DEPARTMENT OF COMMERCE
UNITED STATES OF AMERICA

Report to Congress:
Mercury Contamination in the Great Lakes

Mark D. Cohen
Richard S. Artz
Roland R. Draxler

Air Resources Laboratory
Silver Spring, Maryland
April 17, 2007

noaa National Oceanic and Atmospheric Administration / Office of Oceanic and Atmospheric Research

UNITED STATES DEPARTMENT OF COMMERCE
Chief Financial Officer
Assistant Secretary for Administration
Washington, D.C. 20230

MAY 14 2007

The Honorable Barbara A. Mikulski
Chairman
Subcommittee on Commerce, Justice,
Science and Related Agencies
Committee on Appropriations
United States Senate
Washington, D.C. 20510

Dear Madam Chairman:

Enclosed is the National Oceanic and Atmospheric Administration's (NOAA) report, Mercury Contamination in the Great Lakes, as required by the Conference Report accompanying the Consolidated Appropriations Act, 2005 (H. Rpt. 108-792). The enclosed report summarizes the recent work done at NOAA indicating atmospheric deposition is a significant means for introducing mercury into the Great Lakes.

Please contact me at (202) 482-4951 if you have any questions. Thank you for your continued support of the Department of Commerce and its programs.

Sincerely yours,

Otto J. Wolff
Chief Financial Officer and
Assistant Secretary for Administration

Enclosure

UNITED STATES DEPARTMENT OF COMMERCE
Chief Financial Officer
Assistant Secretary for Administration
Washington, D.C. 20230

MAY 1 4 2007

The Honorable Richard C. Shelby
Ranking Minority Member
Subcommittee on Commerce, Justice,
Science and Related Agencies
Committee on Appropriations
United States Senate
Washington, D.C. 20510

Dear Senator Shelby:

Enclosed is the National Oceanic and Atmospheric Administration's (NOAA) report, Mercury Contamination in the Great Lakes, as required by the Conference Report accompanying the Consolidated Appropriations Act, 2005 (H. Rpt. 108-792). The enclosed report summarizes the recent work done at NOAA indicating atmospheric deposition is a significant means for introducing mercury into the Great Lakes.

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UNITED STATES DEPARTMENT OF COMMERCE
Chief Financial Officer
Assistant Secretary for Administration
Washington, D.C. 20230

MAY 14 2007

The Honorable Alan B. Mollohan
Chairman
Subcommittee on Commerce, Justice,
Science and Related Agencies
Committee on Appropriations
U.S. House of Representatives
Washington, D.C. 20515

Dear Mr. Chairman:

Enclosed is the National Oceanic and Atmospheric Administration's (NOAA) report, Mercury Contamination in the Great Lakes, as required by the Conference Report accompanying the Consolidated Appropriations Act, 2005 (H. Rpt. 108-792). The enclosed report summarizes the recent work done at NOAA indicating atmospheric deposition is a significant means for introducing mercury into the Great Lakes.

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Assistant Secretary for Administration

Enclosure

UNITED STATES DEPARTMENT OF COMMERCE
Chief Financial Officer
Assistant Secretary for Administration
Washington, D.C. 20230

MAY 14 2007

The Honorable Rodney P. Frelinghuysen
Ranking Member
Subcommittee on Commerce, Justice,
Science and Related Agencies
Committee on Appropriations
U.S. House of Representatives
Washington, D.C. 20515

Dear Representative Frelinghuysen:

Enclosed is the National Oceanic and Atmospheric Administration's (NOAA) report, Mercury Contamination in the Great Lakes, as required by the Conference Report accompanying the Consolidated Appropriations Act, 2005 (H. Rpt. 108-792). The enclosed report summarizes the recent work done at NOAA indicating atmospheric deposition is a significant means for introducing mercury into the Great Lakes.

Please contact me at (202) 482-4951 if you have any questions. Thank you for your continued support of the Department of Commerce and its programs.

Sincerely yours,

Otto J. Wolff
Chief Financial Officer and
Assistant Secretary for Administration

Enclosure

Preface

The Conference Report accompanying the consolidated Appropriations Act, 2005 (H. Rpt. 108-792) requested that the National Oceanic and Atmospheric Administration (NOAA), in consultation with the U.S. Environmental Protection Agency (EPA), report to Congress on mercury contamination in the Great Lakes, with trend and source analysis. This report does not attempt to report on all of the many aspects of mercury contamination in the Great Lakes. It is limited to the following two primary components:

- Analysis of the atmospheric transport and deposition of U.S. and Canadian anthropogenic mercury emissions to the Great Lakes using the NOAA HYSPLIT-Hg model; and
- Illustrative literature data regarding trends in Great Lakes mercury contamination.

There have been extensive (and ongoing) interactions between NOAA-ARL and EPA on Great Lakes mercury issues. The EPA contributed significantly to this report through these interactions – in the form of comments, discussions, conferences, joint projects, data sharing, and use of information in EPA publications – all of which directly involved Great Lakes mercury issues. In addition, an EPA-authored analysis of atmospheric transport and deposition of global mercury emissions to the U.S. -- including the Great Lakes – using the EPA-NOAA CMAQ-Hg model has been included as an Appendix to this report.

The problem of mercury contamination in the Great Lakes is complex and involves both past and present loadings. There are several pathways through which mercury can be introduced to the Great Lakes. These include atmospheric deposition directly to the lake's surface, atmospheric deposition to the watershed with subsequent transfer to the lake, effluent discharge from sewage treatment plants and industrial facilities, and transfer from mercury-containing soils (or other media) in the watershed. Both natural and anthropogenic sources contribute mercury to the Great Lakes. Once mercury is introduced to the Great Lakes, it moves through the ecosystem and undergoes chemical transformation processes. A portion is transformed into methylmercury, a bioaccumulative form of mercury. Humans and wildlife who consume fish with high levels of methylmercury are at risk for neurological development effects and other adverse health consequences (National Research Council, 2000).

Atmospheric deposition is a significant loading pathway for many ecosystems, including the Great Lakes. The Air Resources Laboratory (ARL) of NOAA's Office of Oceanic and Atmospheric Research (OAR) has conducted analyses of the atmospheric transport and deposition of mercury to the Great Lakes as a result of air emissions from U.S. and Canadian anthropogenic sources. As noted above, this report summarizes recent work done at ARL using the HYSPLIT-Hg atmospheric fate and transport model investigating this aspect of the Great Lakes mercury issue. It is recognized that U.S. and Canadian anthropogenic sources are not the only sources contributing to atmospheric mercury deposition to the Great Lakes and their watersheds. Global emissions will also contribute to this deposition, and future work with the NOAA HYSPLIT-Hg model will attempt to include these global sources. The report also includes an EPA-authored section reporting on work with the CMAQ-Hg model in support of the

Clean Air Mercury Rule which attempts to include the effect of global mercury sources (Appendix A).

The Air Resources Laboratory has not generally analyzed mercury trends in the Great Lakes. However, illustrative data from the literature have been assembled regarding trends in Great Lakes mercury, including trends in emissions, deposition, and concentrations in fish, other biota, and sediment.

We gratefully acknowledge the EPA and Environment Canada for providing data regarding mercury air emissions (used as inputs for atmospheric modeling) and atmospheric mercury measurements (used in model evaluation and trend analysis). We thank the Mercury Deposition Network, a consortium of numerous Federal, State, and Local agencies, for providing additional atmospheric mercury measurement data used in model evaluation and trend analysis. We thank the EPA, Environment Canada, the International Joint Commission (IJC) and other agencies for the series of comprehensive summaries of Great Lakes data assembled in the ongoing Lakewide Management Plan (LaMP) process. We also thank the EPA, NOAA, IJC, and CEC for financially supporting the mercury modeling work discussed in this report. Finally, we express appreciation to our colleagues in the EPA, NOAA, IJC, Commission for Environmental Cooperation (CEC), Environment Canada, Ontario Ministry of Environment, and the Meteorological Synthesizing Centre – East (MSCE) for many useful discussions regarding the atmospheric fate and transport of mercury.

Executive Summary

The Conference Report accompanying the consolidated Appropriations Act, 2005 (H. Rpt. 108-792) requested that the National Oceanic and Atmospheric Administration (NOAA), in consultation with the U.S. Environmental Protection Agency (EPA), report to Congress on mercury contamination in the Great Lakes, with trend and source analysis. This report has been prepared in response to this request.

Mercury is a pollutant of concern in the Great Lakes, contributing, for example, to numerous fish consumption advisories. Although there are many way in which mercury is introduced into the Great Lakes ecosystem, atmospheric deposition is believed to be one of the most significant current loading pathways. Deposition impacts from any mercury emissions source appear to depend greatly on the relative proportions of the different forms of mercury emitted (ionic > particulate > elemental) and are highly variable in space and time. Based on current understanding, emissions of ionic mercury appear able to create large local and regional impacts.

Source-attribution information regarding atmospheric deposition is needed to determine the relative importance of different source types and source regions. Atmospheric fate and transport models have the potential of providing such source-attribution information in the most comprehensive and detailed manner. At present, there are a number of scientific uncertainties in the chemical and physical processes governing mercury's behavior in the atmosphere; in addition, input data for these models – e.g., emissions inventories and meteorological data – have potentially significant uncertainties. A number of steps could be taken to reduce uncertainties in model physics, chemistry, and inputs. In general, ambient measurements are required for "ground-truthing" and model improvement, but due to the scarcity of available data, such analyses have been very limited to date. Therefore, the accuracy of model results – and the significance of the uncertainties in introducing errors into the simulation – can only be roughly estimated. A nationwide monitoring network measuring speciated ambient atmospheric mercury concentrations to comprehensively evaluate and improve atmospheric mercury models does not yet exist. However, initial steps towards the establishment of such a network are being made by EPA, NOAA and other agencies.

The atmospheric fate and transport of mercury emitted from anthropogenic sources in the United States and Canada has been simulated with the NOAA HYSPLIT-Hg model – funded by U.S. EPA, NOAA, the International Joint Commission (IJC), and the Commission for Environmental Cooperation (CEC) – and the results are presented and discussed in this report. Emissions data were obtained from the U.S. EPA and Environment Canada. Ambient measurement data used for model evaluation and trend analysis was obtained from the U.S. EPA, the Mercury Deposition Network and other sources. In spite of many potentially significant uncertainties, the NOAA HYSPLIT-Hg model, and most other atmospheric mercury models, appear to be able to produce results reasonably consistent with ambient measurements. HYSPLIT-Hg results to date suggest that of anthropogenic sources in the U.S. and Canada, U.S. coal-fired power plants contribute the most to atmospheric mercury deposition to the Great Lakes. This is not surprising, due to the fact they are reported to be responsible for ~50 percent or more of the estimated ionic mercury emissions in the Great Lakes region. The estimated contribution of U.S. coal-fired power plants to the Great Lakes estimated by the HYSPLIT-Hg model is consistent with recent U.S. EPA model estimates developed in support of the 2005 Clean Air Mercury Rule. A number of additional modeling analyses using the NOAA HYSPLIT-Hg model are being initiated to provide more accurate and detailed information regarding the transport and deposition of mercury to the Great Lakes.

Relevant temporal trend data for mercury in the Great Lakes region was assembled for the following: (a) mercury air emissions; (b) mercury deposition; and (c) mercury concentrations in sediments, fish, and other biota. The primary sources of these data were NOAA, the U.S. EPA, Environment Canada, the Ontario Ministry of the Environment, the Mercury Deposition Network, and the scientific literature.

Atmospheric mercury emissions in the Great Lakes region are estimated to have risen to a peak in 1945-1970 and decreased since then. Detailed, recent temporal trend data on mercury emissions are somewhat limited. U.S. data – currently available only for the period 1990-1999 – indicate a significant decrease in emissions from municipal and medical waste incinerators. Over the same period, emissions from coal-fired electricity generation and other source categories were relatively constant. From 1990-2000, Canadian emissions are reported to have decreased by ~75 percent, largely due to process changes at metal smelting facilities. It is anticipated that significant reductions in emissions from U.S. coal-fired power plants will occur as a result of the Clean Air Interstate Rule (CAIR) and the Clean Air Mercury Rule (CAMR).

The longest available wet deposition data records in the Great Lakes region are for 1996-2003 at five Mercury Deposition Network sites. According to EPA emissions inventories, there were only moderate changes in estimated ionic mercury emissions in the vicinity of these sites between 1995-1996 and 1999-2001 – largely due to emissions reductions at municipal waste incinerators and medical waste incinerators -- but the precise timing of these changes is not known. Thus, it is difficult to determine if the trends in precipitation mercury concentrations are related to these reductions. Overall, there may have been a decrease in concentration at these five sites between 2000 and 2001, and this *may* have been related to decreases in regional mercury emissions from waste incinerators (i.e., if the emissions reductions at the relevant incinerators occurred at this time). Detailed atmospheric fate and transport modeling could be done to investigate this issue. However, an accurate, time-resolved emissions inventory for each of the large emissions sources in the region would be required.

Model-estimated deposition to the Great Lakes decreased significantly between 1995-1996 and 1999-2001, primarily due to decreases in mercury emissions from U.S. municipal and medical waste incinerators. Although this report contains significant uncertainties and highlights the need for further study, in the modeling results for both periods, U.S. sources contributed much more to Great Lakes atmospheric mercury deposition than Canadian sources.

Data on mercury levels in Great Lakes fish and the eggs of the Herring Gull (a fish eating bird) are generally available starting in the 1970's. There are variations among species and among lakes, but in general, the data seem to show a significant reduction from 1970 to the mid-1980's, with little change since the mid-1980's to the present. Consistent with this pattern, mercury concentrations in mussels in the Great Lakes region do not appear to show significant changes over the period 1992-2004. Sediment mercury concentrations in the Great Lakes typically show a

1940-1960 peak, and in some cases there are also secondary peaks in the 1970's. Since the 1970's sediment mercury concentrations have generally been decreasing in the Great Lakes. The trends seen in sediments and biota are most likely due, at least in part, to the substantial reduction occurring in the 1970's in effluent discharges to the Great Lakes (and their tributaries) from a number of sources (e.g., chlor-alkali plants).

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1. Introduction

Mercury is a contaminant of significant concern in the Great Lakes (IJC, 2004; Gilbertson and Carpenter, 2004). A number of actions have been taken to address this concern, including the following: (a) the International Joint Commission includes it as one of the top priority chemical substances targeted for virtual elimination under the *Great Lakes Water Quality Agreement*; (b) the United States and Canada (1997) have established the *Great Lakes Binational Toxics Strategy* to eliminate releases of mercury (and other high priority toxic pollutants) with specific goals for the period 1997-2006; (c) the *Great Lakes Mercury Reduction Act* was introduced in the House of Representatives by Reps. Kirk (R-IL), Upton (R-MI), Stupak (D-MI), and Kind (D-WI) in 2002 (e.g., Kirk, 2002); and (d) the *Great Lakes Regional Collaboration* was recently established as a "wide-ranging, cooperative effort to design and implement a strategy for the restoration, protection and sustainable use of the Great Lakes"[1].

The amounts, forms, and sources of mercury introduced into the Great Lakes are poorly understood, as are the temporal and spatial variations of these loadings. There are several pathways through which this loading can take place, including: (a) atmospheric deposition directly to the water surface; (b) atmospheric deposition to the watershed and subsequent transfer to the lake; (c) direct liquid or solid effluent discharge from an industrial or agricultural facility; (d) run-off from urban areas. Both natural and anthropogenic activities contribute to these loadings. Mercury cycling, transformation, and bioaccumulation processes vary from watershed to watershed and lake to lake and are only partially understood.

The primary cause for concern is exposure of humans and wildlife to methylmercury. Methylmercury can be formed within an aquatic ecosystem, e.g., in sediments, and can also be formed in watersheds and delivered to a waterbody. Biological processes – i.e., methylating bacteria – transform a portion of the inorganic mercury in watersheds and aquatic ecosystems to methylmercury. Once methylmercury enters the food chain, e.g., through sediment-dwelling invertebrates, it bioaccumulates (i.e., it reaches higher and higher concentrations in species at higher and higher trophic levels).

The National Academy of Sciences (NAS, 2000) has summarized the public health implications of methylmercury (MeHg) exposure to humans in the following way:

> The committee's margin-of-exposure analysis based on estimates of MeHg exposures in U.S. populations indicates that the risk of adverse effects from current MeHg exposures in the majority of the population is low. However, individuals with high MeHg exposures from frequent fish consumption might have little or no margin of safety (i.e., exposures of high-end consumers are close to those with observable adverse effects). The population at highest risk is

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[1] . In December 2004, a newly formed Federal Interagency Task Force dealing with the Great Lakes, the Council of Great Lakes Governors, the Great Lakes Cities Initiative, Native American Tribes, and the Great Lakes Congressional Task Force signed a *Declaration* and agreed to a *Framework Document* that signified the convening of the Collaboration. In December 2005, a *Strategy to Restore and Protect the Great Lakes* was released by the group. More information can be found at: http://www.glrc.us

> the children of women who consumed large amounts of fish and seafood during pregnancy. The committee concludes that the risk to that population is likely to be sufficient to result in an increase in the number of children who have to struggle to keep up in school and who might require remedial classes or special education.

Results from the Centers for Disease Control's (CDC's) National Health and Nutrition Examination Survey (NHANES) for 1999-2002 indicated that approximately 6% of U.S. women of childbearing age had blood-mercury levels at or above the Environmental Protection Agency's Reference Dose of 5.8 µg/liter (CDC, 2004).

Historically, direct effluent discharges [e.g., from the pulp and paper industry and chlor-alkali facilities] were a large source of loading to the Great Lakes. By the 1970's, these discharges had been significantly reduced. Highly mercury-contaminated sediments in a number of Great Lakes areas remain today as a legacy of these industrial discharges.

Atmospheric deposition is generally a significant mercury loading pathway to ecosystems and in many cases is the dominant loading pathway. Available evidence suggests that this is true for many of the Great Lakes, particularly since the 1970's, when direct discharges were lowered. Mass balance estimates for Lake Michigan (Mason and Sullivan, 1997) and Lake Superior (Dolan *et al*., 1993; Rolphus *et al.*, 2003) indicate that direct atmospheric deposition accounts for ~75 percent of the overall mercury loading to these lakes. No estimates could be found for Lake Huron, but it is likely that atmospheric deposition is comparably important for this lake. For Lake Ontario, Sunderland and Foley (2003) estimated that direct atmospheric deposition accounts for ~35 percent of the current loading. No mass balance estimates could be found for Lake Erie in the scientific literature or regulatory/policy documents [e.g., Lake Erie Lakewide Management Plan (LaMP)].

A number of pollutants – including mercury -- are responsible for fish consumption advisories in the Great Lakes region, as summarized in Figure 1.

Figure 1. Contaminants causing fish advisories in the Great Lakes region. Source: U.S. EPA Great Lakes National Program Office (GLNPO). Downloaded September 21, 2006 from: http://www.epa.gov/glnpo/glindicators/fishtoxics/sportfishb.html

Fish consumption advisories due to mercury contamination have been established throughout the Great Lakes region (summarized in Figure 2). States, Provinces and Tribes have the responsibility for establishing fish advisories, and the most current information can be obtained from them. In addition to the references listed in Figure 2, there are several summaries of and assemblages of useful links to this information, including the following:

- Great Lakes Information Network
  http://www.great-lakes.net/envt/flora-fauna/wildlife/fishadv.html

- U.S. Environmental Protection Agency
  http://www.epa.gov/waterscience/fish/states.htm
  http://www.epa.gov/ost/fishadvice/advice.html
  http://www.epa.gov/waterscience/fish/advisories/factsheet.pdf

- Great Lakes Indian Fish and Wildlife Commission
  http://www.glifwc.org/

- Environment Canada
  http://www.ec.gc.ca/MERCURY/EN/fc.cfm

- The Ontario Ministry of the Environment
  http://www.ene.gov.on.ca/envision/guide/

Fish consumption advisories are typically differentiated for women of child-bearing age, children, and the general population, and the guidelines for each group have been based on a number of different fish mercury concentration thresholds. EPA has proposed a fish-tissue mercury criterion of 0.3 mg methylmercury per kg of fish tissue (wet weight) for the protection of human health (EPA 2001). In August 2006, EPA published draft guidance to states and tribes on how to use this recommended fish tissue criterion as they develop their own standards for mercury (EPA 2006).

Figure 2. Summary of mercury-related fish consumption advisories in the Great Lakes region. In some states, there is a statewide mercury-related fish consumption advisory for lakes (L) and/or rivers (R), and in other cases, advisories have been issued for specific waterbodies. In the case of statewide advisories, the year the advisory was established is given. It is noted that Pennsylvania's statewide advisory was established for a number of pollutants, including mercury, and is not necessarily considered to be only a mercury-specific statewide consumption advisory. Mercury-related advisories for specific fish species have also been established by one or more states and provinces for each of the Great Lakes. Sources of information for this figure: Illinois Department of Public Health (2006); Indiana State Department of Public Health et al. (2006); Michigan Department of Community Health (2006); Minnesota Department of Health (2006); New York State Department of Health (2006); Ohio EPA Division of Surface Water (2006); Ontario Ministry of the Environment (2006a); Pennsylvania Department of Environmental Protection (2006); USEPA (2005f); and Wisconsin Department of Natural Resources (2006).

All things being equal, mercury concentrations tend to be highest in larger (older) fish and in fish at higher trophic levels (i.e., higher in the food chain). Examples of this increase in mercury concentration with fish length (i.e., age) are given in Figure 3.

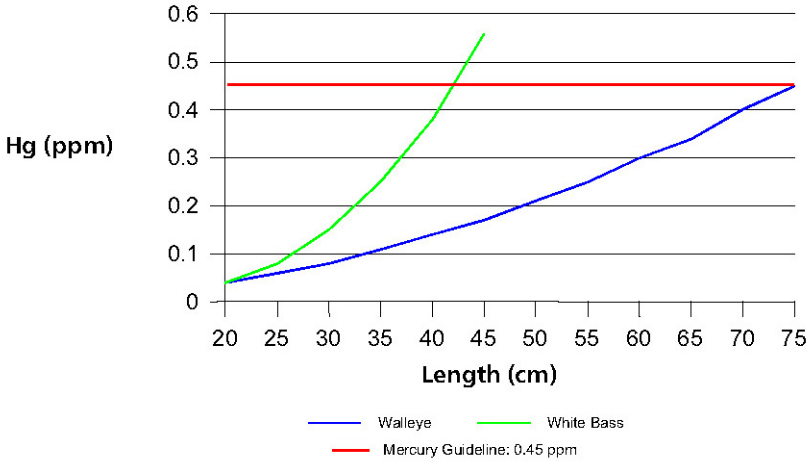

Figure 3. Mercury concentration vs. length for Lake Erie walleye and bass. From the Lake Erie LaMP (2002), for fish caught in Lake Erie Block 1 (a particular subregion of the lake). The "Mercury Guidance" of 0.45 ppm shown in this figure is simply an illustrative threshold used by the authors of the above document.

2. Scope of this Report

This report does not attempt to report on all of the many aspects of mercury contamination in the Great Lakes. It is limited to the following two primary components:

- Analysis of the atmospheric transport and deposition of U.S. and Canadian anthropogenic mercury emissions to the Great Lakes using the NOAA HYSPLIT-Hg model;
- Illustrative literature data regarding trends in Great Lakes mercury contamination.

There have been extensive (and ongoing) interactions between NOAA-ARL and EPA on Great Lakes mercury issues. The EPA contributed significantly to this report through these interactions – in the form of discussions, conferences, joint projects, data sharing, and use of information in EPA publications – all of which directly involved Great Lakes mercury issues. In addition, an EPA-authored analysis of atmospheric transport and deposition of global mercury emissions to the U.S. -- including the Great Lakes – using the EPA-NOAA CMAQ-Hg model[2] is included as an Appendix to this report.

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[2] . Extensive atmospheric mercury modeling has also been conducted by the NOAA Air Resources Laboratory in collaboration with the EPA using the Community Multiscale Air Quality Model (CMAQ-Hg) (e.g., Bullock and Brehme, 2002; USEPA, 2005a). The EPA has prepared a summary of this work, and this summary is included in this report as Appendix A.

3. The Atmospheric Transport and Deposition of Mercury to the Great Lakes

A. Introduction

Atmospheric deposition of gas-phase and particulate-phase pollutants occurs via two processes – wet and dry. Wet deposition is a process in which pollutants are removed from the atmosphere by precipitation (rain, snow, etc.). Dry deposition is a process in which pollutants are removed from the atmosphere by being absorbed or by sticking to trees, soil, water, or other surfaces. For mercury, both types of deposition are important.

Wet deposition can be measured directly, and there is a nationwide network of sites measuring the wet deposition of mercury – the Mercury Deposition Network (MDN). Figure 4 shows current MDN sites, and it can be seen that there are a number of sites in the Great Lakes region.

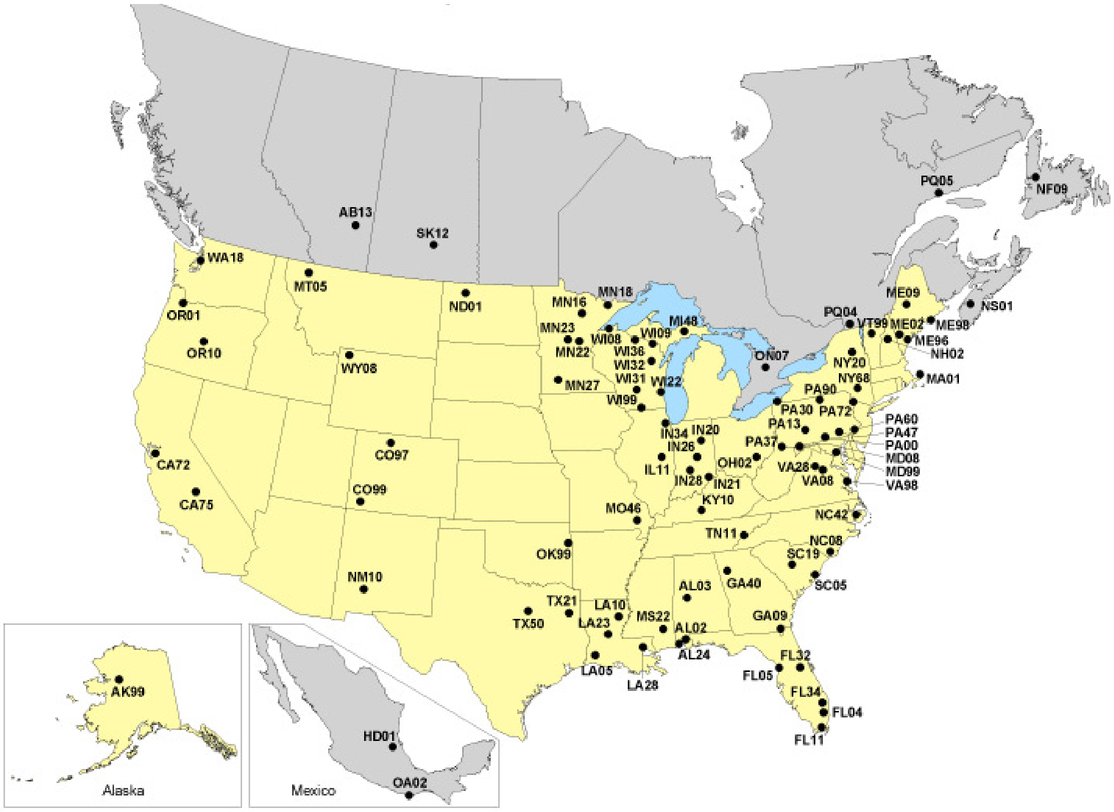

Figure 4. Mercury Deposition Network sites.
From the MDN website: http://nadp.sws.uiuc.edu/mdn/

Dry deposition depends on the concentration of the pollutant in the atmosphere near the Earth's surface, on the meteorological conditions, and the nature of the surface being deposited to. Dry deposition is difficult to measure directly but can be estimated using generalized methods developed for a range of pollutants. In these methods, the concentration of the gas-phase and/or particulate-phase pollutant (in this case, mercury) is measured in the air at a given location, and the dry deposition is estimated with standard algorithms. The algorithms rely on two different types of information: (1) generalized parameters – used for all pollutants – based on many field/laboratory measurements of a number of different pollutants; (2) pollutant-specific parameters that depend intimately on the nature of the pollutant being deposited. There are many uncertainties in estimation of dry deposition (discussed later in this report), but to make any estimate at a given location, air concentrations are generally required. For particulate-phase deposition, in addition to overall concentration measurements, more accurate estimates can be made if size distribution information is obtained. As is discussed in great detail later in this document, different atmospheric mercury forms – elemental, reactive gaseous, and particulate -- appear to exhibit dramatically different deposition behavior. Thus, it is critical to measure the concentrations of these different forms. Unfortunately, concentration data for the different forms of mercury are scarce in the Great Lakes region. There are a few sites in the region at which ambient mercury concentrations are measured from which dry deposition could be estimated. However, these data are largely collected within long-term research projects and their availability to the broader scientific community has been limited.

For the Great Lakes and other aquatic ecosystems, there are two different pathways through which atmospheric deposition can contribute mercury. First, deposition can occur directly to the water surface. Second, mercury can be deposited to the watershed, and a portion of this mercury can be transferred to the water body. The relative efficiency with which mercury deposited to the watershed is delivered to the water body depends on the detailed nature of the deposition and the characteristics of the watershed. Moreover, the processes by which methylmercury is formed in the watershed and in the waterbody and is incorporated into the food chain are highly dependent on the detailed characteristics of the deposition (i.e., the form of mercury deposited) and the watershed and waterbody ecosystems.

Regarding the atmospheric deposition process itself -- directly to the Great Lakes, to the watersheds of the Great Lakes, or to any other ecosystem of interest -- there are two primary groups of questions:

(1) *Amount being Deposited*
  - How much mercury is being deposited?
  - What are the spatial and temporal variations of this deposition?
  - What are the deposition rates for different species or forms of mercury?

(2) *Source-Attribution*
  - What is the relative importance of different source types in contributing to the overall deposition?
  - What is the relative importance of different source regions in contributing to the overall deposition?

The first group of questions – regarding the amount of deposition – is important for answering questions regarding the relative importance of the atmospheric pathway relative to other loading pathways to the Great Lakes. The second group of questions – regarding sources – is obviously important for prioritizing remediation alternatives.

