentrations: because RHg emissions are highest in winter, with stable Hg\(^0\) concentrations year-round, a summer peak in surface concentrations due to chemical production must be by way of seasonal species, such as O\(_3\), \(^{\cdot}\)OH and H\(_2\)O\(_2\).

Figure 4-6 shows the average concentration of the three main oxidizing species and background mercury concentrations at the surface for April and July (from Case IMPT results). Spatial patterns suggest that O\(_3\) is not as important for oxidation as would be anticipated from the lifetime calculated above. Because CMAQ does not model any Hg\(^0\) dry deposition to the lakes and wet deposition is not continuous, the only Hg\(^0\) removal mechanisms over the waterbodies is through chemical oxidation. Additionally, ozone is known to build up over the lakes in the summer, a processes captured in the CMAQ model,
and RHg dry deposition to the lakes is low as well. Thus, the surface layer over the Great Lakes should provide an ideal location for considerable RHg production, if O₃ oxidation is a significant source for RHg. However, high model ozone concentrations over the lakes in July do not led to an increase in RHg concentrations. Analogous high O₃ trends in the Ohio River Valley also do not show a signal in RHg concentrations. Conducting similar analysis for H₂O₂, high concentrations in the south west of the domain are not seen in RHg results. In fact, surface H₂O₂ concentrations show spatial patterns nearly opposite of those for RHg. Thus, neither gas phase O₃ nor gas phase H₂O₂ have a strong spatial relationship with RHg concentrations. Spatial trends for 'OH surface concentrations, however, are comparable. Unlike for O₃ and H₂O₂, there are no significant areas of high 'OH concentrations that do not show increased RHg concentrations as well. From this analysis, 'OH is likely the strongest oxidant, a conclusion further supported by previous studies and the reaction rates for gas-phase oxidation of Hg⁰ in CMAQ version 4.6.

To look at spatial relationships more closely, spatial correlations were calculated for Hg⁰ and RHg with each of the three chief oxidants according to the formula

\[ \text{cor} = \frac{\sum (H_{g_{i,j}} - \overline{Hg})(O_{x_{i,j}} - \overline{Ox})}{\sigma_{Hg}\sigma_{Ox}}, \]

where \( H_{g_{i,j}} (O_{x_{i,j}}) \) is the monthly average concentration of a given mercury species (oxidant) at location \( i,j \) with domain mean monthly average \( \overline{Hg} (\overline{Ox}) \), and standard deviation \( \sigma_{Hg} (\sigma_{Ox}) \). Values nearest 1 and -1 indicate strong relationships, while values near 0 indicate little to no statistical relationship. Correlations were calculated using results from the base case run, and Figure 4-7 shows the spatial correlation between mercury species and
oxidants at each model layer for each month. These spatial correlations must be interpreted bearing in mind the concentration maps in Figure (since correlations may indicate common causes and/or dependence\(^2\)), as well as the products from the oxidation reactions (e.g. \(\cdot\)OH oxidation of Hg\(^0\) creates both RGHg and PHg, while H\(_2\)O\(_2\) oxidation produces only RGHg).

As expected, mercury concentrations in the planetary boundary layer\(^3\) show strong positive correlations with all oxidant concentrations in the summer when higher solar radiation and temperatures lead to greater concentrations of \(\cdot\)OH, H\(_2\)O\(_2\) and O\(_3\). As a yearly average, \(\cdot\)OH and PHg show the strongest positive correlation, with a value of 0.4255, followed by O\(_3\) and RGHg at 0.3402. For \(\cdot\)OH and H\(_2\)O\(_2\), there is also a stronger negative correlation with Hg\(^0\); the annual average correlation with Hg\(^0\) is -0.2170 for \(\cdot\)OH, and -0.2174 for H\(_2\)O\(_2\), compared to a slight positive correlation of Hg\(^0\) with O\(_3\) of 0.1566 as an annual average. For Hg\(^0\) and O\(_3\), correlations change with altitude (i.e. are positive in the PBL, switch to negative at in the lower free troposphere and become more positive in the higher free troposphere), and are relatively stable at each model layer throughout the year. These patterns are likely due to changes in concentrations with altitude. Ozone can be high near the surface due to anthropogenic emissions and higher again in the upper troposphere where stratospheric ozone starts to mix down and/or is imported from anthropogenic sources; Hg\(^0\) will also be higher at the surface due to anthropogenic sources, many of which are spatially similar to ozone emissions.\(^4\) In the upper troposphere, both ozone and Hg\(^0\) are well-

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\(^2\) For example, reactive mercury concentrations have a strong spatial correlation with SO\(_2\) because they have similar emissions sources not because they have interdependent chemical cycling

\(^3\) Model layers 1-9 roughly correspond to the planetary boundary layer, and the remaining layers can be considered representative of the free troposphere.

\(^4\) Urban centers, however, are an exception. Mercury emissions are higher over urban centers, while ozone tends to be lower over cities due to higher NO\(_x\) emissions, which limit ozone production.
mixed and influenced by global pools – albeit Hg\(^0\) concentrations are associated with long-range transport of foreign emissions, and O\(_3\) with stratospheric subsidence.

Temporal patterns are clear for PHg correlations with all oxidants, showing strong positive correlations in the summer. For H\(_2\)O\(_2\), however, this is not due to direct production, since H\(_2\)O\(_2\) oxidation creates only RGHg. Similar seasonal patterns are visible for RGHg correlations with O\(_3\) and 'OH, but H\(_2\)O\(_2\) shows no significant seasonal pattern in the planetary boundary layer. In the free troposphere (model layers 10-15), 'OH shows stronger correlations with PHg in the winter, and H\(_2\)O\(_2\) demonstrates no notable relationships to either PHg or RGHg, while O\(_3\) shows stable positive correlations with RGHg and negative correlations with PHg throughout the year.

Contrasting correlations for reactive species and Hg\(^0\) further supports the dominance of 'OH as the main oxidating species in this CMAQ parameterization. Hg\(^0\) shows no relationship with 'OH in the PBL, and a strong negative correlation in the free troposphere. The negative correlation in higher model layers is complemented by high correlations with RGHG in those same areas. The absence of any relationship in the PBL may be explained by low concentrations of 'OH, which may oxidized Hg\(^0\), but those losses are small relative to the entire Hg\(^0\) pool.

Correlations at the surface further support the conclusion that 'OH oxidation is a significant source for RHg concentrations. Average surface correlations during warmer months (April-September) show strong relationships between 'OH and both reactive species, with correlations of 0.4180 for PHg and 0.3434 for RGHg. Hydrogen peroxide also shows high positive correlations with surface PHg (correlation of 0.4884), but this is not due to direct production, as mentioned earlier.
Based on lifetime analysis, surface concentration distribution of reactive mercury species, and correlations with major Hg\(^0\) gas-phase oxidants, local production of RHg from global Hg\(^0\) pools is likely to be a significant source for surface concentrations. Further, high uncertainty for oxidation reaction rates allows the possibility that local production is unrealistic, and can explain model error when results are compared with observations. In sum, analysis shows that chemical production, via Hg\(^0\) oxidation, is strongly linked to RHg concentrations and over-production is a likely explanation for model over-prediction at the surface.

**CMAQ Deposition and Transport**

A second possible source of surface over-prediction is slow removal processes. Since model experiments showed non-local mercury pools as the main source of ambient concentrations and deposition, slow removal of ambient pools may cause model over-prediction. Examining the connection between removal processes and surface concentrations is difficult, however, because there is little data on mercury dry deposition, and because wet deposition is reported only as total mercury. Thus, mercury dry deposition rates are highly uncertain, but are thought to be as effective as wet deposition for removing reactive mercury. Total wet deposition is known with some confidence due to the MDN reporting, but model totals are dependent on uncertain aqueous chemistry.