There are three types of methodologies used to address the above questions: (a) atmospheric monitoring alone; (b) back-trajectory and other receptor-based methods coupled with atmospheric monitoring; and (c) comprehensive atmospheric fate and transport modeling.

With the atmospheric monitoring alone – as described above – one can estimate the atmospheric deposition of mercury at the monitoring site for the time period that the monitoring was carried out. However, in general there can be large spatial variations, and so it is unlikely that a few measurement sites will be able to represent the deposition over a large region. Moreover, measurements are not always continuous in time. Since there can be large temporal variations, such discontinuities raise additional questions regarding the representativeness of the monitoring data (i.e., are peaks missed or are they over-represented in the samples?). In sum, monitoring data by itself can provide detailed information about the deposition amount at a given site, but since the number of sites is necessarily limited, monitoring alone is unlikely to be able to provide accurate deposition data for large regions such as the Great Lakes.

By itself, monitoring cannot generally be used to estimate source attribution data. However, one can couple monitoring with back-trajectory and other receptor-based techniques in an effort to do so. In the back-trajectory technique, models using observed wind-direction data are used to estimate the origins of air parcels arriving at the monitoring site for each sample. Information about the relative importance of source regions is then obtained, for example, by comparing the air parcel origin locations for high-concentration samples with those for low-concentration samples. Sophisticated methodologies are often employed in carrying out these procedures. However, these techniques are somewhat limited by several factors, including the following: (a) one cannot be sure *where* on any upwind pathway a contributing or non-contributing source region may lay; (b) factoring in chemical transformations, wet and dry deposition, and dispersion is very difficult – and not generally even attempted – with back-trajectory analyses. Indeed, implicit in the methodology normally used for such calculations are the assumptions that the pollutant is chemically inert, does not deposit along the trajectory, and stays entirely on the centerline of the trajectory. Thus, while some information can certainly be obtained from this approach, the information is somewhat limited for mercury, as it is not chemically inert, does deposit along the trajectory, and is dispersed around the trajectory centerline.

Ultimately, perhaps the best approach to estimating atmospheric deposition is through the use of comprehensive atmospheric fate and transport models. These models start with an emissions inventory and then attempt to simulate the atmospheric behavior of the pollutant after it is emitted. Information about chemical transformations, wet and dry deposition, downwind transport, and dispersion are all coupled together in these models. These models have the potential of estimating wet and dry deposition over large regions. In addition, such models also have the potential for developing detailed source-attribution information.

A key factor in the use of such models, however, is that ambient monitoring data be available for model evaluation, or "ground-truthing". The simulated concentrations and deposition are compared against the actual measurements. The degree to which the model's estimates match the measurements – taking into account the degree of uncertainty in the measurements themselves –

gives a measure of the validity of the model. The scarcity of such data for mercury is a major impediment to the development and testing of atmospheric mercury models.

In the current understanding of atmospheric mercury, there are three different forms – elemental, ionic, and particulate. Elemental mercury (Hg^0) generally makes up most (greater than ~ 90 percent) of the total Hg in atmosphere. It exists primarily in the vapor phase. It is not very water soluble, so it is not wet deposited very efficiently. It has a relatively high vapor pressure and is not very "sticky" and so it is not dry deposited very efficiently. In most – but not all -- situations, reactions that convert it to other forms of mercury are believed to be relatively slow. These features result in a relatively long average atmospheric lifetime for elemental mercury – on the order of 0.5-1 year. With such a long lifetime, it can be globally distributed. These considerations are in accord with ambient measurements that show a reasonably consistent background concentration over the entire globe (e.g., Kim *et al*., 2005; Slemr *et al*. 2003). The global distribution of mercury also means that distant sources can contribute to the deposition at any given location.

Ionic mercury is generally present at a much lower concentration than the elemental form and typically constitutes only 1-5 percent of the total mercury in the atmosphere. It exists in both the vapor phase, the droplet phase, and the particulate phase in the atmosphere. When in the vapor-phase, ionic mercury is sometimes referred to as reactive gaseous mercury (RGM). As defined here, this form of mercury does not consist only of true ions but includes the following groups of compounds:

- Vapor-phase Hg(II) molecules -- e.g., $HgCl_2$(gas), $Hg(OH)_2$(gas), etc.
- Aqueous-phase (dissolved) Hg(II) molecules -- e.g., $HgCl_2$(aq), $Hg(OH)_2$(aq), etc.
- Aqueous-phase (dissolved) Hg(II) ions – e.g., Hg^{+2}(aq)
- Hg(II) species reversibly adsorbed to the surface of dry particles
- Hg(II) species reversibly adsorbed to the surface of the insoluble mineral or soot core of an atmospheric droplet.

There are a number of individual mercury species making up the total pool of ionic mercury in the atmosphere. A principal species is believed to be $HgCl_2$, but little progress has been made to date in the identification of the actual species comprising ionic mercury. As a result, ionic mercury is defined operationally, i.e., by its properties. Ionic mercury is very water soluble and is therefore wet deposited very efficiently. It is also very "sticky", so it can also dry deposit very efficiently. As a result of these relatively fast deposition processes, it has a much shorter typical *average* atmospheric lifetime – on the order of 1-10 days.[3] Also, as a result of this enhanced deposition, pound for pound, emissions of this form of mercury are believed to have higher local and regional deposition effects than elemental mercury.

Particulate mercury also generally comprises only a few percent of the total mercury in the atmosphere at any given location. This form of mercury is not pure particles of mercury, but rather consists of mercury compounds associated with atmospheric particulate matter. Like ionic

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[3] While the average atmospheric lifetime may be in the range of 1-10 days, portions can deposit on much faster time scales, e.g., within minutes of emissions or formation.

mercury, the actual species are not generally known. One species may be HgO, mercuric oxide. Like ionic mercury, it is defined operationally -- a filter is used to collect particulate matter, and then the particulate matter is analyzed for mercury. All the mercury found in this way is considered to be in the particulate form. The deposition behavior of particulate mercury is the same as that of atmospheric particulate in general. These processes depend on particle size, and so the overall deposition rate of particulate mercury depends on the particle size distribution of Hg(p), i.e., what fraction of the total Hg(p) is present on any given sized particle. On average, pound for pound, the deposition of this form of mercury is believed to be faster than that of elemental mercury but slower than that of ionic mercury under most conditions. Its typical average atmospheric lifetime is on the order of 1-2 weeks. Thus, this form of mercury can have some local and regional deposition effects. This form of mercury is not considered to be water soluble to a significant extent, as water soluble compounds would be considered to be part of the ionic mercury group discussed above. As a result, its bioavailability after deposition may be less than that of ionic mercury.

B. Atmospheric Emissions

Mercury is a naturally occurring element and there is a “natural” mercury biogeochemical cycle. In this cycle, mercury is emitted to the atmosphere from natural sources. Volcanoes are a potentially significant source of “natural” mercury emissions to the atmosphere, as are regions with high mineral mercury content. Most of the natural mercury emissions to the atmosphere are generally believed to be of the elemental form. After being emitted, this mercury is transported and dispersed throughout the atmosphere, and undergoes chemical transformations. Some of the mercury is eventually deposited. The deposited mercury will have a variety of fates – e.g., incorporation into the food chain, sequestration into soils or sediments, re-emissions back to the atmosphere, etc. Because of the natural mercury cycle, there likely has always been some mercury in fish.

Anthropogenic activities can result in mercury emissions. For example, mercury is contained within coal and is emitted when the coal is combusted to produce energy. Mercury is also contained in other fossil fuels and is similarly emitted when they are burned. Mercury is mined and is associated with other metals that are mined, and metallurgical operations (mining, smelting, etc.) can be significant sources of mercury emissions. Mercury is used in some industrial processes – e.g., in one type of chlor-alkali production process – and these facilities can be significant mercury emissions sources. Mercury incorporated into products can be emitted during the production, use, or disposal of the product. Anthropogenic emissions, once deposited, can be re-emitted. Like natural emissions, these re-emissions are believed to be largely in the form of elemental mercury.

The overall totals for emissions (natural and anthropogenic) and anthropogenic re-emissions are very uncertain. It is beyond the scope of this report to review this topic, but one example will be provided. Lamborg *et al*. (2002) have estimated the global totals for emissions and re-emissions, and these estimates are shown in Figure 5. It can be seen that anthropogenic emissions and re-emissions (~3200 metric tons/year) account for ~70 percent, and natural processes (~1400 metric tons/year) account for ~30 percent of global mercury emissions.

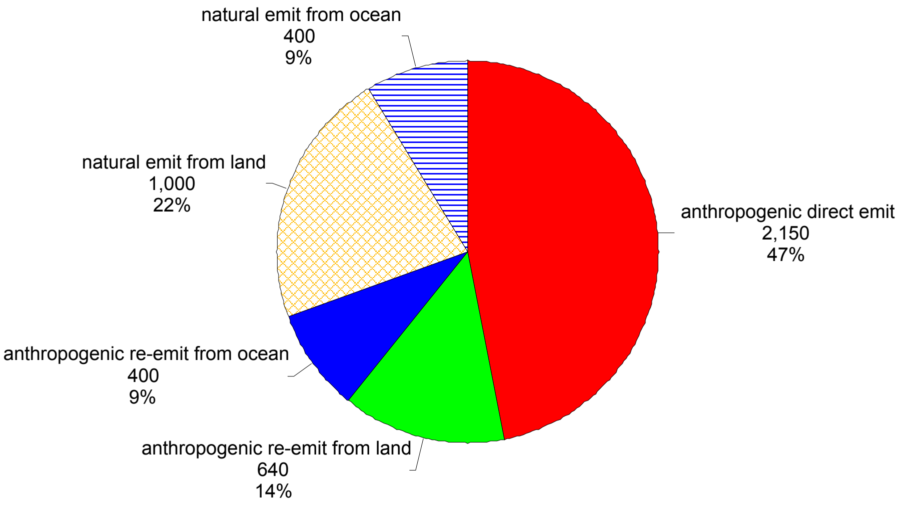

Figure 5. Global natural and anthropogenic emissions of mercury. Estimates in this figure are taken or inferred from Lamborg et al. (2002), and are for ~1990. All values are in metric tons per year.

Figure 6 shows an estimate of the global distribution of natural emissions. Note that for the data set mapped in this figure, the total natural emissions were 1800 metric tons/year – 1000 metric tons/year from land surfaces and 800 metric tons/year from ocean surfaces – slightly different than the estimates shown in Figure 5.

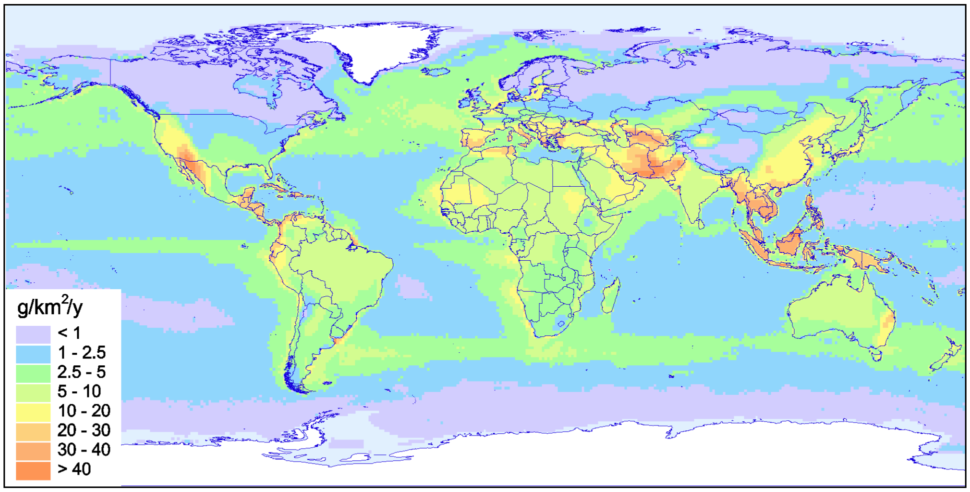

Figure 6. Global natural emissions of mercury.
Estimated for use in the EMEP Mercury Model Intercomparison Study (Ryaboshapko *et al*., 2005). Note that this data includes estimated anthropogenic re-emissions (~400 metric tons/yr) from the ocean.

Table 1 shows estimates of direct global anthropogenic emissions. A version of this table appeared in the IJC's 12th Biennial Report (IJC, 2004) and is based on data from Pacyna *et al.,* (2003). According to these estimates, more than 50 percent of the anthropogenic emissions in 1995 are estimated to have come from Asia, while North America is estimated to have accounted for ~10 percent. Maps of the global distribution of 1995 and 2000 estimated emissions are shown in Figure 7 and Figure 8, from Pacyna *et al*. (2005).

Continent	Stationary Combustion	Non-ferrous Metal Production	Iron and Steel Production	Cement Production	Waste Disposal	Total	Percent
Europe	186	15	10	26	12	250	13
Africa	197	8	0.5	5		211	11
Asia	860	87	12	82	33	1074	56
North America	105	25	5	13	66	214	11
South America	27	25	1.4	6		59	3
Australia and Oceania	100	4	0.3	1	0.1	106	5
Total for 1995	1475	166	29	132	111	1913	
Total for 1990	*1295*	*394*	*28*	*115*	*139*	*1971*	

Table 1. Global anthropogenic mercury emissions for five major source categories.
Data are for 1995, unless otherwise indicated, are given in metric tons per year, and are from Pacyna *et al.* 2003. Totals may not appear exact due to rounding. The estimated total for 1990 shown in the table (1971 metric tons) is just for the five major source categories in the table. Pacyna reported an additional 171 metric tons emitted from chlor-alkali plants and other less significant sources globally in 1990, for a total global anthropogenic emissions of 2143 metric tons/year. These additional source categories were not included in the estimates for 1995.

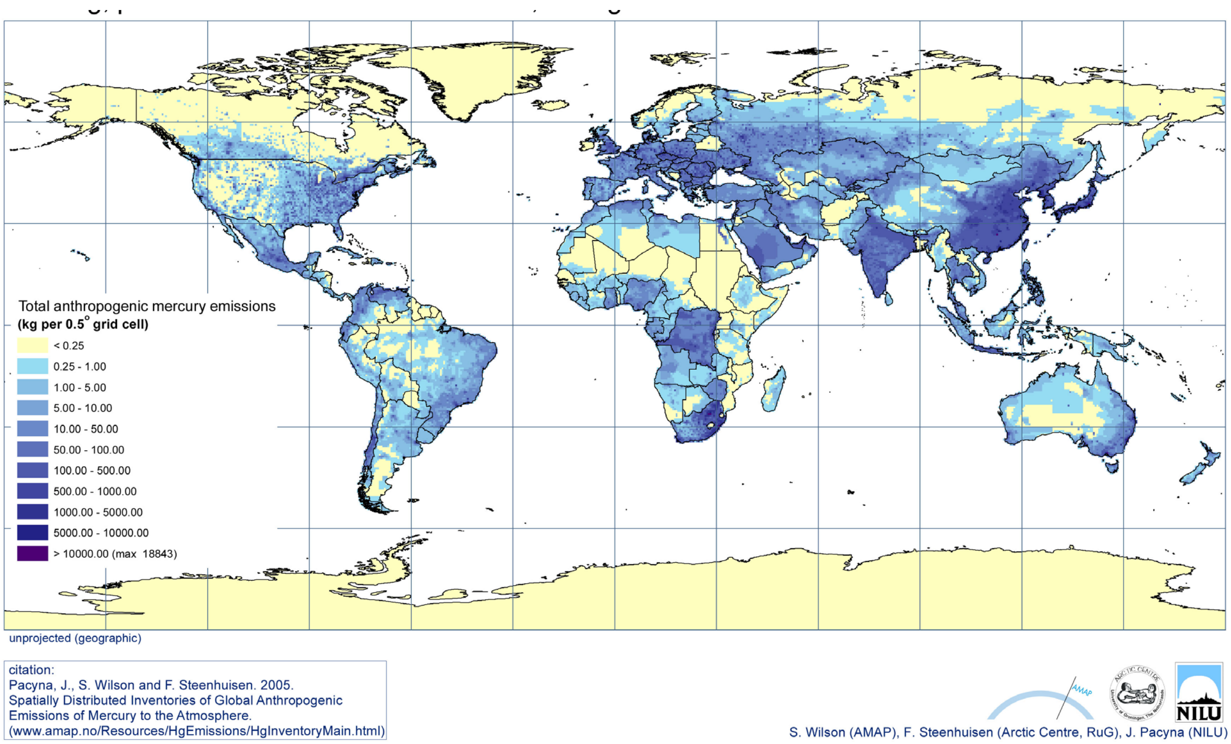

Figure 7. Global direct anthropogenic emissions of mercury to the atmosphere (1995).

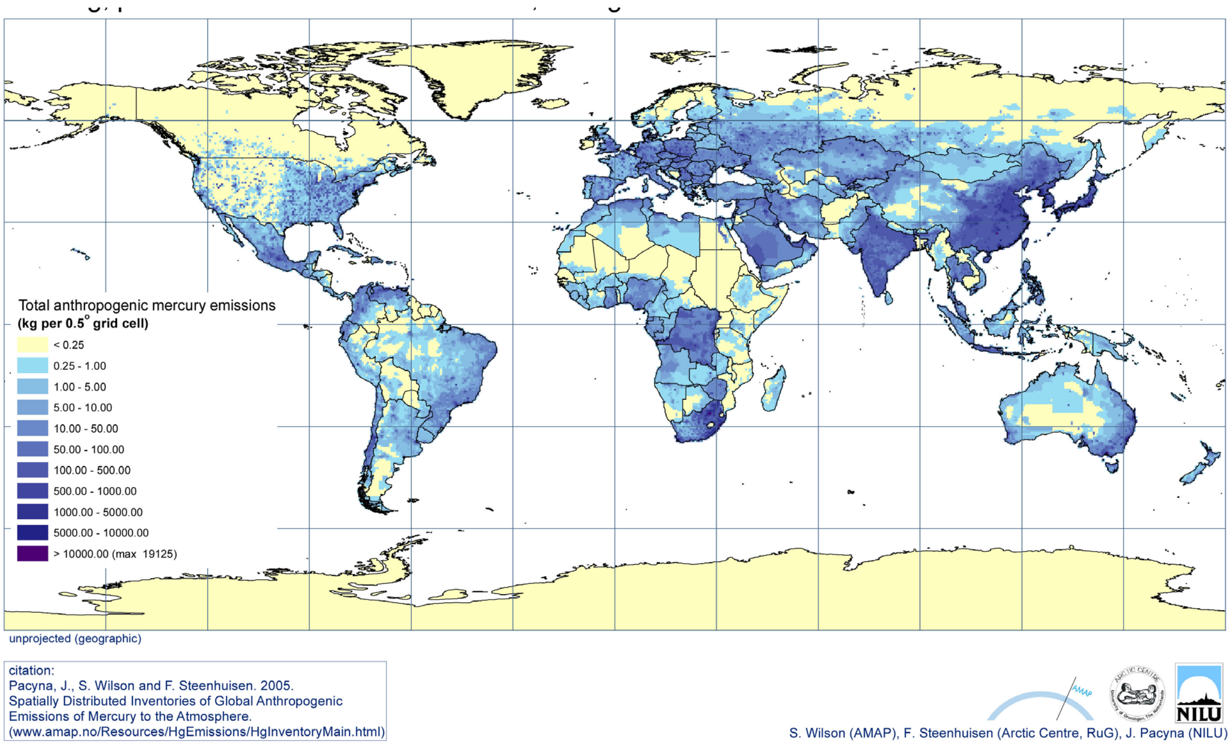

Figure 8. Global direct anthropogenic emissions of mercury to the atmosphere (2000).

Figure 9 shows the estimated U.S. mercury emissions (nominally for 1999), broken down by different source categories, based on the U.S. EPA National Emissions Inventory (NEI) (Pope, 2003). Emissions from municipal and medical waste incinerators are believed to have reduced significantly, starting in the 1990's, but the exact timing of these reductions has not been precisely characterized. It is believed that the 1999 estimates of emissions from municipal and medical waste incinerators may have been slightly too optimistic, and the reductions to the levels shown were not actually achieved until sometime later (~2000-2001)[4]. In any event, it can be seen that coal-fired power plants are the largest source category of emissions in the U.S.

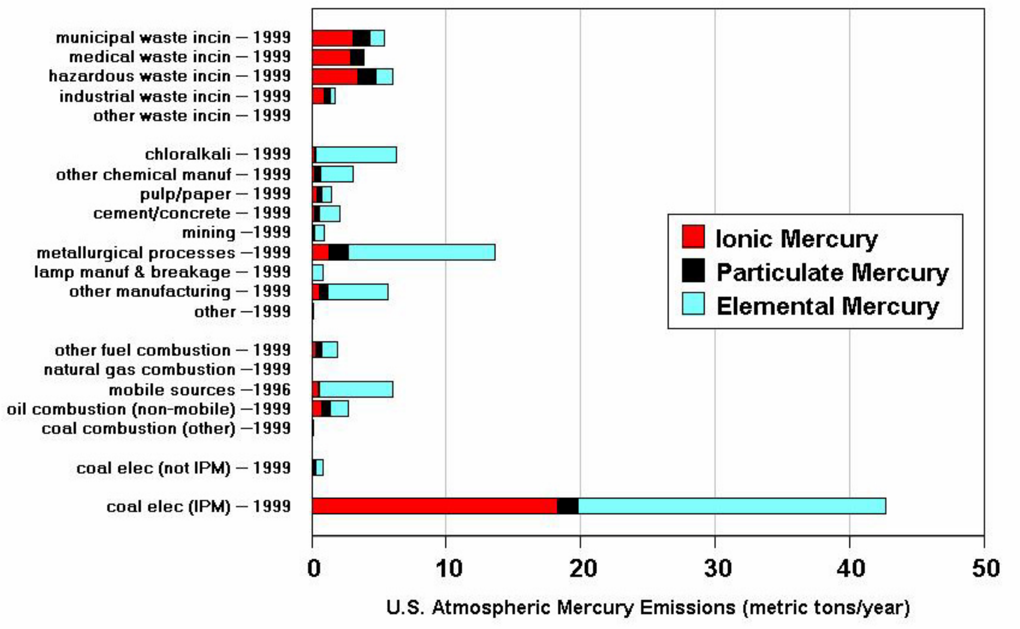

Figure 9. U.S. atmospheric mercury emissions (1999-2001).
"coal elec (IPM)" refers to large coal-fired electricity generating facilities identified by the U.S. EPA for inclusion in their Integrated Planning Model (for emissions, fuel use, and economic projections). Estimates for mobile sources were not included in this inventory, and so data from the 1996 U.S. EPA mercury inventory were used for this source category.

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[4] For example, the EPA reports that retrofits at large municipal waste combustors were not completed until 2000, but that the estimated reductions arising from those retrofits were factored into the 1999 National Emissions Inventory (USEPA, 2005b).

Figure 10 shows comparable data for estimated Canadian emissions. These estimates are based on a 1995 Canadian inventory (Niemi, 2001). An attempt was made to update the largest sources to ~2000 using NPRI data (Cohen and Miller, 2003). The official Environment Canada 2000 mercury emissions inventory was not yet available at the time these calculations were performed.

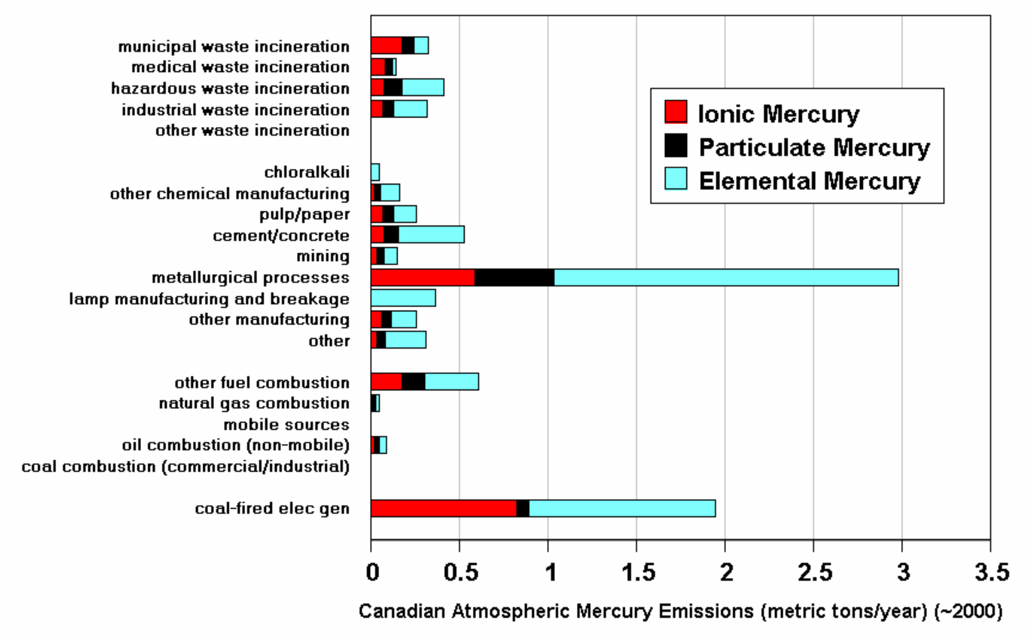

Figure 10. Canadian atmospheric mercury emissions (~2000)

Figure 11 shows the geographical distribution of the U.S. and Canadian emissions based on the aforementioned data sources (the same data as was used for Figures 9 and 10 above). Based on these same data sources, Figure 12 through Figure 15 show the locations and general source category of the largest sources in these U.S. and Canadian inventories for emissions of total, ionic, particulate, and elemental mercury, respectively. As discussed in detailed below [Section D, beginning on page 36], emissions of ionic mercury [Figure 13] are believed to have the highest potential for local and regional deposition impacts.

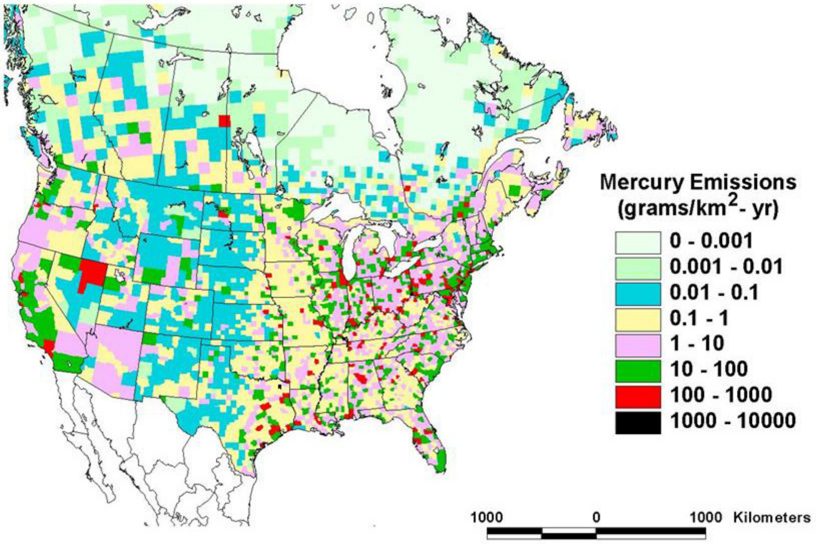

Figure 11. U.S. and Canadian anthropogenic mercury emissions (map) As discussed in the text, the data generally represent emissions for 1999-2000. The data are summarized at the county level in the U.S. In Canada, the data in this figure are summarized on a 50 km grid in the Great Lakes region and a 100 km grid throughout the rest of Canada.

It must be noted that there are substantial uncertainties in mercury air emissions inventories for the U.S., Canada, and the rest of the world. Shortcomings include the following: (a) infrequent updates; (b) scarcity of stack-test data – and emissions factor[5] estimates – for overall mercury emissions; (c) extreme scarcity of stack-test data – and emissions factor estimates – for speciated mercury emissions (e.g., broken down into elemental, ionic, and particulate mercury forms); significant uncertainties in activity rates (e.g., tons of waste burned per year at a given incinerator); (d) lack of information on significant discontinuities in emissions (e.g., temporary facility shutdowns due to maintenance); (e) lack of other temporal information (e.g., diurnal, weekly, and/or seasonal variations; (f) omitted sources; (g) erroneous records (e.g., double-counted facilities; inclusion of facilities that have closed); and (h) a general lack of transparency in the methodology underpinning any individual emissions estimate. These uncertainties

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[5] An *emissions factor* is an estimate of emissions per unit of activity, e.g., for a waste incinerator, an emissions factor might be expressed as a certain number of grams of mercury emitted per metric ton of waste burned. Emissions factors are typically based on stack tests, and allow – sometimes with substantial uncertainty – the stack test data to be used to estimate emissions at other times (at the tested facility) and for other similar facilities.

constitute a serious impediment to understanding and modeling atmospheric mercury, and they are discussed further in Section F – *Model Uncertainties* – below.

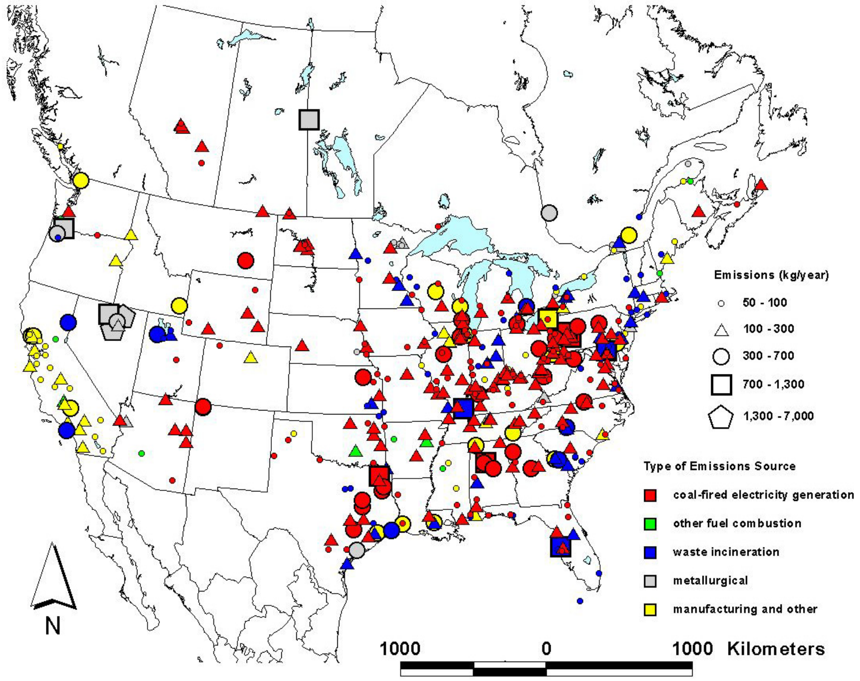


Figure 12. Largest sources of total mercury emissions to the air in the U.S. and Canada. As discussed in the text, the data generally represent emissions for 1999-2000.

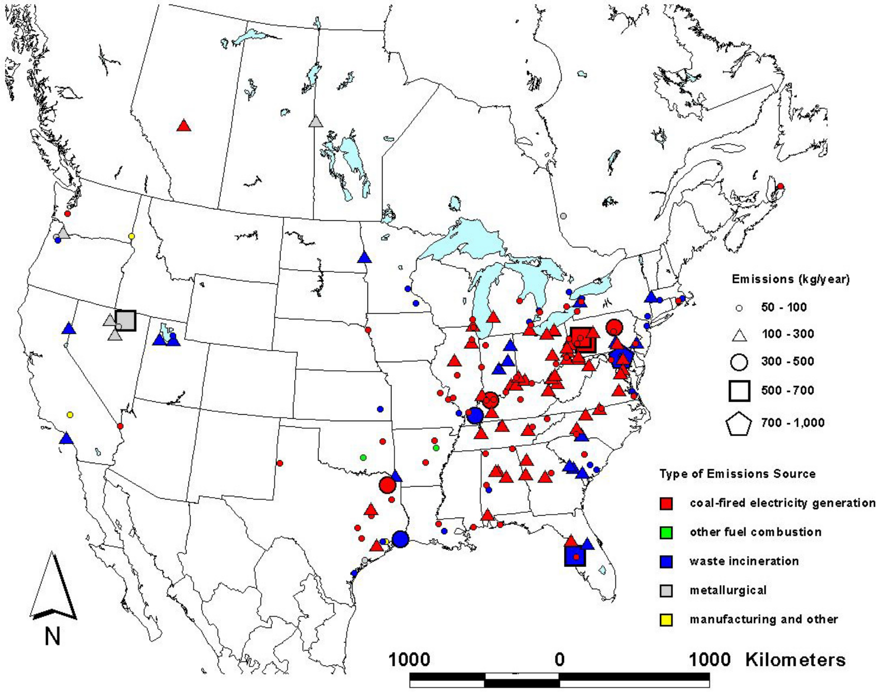


Figure 13. Largest sources of ionic mercury emissions to the air in the U.S. and Canada. As discussed in the text, the data generally represent emissions for 1999-2000.

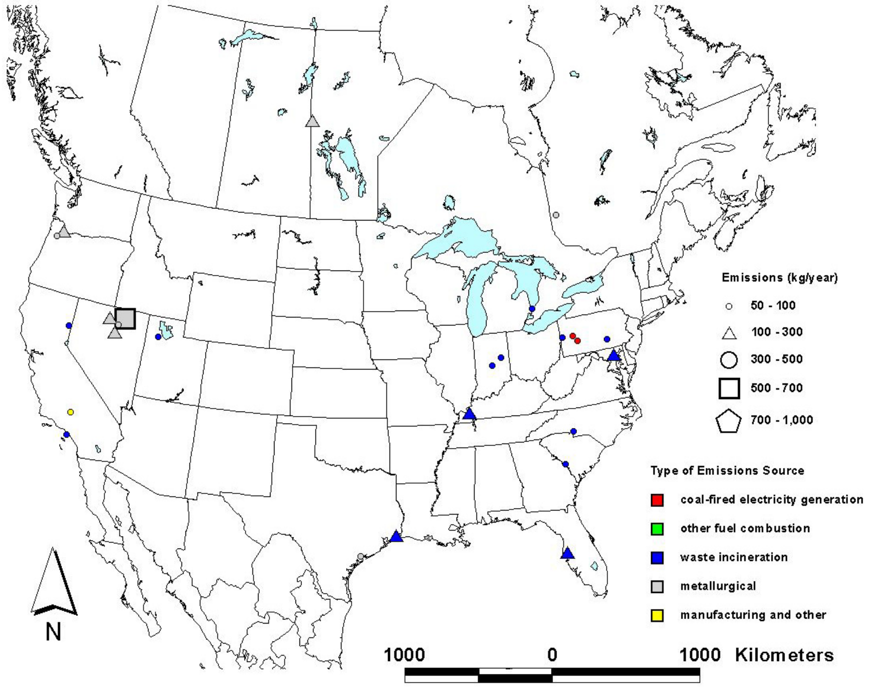


Figure 14. Largest sources of particulate mercury emissions to the air in the U.S. and Canada. As discussed in the text, the data generally represent emissions for 1999-2000.

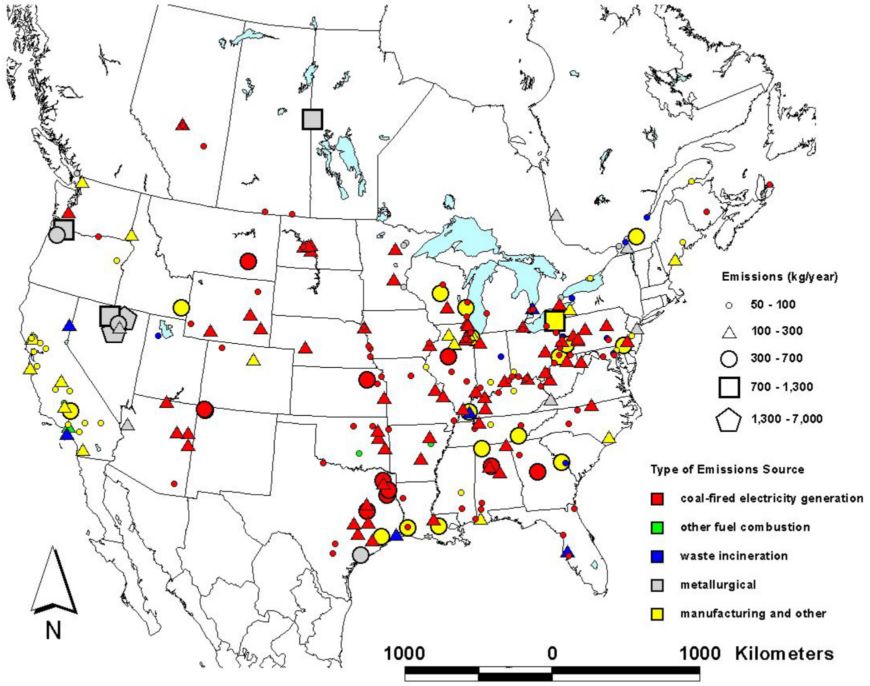


Figure 15. Largest sources of elemental mercury emissions to the air in the U.S. and Canada. As discussed in the text, the data generally represent emissions for 1999-2000.

C. Overview of Atmospheric Mercury Modeling

There have been several atmospheric mercury modeling efforts for North America (e.g., the EPA analysis conducted for the Clean Air Mercury Rule (Appendix A); Bullock et al., 1998; Bullock and Brehme, 2002; Dastoor and Larocque, 2004; Dvonch et al., 1998; Lin et al., 2001; Lin and Tao, 2003; Pai et al., 1997; Seigneur et al., 2001, 2004; Shannon and Voldner, 1995; U.S. EPA, 2005a; Xu et al., 2000a,b,c) and this is an area of ongoing research and development. However, there has been only limited progress in developing the detailed source-receptor relationships for the Great Lakes needed for policy development and required in Annex 15 of the Great Lakes Water Quality Agreement (see Appendix B) and the Clean Air Act, Title III, Sections 103 and 109 (see Appendix C).

An attempt to develop such detailed source-attribution information is being carried out by the NOAA Air Resources Laboratory using a specially configured version of the NOAA HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) atmospheric fate and transport model – HYSPLIT-Hg.

The HYSPLIT model (Draxler and Hess, 1998) has been developed at NOAA and used for many applications. Examples include simulations of the atmospheric fate and transport of sulfur dioxide (Rolph *et al*., 1992, 1993), ozone (Draxler, 2000; Stein *et al*., 2000), smoke plumes (Draxler *et al*., 1994; McQueen and Draxler, 1994), dioxin (Cohen et al., 1995, 2002), and atrazine (Cohen et al., 1997). The model was evaluated in each of the above applications and has also been evaluated in several field tests (e.g., Draxler, 1991).

Initial mercury modeling results for the Great Lakes have been published for 1996 (Cohen et al., 2004), and so the methodology will only be briefly reviewed here. A preliminary 1999 update has been prepared to supplement the published 1996 results, and the results of this update will be presented below (in section H, beginning on page 63).

Figure 16 shows a schematic of many of the phenomena considered in the model. In this figure, the three forms of atmospheric mercury – elemental, ionic (referred to as *RGM* and *Hg(II)* in the figure), and particulate mercury are shown separately. First, all three forms are emitted from anthropogenic sources. In the vapor phase, elemental mercury can be oxidized to ionic mercury and particulate mercury by several reactants (e.g., O_3, H_2O_2, Cl_2, and OH•). When droplets are present (e.g., inside a cloud or at high humidities even without a cloud), the ionic mercury is preferentially absorbed into the aqueous phase. The droplets are grown around particles, and so the particulate mercury associated with these particles finds itself inside the droplet. The degree of solubility of particulate mercury in the droplet phase is not well understood at present. In the HYSPLIT-Hg model, it was determined through initial evaluation exercises that the model appears to give the most realistic results when it is assumed that the particulate mercury is essentially insoluble. However, different assumptions regarding this phenomenon are made in other models (e.g., Ryaboshapko *et al*., 2005).

In the aqueous phase inside a droplet, ionic mercury can be reduced to elemental mercury by dissolved SO_2 and by sunlight. At the same time, elemental mercury can be oxidized to dissolved Hg(II) species and relatively insoluble Hg(p) species by dissolved O_3, OH•, HOCl and OCl^{-1}.

The relative importance of the competing oxidation and reduction processes depends on the relative concentrations of the various reactants. The chemical reactions included in the model are presented in Table 2. In addition, ionic mercury can be absorbed onto the insoluble particulate core of the droplet, primarily onto the soot component of this core. The absorption is reversible, however, and the net direction of the flux depends on the relative concentrations of ionic mercury in the two phases. While on the particulate core, ionic mercury is assumed to be essentially inert (i.e., is not subject to reduction by SO_2). The model also includes dry and wet deposition processes.

The scientific understanding of atmospheric mercury continues to evolve. For example, there is emerging evidence that significant mercury transformation processes may be occurring in the upper atmosphere. The extent or mechanism(s) of these transformations have not been well characterized. This phenomenon is tentatively included in Figure 16, but it is recognized that this is a particularly uncertain fate process.

A conceptual schematic of the HYSPLIT-Hg fate and dispersion model is given in Figure 17. In the model, puffs of air containing mercury are emitted at periodic intervals at a given source location. The puffs are transported downwind, based on meteorological data. The puffs are also dispersed horizontally and vertically, based on the degree of turbulent mixing in the atmosphere at any location, as estimated from meteorological data. Within the puff, the mercury undergoes the various chemical and physical transformations discussed above and is subjected to wet and dry deposition processes. Numerical models such as this operate with time steps at which calculations are performed. A typical time step used in the HYSPLIT-Hg modeling is 15 minutes. At each time step, the puff's position and size are estimated, as is the ongoing fate of the mercury within it due to transformation and deposition processes.

The fate and transport of a given puff is followed until it leaves the model domain or until all the mercury within it has been removed by wet and dry deposition. The emission sources being simulated here generally emit mercury continuously, however, and so additional puffs are released periodically throughout the modeling period. This is shown conceptually in Figure 18. In the modeling described here, the simulations were performed for an entire year, and puffs were released every 7 hours from a given source location. Based on a series of numerical experiments, it was found that this frequency of puff release was sufficient to simulate the fate and transport of mercury within this model, while at the same time allowing the computations to proceed as efficiently as possible.

Meteorological data used as input for the simulations was a full year (1996) of meteorological output from NOAA's Nested Grid Model (NGM) (Rolph, 1997). These data had a horizontal resolution of 180 km, 11 vertical levels up to 6000 meters elevation, and a temporal resolution of two hours. The NGM model was initialized with observations every 12 hours, and the periods in between initializations represent forecast data. All precipitation data in the NGM archive is forecast only, i.e., observed precipitation was not factored into the NGM simulation. The use of more highly resolved and/or more highly observation-assimilated meteorological data would no doubt improve the accuracy of the simulation, especially in the prediction of concentrations and deposition at specific locales and times (e.g., in the model evaluation exercises described below). It is believed that the *annually-averaged* deposition and source-attribution information for the

Great Lakes described here would not be significantly affected, but this hypothesis could be tested in future work.

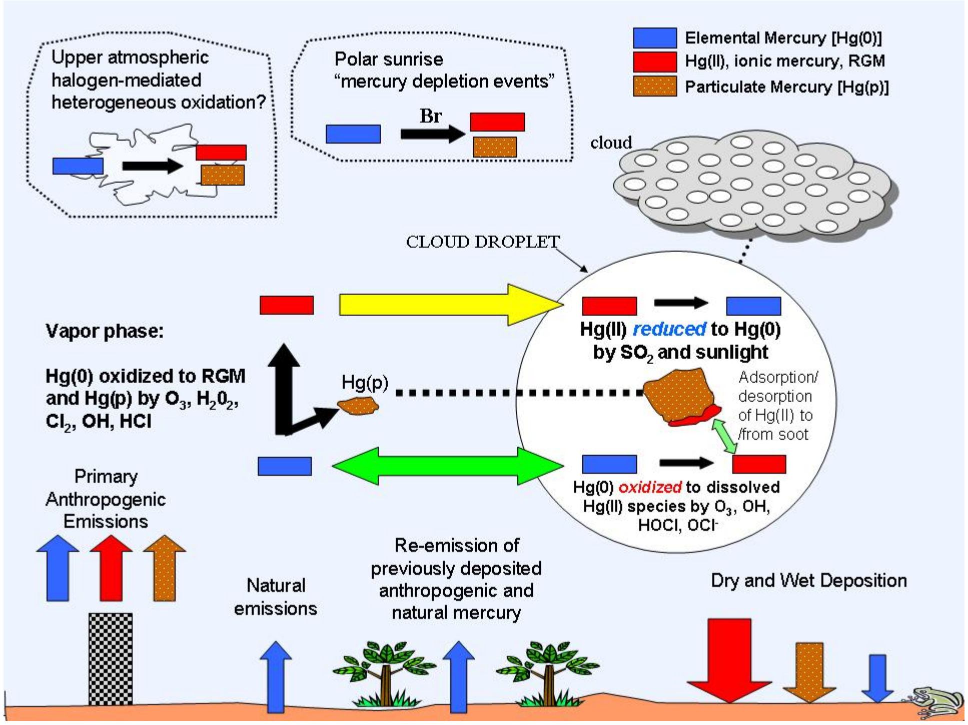


Figure 16. Atmospheric behavior of mercury.

Reaction	Rate	Units	Reference
GAS PHASE REACTIONS			
$Hg^0 + O_3 \rightarrow Hg(p)$	3.0E-20	cm^3/molec-sec	Hall (1995)
$Hg^0 + HCl \rightarrow HgCl_2$	1.0E-19	cm^3/molec-sec	Hall and Bloom (1993)
$Hg^0 + H_2O_2 \rightarrow Hg(p)$	8.5E-19	cm^3/molec-sec	Tokos et al. (1998) (upper limit based on experiments)
$Hg^0 + Cl_2 \rightarrow HgCl_2$	4.0E-18	cm^3/molec-sec	Calhoun and Prestbo (2001)
$Hg^0 + OH\bullet \rightarrow Hg(p)$	8.7E-14	cm^3/molec-sec	Sommar et al. (2001)
AQUEOUS PHASE REACTIONS			
$Hg^0 + O_3 \rightarrow Hg^{+2}$	4.7E+7	$(\text{molar-sec})^{-1}$	Munthe (1992)
$Hg^0 + OH\bullet \rightarrow Hg^{+2}$	2.0E+9	$(\text{molar-sec})^{-1}$	Lin and Pehkonen(1997)
$HgSO_3 \rightarrow Hg^0$	$T*e^{((31.971*T)-12595.0)/T)}$ sec^{-1} [T = temperature (K)]		Van Loon et al. (2002)
$Hg(II) + HO_2\bullet \rightarrow Hg^0$	~ 0	$(\text{molar-sec})^{-1}$	Gardfeldt & Jonnson (2003)
$Hg^0 + HOCl \rightarrow Hg^{+2}$	2.1E+6	$(\text{molar-sec})^{-1}$	Lin and Pehkonen(1998)
$Hg^0 + OCl^{-1} \rightarrow Hg^{+2}$	2.0E+6	$(\text{molar-sec})^{-1}$	Lin and Pehkonen(1998)
$Hg(II) \leftrightarrow Hg(II)_{(soot)}$	9.0E+2	liters/gram; t = 1/hour	**eqlbrm:** Seigneur et al. (1998) **rate:** Bullock & Brehme (2002).
$Hg^{+2} + h\nu \rightarrow Hg^0$	6.0E-7	$(sec)^{-1}$ (maximum)	Xiao et al. (1994); Bullock and Brehme (2002)

Table 2. Atmospheric chemical reactions of mercury.

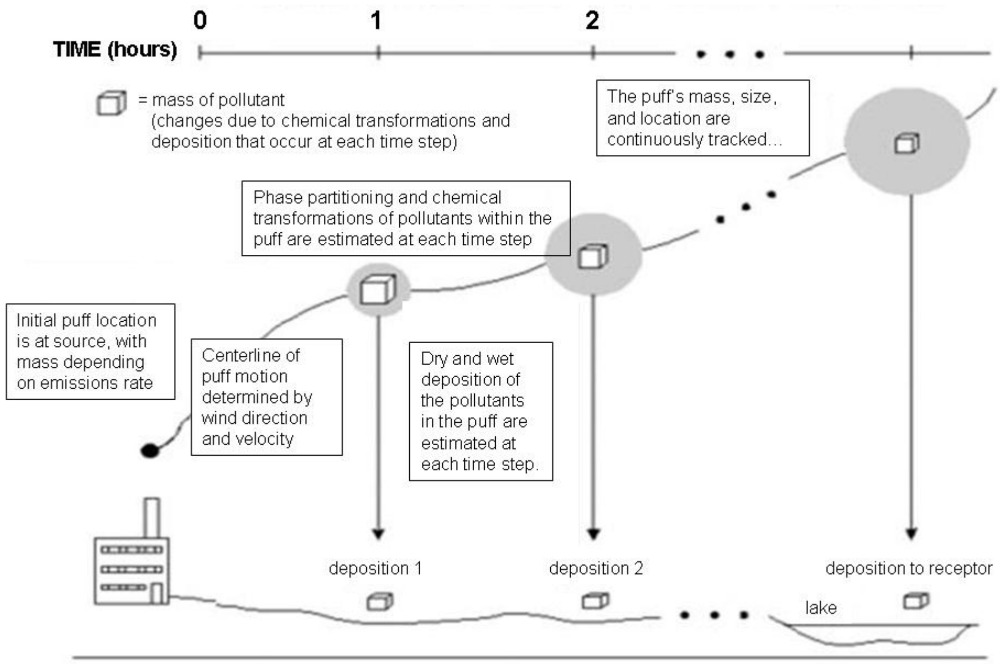


Figure 17. Schematic of Lagrangian puff modeling.

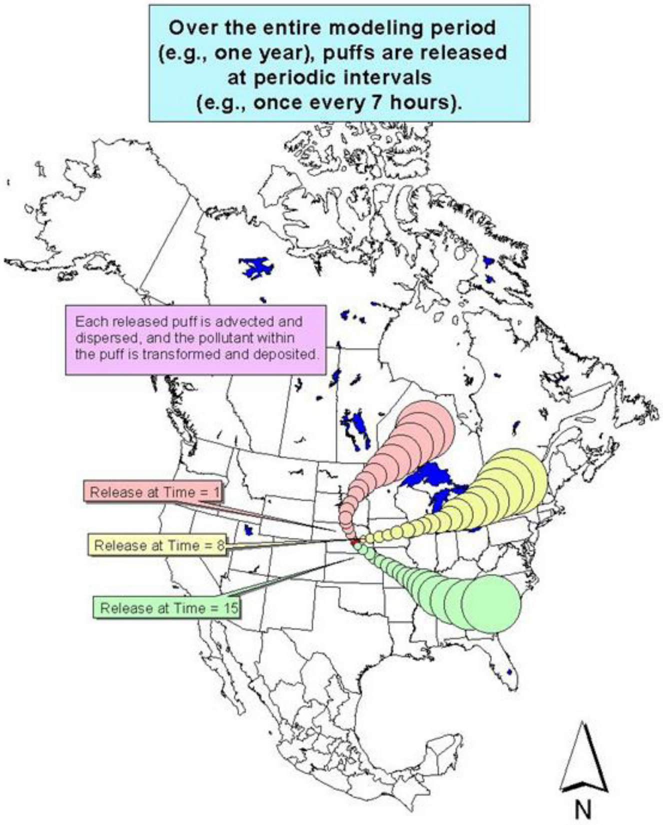


Figure 18. Multiple puff releases from a single source.

D. Illustrative Modeling Results for a Single Source

Deposition impacts of any emissions source on any receptor are (1) highly variable in space and time and (2) strongly dependent on the form of mercury emitted. To illustrate these points, a number of hypothetical, simplified modeling simulations of the fate and transport of mercury from a single source will be briefly discussed in this section. The simulations discussed in this section share many of the same features, including the following:

- Archived NGM meteorological data for 1996 were used (with 180 km spatial resolution);
- The modeling period was for the entire year 1996;
- Unless otherwise noted, the simulations were done with an effective stack height of 250 meters, a typical stack height for large coal-fired power plants;
- All simulations were done for a hypothetical, continuous, 1 kg/day source of either elemental, particulate, or ionic mercury, as noted; in any given simulation, only one form of mercury was emitted, but the mercury was allowed to be transformed into other forms as discussed above;
- The hypothetical source was located at the center of the modeling domain, at North Latitude 42.5, West Longitude 97.5.
- In some of the simulations, the results were tabulated on a 1^{o} x 1^{o} grid (approximately 100 km x 100 km) over the entire modeling domain [see Figure 19], while in others, the results were tabulated on a 0.1^{o} x 0.1^{o} grid (approximately 10 km x 10 km) over a smaller region [see Figure 20]. Note that the underlying physics and chemistry of these simulations were the same – only the spatial resolution of the output was varied.

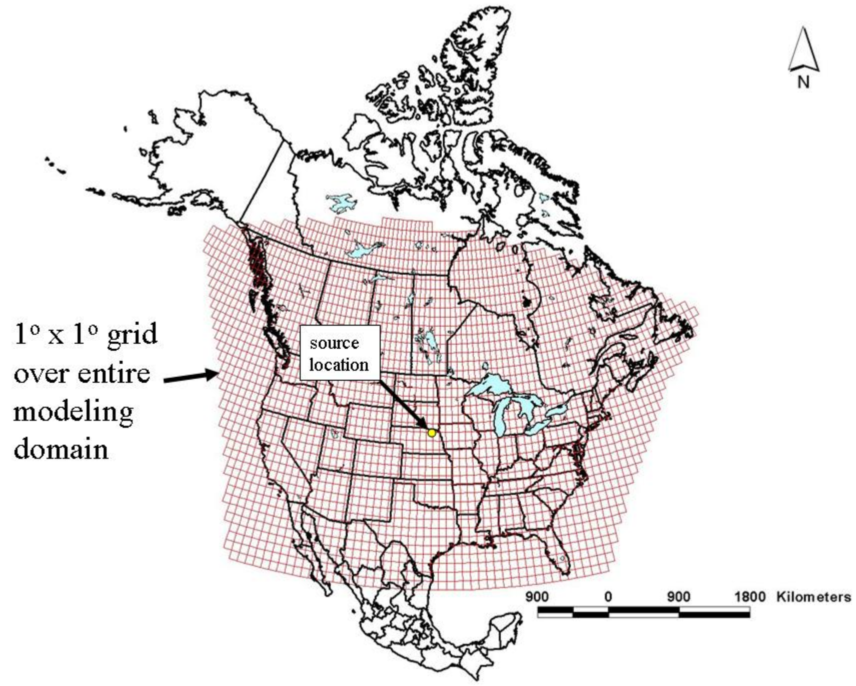


Figure 19. 1° x 1° grid for whole-domain analysis.

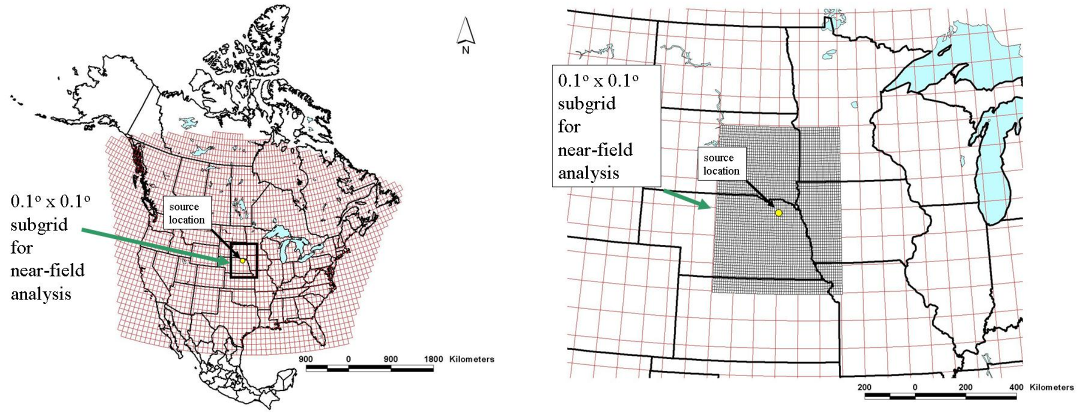


Figure 20. 0.1° x 0.1° subgrid for near-field analysis.

To illustrate the spatial and temporal variability of atmospheric deposition impacts from any given source, Figure 21 shows the daily deposition arising from a single, continuous, hypothetical source in the middle of the modeling domain for a period of 15 days. It can be seen that there are large spatial variations, and that the pattern changes – sometimes rather dramatically – from day to day.

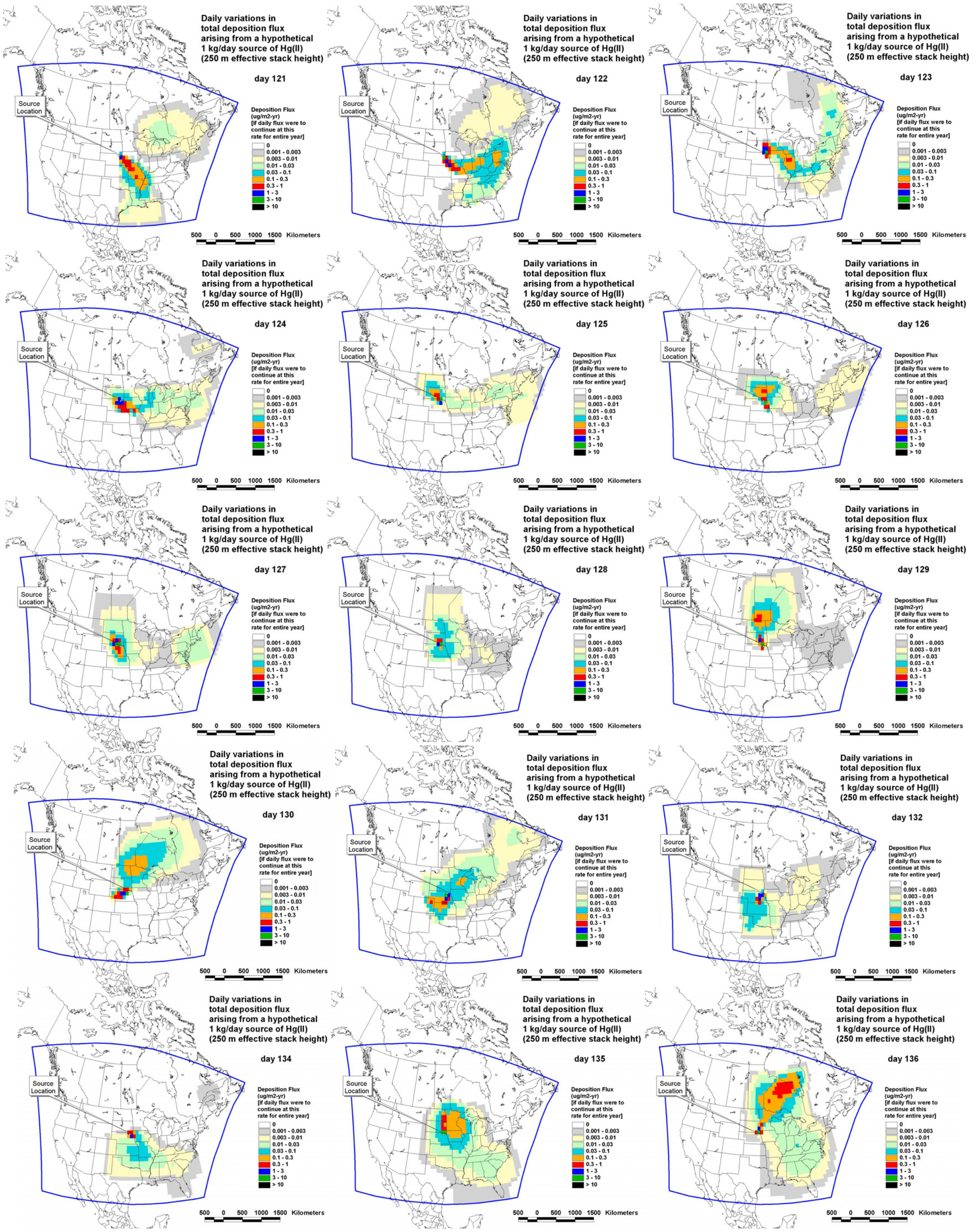


Figure 21. Daily maps of deposition arising from ionic mercury emissions.
The maps shown are for simulations of the atmospheric fate and transport of emissions from a single, hypothetical, continuous, 1 kg/day, 250 meter effective stack height source of ionic mercury. While the simulation was carried out for an entire year, only a 15-day period during the middle of the year is shown here for brevity (days 121-135). Thus, it is noted that a portion of the deposition shown for each day arose from emissions before the 15-day period shown.