Chapter 3 evaluated CMAQ wet deposition and showed that model results corresponded well with total mercury wet deposition and precipitation observations. Case IMPT and Case EMIS results showed that CMAQ wet deposition is mainly composed of non-local RGHg and PHg. If total mercury wet deposition and precipitation levels are to remain unchanged while reducing surface concentrations, aqueous chemistry is the most
likely source of error, which has already been demonstrated as a likely source of high surface concentrations.

Without observations to similarly constrain analysis, model performance for dry deposition is difficult to examine. A lifetime analysis provides a quick method to inspect model behavior. Model dry deposition of PHg is low compared to RGHg and Hg$^0$, with 160 kg of PHg dry deposited to the entire Great Lakes domain throughout the modeled year, compared to total mercury dry deposition of 4,278 kilograms – less than 4%. For this reason, dry deposition lifetimes were only calculated for surface RGHg and Hg$^0$ using the formula,

$$\tau = \frac{h}{V_D},$$

where $\tau$ is the lifetime (s), $V_D$ is the dry deposition velocity (m/s) from MCIP, and $h$ is the mid-layer altitude (m) of the surface model layer. Monthly average dry deposition lifetimes for gaseous mercury over the Great Lakes range from less than 10 minutes for RGHg to over two weeks for Hg$^0$, and on average, surface RGHg is deposited within an hour and Hg$^0$ deposition to land occurs in about two and a half days. Figure 4-8 shows spatial variation in RGHg and Hg$^0$ dry deposition lifetime throughout the year. The high rate of deposition for RGHg is due to its volatility, and compared to other gaseous species dry deposition lifetimes, surface concentrations of RGHg are removed rapidly. Table 4-2 compares dry deposition lifetimes for a few chemical species for comparison.

Dry deposition to the lake bodies is much slower than to land for RGHg, and is effectively zero for Hg$^0$. This is because high surface flux of mercury makes net deposition very small for both species, a process observed in various studies [e.g. Poissant and Casimir, 1998]. Dry deposition for both RGHg and Hg$^0$ is seasonal, with both showing higher dry
deposition velocities in the winter over the Great Lakes domain. Snow cover appears to be driving the higher modeled winter dry deposition, but it is not clear how this process actually occurs due to the volatility of mercury in snow [Witherow and Lyons, 2008; Lalonde et al., 2002]. Dry deposition occurs more rapidly to forested areas, due to greater surface area, and higher moisture content also encourages deposition.

If Hg\textsuperscript{0} dry deposition is underestimated, surface Hg\textsuperscript{0} will increase, and may explain high surface RHg depending on the efficiency of Hg\textsuperscript{0} oxidation. PHg dry deposition lifetimes were not calculated explicitly due to complications in assigning particle size, which drives deposition rates for aerosols, but low PHg dry deposition totals indicate that PHg dry deposition lifetimes are longer than those of RGHg. These longer removal rates for PHg may lead to over-prediction of both PHg and RGHg concentrations since CMAQ includes mechanisms for cycling between gas and particle phase for reactive mercury.

A second analysis for dry deposition rates uses information on advection processes to compare actual RHg lifetimes with those in CMAQ. This investigation will focus on Devil’s Lake since local emissions are effectively zero, and thus any reactive mercury reaching the site must be either advected or locally produced from background Hg\textsuperscript{0}.

As shown in Chapter 3, observed RHg concentrations were highest in April and the first half of May. [See Chapter 3, Figure 3-16] Wind direction measurements taken at the site show that winds were predominantly out of the east for April and early May, compared to prevailing westerly winds the rest of the year shown in Figure 4-9a. During the easterly wind events, the Devil’s Lake measured RHg concentrations show a significant increase, most likely reflecting advection from high-emitting areas to the east (e.g. Milwaukee) [Rutter et al. 2007]. Average modeled monthly winds over the Great Lakes region also show surface
winds from the east in April and early May over southern Wisconsin, and monthly average surface winds over Devil’s Lake come out of the west/southwest from June-December, as in observations. [Figure 4-9b] Further, Milwaukee and regions to the east of Devil’s Lake have higher RHg concentrations throughout the year as well. Thus, while CMAQ shows similar wind patterns to observations and higher concentrations to the east, this combination does not result in an increase in either RGHg or PHg surface concentration in the Devil’s Lake region, as demonstrated in surface measurements. This suggests that the modeled RHg lifetime is shorter than actual timescales, a possible result of high dry deposition rates.