In Figure 22, the daily values for a single location 40 km "downwind" of the same source are plotted. The weekly average deposition for the same site is also shown. It can be seen that the deposition varies dramatically over the course of the year. The behavior illustrated in these figures is not unique to mercury – it is a relatively general phenomenon for pollutants because of the inherent variability of weather patterns. Recently, data have been published that demonstrate these spatial and temporal variations of source impacts for mercury (Gildemeister et al., 2005). This phenomenon is important to consider when designing or interpreting monitoring data at any given site. Short term or discontinuous measurements may not be representative of the long-term average impacts at any given site.

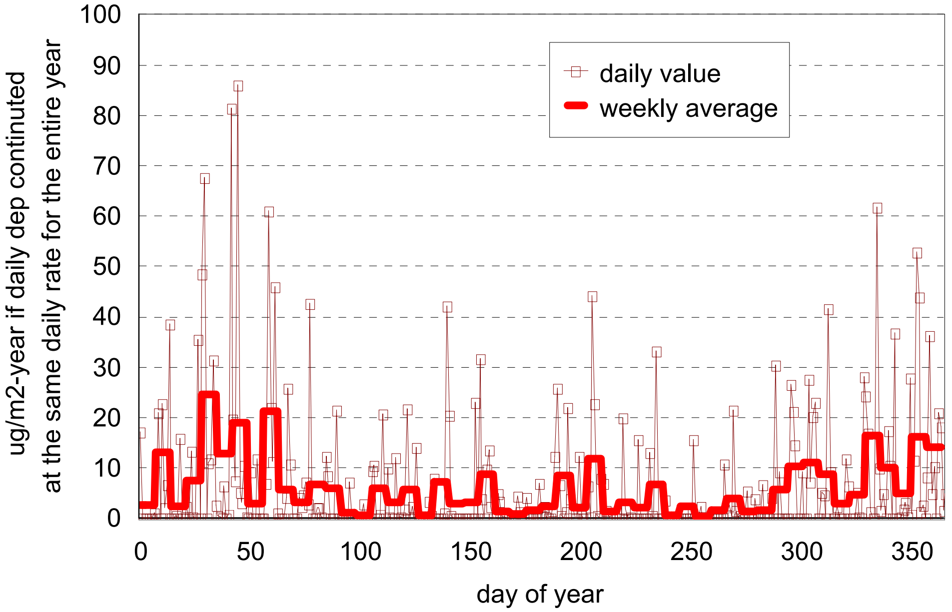


Figure 22. Daily variations in mercury deposition impacts. This figure shows the total deposition of mercury at a particular fixed location 40 km away from a 250 meter high, 1 kg/day continuous source of ionic mercury.

The second general point regarding mercury's atmospheric behavior – discussed above in the introduction to this modeling section (Section 3) -- is that the type of mercury emitted strongly influences the downwind fate and transport. To illustrate this point, annual total deposition fields arising from emissions of elemental, particulate, and ionic mercury are shown for the whole domain in Figure 23 and for the near-field domain in Figure 24. As noted earlier, the simulations in these two figures were essentially the same – only the resolution and extent of the output was varied. Noting that the color scale in these figures is logarithmic, it can be seen that there is a rather dramatic difference in the deposition fields arising from emissions of the different forms of mercury.

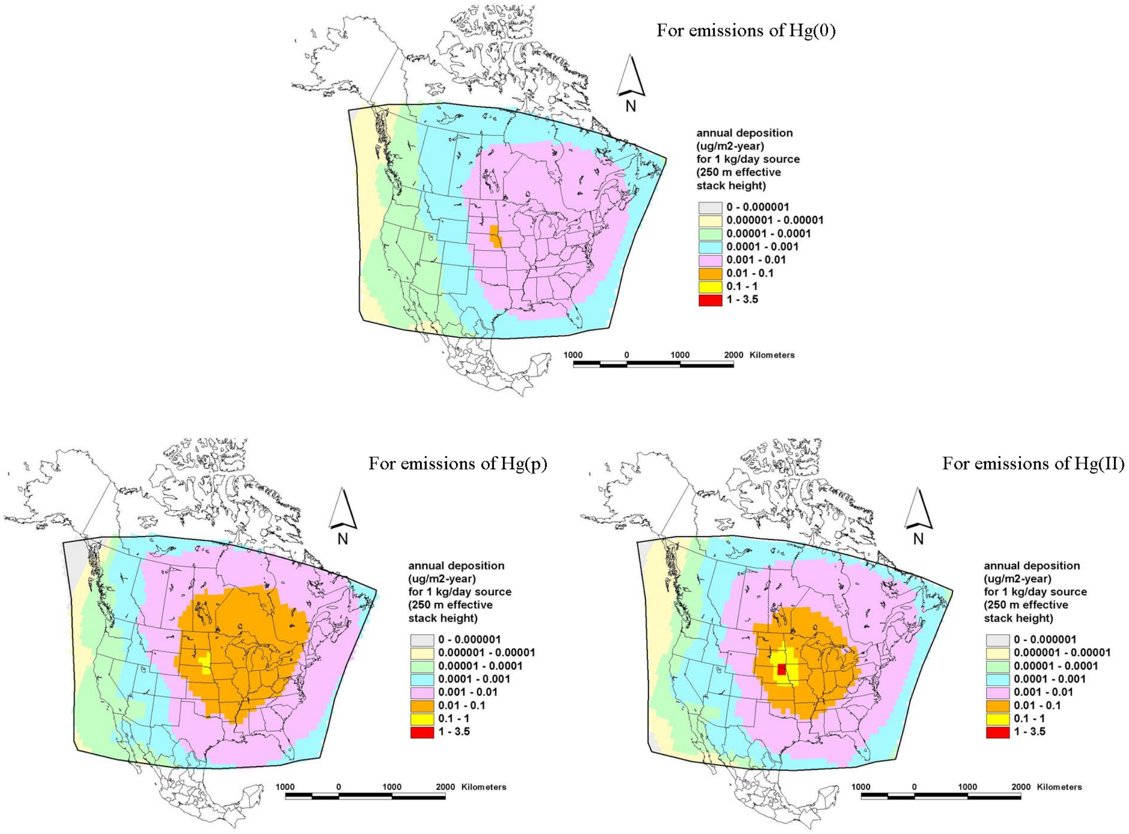
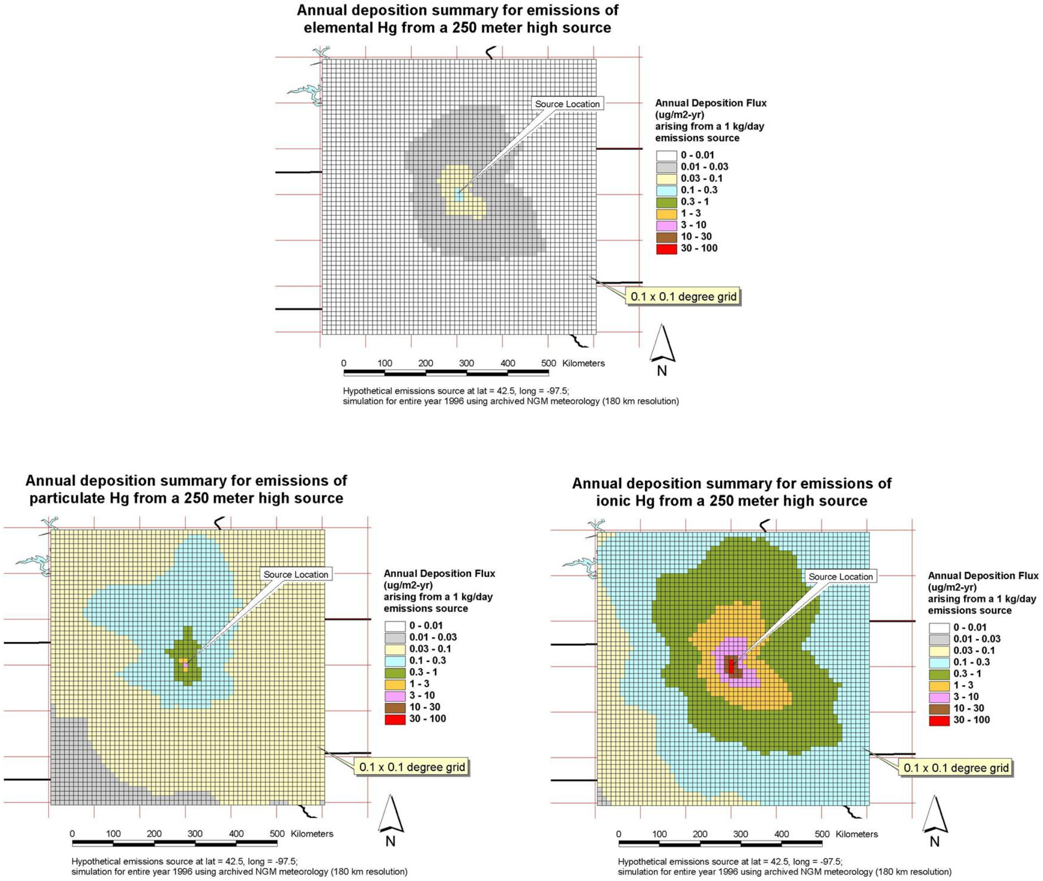


Figure 23. Large scale deposition impacts of different types of Hg emissions. In this figure, Hg(0) refers to elemental mercury, Hg(p) refers to particulate mercury, and Hg(II) refers to ionic mercury.



Annual deposition summary for emissions of elemental Hg from a 250 meter high source

Annual deposition summary for emissions of particulate Hg from a 250 meter high source

Annual deposition summary for emissions of ionic Hg from a 250 meter high source

Hypothetical emissions source at lat = 42.5, long = -97.5;
simulation for entire year 1996 using archived NGM meteorology (180 km resolution)

Figure 24. Near-field deposition arising from mercury emissions. In the top two maps, the sub-domain used for this near-field analysis is shown. In the other maps, results for emissions of elemental, particulate, and ionic mercury are shown.

The near-field results are presented in another way in the following figures. Figure 25 and Figure 26 show the average deposition flux at different distances away from a hypothetical source of ionic mercury for three different effective stack heights[6] (50, 250, and 500 meters). Figure 25 presents the data using a logarithmic scale (0.001, 0.01, 0.1, …) while Figure 26 presents exactly the same data using a linear scale (10, 20, 30, …). It can be seen that stack height primarily influences deposition in the region closest to the source. Figure 27 (logarithmic) and Figure 28 (linear) present data for emissions of ionic, particulate, and elemental mercury for the same effective stack height (250 meters). It can be seen that there is a dramatic difference between the deposition fluxes of ionic, particulate, and elemental mercury – pound for pound, emissions of ionic mercury result in deposition fluxes approximately an order of magnitude greater than those arising from emissions of particulate mercury, and deposition fluxes arising from emissions of elemental mercury are approximately an order of magnitude lower than those for particulate

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[6] The "effective" stack height includes plume rise, i.e., the height to which the emitted material rises shortly after leaving the stack due to the fact that the emitted material may be hotter than the ambient air and that the emitted material may be blown out the stack at significant velocities.

mercury emissions. It should be noted that data in these four figures are averaged over the entire distance range (i.e., in all directions away from the source). At any given distance from the source, the deposition would be higher at locations typically downwind and lower at locations normally upwind of the source.

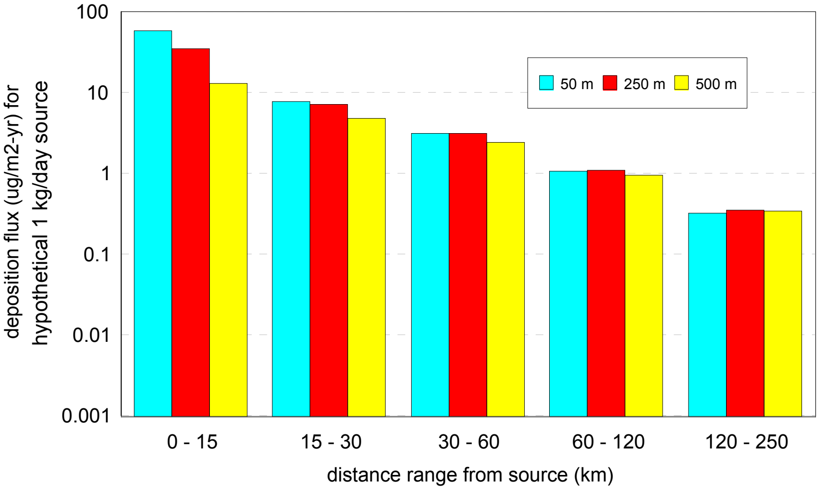


Figure 25. Deposition vs. distance for emissions of ionic mercury (logarithmic). Data for three different effective stack heights are presented.

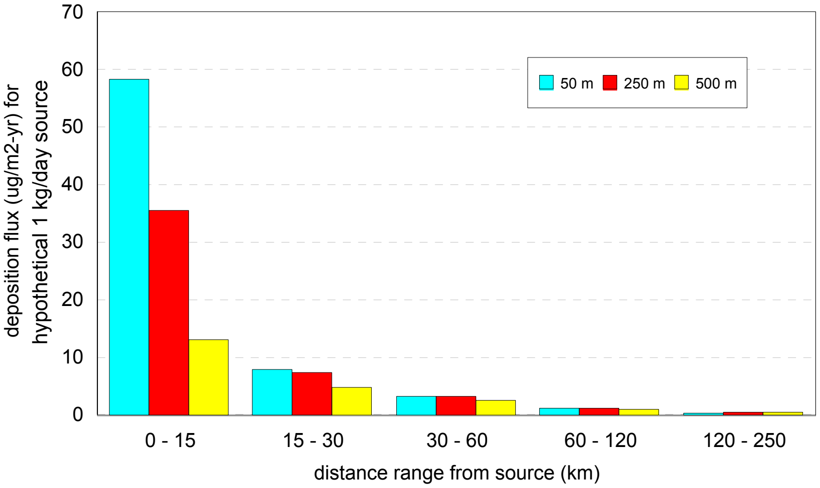


Figure 26. Deposition vs. distances for emissions of ionic mercury (linear). These are the same data as shown in the previous figure, but expressed on a linear scale. As in the previous figure, data for three different effective stack heights are presented.

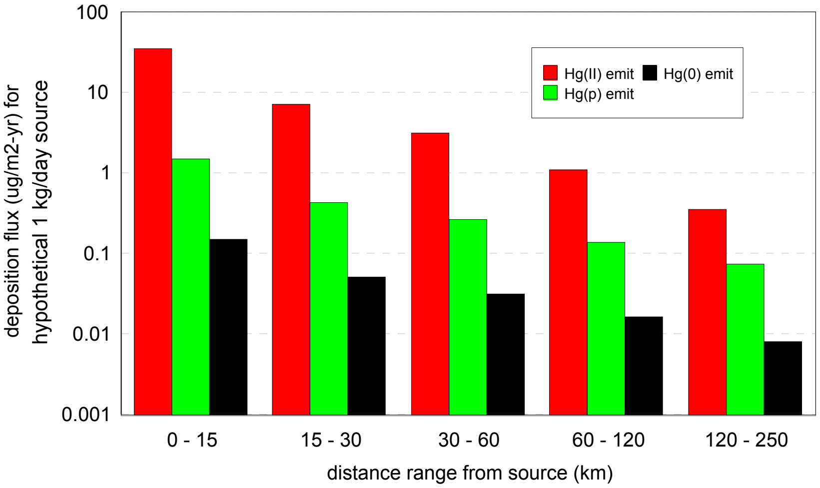


Figure 27. Deposition vs. distance for emissions of different mercury forms (logarithmic). These data are for Hg(II) [ionic], Hg(p) [particulate], and Hg(0) [elemental] emissions from an effective stack height of 250 meters.

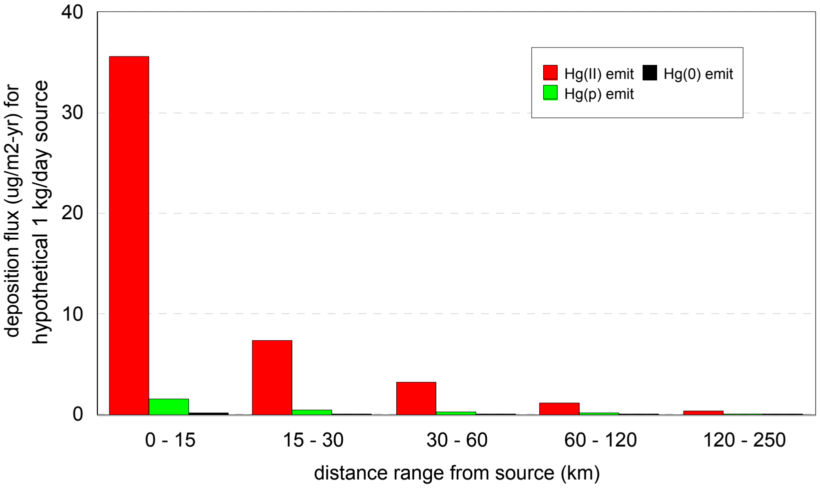
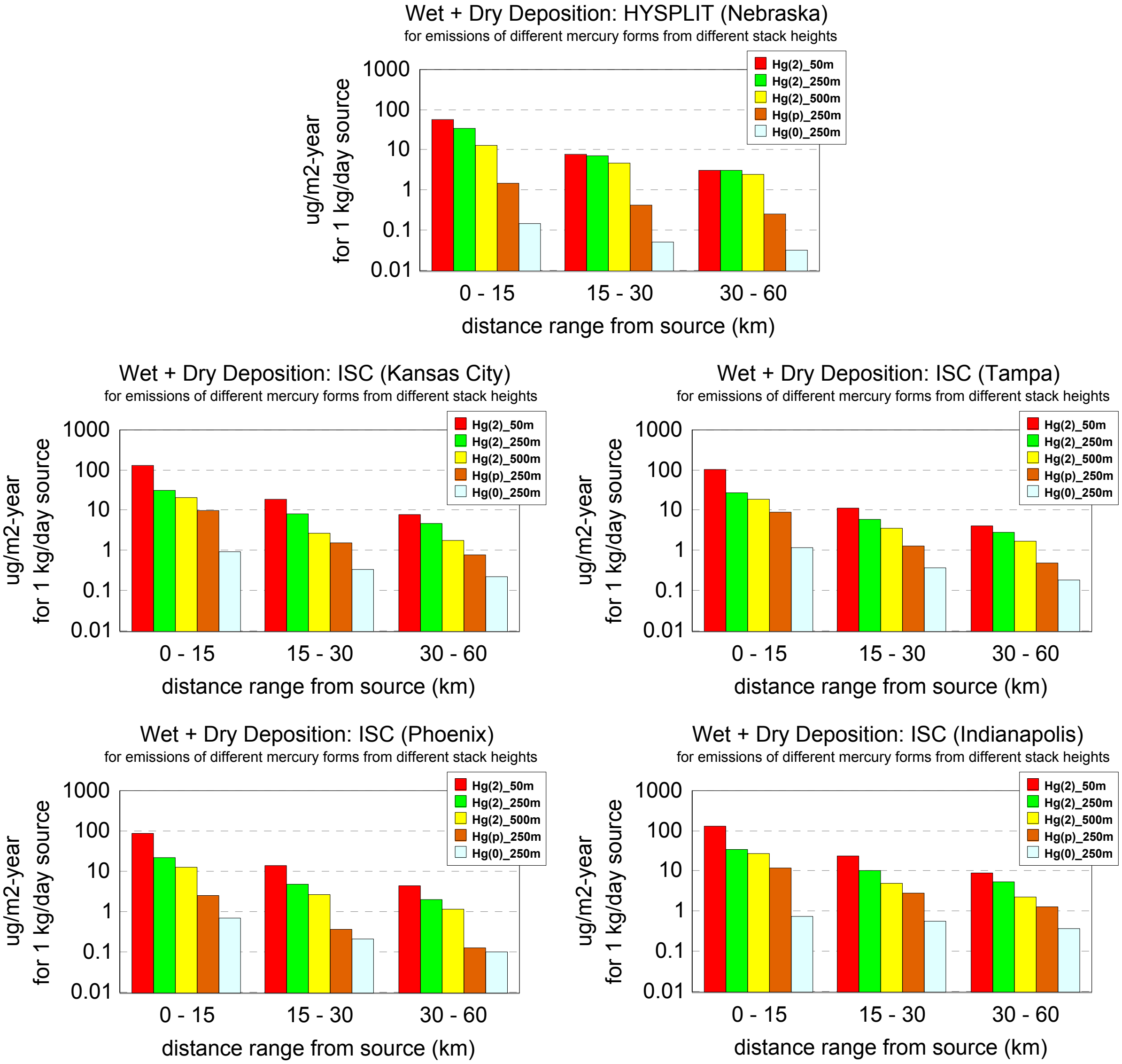


Figure 28. Deposition vs. distance for emissions of different mercury forms (linear). These are the same data as shown in the previous figure, but a linear scale is used. As in the previous figure, these data are for Hg(II) [ionic], Hg(p) [particulate], and Hg(0) [elemental] emissions from an effective stack height of 250 meters.

The U.S. EPA has performed a similar near-field deposition analysis with the Gaussian plume Industrial Source Complex (ISC) model (U.S. EPA 2005c) for hypothetical mercury sources at four different locations. Detailed results from this analysis were obtained from the EPA (U.S. EPA 2005e). For comparison purposes, the ISC results were "mapped" onto the HYSPLIT grid.

The results are shown in Figure 29. The HYSPLIT and ISC simulations were performed for different locations; also, meteorological data used for the EPA analyses were for 1990-1994, while 1996 data were used for the HYSPLIT simulations. Given that both the HYSPLIT and ISC models are highly sensitive to meteorological conditions, and these conditions naturally vary from location to location and from one year to the next, it is not expected that the results would be identical. Nevertheless, it can be seen that the results from the two models are reasonably consistent. To provide a more rigorous comparison, additional analyses could be conducted to compare the models for the same location and time period.



Wet + Dry Deposition: HYSPLIT (Nebraska)

for emissions of different mercury forms from different stack heights

Wet + Dry Deposition: ISC (Kansas City)

for emissions of different mercury forms from different stack heights

Wet + Dry Deposition: ISC (Tampa)

for emissions of different mercury forms from different stack heights

Wet + Dry Deposition: ISC (Phoenix)

for emissions of different mercury forms from different stack heights

Wet + Dry Deposition: ISC (Indianapolis)

for emissions of different mercury forms from different stack heights

Figure 29. Near-field deposition estimated by ISC and HYSPLIT models. The top graph shows HYSPLIT model results, where the hypothetical source was at a location in Nebraska, and the other graphs show the ISC model results, for the four different locations analyzed by the EPA (Kansas City, Tampa, Phoenix and Indianapolis).

Figure 30 combines data from the HYSPLIT-Hg near-field and whole-domain hypothetical simulations to show the cumulative fraction deposited at different distance ranges arising from emissions of different forms of mercury. Again, there is a dramatic difference between the results for emissions of the different forms of mercury.

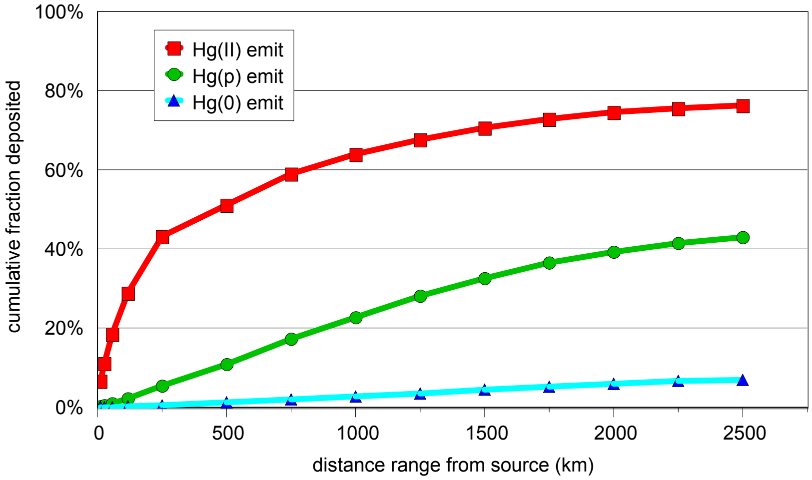


Figure 30. Cumulative fraction of emissions deposited out to 2500 km. Results are for a 250 meter effective stack height for emissions of different forms of mercury. As with the previous data presented in this section, the hypothetical source emitted at a rate of 1 kg/day and was located at the center of the modeling domain (latitude 42.5, longitude -97.5). Also, as with the previous figures, the simulation was for the entire year 1996, using NGM meteorological data.

Given the critical importance of the form of emitted mercury on depositional impacts – and the enhanced local and regional deposition arising from Hg(II) (aka “ionic”, “RGM”) emissions, it is instructive to consider the sources of this form of mercury in the Great Lakes region. An example is shown in Figure 31 for anthropogenic sources in the Great Lakes States and Provinces.

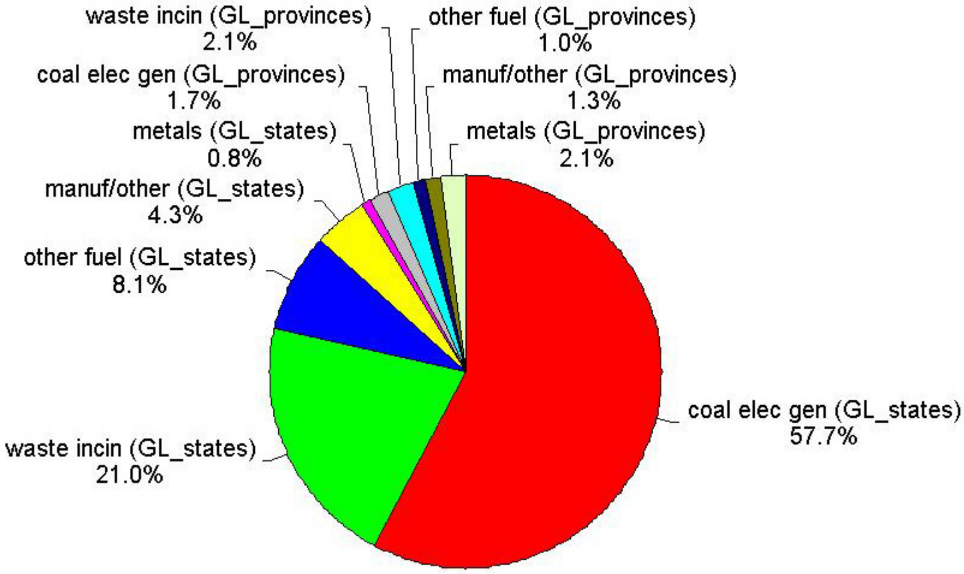


Figure 31. Emissions of ionic mercury in the Great Lakes region. Ionic mercury emissions are tabulated for different source sectors and for the Great Lakes states (MN, WI, IL, IN, MI, OH, PA, and NY) and the Great Lakes provinces (ON, PQ). U.S data is for 1999-2001 and Canadian data is for 2000. The total anthropogenic inventoried ionic mercury emitted from these states and provinces is 13.4 metric tons/year.

E. Overall Modeling Methodology

In the atmospheric mercury modeling done to date for the Great Lakes at the NOAA Air Resources Laboratory with the HYSPLIT model, only anthropogenic emissions from the U.S. and Canada have been considered. The impact of global emissions sources, as well as natural and re-emissions sources could be added to the simulations in the future.

Conceptually, the overall modeling procedure involves modeling the emissions of mercury from each source in the inventory, similar to the types of simulations presented above for a single hypothetical source. However, because there are more than 100,000 sources in the combined U.S. and Canada emissions inventory, it is not feasible to explicitly model each individual source with its own simulation. A procedure has been developed that allows the individual impacts of each source in the inventory to estimated, based on a more limited set of simulations (Cohen et al., 2002, 2004). In this technique, an interpolation procedure is used to estimate detailed source-receptor relationships. To conduct the analysis, explicit HYSPLIT simulations of emissions – similar to those discussed in the previous section – were performed for a limited number of *standard source locations.* Then, the impact of any given source – at other locations – on the Great Lakes was estimated based on a weighted average of the impacts of the nearest explicitly modeled *standard source locations* nearest to that given source. This procedure is illustrated in Figure 32.

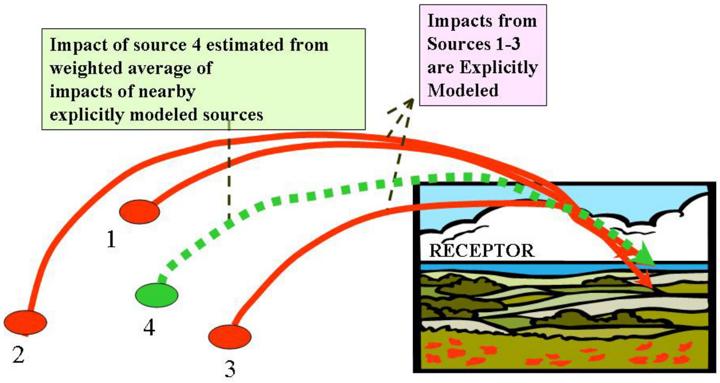


Figure 32. Spatial interpolation.

To account for the varying proportions of different mercury forms being emitted from different sources, separate unit-emission simulations of Hg(II), Hg^0, and Hg(p) emissions were made at each standard source location. The impact of a source emitting a mixture of Hg^0, Hg(II), and Hg(p) was estimated based on a linear combination of these pure-component unit emissions simulations. An example of this procedure is illustrated in Figure 33.

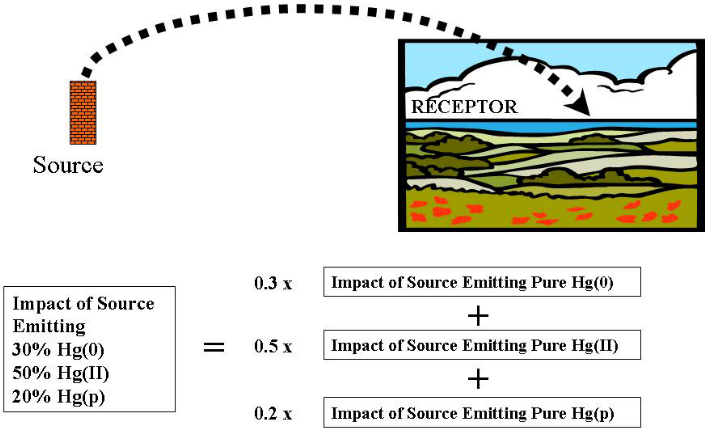


Figure 33. Chemical interpolation.

In sum, both spatial and chemical interpolation procedures were used to estimate the impact of each source in the inventory on each of the Great Lakes. This spatial and chemical interpolation methodology relies on the "assumption" that the atmospheric fate and transport of mercury from any given source is not influenced by the mercury emissions from any other source. This assumption is consistent with the current understanding of atmospheric mercury.

Concentrations of key reactants influencing the atmospheric chemistry of mercury (e.g., O_3, OHC, SO_2, Cl_2) were estimated using a variety of empirical methods, as described elsewhere (Cohen et al., 2004).

Only the direct deposition to the lake surfaces has been estimated in the modeling analysis described here. Indirect atmospheric contributions, resulting from deposition to a lake's watershed and subsequent transfer to the lake, have not been estimated as part of the modeling to date. Due to the relatively small size of their watersheds, this pathway may be less important for the Great Lakes than for other water bodies.

Estimating the amount of mercury loading to the Great Lakes contributed through the indirect watershed-mediated pathway is very uncertain, as there are few measurements of runoff and tributary inputs to the lakes. Moreover, determining the portion of such input that arises as a result of atmospheric deposition as opposed to direct discharges to the tributaries or natural mercury present in the ecosystem is difficult. Rolfhus *et al*. (2003) have estimated that total tributary input to Lake Superior represented approximately 27 percent of the total loading to the lake, based on measurements made in 2000. Landis and Keeler (2002) estimated that tributary inputs account for approximately 16 percent of the loading to Lake Michigan, based on 1994-95 measurements. Indirect atmospheric deposition would account for a portion of these contributions, but the fraction is unknown.

F. Model Uncertainties

There are a number of uncertainties in atmospheric mercury models. In the following section, these uncertainties will be discussed, along with potential actions that could be taken in an attempt to reduce them. In general, these uncertainties apply to any atmospheric mercury model, but details specific to the HYSPLIT-Hg modeling presented here will be provided as appropriate.

It is important to point out that virtually all of the issues discussed below are simply a reflection of the current state of the art. They are not insurmountable. Essentially all of the uncertainties below could be reduced significantly in the future as more research and data become available. In some cases, the steps necessary to address the issues are relatively straightforward, and in others, more complex. Examples of actions to reduce uncertainties will be noted in the following discussion.

Since there are uncertainties in model physics and chemistry, there are uncertainties in the overall results of the modeling (e.g. source attribution estimates). However, due to the scarcity of data for model evaluation – discussed in detail in the next section – it is difficult to gauge the overall significance of the uncertainties discussed below.

1) Emissions

There are many uncertainties in anthropogenic emissions inventories. First, there have been relatively few measurements of the proportion of the three forms of mercury emitted from various source categories, and so this aspect of the inventory is particularly uncertain. As is discussed above, the atmospheric fate of the different emitted forms is quite distinct; accordingly, source-receptor relationships are strongly dependent on the emissions profile of each source. Second, while emissions estimates from a few source categories (e.g. coal fired power plants) are based on a relatively large set of measurements, estimates for most other source categories are based on relatively few (if any) measurements. As a result, estimates of the proportion of different mercury forms emitted – and even the annual total emissions of all forms combined – are very uncertain for many sources.

In addition, information on the temporal variation of emissions is generally not available. So, simple (and perhaps unrealistic) assumptions have to be made. In the modeling presented here, the emissions from each source were assumed to have been continuous and constant throughout the year. This assumption is used in most mercury modeling because temporally resolved emissions data is generally not available. However, the validity of this assumption is uncertain for any given source. Even for sources that are relatively continuous, maintenance or upset-related shut downs do occur. Since deposition impacts from any given source are highly episodic (see subsection D above), temporal variations in emissions may introduce significant errors in estimates of source-receptor relationships. For example, the model might estimate that a particular source would contribute significant deposition at a certain site, assuming continuous emissions, on a limited number of days per year [e.g., see Figure 22 (page 39) above]. If the facility happened to be shut down on one or more of those days – or if the emissions were higher or lower than average -- the accuracy of the simulation could be strongly affected. Due to a lack of data, these types of errors are difficult to diagnose and fix, and can be particularly important in comparing model predictions against actual measurements at any particular location and time. If the model does not agree with the measurement, it may simply be that the emissions for one or more of the sources contributing significantly to that site have been incorrectly characterized for that time period.

Additional measurements, data collection, and data assembly would be required to reduce the uncertainty in the amounts, forms, and timing of mercury emissions from any given source. Technologies for continuous emissions monitoring of different mercury forms are now available and have been installed on several large coal-fired power plants. Based on these measurements, it has been found that there can be significant temporal variations in mercury emissions over time scales of minutes to hours, as well as variations on longer time scales. An example of such data is shown in Figure 34 (Keller, 2006).

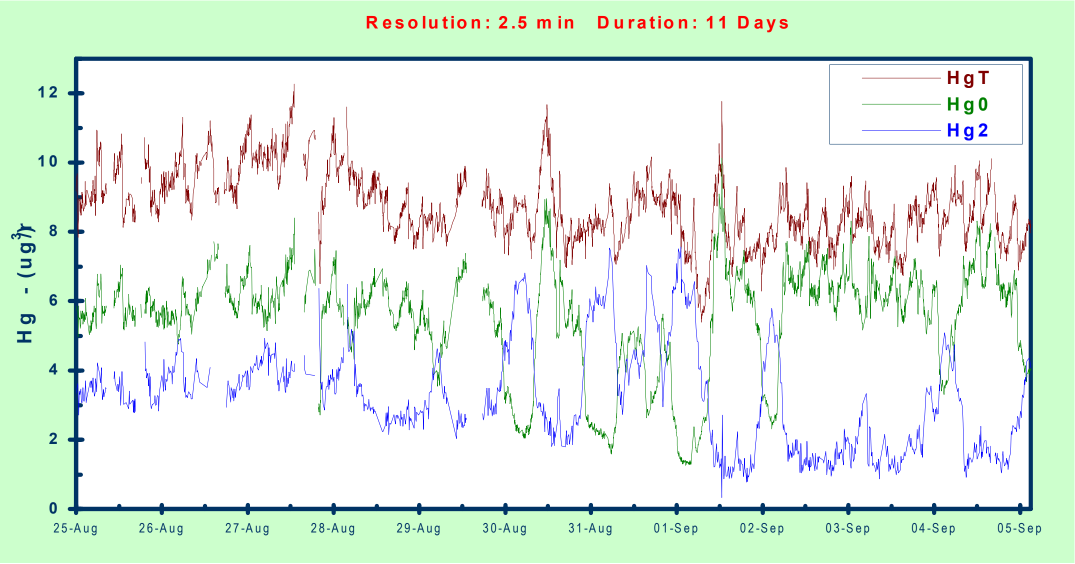


Figure 34. Temporal variations in Hg emissions from a coal-fired power plant.

Finally, emissions inventories are not static – they can change significantly over time. The EPA reports that they have individual facility mercury emissions estimates for 1990, 1996, 1999 and 2002. The source sectors believed to have changed the most significantly over the past 10-15 years are municipal and medical waste incinerators. Overall, it is believed that substantial reductions in mercury emissions occurred during the period from the early 1990's through ~2001-2002 (e.g., see Figure 76, page 92). However, the precise timing of these reductions is not well known. For example, both the ~1996 and ~1999 EPA inventories may have underestimated the overall mercury emissions from these sources – i.e., they may have been too optimistic regarding the timing of the reductions. More importantly, the changes in emissions between any two inventories (e.g., for 1995, or 1997) and within the year of any given inventory are not available. This complicates the interpretation of trend data at measurement sites. One might expect, for example, to see the effect of reductions at a particular monitoring site downwind of a particular incinerator. But, if the exact time-course of emissions from the incinerator is not well known, it is difficult to glean meaningful information regarding local and regional impacts of the facility from local and regional ambient measurements. An accurate, continuous estimate of facility-specific emissions from significant sources in the U.S. (and elsewhere) -- from the initial operation of each facility up to the present -- has not been assembled. Therefore, interpretation of trends in monitoring data is extremely difficult. Examples of analyses interpreting time trends in monitoring data in relation to time trends in local source emissions have recently been provided by Prestbo *et al.* (2006) and Bookman *et al.* (2006).

The nominal schedule for EPA mercury inventory updates in the U.S. is once every three years, and the issuance of the inventory is not done for many years after the inventory year. The infrequent and delayed updates complicate the modeling process. Only certain years can be attempted, and these attempts can only occur years after the actual emissions. In the past, Canadian emission inventories have been compiled by Environment Canada once every five years. Until recently, the latest available national mercury inventory was for 1995. However, the 2000 inventory is now becoming available. Future inventories may be made available annually (Niemi, 2005). Global emissions inventories are currently being updated on a 5-year schedule by an international group led by Jozef Pacyna of the NILU institute in Norway. The latest global inventory data available at the time of this writing is for 2000.

Once anthropogenically emitted mercury is deposited, it can be re-emitted. The temporal and spatial patterns of these re-emissions are very poorly understood. It is believed that most re-emissions are in the form of elemental mercury. The re-entrainment of dust may result in re-emissions of particulate mercury, but the relative significance of this process is unknown. A complex suite of factors will influence the relative re-emissions flux at any given location, including the amount, speciation, and distribution of mercury that has already been deposited, the time course of the deposition history, meteorological conditions, soil and vegetation characteristics, and a number of chemical and biological processes. However, all things being equal, it is likely that emissions will be higher in regions that have experienced the greatest deposition. And, all things being equal, as the deposited mercury is depleted, re-emissions may diminish over time. Given the above, and the fact that deposition close to the source is generally the greatest (e.g., see Figure 28, page 43), at first order, the spatial distribution of the re-emissions field may be similar to that of the direct anthropogenic emissions. This is an assumption that is commonly used (e.g., Ryaboshapko, 2005), although the relative emission rate is very uncertain. Lamborg *et al.* (2002) estimate that globally, annual re-emissions may be as much as 30 percent of the annual direct emissions.

Given current understanding, it is difficult at present to improve on the simple and potentially inaccurate treatment described above. There are insufficient data -- on the fluxes from contaminated soils, the spatial and temporal variations of different forms of mercury in soil and other media and the processes that influence the behavior of mercury in soils -- to make realistic estimates of re-emission fluxes for input to large-scale models.

A closely related emissions issue concerns emissions from soils and sediments directly contaminated through anthropogenic activities, e.g., liquid and solid industrial waste discharges, mine tailings, etc. Emissions from these sources are poorly understood. To characterize them, the same type of approach would be required, i.e., monitoring, process-related studies, and modeling.

Uncertainties in natural emissions are similar to those for other types of emissions. As a result, the amounts, time-course, and spatial distribution of these emissions are poorly understood. However, new information and techniques for estimating natural emissions are emerging (e.g., Tsiros 2002; Scholtz *et al*., 2003; Bash *et al*., 2004; and Gustin *et al*., 2004) and it is hoped that accurate estimates will be available in the future as inputs to atmospheric mercury models. Coordinated national and international programs to develop periodic estimates of natural mercury emissions, similar to existing efforts for current anthropogenic emissions, do not yet exist.

At any given location, the net flux of each form of mercury will be made up of the following components:

- A downward flux of anthropogenic mercury being deposited;
- A downward flux of natural mercury being deposited;
- An upward flux being emitted from natural sources; and
- An upward flux being re-emitted from previously deposited anthropogenic emissions.

This presents a difficulty, as it may be difficult in most cases to determine the separate magnitudes of these different components. This is especially true for elemental mercury, for which the upward flux components may be the most significant. However, models and measurements can be used together to estimate the magnitudes of the different components of the net surface exchange flux.

2) Atmospheric Phase Behavior

There are several ways in which atmospheric phases can be delineated, but for the purposes of this discussion, we will assume that there are three main atmospheric phases: vapor, particulate (solid), and, in some cases, aqueous droplets (e.g., clouds, fogs). In general, at any given time and location in the atmosphere, all forms of mercury co-exist and are present in differing proportions in each existing phase. Each form of mercury will move from one phase to another in response to thermodynamic driving forces, forces that are changing continuously in the atmosphere as the conditions change (e.g., relative humidity, temperature).

These phenomena are important because mercury’s chemical transformations and deposition processes can differ greatly from phase to phase. For example, chemical transformation reactions for elemental and ionic mercury are usually faster in the aqueous phase than the vapor phase, and are believed to be essentially non-existent in the particulate phase. As another example, dry deposition of vapor-phase ionic mercury is usually faster than that of ionic mercury associated with typical atmospheric particles or droplets. For models to be able to estimate chemical transformation and deposition, then, the phase behavior of the different forms of mercury must be simulated accurately.

There are a number of fundamental uncertainties related to mercury's atmospheric phase behavior. These include, but are not necessarily limited to, the following:

- When a droplet forms around a particle at high humidity, what fraction of the particulate mercury becomes dissolved in the aqueous phase? In the HYSPLIT-Hg model, it is currently assumed that the particulate mercury is completely insoluble. Some models have adopted different assumptions, e.g., 50 percent dissolved (Ryaboshapko et al., 2003). In general, this remains an unanswered question.

- When a droplet dries out, what happens to the aqueous phase mercury? In the HYSPLIT-Hg model, it is currently assumed that this mercury is more or less completely liberated to the vapor phase. This same assumption is made in the CMAQ-Hg model, but the opposite assumption – that all the dissolved mercury remains with the particle upon evaporation -- is made in the MSCE-Hg model (Ryaboshapko et al., 2003).

- Within a droplet, what are the thermodynamic driving forces and mass transfer rates of different mercury species between the aqueous phase and the insoluble core of the particle (e.g., mineral and/or soot) and how do these depend on the chemical composition and other characteristics of that core?

- When "reactive gaseous mercury" (RGM) is measured using the annular denuder technique (Landis et al., 2002) – the most common methodology currently in use – are dissolved ionic mercury compounds measured as well? That is, if the measurements are being made in a high humidity environment, and aqueous droplets are present containing dissolved Hg(II) species, what is the fate of these dissolved compounds in the measurement system? In evaluation of HYSPLIT-Hg modeling results against measurement data, it is assumed that the dissolved Hg(II) compounds are measured as RGM by these devices. The rationale for assuming that the dissolved compounds are counted as RGM relies on the following: (a) that the inlet sampling tubes are heated, leading to evaporation of any incoming droplets; (b) that upon evaporation, the dissolved Hg(II) species in the droplets are then liberated to the vapor phase (as noted above, a matter of some uncertainty); and (c) that the vapor phase Hg(II) compounds are then measured along with any incoming vapor phase Hg(II) compounds as RGM. This is a matter of some disagreement in the scientific community, however. This controversy could likely be resolved by a carefully controlled laboratory experiment in which the measurement efficiency of vapor phase Hg(II) introduced to the device is compared with the measurement efficiency of droplet phase Hg(II) introduced to the device.

- How accurate are the Henry's Law coefficients used to estimate gas-liquid partitioning, and how do these depend on temperature? Can Henry's Law approach even be used – i.e., assuming equilibrium is maintained between the vapor and liquid phases for a particular mercury compound -- or must mass transfer limitations be considered, introducing delays in the system's approach to any given equilibrium state?

3) Atmospheric Chemistry

While much has been learned about the atmospheric chemistry of mercury (e.g., Lin and Pehkonen, 1997; Gardfelt, 2003), there are still many questions and our understanding is evolving. Some of the key chemistry issues currently confronting atmospheric models include the following:

- The actual chemical species comprising atmospheric “ionic mercury” and “particulate mercury” are not really known, nor are there any measurement techniques which can currently determine the relative abundance of the actual species involved. There is speculation about what the important species might be, but uncertainty is high. Moreover, the relative importance of different ionic or particulate compounds most likely changes dramatically over time and space in the atmosphere.

- In general, it is not known if all significant reactions have been determined. That is, are there any reactions that need to be added to the models? Increasing evidence for the importance of bromine in oxidizing elemental mercury to ionic mercury is emerging. However, most models – including the HYSPLIT-Hg model – have not yet been able to include bromine-mediated reactions.

- What is the reaction rate of each reaction, and how does the rate vary with temperature? Due to the difficulties in making such measurements, there is a fair amount of uncertainty in most if not all of the reaction rates. Even for the few reactions that have been studied more than others, there can be large differences between different experimental measurements, and in such cases, it is generally difficult to determine which data to utilize.

- Most models use somewhat similar chemistry schemes (e.g., Ryaboshapko et al., 2002, 2003, 2005), but there are some differences. For example, a reaction involving the hydroperoxyl radical (HO_2•) – previously thought to be significant in reducing ionic to elemental mercury in atmospheric aqueous droplets -- has been reported to be not significant in the atmosphere in a recent laboratory and theoretical study (Gardfelt and Jonsson, 2003). As a result, most atmospheric mercury models that utilized this reaction have now removed it. If the Gardfeldt and Jonnson contention is true, and the reaction is indeed unimportant, then – all other things being equal -- models that included this reaction would tend to underestimate mercury deposition. The CMAQ-Hg model’s inclusion of this reaction may partly explain its systematic underprediction of mercury wet deposition in spite of a tendency to overpredict precipitation (Appendix A; U.S. EPA, 2005a).

- Calvert and Lindberg (2005) have recently suggested that the two of the key chemical reactions converting Hg^0 to RGM in atmospheric chemistry models may be significantly slower than currently used estimates. If this is true, current estimates of the impact of global – i.e., very distant -- sources may be overpredicted. These distant impacts are simulated by models either by conducting global simulations (e.g., Dastoor and Larocque, 2004) or by using estimated boundary conditions for regional models (e.g., the

CMAQ-Hg analysis presented in Appendix A). In the boundary condition method, distant impacts could be overestimated if the processes converting Hg^0 to RGM are overestimated in the regional model. In essence, in such a situation, Hg^0 from distant sources is allowed to reach the boundary of the regional model – as represented by the boundary conditions utilized -- but once it enters the regional model, it is too-rapidly oxidized and deposited [see, for example, the analysis by Bullock (2004)].[7]

- Boundary conditions for regional models are sometimes estimated using empirical data. However, in some cases, global models are used to provide boundary conditions for regional models (e.g., Seigneur et al, 2001, 2004; U.S. EPA 2005a; Appendix A). When this is done, while the current understanding of atmospheric mercury chemistry is incomplete, it is important that the global and regional models use the "same" atmospheric mercury chemistry and physics. If this is not done, errors can be introduced in the overall simulation that might affect the source-attribution results. For example, if the regional model has a faster rate of Hg^0 oxidation than the global model, the relative importance of elemental mercury reaching the regional model and subsequently oxidized and deposited might be biased high. Similarly, if the global model had a slower rate of ionic mercury reduction (or removal via deposition), the relative importance of ionic mercury reaching the regional model and subsequently being deposited might be biased high.

- Each of the above two points are examples of the problems that can occur if the chemistry or physics of the regional model are not consistent with the model-estimated or empirically-derived boundary conditions used to account for the influence of sources outside the regional model domain. Clearly, inconsistencies can affect a regional model's estimation of the relative importance of sources outside its domain. In the examples above, the relative importance of sources outside the regional domain could be biased high.

- It is difficult to determine the extent of consistency between global and regional models if the relevant details of each model are not explicitly compared. However, even in cases where the details are not transparent, evidence can sometimes be found regarding possible inconsistencies. As an example, evidence of such possible inconsistencies may be present in the modeling done in support of the U.S. EPA Clean Air Mercury Rule (U.S. EPA 2005a; Appendix A). As can be seen in Figure 3 of Appendix A, there are deposition patterns near some of the boundaries of the domain that appear to be unexpected (e.g., high deposition at parts of the eastern boundary). Absent other explanations, such boundary effects can be evidence of inconsistencies.

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[7] . In the case of a global model, the effect of the overestimated oxidation rates is not obvious. On the one hand, less elemental mercury would be transported long distances – due to enhanced oxidation and subsequent deposition – but the elemental mercury that did get transported long distances would be oxidized and deposited at enhanced rates. These two countervailing phenomena would balance out, to a certain extent, and the net effect on model-predicted distant impacts is therefore difficult to predict.

- What are the concentrations of key reactants (e.g., hydroxyl radical, ozone, sulfur dioxide, etc.) at any given place, time, and phase in the atmosphere? This is a particularly difficult matter for reactive bromine and chlorine compounds. As reactions involving these compounds are believed to be among the most important for atmospheric mercury, these uncertainties may be very significant.

- Dissolved mercury species are involved in a number of chemical equilibrium processes. It is uncertain whether the equilibrium constants for all identified processes are accurately known – including their dependence on temperature and other variables -- and if all significant processes have even been identified.

4) Wet and Dry Deposition

Of all the phenomena associated with atmospheric mercury, perhaps wet deposition is the least difficult to measure. A reliable and scientifically sound methodology has been developed and the Mercury Deposition Network is a very successful and important measurement program. It has operated since 1995 and has been growing steadily since then. There are now ~80 sites in the U.S., 5 sites in Canada, and recently, a few sites have been established in Mexico. The monitoring equipment is relatively inexpensive, and the total costs associated with a Mercury Deposition Network site are usually less than $20,000 per year. Thus, most of the data available on atmospheric mercury in the U.S. is for wet deposition.

However, the relative ease of measurement belies the difficulty in modeling this phenomenon.[8] First, the amount of precipitation is known accurately only at precipitation monitoring sites. Precipitation at any other location must be estimated, and this is a difficult and uncertain task. Moreover, the meteorological datasets used to drive atmospheric models often do not match the precipitation observed at the monitoring sites. Thus, even if the processes involved with mercury wet deposition were understood perfectly, uncertainties in the precipitation amount would introduce errors into model estimates. Of course, the wet deposition processes are not well understood, and so there are a number of additional uncertainties in the simulation of this phenomenon by models. While there are many measurements of the "results" of wet deposition – i.e., the amount of mercury in precipitation reaching Earth's surface – there have been very few measurements of process-related phenomena (e.g., concentrations of mercury in cloud water, cloud processing of mercury, scavenging of mercury from the atmosphere below clouds as precipitation falls on its way to the ground). Thus, there is little actual empirical data upon which to design or evaluate model algorithms describing these phenomena. Additional uncertainties are involved with the meteorological data. Not only is the *amount* of precipitation uncertain at any location, but other aspects are uncertain as well, including (a) the vertical and horizontal extent of clouds; (b) the liquid water content of clouds; (c) the droplet size distribution of clouds and precipitation; and (d) the time course of precipitation intensity. These parameters influence the wet deposition process but are rarely known with any accuracy.

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[8] Most of the following issues are not unique to mercury but are applicable to wet deposition modeling of any pollutant. However, in contrast to some pollutants (e.g., sulfate and nitrate), there have been very few process-related measurements investigating mercury wet deposition.

The situation with dry deposition is perhaps more difficult, as routine methods to measure this phenomenon – analogous to the MDN – are not available. Thus, not only are process-related measurements generally not available, even the results of the processes (i.e., the total dry deposition) are not available. Dry deposition estimates are generally made using the resistance method (Hicks et al., 1987; Wesely, 1989), but this methodology has not been adequately evaluated in its application to mercury. The method involves three "resistances" to deposition:

- The *aerodynamic resistance* (R_a) associated with the difficulty of the pollutant to make its way down to the ground or canopy level; R_a varies with meteorological conditions in any given situation but is the same in any given situation for all pollutants. Thus, its use in estimating dry deposition of mercury is no more uncertain than that for any other pollutant.

- The *laminar sublayer resistance* (R_b) associated with the difficulty of the pollutant to make its way across the thin layer of nearly stagnant air that generally exists near any surface. For particles, R_b depends on particle size, shape, and density but is independent of the chemical constituents of the particle. For vapors, it depends on the diffusivity of the pollutant in air, a parameter that can be reasonably well estimated for any pollutant. The estimation of R_b is most uncertain for particles, both because the theoretical understanding of the process is relatively poor and because the most important influence on the process – particle size – is rarely known any degree of certainty. There are a few measurements of particulate mercury, but essentially none of the *size distribution* of particulate mercury.

- The *canopy resistance* (R_c) associated with the difficulty of the pollutant to be dry deposited to a given surface once it has successfully traversed the lower atmosphere and the laminar sublayer. R_c is generally assumed to be zero for particles but can be important for gases. The canopy resistance is very dependent on the nature of the surface being deposited to and is also by far the most chemical-specific of the resistances. The algorithm used to estimate R_c was originally developed for deposition of sulfur dioxide and ozone, and was calibrated using extensive empirical data. While its theoretical framework and extension to mercury species appears to be reasonable, there are essentially no empirical dry deposition data for mercury to calibrate the algorithm. So, pollutant-specific parameters -- such as the "surface reactivity" – are not known. Of course, as noted above, other than elemental mercury, the actual vapor phase mercury species are generally not known. Like dry deposition estimates for any vapor, uncertainties in the nature of the surface will introduce errors in the simulation.

5) Meteorological Data

Meteorological data – e.g., wind speed and direction, temperature, relative humidity, degree of turbulent mixing, precipitation form and amount, liquid water content – are generally used as inputs to any comprehensive atmospheric fate and transport model. The data are normally gridded – at a given spatial and vertical resolution – and are produced using numerical weather models (e.g., MM5, RAMS, etc.). The numerical weather models utilize existing weather measurements and detailed theoretically-based calculations to estimate the behavior of the whole atmosphere within any given modeling domain.

As discussed above in relation to wet deposition, there are many uncertainties in the precipitation data. Perhaps the most significant additional uncertainty in the use of meteorological data concerns the spatial and temporal resolution of the grid on which they are provided to the model. For example, the 1996 meteorological data used for the atmospheric mercury modeling detailed in this report, the grid points were spaced ~180 km apart. This somewhat coarse resolution has been generally found to be adequate in model simulations in capturing the large scale features of the atmosphere. However, the actual situation at locations inside any grid square may be highly variable, due to a variety of factors (e.g., complex terrain). So, the 180 km data used in this modeling is likely able to support a reasonable simulation of the fate and transport of mercury over distances of ~100-200 km and greater.

The data are of course also used in this application to estimate the fate and transport of mercury emitted from a given source starting right at the emissions location. The use of such coarse data for near-field dispersion is less than ideal. It is expected that the long-term averages (e.g., over the course of a year) will be reasonably well simulated, but the short-term variations in concentrations and deposition at any particular location downwind of the source are unlikely to be well characterized. Thus, in the data discussed above regarding near-field deposition (e.g., Figure 24) the precise deposition at any *actual* location near the source is unlikely to be precisely correct; however, it is likely that the general features of the deposition pattern are reasonably well simulated, even with such coarse data. That is, even with the use of such coarse data, the amount deposited within a given distance of the source may be well simulated even if the precise spatial distribution within that distance range is not well characterized.

The consequence of this type of uncertainty is not believed to be very significant for estimates of deposition to large receptors like the Great Lakes. However, it may be very important for the model estimates of deposition at any particular location (e.g., at a Mercury Deposition Network site). If the model estimates are not consistent with the measurements, it may simply be that the wind direction supplied to the model was not sufficiently accurate.

However, for other types of uncertainties, the use of coarse data may be more significant for the Great Lakes. For example, dry deposition may be relatively less important for the Great Lakes during warm conditions (e.g., summer). This is because the lakes are generally colder than the atmosphere during those periods, and therefore the lower levels of the atmosphere are relatively stable. Since dry deposition depends on the level of mixing in the lower atmosphere, the enhanced stability can lead to lower dry deposition rates. These phenomena are included in the model through the meteorological data and the dry deposition algorithms that utilize these data. It is recognized that the relatively coarse meteorological data utilized in this preliminary modeling may not have captured this phenomena precisely.

Currently, data for much of North America are available on much finer grid scales than the 180-km data used here (e.g., 40 km). In addition, models such as MM5 and RAMS could be utilized to produce data of finer resolution if needed. Future modeling could use one or more of these higher resolution data sets to potentially improve the accuracy of the simulations.

G. Model Evaluation

Given the uncertainties in emissions, fate processes, meteorology and other model inputs and algorithms described above, models must always be "ground-truthed" against actual measurements. The extent to which the model results are consistent with the measurements is an indication of the overall performance of the model.

Model evaluation exercises also serve as overall tests of our understanding. If models do not agree with valid measurements, then this may indicate one or more fundamental errors in our understanding of the fate and transport of atmospheric mercury.

To comprehensively evaluate the simulation accuracy of any atmospheric mercury model, the following data are required:

- inputs of high quality, temporally-resolved, speciated emissions data and high resolution meteorological data;
- time-resolved measurements of the atmospheric concentrations of mercury and measurements of wet deposition, to compare the model predictions against, at a number of qualitatively different locations throughout the modeling domain, e.g., coastal and inland, over-water and over-land, source-impacted and remote, ground level and different elevations in the atmosphere [for the most comprehensive analysis, data on individual mercury species would be required, e.g., $HgCl_2$, $Hg(OH)_2$, HgO, etc; however, since this is not possible at present, data are at a minimum required for the three different forms of atmospheric mercury (elemental, ionic, and particulate)];
- comparable measurements of all significant reactants affecting the behavior of mercury in the atmosphere (e.g., O_3, SO_2, etc.);
- process-related measurements to evaluate specific model algorithms (e.g., chemistry, dry and wet deposition, phase partitioning).

Unfortunately, the only data routinely available in the U.S. for model evaluation are weekly wet deposition measurements at the ~80 non-source-impacted sites of the Mercury Deposition Network. To date, essentially all evaluations of atmospheric mercury models covering the U.S. have been limited to comparisons against these MDN data. These data are *extremely* useful, and the scientific community is well served by the presence of this network, but the MDN data are only a small part of the data required to properly evaluate atmospheric mercury models. First, the weekly time-resolution is less than ideal for model evaluation – more frequent (e.g., daily) measurements would be more useful. Second, there are large regions of the country with few or no measurements – the geographical coverage of the network needs to be improved. Third, in addition to the regional background sites already included in the network, a number of source-impacted sites should be added. Finally, only total mercury in precipitation is measured at most MDN sites – it would be extremely useful if additional chemical and physical information could be obtained, e.g., particulate vs. dissolved mercury in precipitation. Most importantly, a systematic network of ambient mercury concentration data in air does not exist, and even small amounts of such data are rarely available for model evaluation. *Thus, it has not been possible to date to evaluate atmospheric mercury models in any comprehensive way.*

A number of agencies and research organizations are collectively taking initial steps to establish a large-scale network -- analogous to the MDN -- to measure mercury concentrations in ambient air and provide data to the scientific community in a timely fashion. Wherever possible, the “new” network will try to incorporate existing measurement efforts. Secondly, wherever possible, the new network will co-locate the new speciated mercury concentration measurements at existing monitoring site, e.g., at MDN sites. Several meetings have been held during 2006 discussing plans and guiding principles for the potential new network (NADP, 2006). Toward this end, EPA and NOAA are collaborating to establish a new site in Beltsville Maryland, the Canaan Valley Institute (CVI) and NOAA are collaborating on a new site at CVI in West Virginia, and NOAA is collaborating with local partners to establish a new site at the Grand Bay National Estuarine Research Reserve in Mississippi. These three sites have been pledged to the new network. Although the network is still in its infancy, it is anticipated that other institutions will contribute additional sites. It is noted that an instrument suite capable of measuring total gaseous mercury, reactive gaseous mercury, and particulate mercury is commercially available.