This analysis indicates that dry deposition rates may be a contributing factor to high surface concentrations, but not because they are too slow, rather, it is more likely that deposition occurs to quickly in the CMAQ model. A slower dry deposition rate would in turn allow for less chemical production of RHg while still providing a source of reactive mercury to maintain levels of wet deposition. Since total mercury wet deposition has historically been the only tool for model evaluation, it is reasonable to assume that model parameterization may be tuned to wet deposition, but in doing so, incorrectly assumes high rates of deposition and production. Thus, in explaining model over-prediction, the chemical production of mercury remains the most likely direct cause, and dry deposition rates were over-estimated to maintain appropriate levels of wet deposition.

Conclusions and Next Steps

As shown in Chapter 3, CMAQ generally captures total wet deposition as compared to MDN measurements, and model experiments presented here demonstrate that wet deposition is driven by imported reactive mercury pools. These imported RHg pools are chemically produced from the global Hg\(^0\) pool, driven the oxidant \(^{\cdot}\)OH. In the analysis of
RHg transport, CMAQ shows little influence from advected RHg, while observations are influenced by regional emissions. This analysis points to high dry deposition rates in the model that do not reflect actual atmospheric processes. In this case, lowering RGHg dry deposition rates\(^5\) would require reductions in Hg\(^0\) oxidation rates in order to maintain wet deposition values, thus decreasing local production of RHg. These modifications may bring ambient concentrations within range of ambient concentration observations, although further study is needed to identify appropriate rates of deposition and oxidation.

Therefore, this analysis underscores the need for further investigation into dry deposition and the inter-species chemical cycling of mercury. The agreement between model and observed wet deposition is likely due to compensating errors, given the demonstrated over-prediction of surface concentration, and this evaluations casts doubt on the ability of CMAQ version 4.6 to capture actual atmospheric mercury processes. In this sense, the chemical processes for atmospheric mercury remain uncertain and advanced research into the chemical kinetics would aid modeling efforts. As other modeling studies have echoed [e.g. Bullock et al., 2009; Sunderland et al., 2008; Lin et al., 2007] a better understanding of dry deposition for all mercury species is paramount. Surface exchanges of mercury have proven complex and capturing these processes is no small task, but dry deposition rates play an important role in determining atmospheric concentrations.

From the analysis presented here and in previous chapters, it is clear there is considerable room for model development. Modeling efforts to date have taken advantage of the most up-to-date science, but real understanding of the atmospheric mercury cycle is

\(^5\) Recall that PHg is dry deposited based on particle size and PHg deposition rates cannot be changed without altering the particle size distribution of PHg.
limited by both its complexity and minimal measurement data. Interpreting model results is difficult in light of such uncertainty, but as demonstrated here, all contributions are of value.
Figure 4-1 – Average Monthly Surface Concentrations

<table>
<thead>
<tr>
<th>Base Case</th>
<th>Case EMIS</th>
<th>Case IMPT</th>
</tr>
</thead>
<tbody>
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<td><img src="image9.png" alt="Map" /></td>
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</tbody>
</table>

Figures a₁-c₃ show average surface concentration for April, and d₁-f₃ are for July. Each row is a different mercury species (e.g. a₁-a₃ are Hg⁰ concentrations) and each column is a different model run (e.g. a₁-f₁ are all base case results).
Figures a₁-c₃ show average surface concentration for April, and d₁-f₃ are for July. Each row is a different mercury species (e.g. a₁-a₃ are Hg⁰ concentrations) and each column is a different model run (e.g. a₁-f₁ are all base case results).
Figure 4-2 – Surface Concentration at Devil’s Lake and Milwaukee*
CMAQ shows the actual grid cell containing the Milwaukee measurement site as over the lake. However, the differences in concentration and emissions between the actual grid cell and those to the immediate west or south are negligible. Figure a3 is for the grid cell containing the measurement site.

Figures a1 and a2 show RHg surface concentrations at Devil’s Lake and compare hourly values from observations and the three model runs for April and July respectively. Figure a3 compares the three model runs over Milwaukee. As expected emitted and imported mercury are equally influential in Milwaukee, while imported mercury dominates for the Devil’s Lake site. The Devil’s Lake data (a1 and a2) are from 2003, while the Milwaukee data (b) uses observations from 2004 and model results from 2003. Figure a3 should not be considered a one-to-one comparison but only an order of magnitude approximation.
Figure 4-3 – Scaled Surface Concentration at Devil’s Lake

Figure a and b show scaled Case IMPT surface concentrations for RGHg and PHg, respectively, over Devil’s Lake for July. These figures can be compared with Figure 3-17 in Chapter 3.
Figure 4-4 – Weekly Wet Deposition* over Great Lakes Domain

One data point beyond April chart limits and two data points beyond July chart limits; values are listed in the lower right-hand corner.

Figures a and b compare weekly total wet deposition from the MDN over the entire Great Lakes domain for each of the three model runs. The substantial decrease in wet deposition totals for Case EMIS demonstrates model dependence on imported mercury in order to capture wet deposition values similar to observations.
Figure 4-5 – Total Dry Deposition and Source Contribution
Figures a1-a5 show dry deposition totals, and species and source contribution for April, and figures b1-b5 show the same series for July. Figure a1 is the total dry deposition for April from all sources. The remaining figures show percent contribution to monthly totals for RHg and Hg⁰ depending on source. The figures show: a2) imported RHg April percent contribution, a3) imported Hg⁰ April percent contribution, a4) emitted RHg April percent contribution, and a5) emitted Hg⁰ April percent contribution.
Figures a1-a5 show dry deposition totals, and species and source contribution for April, and figures b1-b5 show the same series for July. Figure b1 is the total dry deposition for July from all sources. The remaining figures show percent contribution to monthly totals for RHg and Hg0 depending on source. The figures show: b2) imported RHg July percent contribution, b3) imported Hg0 July percent contribution, b4) emitted RHg July percent contribution, and b5) emitted Hg0 July percent contribution.
Table 4-1 – Lifetime for Hg\(^0\) due to Gas Phase Oxidation

a

<table>
<thead>
<tr>
<th>Oxidant* (Reaction(^\S))</th>
<th>O(_3) (RG1)</th>
<th>H(_2)O(_2) (RG3)</th>
<th>OH (RG4)</th>
<th>Total</th>
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<tr>
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<td>5.70 days</td>
<td>1468 days</td>
<td>709.9 days</td>
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<td>February</td>
<td>5.54</td>
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<td>135.8</td>
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</tr>
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<td>May</td>
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<td>70.9</td>
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</tr>
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<td>June</td>
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<td>September</td>
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<td>December</td>
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b

<table>
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<tr>
<th>Oxidant (Reaction)</th>
<th>O(_3) (RG1)</th>
<th>H(_2)O(_2) (RG3)</th>
<th>OH (RG4)</th>
<th>Total</th>
</tr>
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<tbody>
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<td>9.94 days</td>
<td>4004 days</td>
<td>577.4 days</td>
<td>9.71 days</td>
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<tr>
<td>February</td>
<td>10.06</td>
<td>4328</td>
<td>387.0</td>
<td>9.75</td>
</tr>
<tr>
<td>March</td>
<td>10.07</td>
<td>4224</td>
<td>257.0</td>
<td>9.65</td>
</tr>
<tr>
<td>April</td>
<td>10.09</td>
<td>4216</td>
<td>187.8</td>
<td>9.53</td>
</tr>
<tr>
<td>May</td>
<td>10.09</td>
<td>4545</td>
<td>156.3</td>
<td>9.43</td>
</tr>
<tr>
<td>June</td>
<td>10.24</td>
<td>4272</td>
<td>137.5</td>
<td>9.47</td>
</tr>
<tr>
<td>July</td>
<td>10.27</td>
<td>3566</td>
<td>139.7</td>
<td>9.51</td>
</tr>
<tr>
<td>August</td>
<td>10.29</td>
<td>3092</td>
<td>135.5</td>
<td>9.50</td>
</tr>
<tr>
<td>September</td>
<td>10.30</td>
<td>4098</td>
<td>202.2</td>
<td>9.75</td>
</tr>
<tr>
<td>October</td>
<td>10.03</td>
<td>4210</td>
<td>332.4</td>
<td>9.69</td>
</tr>
<tr>
<td>November</td>
<td>10.01</td>
<td>3953</td>
<td>437.8</td>
<td>9.74</td>
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<tr>
<td>December</td>
<td>10.07</td>
<td>3817</td>
<td>568.2</td>
<td>9.85</td>
</tr>
</tbody>
</table>