In the following discussion, we discuss a few limited evaluations that have been carried out for the HYSPLIT-Hg modeling system. In the Great Lakes modeling described here, 1996 meteorological data were used. Therefore, to evaluate the model, 1996 emissions and 1996 measurements must be used. An analysis was carried out for each of the nine sites in the Great Lakes region at which 1996 wet deposition measurements were available. The results are summarized in Cohen *et al*. (2004), and for convenience, the relevant comparison figure of that work (Figure 8) is reproduced here, as Figure 35.

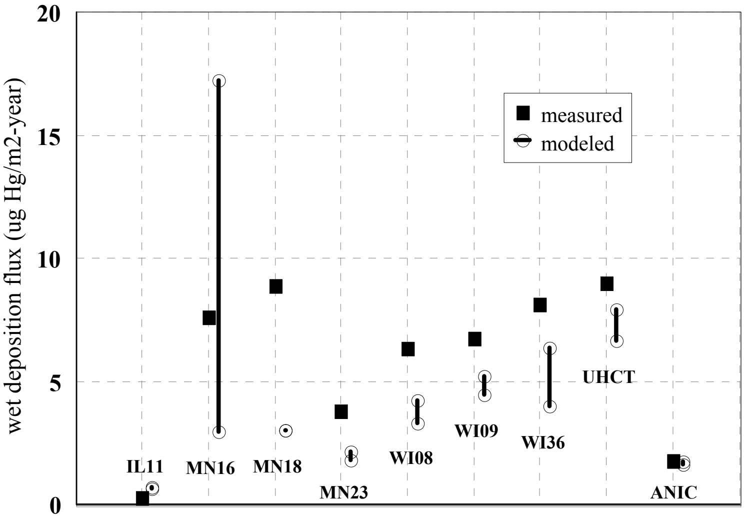

Figure 35. Modeled vs. Measured Wet Deposition.
Comparison of annual model-estimated wet deposition fluxes with measured values at sites within 250 km of the Great Lakes during 1996. The range of modeled estimates shown for each site represents the difference in estimated deposition in using the NGM-forecast *model* precipitation and the *actual* precipitation at the site.

While the degree of agreement between the modeled and measured wet deposition at the nine Great Lakes sites varied, the overall tendency is for the model to underpredict the measured values. This result was expected given that *only* direct U.S. and Canadian anthropogenic emissions sources were considered in the analysis. The total mercury deposition measured at the site would include contributions from these additional sources:

- Direct anthropogenic emissions from sources outside of the U.S. and Canada;
- Re-emitted anthropogenic mercury from U.S. and Canadian sources;
- Re-emitted anthropogenic mercury from sources in the rest of the world;
- Natural emissions in the U.S. and Canada;
- Natural emissions throughout the rest of the world.

The average degree of underprediction (~30 percent) gives some information about the potential impact of these omitted sources[9] That is, based on this evaluation, it would appear that the omitted sources were responsible for ~30 percent of the wet deposition at these nine Great Lakes sites during 1996. Future work could include the omitted sources.

While not directly relevant to the Great Lakes region, European ambient mercury concentration data were made available to modelers in a model evaluation/intercomparison project (Ryaboshapko et al., 2003). The results for most of the participating models, including HYSPLIT-Hg, were reasonably consistent with ambient concentration measurements of elemental and particulate mercury. The agreement was by no means perfect, but the results were encouraging. Examples for HYSPLIT-Hg are shown in Figure 36 and Figure 37. In general – and HYSPLIT-Hg is no exception -- less satisfactory results were found with model predictions of ionic mercury, although this may have been partly caused by uncertainties in the measurements themselves. Figure 38 gives an example of the comparison of HYSPLIT-Hg results against ionic mercury measurements.

While these limited evaluations against wet deposition and ambient concentrations are somewhat encouraging, they can only be regarded as an initial step. Due to the lack of available ground-level and upper-atmosphere data on atmospheric concentrations of elemental, ionic, and particulate mercury, it has not been possible to date to adequately evaluate the HYSPLIT-Hg model.

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[9] . It is interesting to note that a comparable underprediction of wet deposition at MDN sites (~30%) was found in the modeling done in support of the EPA's Clean Air Mercury Rule (U.S. EPA 2005a; Appendix D) even though in this case an attempt was made to include the effects of all – e.g., global – sources.

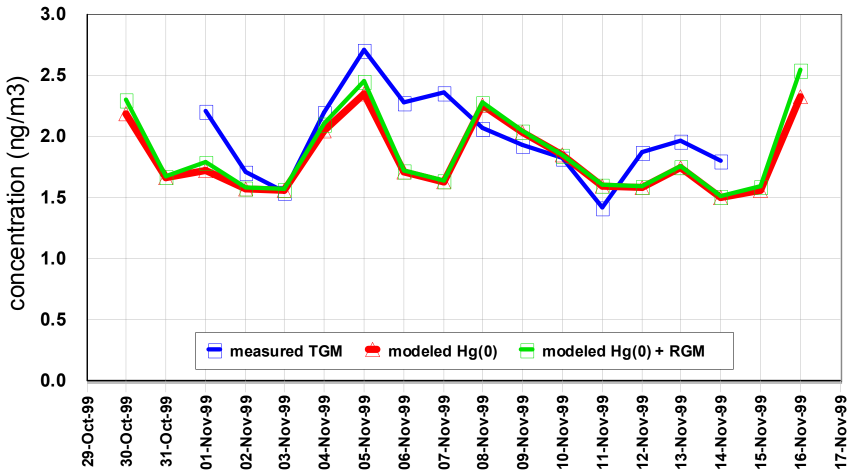

Figure 36. Modeled vs. measured elemental mercury at Neuglobsow.

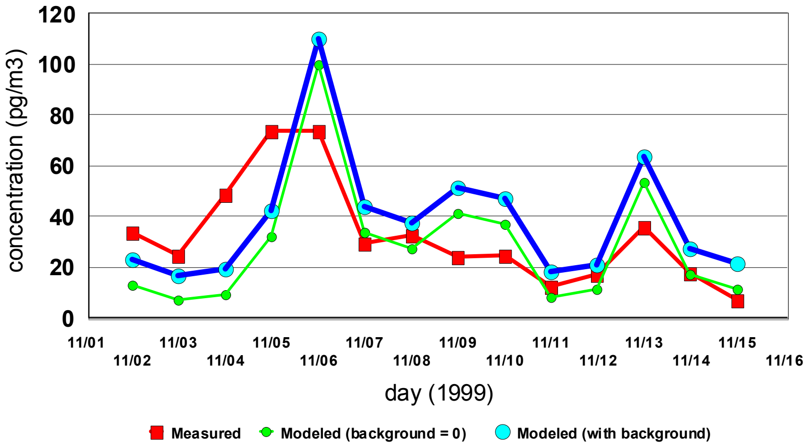

Figure 37. Modeled vs. measured particulate mercury at Zingst.

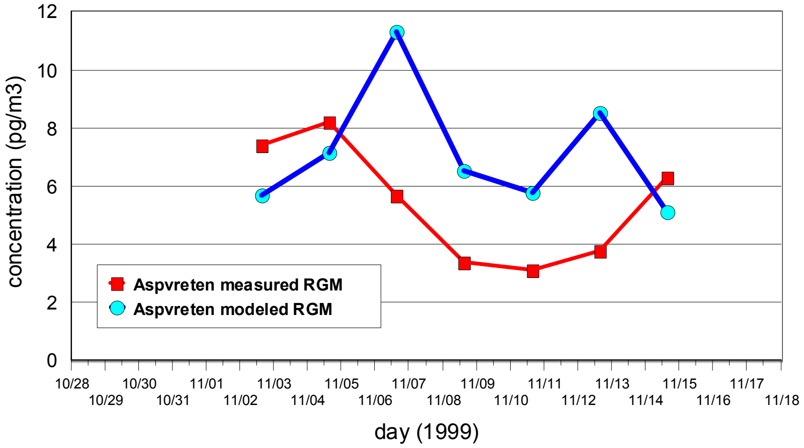

Figure 38. Modeled vs. measured ionic mercury at Aspvreten.

H. Atmospheric Modeling Results

Results for the Great Lakes based on 1996 U.S. and Canadian direct anthropogenic emissions have been presented earlier (Cohen et al., 2004). Here, we will present new results based on the estimated 1999-2001 U.S. emissions[10] and 1995-2000 Canadian emissions described above. For this preliminary analysis, the same 1996 meteorology and gridded chemical reactant concentration data used in the previous analysis are utilized[11]. In essence, the analysis is exactly the same except for the updated emissions inventory. The modeling system estimates the atmospheric deposition contribution to each of the Great Lakes arising from each source in the inventory.

At the outset, it must be stressed that there are a number of limitations in the analysis described here. In addition to the fact that 1996 meteorological and reactant data were used with 1999-2001 emissions, there are a number of additional uncertainties, as described above (section F). These uncertainties could have significant effects on the results presented here. It has not been possible to quantitatively estimate the importance of these uncertainties to the analysis due to a lack of atmospheric mercury data. At the same time, the model appears to be able to produce results reasonably consistent with observations in the Great Lakes region, and moreover, the differences between the model and measurements are in the expected direction. Therefore, with the caveats noted above, the preliminary results will be briefly summarized here.

It is important to note that only direct anthropogenic emissions from the U.S. and Canada have been included in the modeling for the Great Lakes discussed below. Thus, only a portion of the total mercury fluxes are being analyzed. Future work could include global natural and anthropogenic emissions. It is also noted that the EPA has removed estimates of mercury emissions from mobile sources from their inventories, due to a high level of uncertainty. However, estimated emissions from mobile sources – based on earlier 1996 EPA data which has since been withdrawn – are included in the following results.

The U.S EPA has recently conducted a comprehensive modeling analysis of mercury deposition in the U.S. (U.S. EPA 2005a). A summary of this analysis is presented by the EPA in Appendix A, with additional detail for the Great Lakes. In this modeling, one simulation was done with all sources included, and another was done with emissions from U.S. coal-fired utilities removed. The total contribution of U.S. coal-fired utilities – e.g., on each of the Great Lakes – was estimated from the differences between these two simulations. These estimates can be directly compared to results from the HYSPLIT analysis presented here. Although the modeling was conducted for different years, the two sets of results appear to be very similar (see Figure 8 of Appendix A).

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[10] Estimates for mobile sources were not included in the 1999 inventory, and so data from the 1996 U.S. EPA mercury inventory were used for this source category.

[11] 1999 meteorological and chemical reactant concentration data are available and could be used with these 1999 emissions in future work.

In the following, results will first be presented for Lake Michigan, and each of the figures will be briefly described. For brevity, the analogous figures will be presented for each of the other Great Lakes with no additional explanation. In the final sub-section, summary figures for the Great Lakes as a whole will be presented.

As described above, all of the results presented here for the Great Lakes (Figure 39 through Figure 74) are based on the estimated 1999-2001 U.S. emissions and 1995-2000 Canadian emissions described above (Section 3-B, beginning on page 23) and the 1996 meteorology and gridded chemical reactant concentration data described in Cohen *et a*l. (2004).

1) Lake Michigan

In this sub-section, modeling results for Lake Michigan will be summarized in a series of figures. First, the *total* deposition contributions to Lake Michigan arising from emissions in each U.S. county and in each Canadian grid square were determined. These results are mapped – with different scales – in Figure 39, Figure 40, and Figure 41.

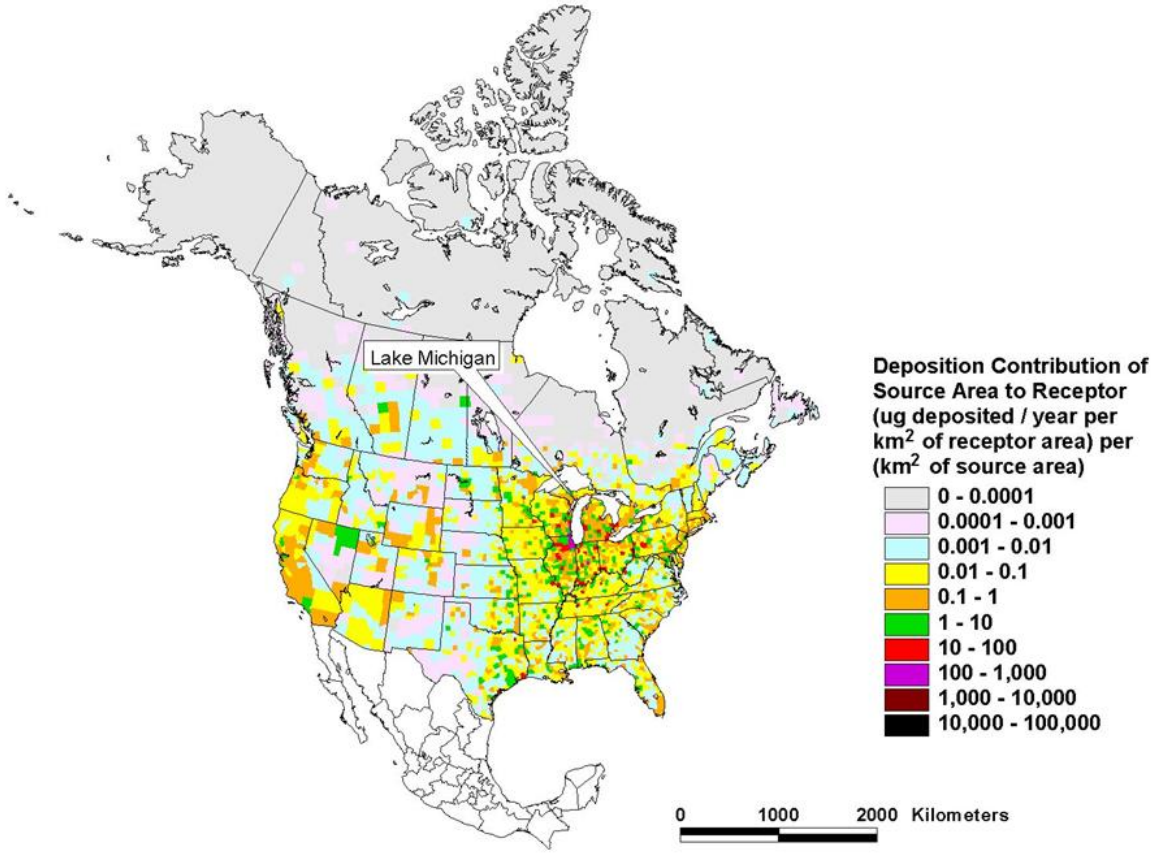


Figure 39. Atmospheric deposition contributions to Lake Michigan.

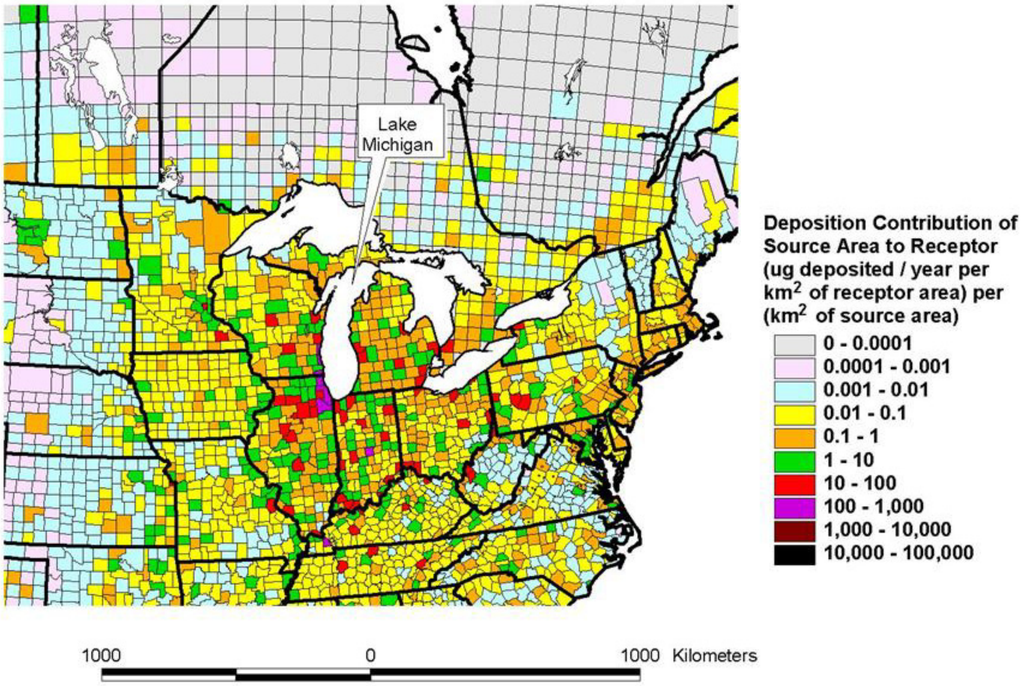


Figure 40. Atmospheric deposition contributions to Lake Michigan (regional view).

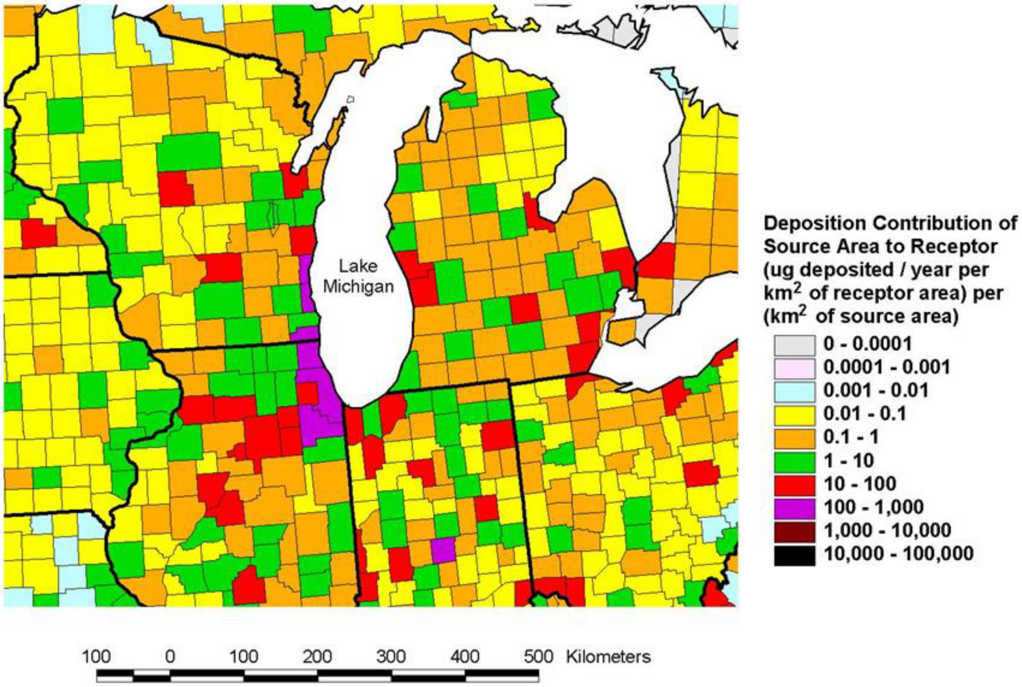


Figure 41. Atmospheric deposition contributions to Lake Michigan (close up).

Figure 42 summarizes the results by showing the total emissions from different distance ranges away from Lake Michigan, and the total deposition arising from those emissions. It can be seen that emissions closer to the lake (e.g., within 100 km) have a bigger relative impact – pound for pound -- than sources farther away. This is certainly an expected result.

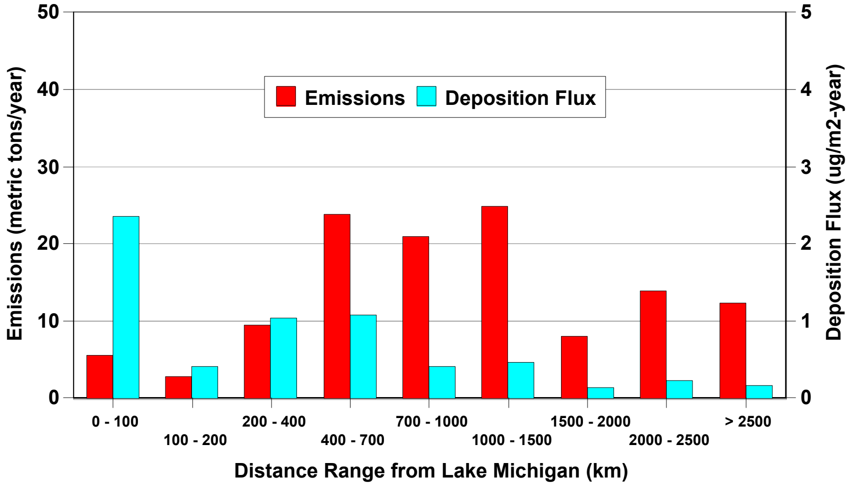


Figure 42. Emissions and deposition arising from different distances from Lake Michigan.

Figure 43 (full view) and Figure 44 (close-up) show the geographical distribution of the largest modeled contributors to Lake Michigan.

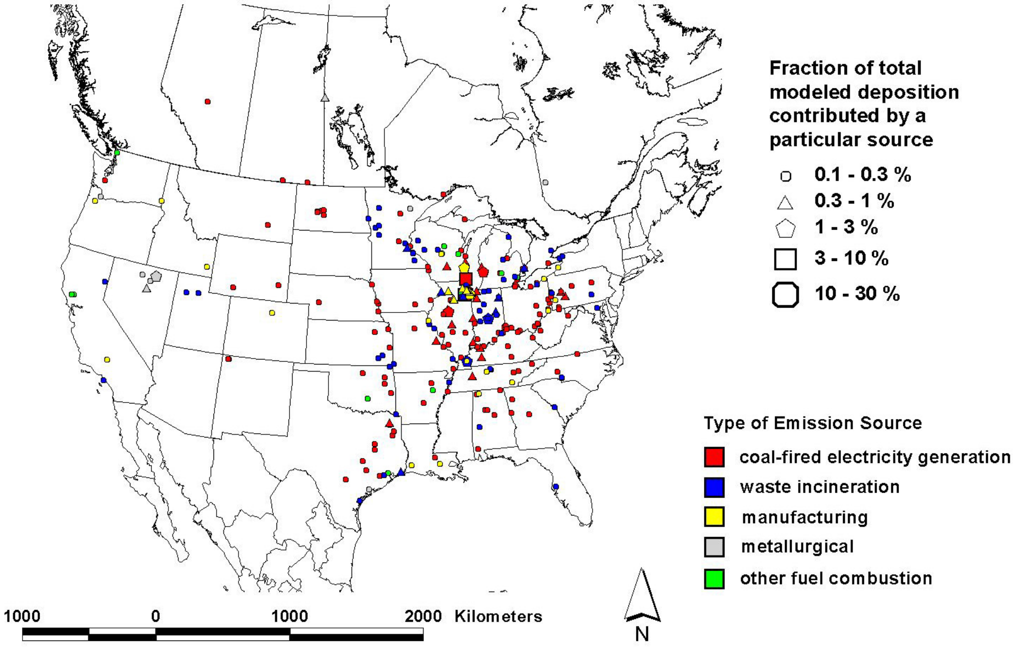


Figure 43. Largest modeled contributors to Lake Michigan (full view).

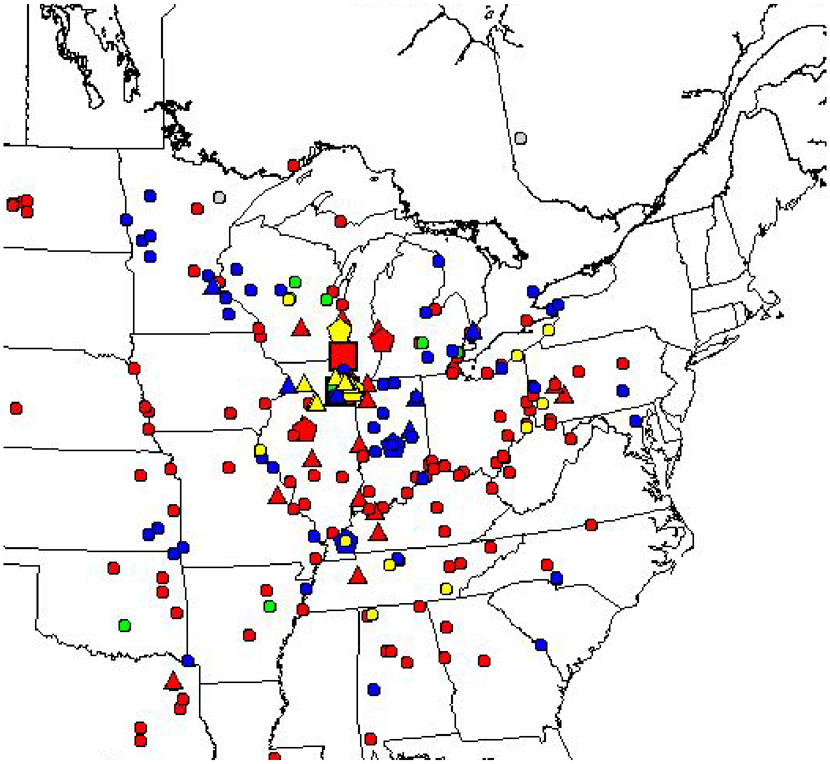


Figure 44. Largest modeled contributors to Lake Michigan (close-up).

Figure 45 summarizes the overall modeling results for Lake Michigan, showing the model-estimated atmospheric deposition flux arising from different source sectors in the U.S. and Canada. As noted above in the discussion of emissions inventories, "IPM" refers to large coal-fired electricity generating facilities identified by the U.S. EPA for inclusion in their Integrated Planning Model (for emissions, fuel use, and economic projections).

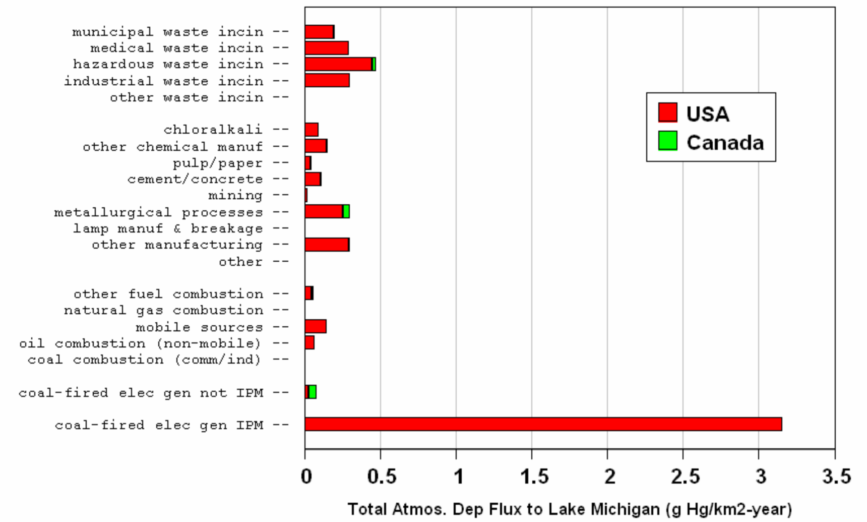


Figure 45. Modeled deposition to Lake Michigan from different source sectors.

Figure 46 shows the cumulative fraction of the total modeled deposition arising from the top 25 modeled contributors to Lake Michigan. The emissions sources are displayed in order of their model-estimated deposition contribution to the lake, e.g., the Pleasant Prairie coal-fired power plant is the top contributor, the Joliet 29 coal-fired power plant is the next highest contributor, etc., based on the model results. The "rank" is shown along the "y-axis". The modeled deposition contributed by each source is added to the total deposition for the preceding sources, so that the cumulative modeled deposition is shown along the "x-axis". For example, the top 10 contributing sources are estimated to contribute about 20% of the modeled deposition. The top 25 sources, i.e., all those shown in the figure, are estimated to contribute over 30% of the modeled deposition. Since the cumulative deposition is shown, the deposition for any one source is the difference between the cumulative deposition between that source and the immediately preceding source. It is seen that the largest contributing sources are responsible for ~3-4% of the total model-estimated deposition, while the individual-source contribution falls to ~1% for lower-ranked sources in the top 25.

This figure is based on the current model configuration and EPA emissions data for 1999-2001. Errors in emissions estimates, meteorological data, and model physics and chemistry could all affect the data shown this figure – sources could move up or down in the rankings; other sources could replace those in the top-25 shown in this figure. As uncertainties in atmospheric modeling are reduced, more and more confidence will be able to be placed in estimates such as these. Thus, the currently available results are presented here, with the understanding that improved estimates could be provided in the future. At the same time, it is noted that the occurrence of the sources shown in Figure 46 in the top-25 contributors to Lake Michigan is not surprising, given that they are among the largest sources of mercury – particularly ionic mercury, with its potential for large local and regional impacts – upwind of Lake Michigan. So, while future simulations will no doubt improve the accuracy of the estimates, it is unlikely that the results will change dramatically.