* Cl\(_2\) is not listed since the average lifetime is greater by many orders of magnitude. The annual average timescale for RG2 to occur in the PBL is 1,108,000,000 years. In the upper troposphere it is twice as long.

\S\ See Chapter 2, Figure 2-6
Figure 4-6 – Average Surface Concentration for RHg and Main Hg$^0$ Oxidants
Figures are a1) average RHg surface concentration due to importer mercury (Case IMPT) for April and a2) July; b2) average O3 surface concentration for April and b2) July; c1) average H2O2 surface concentration for April and c2) July; and d1) average ·OH surface concentration for April and d2) July.
Figure 4-7 – Spatial Correlations for Mercury and Major Gas-Phase Oxidants
Figures are spatial correlations for $a_1$) Hg$^0$ and O$_3$, $a_2$) RGHg and O$_3$, $a_3$) PHg and O$_3$, $b_1$) Hg$^0$ and \textsuperscript{1}OH, $b_2$) RGHg and \textsuperscript{1}OH, $b_3$) PHg and \textsuperscript{1}OH, $c_1$) Hg$^0$ and H$_2$O$_2$, $c_2$) RGHg and H$_2$O$_2$, and $c_2$) PHg and H$_2$O$_2$. 
In CMAQ, Hg₀ dry deposition occurs very slowly to the lakes (on the order of years) and were not included in Figures a-d.

Figures a-d show 2003 monthly Hg₀ average dry deposition lifetime for January (a), April (b), July (c) and October (d). Figures e-h show 2003 monthly RGHg average dry deposition lifetime for January (e), April (f), July (g) and October (h).
Table 4-2 – Dry Deposition Lifetime Comparison

<table>
<thead>
<tr>
<th>Species</th>
<th>Maximum Annual Dry Deposition Lifetime over Great Lakes Domain* (hours)</th>
<th>Minimum Annual Dry Deposition Lifetime over Great Lakes Domain (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>2.53</td>
<td>0.657</td>
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<tr>
<td>Sulfate</td>
<td>6.56</td>
<td>2.53</td>
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<td>HNO₃ &lt;sup&gt;§&lt;/sup&gt;</td>
<td>0.464</td>
<td>0.289</td>
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<tr>
<td>NH₃</td>
<td>1.44</td>
<td>0.494</td>
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<td>PAN</td>
<td>3.71</td>
<td>12.1</td>
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<td>HONO</td>
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<td>0.593</td>
</tr>
<tr>
<td>CO</td>
<td>14.9</td>
<td>1.37</td>
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<tr>
<td>NO</td>
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<td>25.4</td>
</tr>
<tr>
<td>NO₂</td>
<td>29.0</td>
<td>15.3</td>
</tr>
</tbody>
</table>

*Dry deposition to land only

<sup>§</sup> HNO₃ was used as the basis for developing the RGHg dry deposition rate because it has a high rate of deposition.
Figure 4-9 – Modeled and Observed Winds

Figure a1 shows wind direction at Devil’s Lake using model data and Figure a2 shows Devil’s Lake observed wind direction [Rutter et al., 2007]. Wind direction was aggregated such that all directions between 0° and 179° were considered from the east and all wind directions greater than or equal to 180° were labeled as from the west. CMAQ wind direction based on 10-meter wind-speed (variable WSPD10 in MCIP v 3.4 output).
Figure 4-9 – Average Winds

Devil’s Lake 6.0 m/s
Figures show average wind speed and direction for April (b1), May 1-15th (b2), July (b3) and October (b4).
Supplemental Figure 4-A – July Average Concentration over Continental U.S.