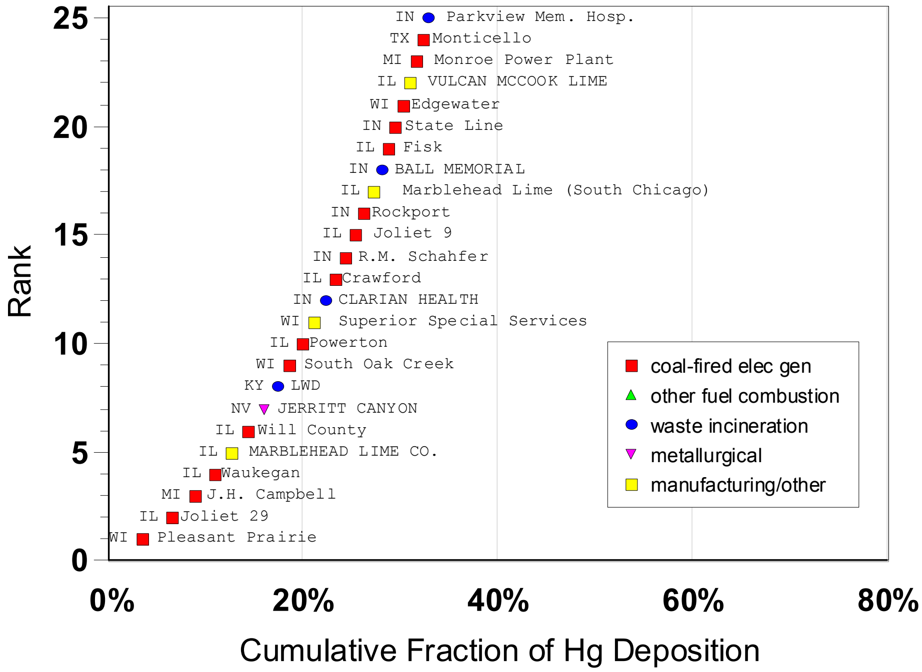


Figure 46. Top 25 modeled atmospheric deposition contributors to Lake Michigan.

2) Lake Superior

In this sub-section, figures summarizing the modeling results for Lake Superior are presented, analogous to those presented above for Lake Michigan. As noted above, to avoid redundancy, the figures will not be described.

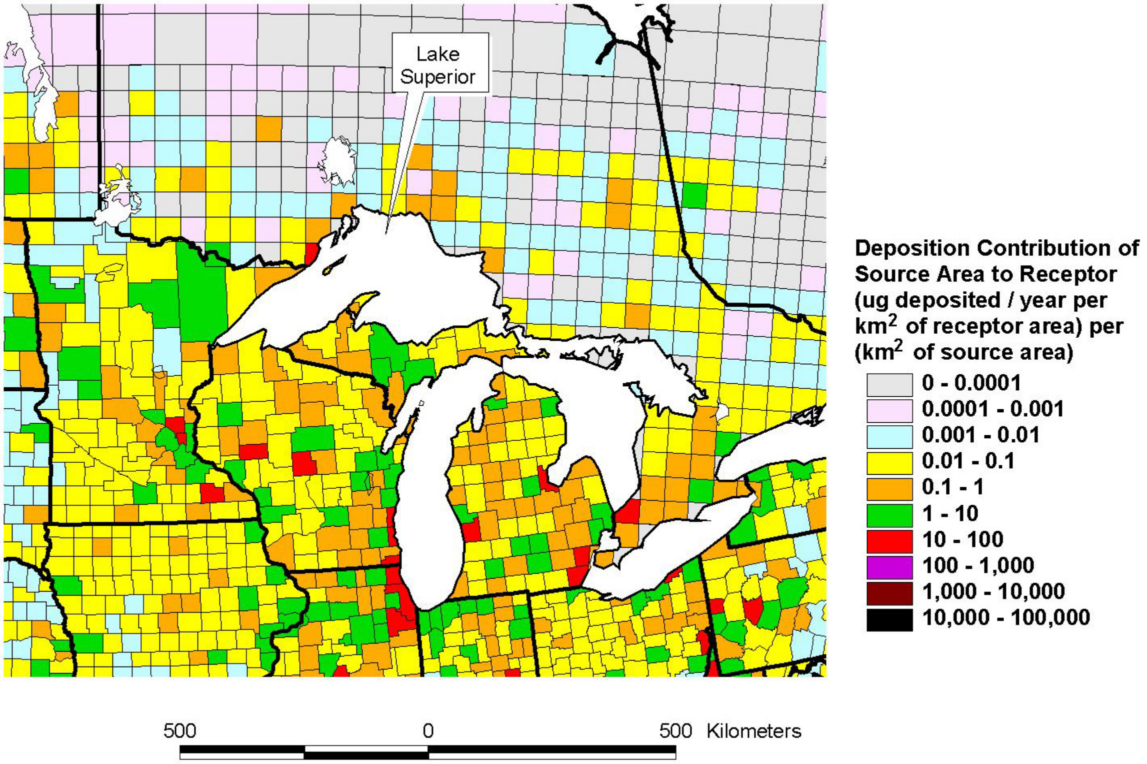


Figure 47. Atmospheric deposition contributions to Lake Superior.

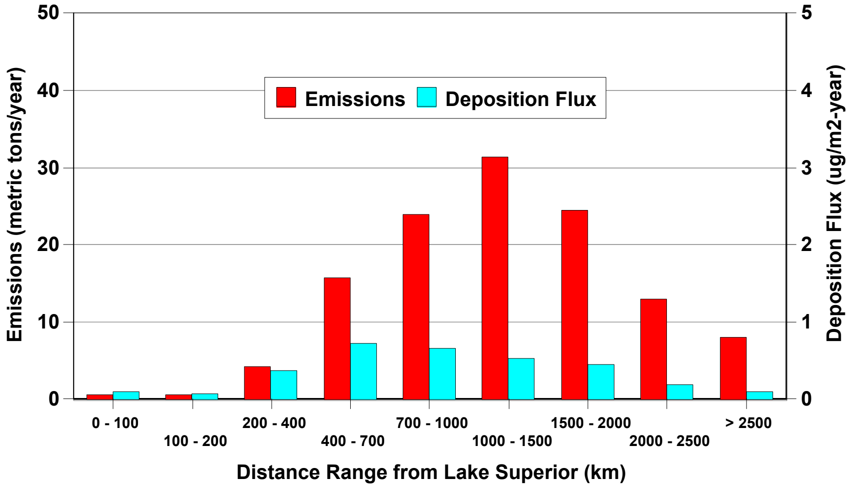


Figure 48. Emissions and deposition arising from different distances from Lake Superior.

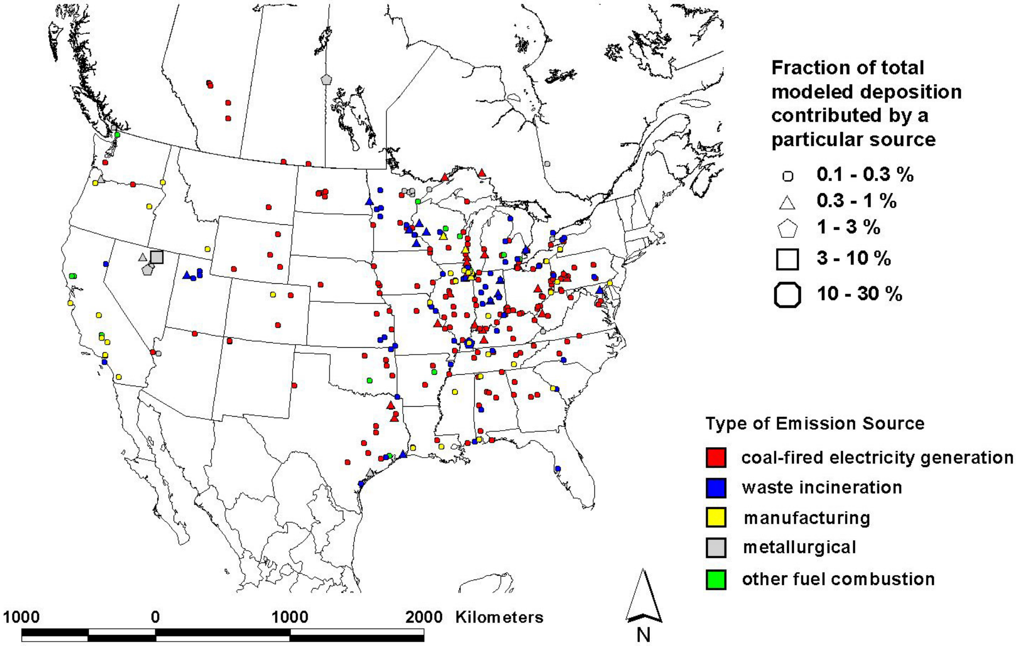


Figure 49. Largest modeled contributors to Lake Superior (full view)

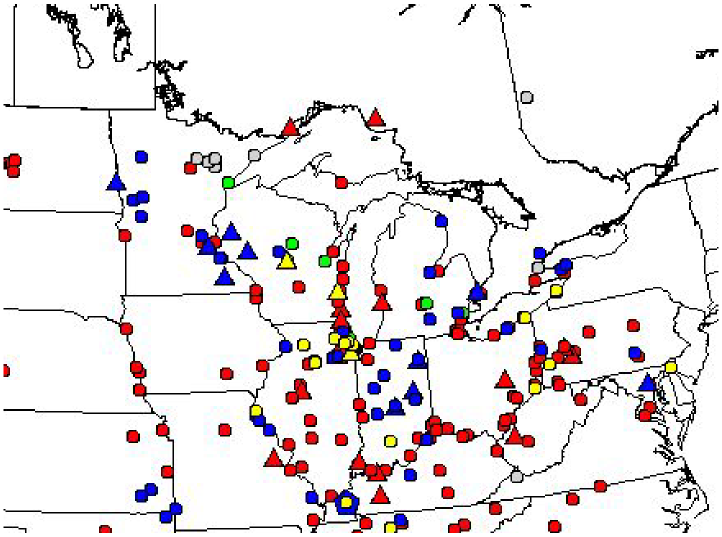


Figure 50. Largest modeled contributors to Lake Superior (close-up)

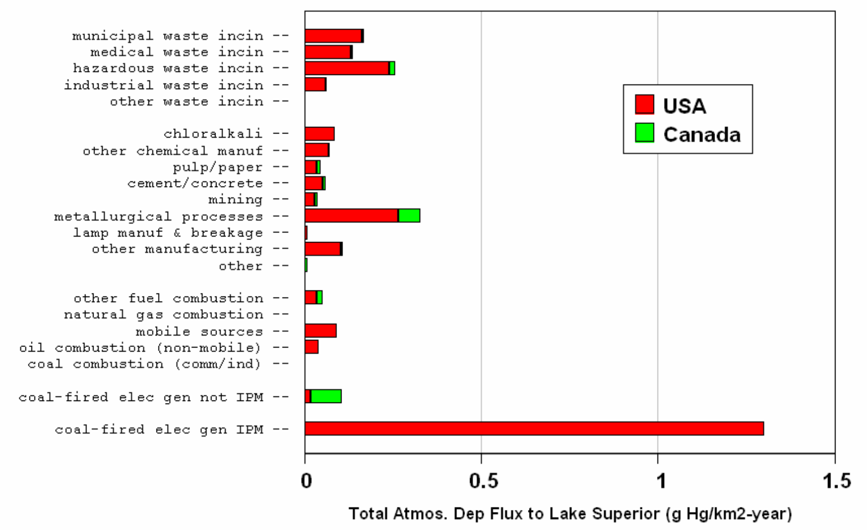


Figure 51. Modeled deposition to Lake Superior from different source sectors.

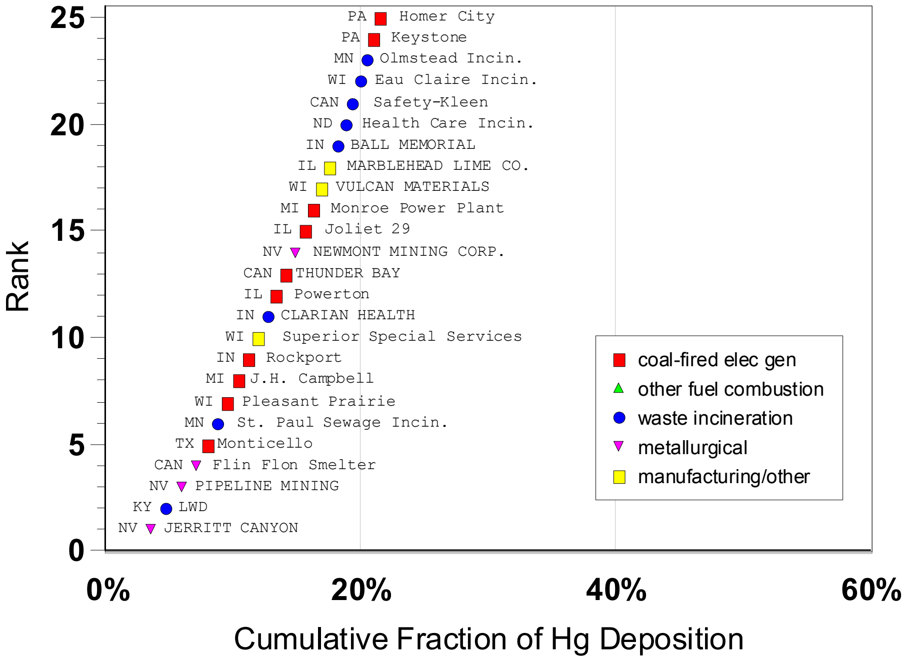


Figure 52. Top 25 modeled atmospheric deposition contributors to Lake Superior.

3) Lake Huron

In this sub-section, figures summarizing the modeling results for Lake Huron are presented, analogous to those presented above for Lake Michigan and Lake Superior. To avoid redundancy, the figures will not be described.

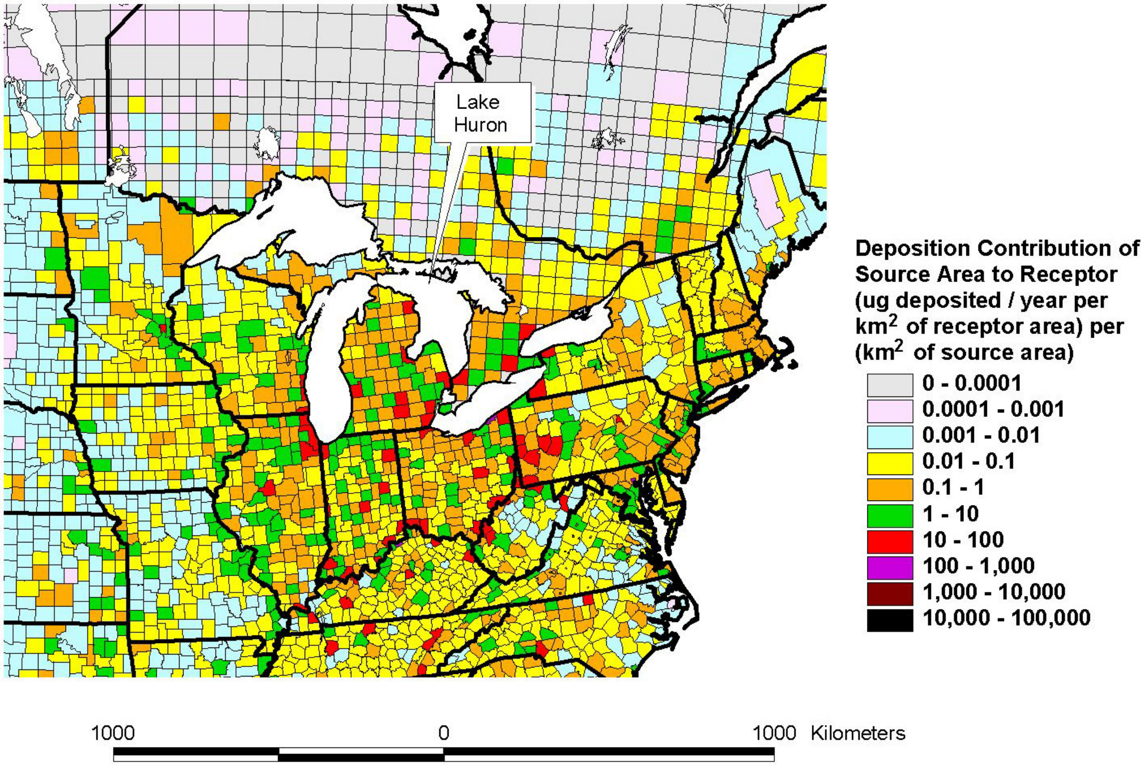


Figure 53. Atmospheric deposition contributions to Lake Huron.

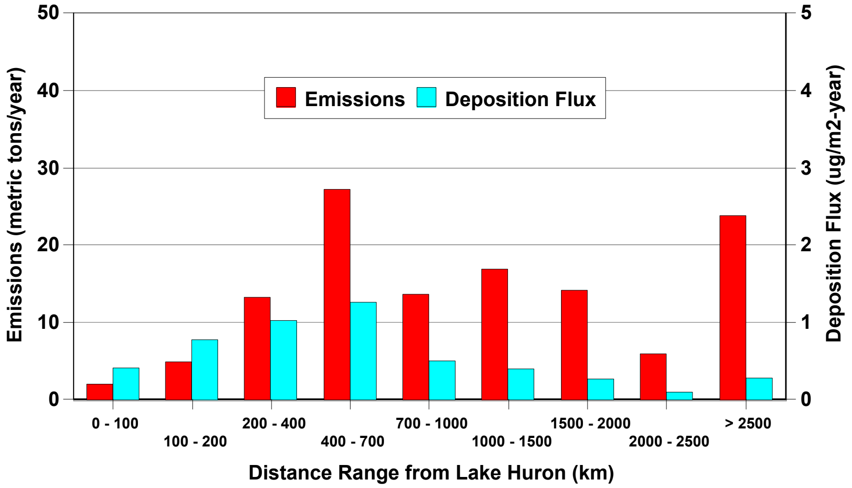


Figure 54. Emissions and deposition arising from different distances from Lake Huron.

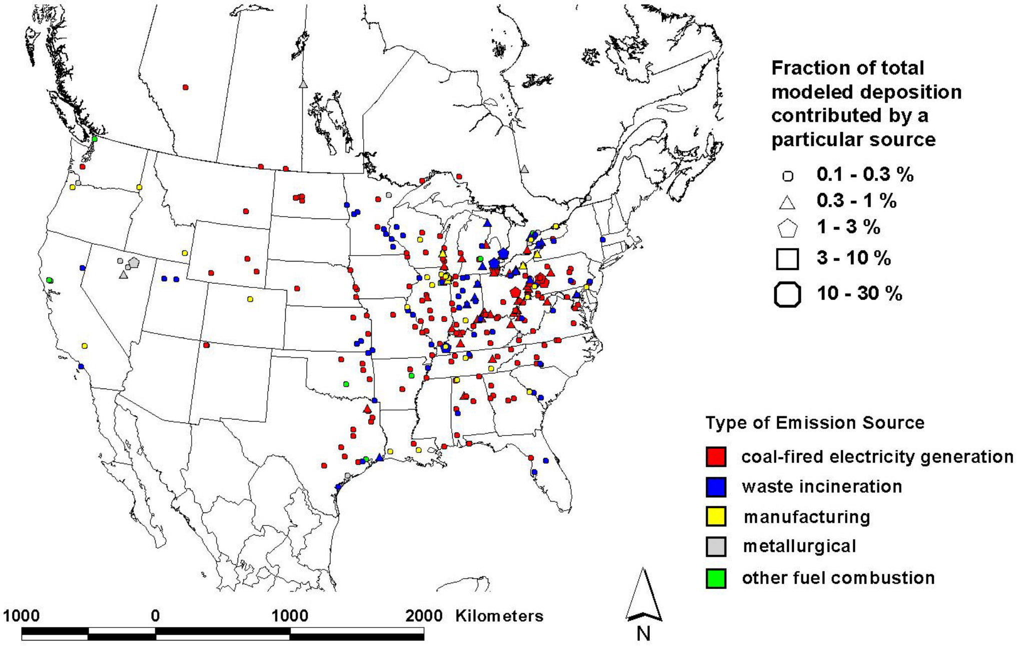


Figure 55. Largest modeled contributors to Lake Huron (full view)

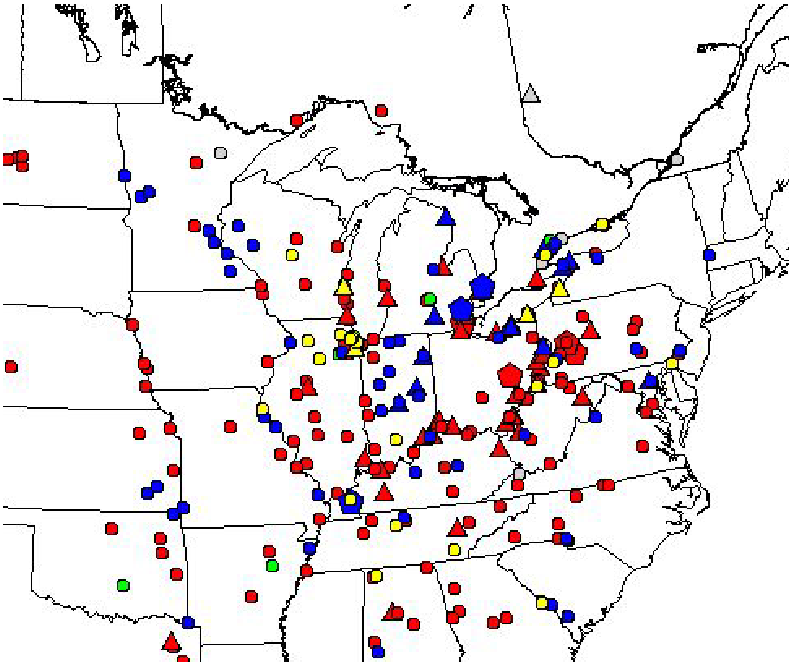


Figure 56. Largest modeled contributors to Lake Huron (close-up)

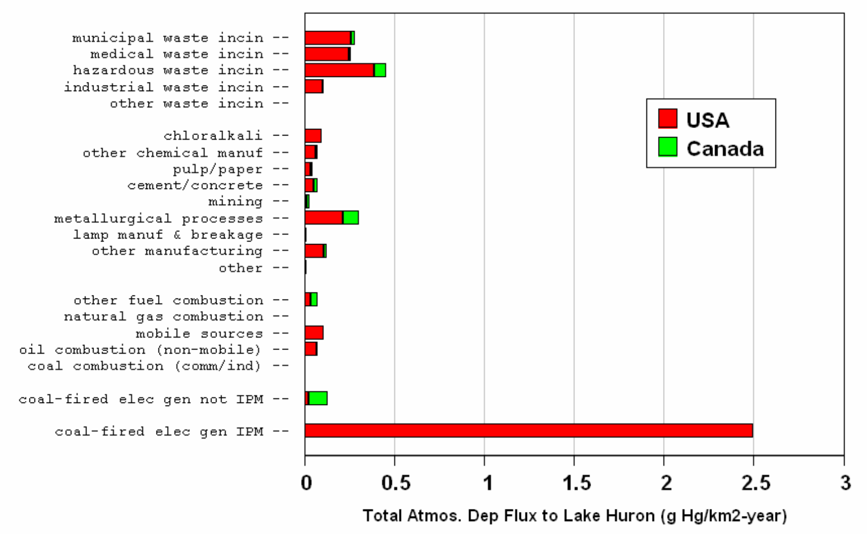


Figure 57. Modeled deposition to Lake Huron from different source sectors.

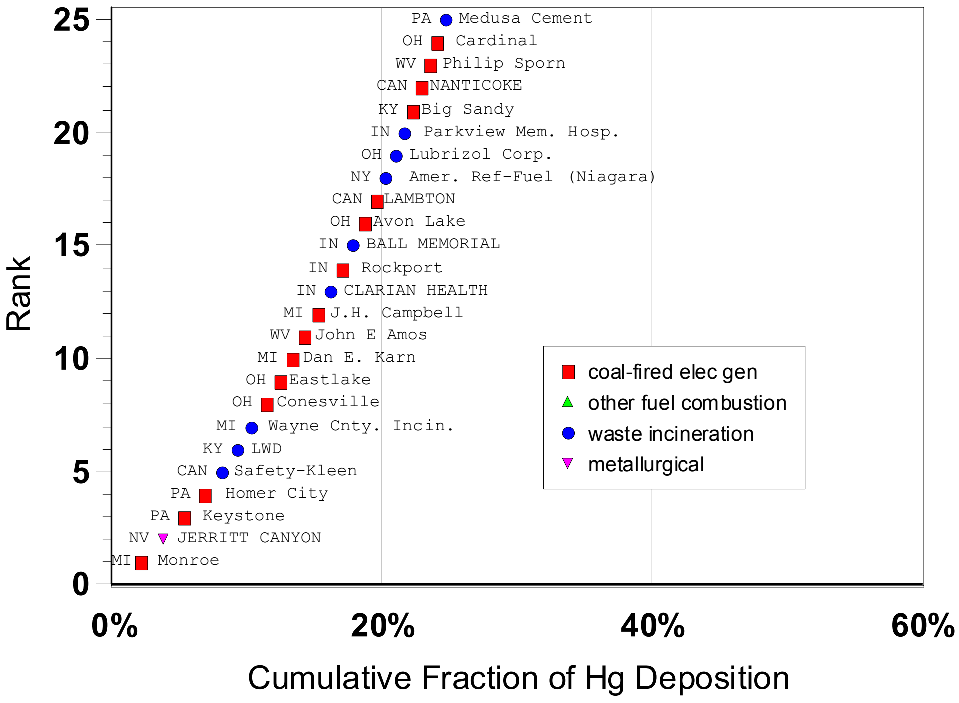


Figure 58. Top 25 modeled atmospheric deposition contributors to Lake Huron.

4) Lake Erie

In this sub-section, figures summarizing the modeling results for Lake Erie are presented, analogous to those presented above for other Great Lakes above.

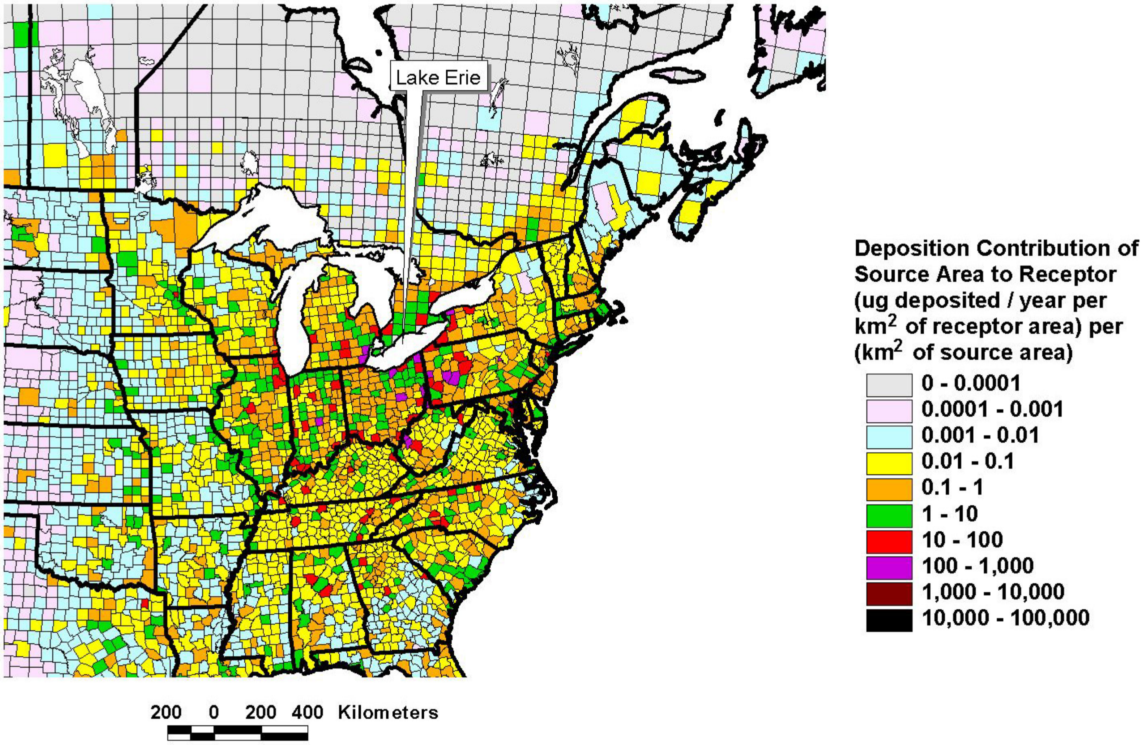


Figure 59. Atmospheric deposition contributions to Lake Erie.

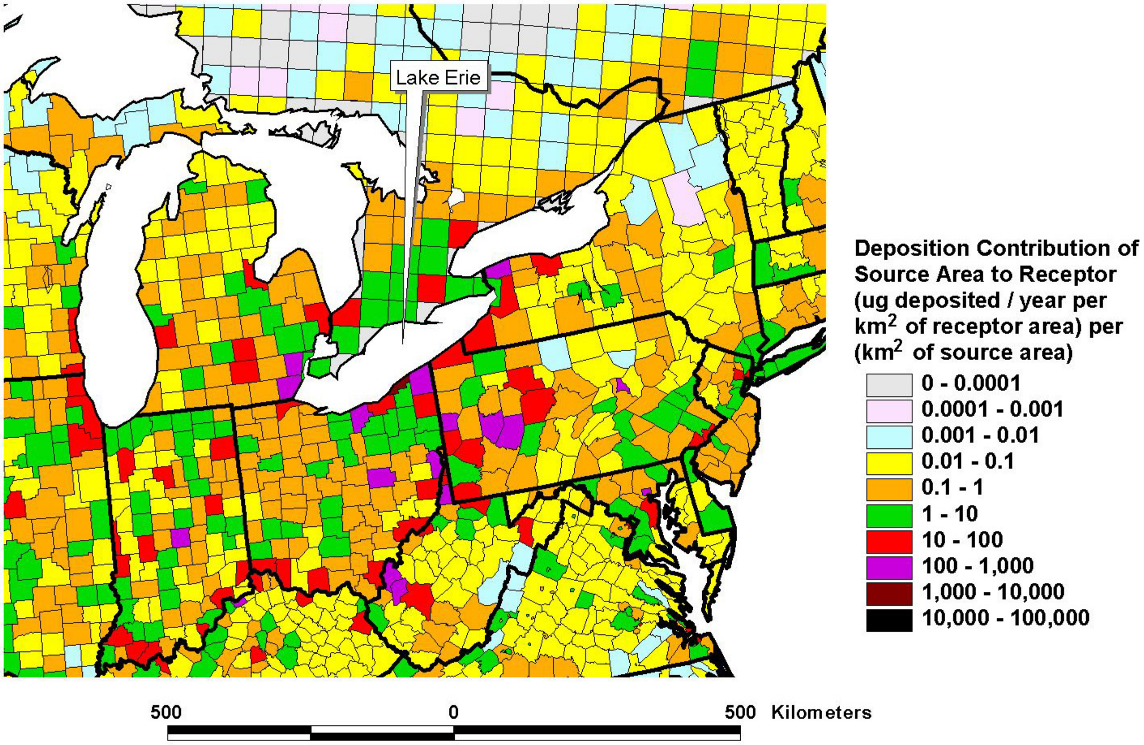


Figure 60. Atmospheric deposition contributions to Lake Erie (close-up).