(a) $Hg^0$ (ppt)

(b) $RGHg$ (ppt)
Figures show average July concentration across all model layers, for a) Hg$^0$, b) RGHg and c) PHg.
Supplemental Figure 4-B – Average Inflow at for Western Boundary of Great Lakes Domain

Figure shows average concentrations along Western boundary as a monthly average across all model layers.
References


Chapter 5

Implications for Atmospheric Mercury Research and Policy

Introduction

Previous chapters have shown that the current mercury chemistry used in regional models can reproduce total mercury wet deposition, but not speciated surface concentrations. Since these processes are not independent, errors in concentration suggest deposition is not reflective of actual processes. Instead, compensating errors in calculating deposition rates likely result in realistic values. Although dry deposition was not directly evaluated since no observational data was available, it can be inferred that modeled dry deposition is also inaccurate as these values depend on surface concentration as well. Thus, the evaluation presented here examines the mercury cycle in the Community Multiscale Air Quality Model (CMAQ) model – a regional chemical model transport model developed by the EPA for the purpose of informing U.S. air pollution policy decisions. The significant error found in the current model system requires further research for all areas of the atmospheric mercury cycle; without attention to these issues, U.S. atmospheric mercury policy may not sufficiently protect human health.

From a public health perspective, this conclusion does not change the fact that atmospheric deposition is a significant source of mercury in aquatic systems, where it can be transformed into the dangerous neurotoxin methylmercury (MeHg). For the Great Lakes Region, MeHg can be a substantial concern given the size of the freshwater system and the number of people that depend on Great Lakes resources. While CMAQ model results point to imported atmospheric mercury as the major source for deposition, comparison with surface concentration data demonstrates that chemical mechanisms in CMAQ 4.6 are unrealistic, and
thus, the deposition results should not be considered robust. Therefore, it remains unclear whether RHg deposition is driven by chemical transformation of imported Hg\(^0\) concentrations, or due to local emission sources.

This uncertainty has profound implications for mercury policy: if chemical production of RHg from global Hg\(^0\) is the largest source of mercury in aquatic systems, then international agreements will be necessary to minimize public health risk; if direct emissions of RHg dominate, then regional or national mercury policies are necessary. Thus, it remains unclear whether policies to reduce mercury in the environment should target local sources or global emissions. With the intention of informing future mercury policy decisions, this chapter will discuss the current U.S. mercury policy, the Clean Air Mercury Rule, and identify areas for future research.

**U.S. Atmospheric Mercury Policy**

The Clean Air Mercury Rule (CAMR) is an emissions cap-and-trade scheme, and the first national policy for atmospheric mercury emissions. The CAMR was passed in March of 2005 and regulates total mercury emissions from electric-generating units (EGUs). The CAMR was designed to build on the Clean Air Interstate Rule (CAIR), and assumes a certain level of mercury emission reductions from this policy as a co-benefit. From the CMAQ model evaluation here, there are two clear areas that may undermine how effectively the CAMR can protect human health: dry deposition rates and the rate of RHg chemical production.

Dry deposition rates have a strong impact on the lifetime of emitted air pollutants. High dry deposition rates will cause air pollutants to deposit close to the emission source, while lower dry deposition rates will allow the species to be transported longer distances
before being deposited. Cap and trade schemes best regulate well-mixed pollutants, such as carbon dioxide (CO$_2$) or chlorofluorocarbons (CFCs). Pollutants that do not mix evenly can create ‘hot spots’ – areas with higher pollutant concentrations relative to other points in time or space with accordingly higher exposures and impacts. The possibility of hot spots is the most litigious aspect of cap-and-trade policy and is often the reason for not pursuing this type of regulation. If RHg dry deposits rapidly, then hot spots will likely exist near mercury emission sources that may lead to an uneven distribution of MeHg exposures.

The CMAQ model assumes a very high RHg dry deposition rate, but this is acknowledged as uncertain [e.g. Lin et al., 2007]. In policy terms, the EPA circumvents the hot spot issue by relying on a different policy – the Clean Air Interstate Rule (CAIR) – to indirectly control RHg emissions. The CAIR regulates sulfur dioxide (SO$_2$) and nitrogen oxides (NO$_x$), and according to the CAMR documentation, the SO$_2$ and NO$_x$ control technologies required for CAIR would have the co-benefit of also reducing RHg emissions [U.S. EPA 2005a]. The end result of the CAMR/CAIR policy is the separation of Hg$^0$ and RHg controls at the national level. If research shows that RHg from EGUs is the main source of MeHg via fast dry deposition, the CAMR/CAIR approach may sufficiently protect public health. Yet it is questionable whether the EPA should rely on an assumption that SO$_2$ and NO$_x$ controls will reduce RHg emissions without explicitly incorporating it into policy measures. If new studies do find that local emissions are the dominant source for MeHg, then relying on an unenforceable co-benefit is likely to be ineffective.

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1 This also recalls the Acid Rain Program (ARP), which inspired the CAMR. The ARP used a cap and trade scheme to regulate sulfur dioxide (SO$_2$) emissions and is widely cited as a success [e.g. Bryner, 2006; Schmalensee et al., 1998]. This success was supported by the existing National Ambient Air Quality Standards (NAAQS), which set local environmental limits that eliminated hot spots. Similar to SO$_2$ emissions regulation using ARP/NAAQS to decrease total emissions (the ARP) and target hot spot creation (the NAAQS), U.S. mercury policy uses the CAMR for general mercury emissions control and CAIR to eliminate RHg hot spots.
Mercury chemical cycling is also relevant to public health by indicating what scale of mercury policy is needed. If production from background Hg\(^0\) concentrations is a larger source of RHg than direct emissions, international policies would be necessary to have an impact on MeHg formation. The research presented here shows that the current CMAQ formulation for total deposition, which is largely due to imported concentrations, is based on incorrect model assumptions and may not reflect actual processes. Given this uncertainty, it is difficult to assess the source and quantity of deposited mercury, and thus equally as difficult to formulate an effective control strategy. This is not to discount atmospheric production as a source of RHg, however, and in the event that future studies are able to better explain chemical cycling of atmospheric mercury, policy will need to reflect that process. If RHg is largely controlled by chemical production from Hg\(^0\), the CAMR may be less effective than an international agreement. One possible path to developing a global approach to atmospheric mercury is through the United Nations Environment Programme (UNEP), and at the 25\(^{th}\) session of the UNEP Governing Council in February 2009, the U.S. proposed that a legally-binding international agreement be developed for mercury. This mercury policy is still in its formative stages, it remains to be seen how the policy may be informed by uncertainty in atmospheric mercury processes. Yet, if evidence shows imported mercury to be the dominant source for MeHg, this nascent international effort can provide a platform for protecting human health worldwide.

Looking Forward – Developing Mercury Policy from Science

This study clearly demonstrates the need for more research into atmospheric mercury science, particularly for dry deposition and chemical cycling. How this science proceeds will change the priority of policy measures, whether towards a national regulation of emissions,
such as the CAMR, or towards global agreements, such as the UNEP policy. While the CAMR focuses solely on EGU emissions and regional emissions, the UNEP policy is broad, building on the larger international policy landscape, which includes the formal recognition of a unified Earth system and the disparate needs of different peoples and nations. More observational data for atmospheric mercury would greatly facilitate model evaluation and constrain model development, which in turn would aid policy-makers in formalizing the best approach to protect human health. Including ambient mercury concentration measurements with other air quality monitoring systems, creating a dry deposition network and continuing laboratory studies will all contribute to increased understanding of the atmospheric mercury cycle, and lead to effective policy to reduce human health impacts.
References