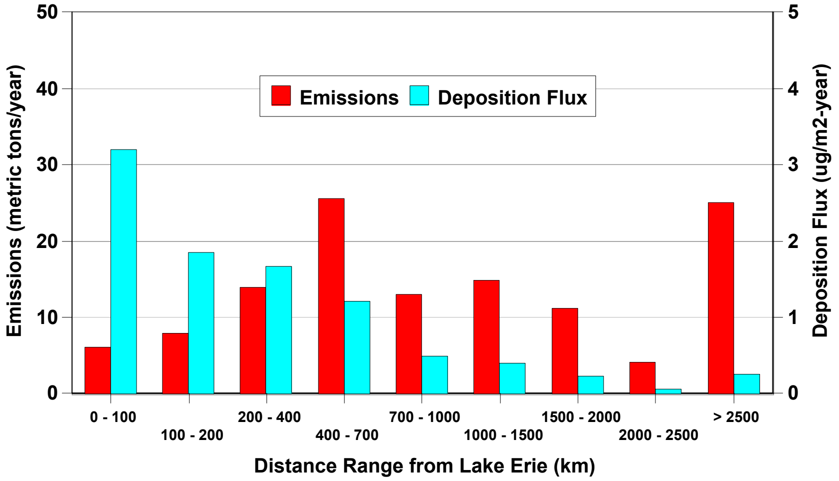


Figure 61. Emissions and deposition arising from different distances from Lake Erie.

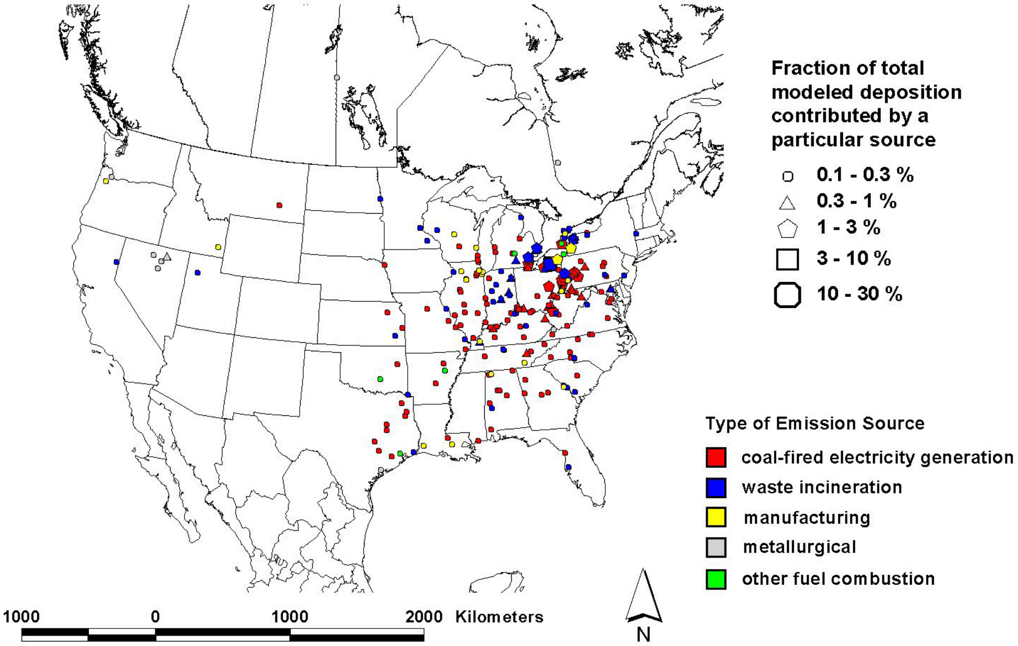


Figure 62. Largest modeled contributors to Lake Erie (full view)

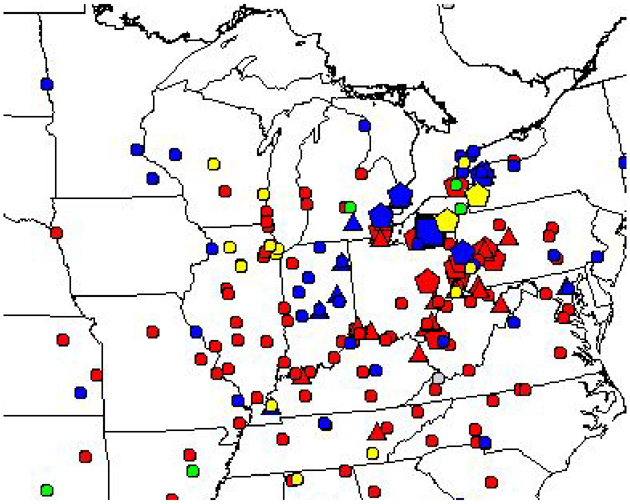


Figure 63. Largest modeled contributors to Lake Erie (close-up)

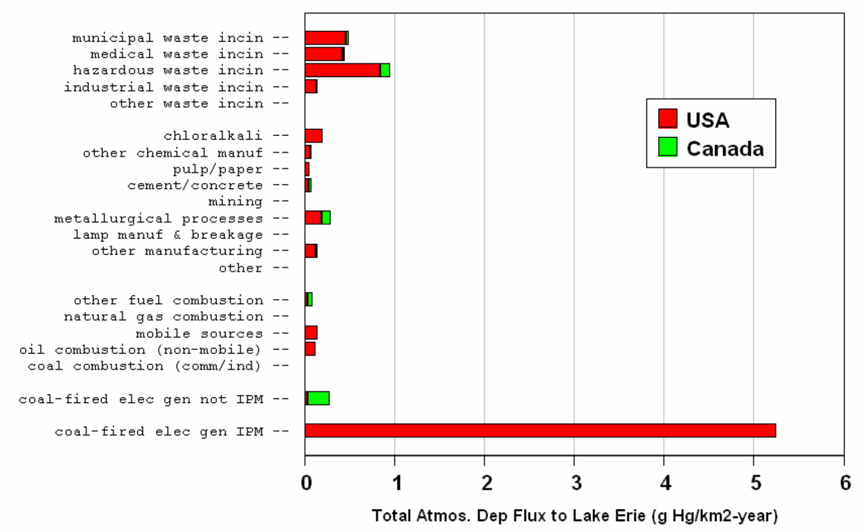


Figure 64. Modeled deposition to Lake Erie from different source sectors.

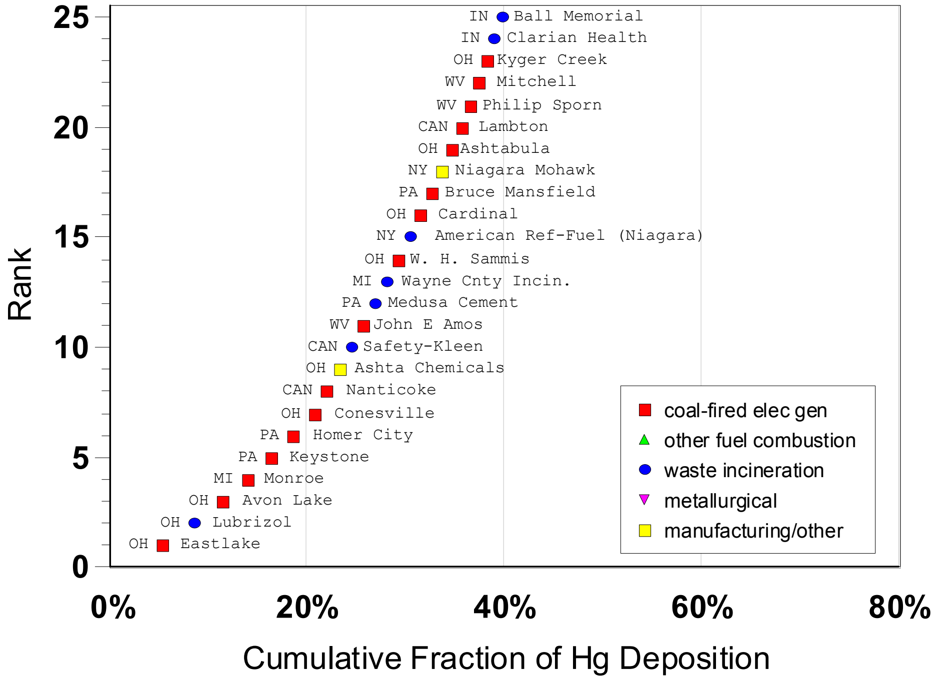


Figure 65. Top 25 modeled atmospheric deposition contributors to Lake Erie.

5) Lake Ontario

In this sub-section, figures summarizing the modeling results for Lake Ontario are presented, analogous to those presented above for other Great Lakes above.

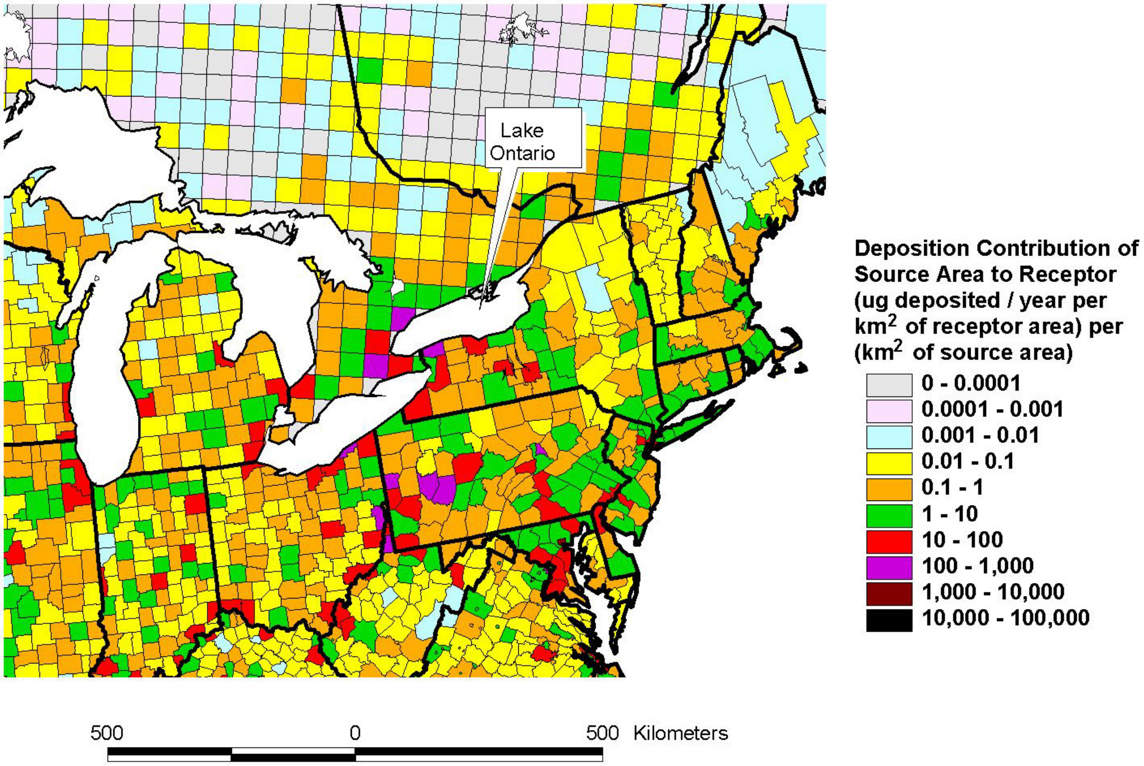


Figure 66. Atmospheric deposition contributions to Lake Ontario (regional view).

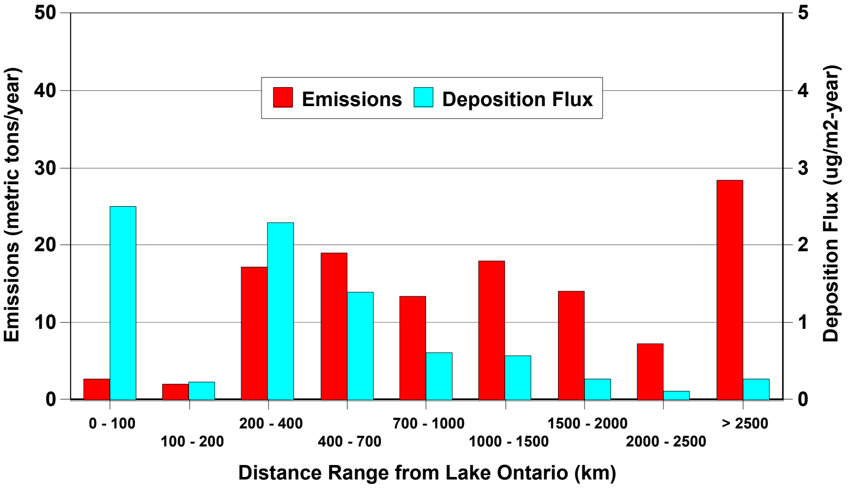


Figure 67. Emissions and deposition arising from different distances from Lake Ontario.

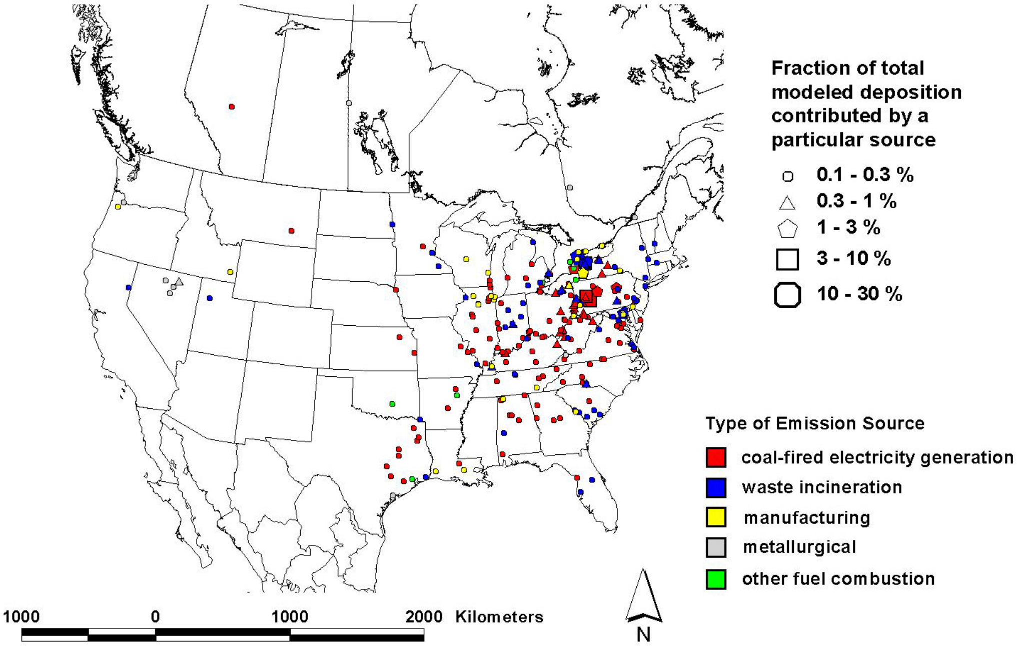


Figure 68. Largest modeled contributors to Lake Ontario (full view).

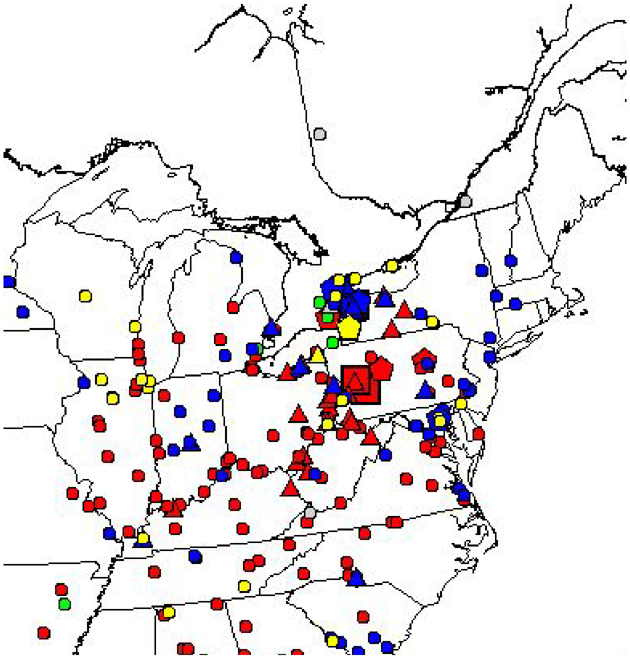


Figure 69. Largest modeled contributors to Lake Ontario (close-up).

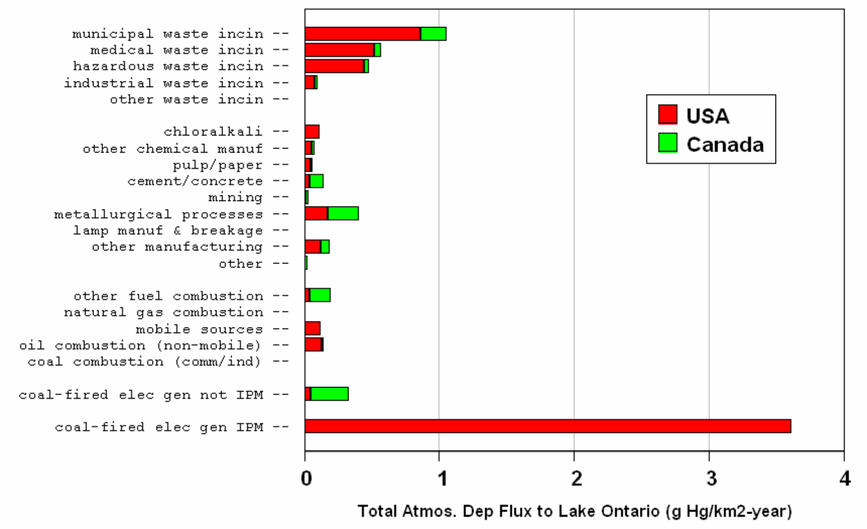


Figure 70. Modeled deposition to Lake Ontario from different source sectors.

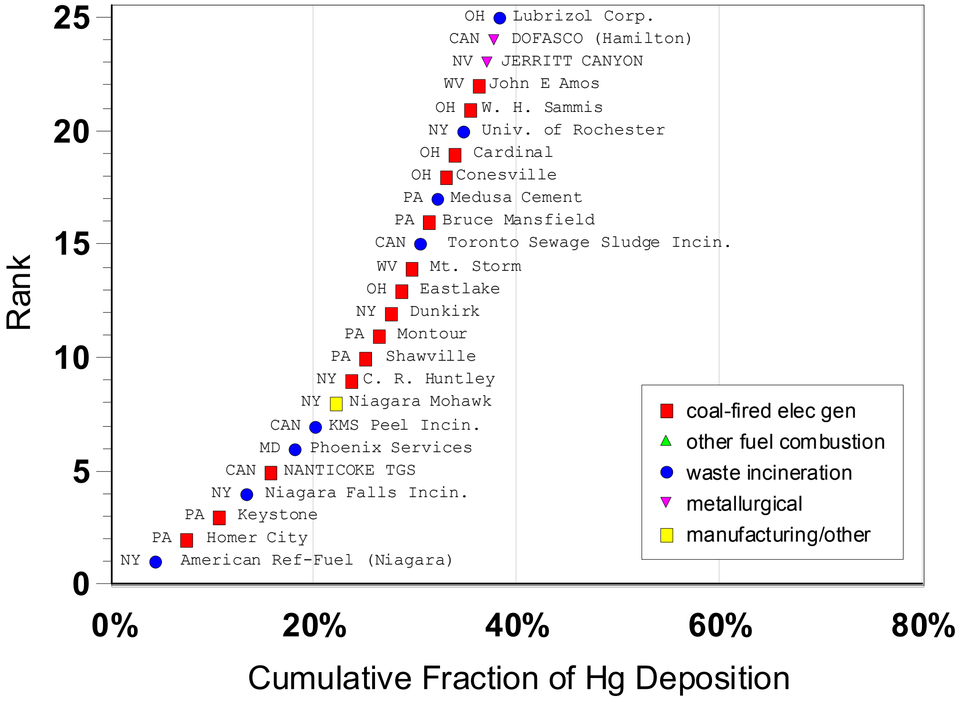


Figure 71. Top 25 modeled atmospheric deposition contributors to Lake Ontario.

6) Combined Great Lakes

In an attempt to summarize these results, the 25 largest contributors to each of the Great Lakes were pooled together in a common list. These sources were mapped and are shown in Figure 72 (full view) and Figure 73 (close-up). In Figure 74, the total modeled deposition to the Great Lakes from different source sectors in the U.S. and Canada is summarized. It can be seen from these figures that on the whole, coal-fired power plants appear to be the most significant contributors to atmospheric deposition of mercury to the Great Lakes. This is not surprising given that the majority of the ionic mercury emitted in the Great Lakes region comes from this source sector (see Figure 31 on page 46).

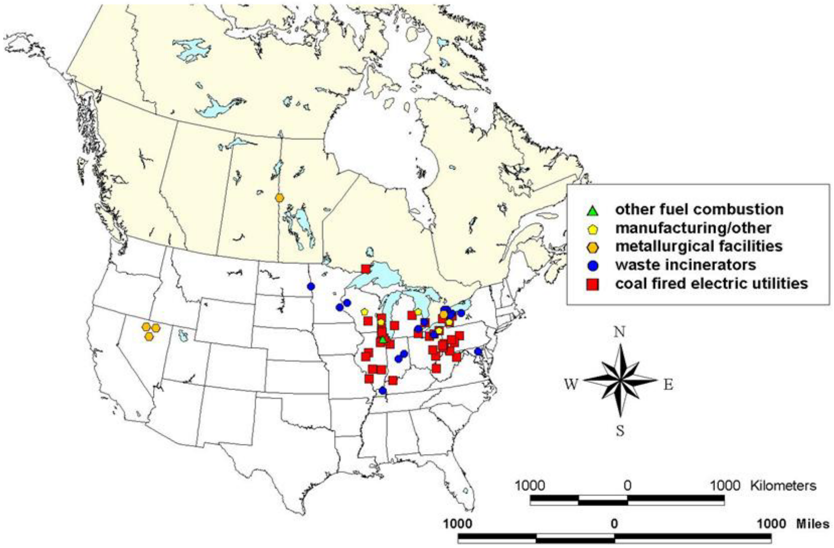


Figure 72. Largest modeled contributors to the Great Lakes (full view). These sources were among the top-25 model-estimated contributors to one or more Great Lakes.

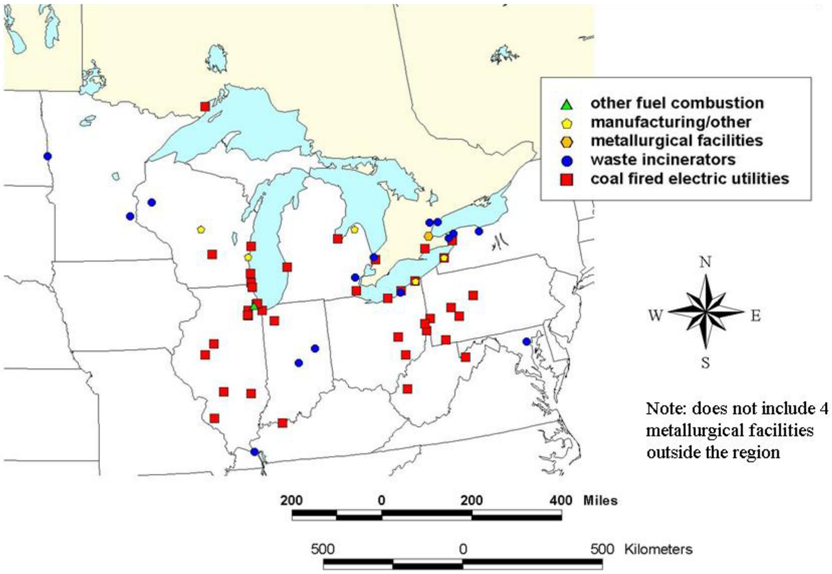


Figure 73. Largest contributors to the Great Lakes (close-up).

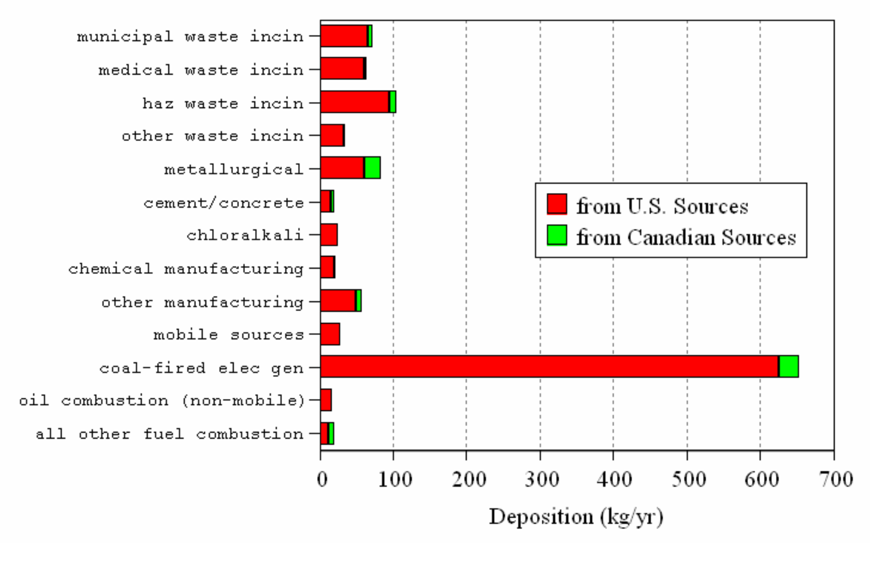


Figure 74. Modeled deposition to the Great Lakes from different source sectors.

I. Potential Next Steps

As resources permit, initial steps are being taken to refine and extend the HYSPLIT-Hg results described above along the following lines:

1. *Extension of the model from its current North American domain to a global extent* to simulate the impacts of sources throughout the world on receptors of interest. This will allow, for example, estimates to be made of the relative importance of domestic vs. international emissions sources to the deposition occurring in the Great Lakes region and elsewhere.

2. *Inclusion of the impact of natural emissions and re-emissions of anthropogenic mercury.*

3. *The use of higher-resolution meteorological data.* To this end, NOAA ARL has recently begun archiving 40-km gridded U.S. meteorological data.

4. *Development of a system for incorporating observed precipitation data into the model* to increase the accuracy of wet deposition estimates throughout the model domain.

5. *Evaluation of the model against additional wet deposition data and ambient concentration data for elemental, ionic, and particulate mercury.* NOAA ARL collected such data during summer 2004 at two sites in the Chesapeake Bay region, and the model is being evaluated against these data. Attempts to obtain comparable data collected by other researchers at other sites are also being made, and if the data are obtained, the model could be evaluated more comprehensively. As described above, a new large-scale monitoring network is being considered, and three new sites have been pledged to this embryonic network. Sites in the network will provide additional data for model evaluation and improvement. All such evaluation exercises require accurate, time-resolved emissions estimates over the relevant time period for all sources that significantly affect the measurements at the site. As weather patterns are highly variable, the required temporal resolution of the emissions estimates are on the order of 1-2 hours, and perhaps even shorter. Inventories such as these do not exist at the present but could be constructed.

6. *Process-related measurements* of atmospheric chemistry, phase-partitioning behavior, and dry and wet deposition to evaluate and refine model algorithms.

7. *Sensitivity tests* -- investigating the influence of uncertainties in model inputs and model algorithms -- to help determine which uncertainties are the most critical for model improvement.

8. *Linkage of the atmospheric model to other mercury models to form a multi-media mercury modeling system* to track mercury from emissions to ecosystem loading to food chain bioaccumulation to human exposure.

9. *Use of updated emissions inventories as inputs to the model*. It is expected that a number of new anthropogenic emissions inventories will soon be available – 2002 U.S., 2000 Canada, 2000 global – and these could be used to develop more updated source-attribution estimates for the Great Lakes and other receptors of interest. It is of course unfortunate that inventories for the same year are not available for all regions of interest. This complicates the model evaluation process.

10. *Estimation of the time-course of atmospheric loading to the Great Lakes* by running the model over long periods using a continuous record of historical emissions. Such estimates would likely need to be made over long periods -- e.g., for the past 50-100 years, or even longer. Continuous, historical emissions inventories are not available at present but could be constructed.

11. *Estimation of the impacts of potential future emissions scenarios*.

12. *Participation in additional model intercomparison studies.* In these studies, participating models are given the same meteorological and emissions inventory data as inputs. Model results are then compared against each other and where possible, against a common set of ambient measurements. Finally, analyses are then conducted to attempt to ascertain the reasons for any significant differences between the models and/or between the models and the measurements.

J. Summary of Great Lakes Atmospheric Mercury Deposition

In the above sections, the transport and deposition of atmospheric mercury has been discussed in general and specific examples for the Great Lakes have been presented. Here we provide a very brief summary of this preceding discussion.

1. Mercury is a pollutant of concern in the Great Lakes, contributing, for example, to numerous fish consumption advisories.

2. Atmospheric deposition is a significant loading pathway for mercury to the Great Lakes.

3. Source-attribution information is needed for this atmospheric deposition to determine the relative importance of different source types and source regions.

4. Deposition impacts from any mercury emissions source appear to depend greatly on the relative proportions of the different forms of mercury emitted (ionic > particulate > elemental), and are highly variable in space and time. Based on current understanding, emissions of ionic mercury in particular appear able to create large local and regional impacts.

5. Atmospheric fate and transport models have the potential of providing the most comprehensive and detailed source-attribution information for atmospheric mercury deposition to the Great Lakes. These models require accurate emission inventories and meteorological data, as well as ambient measurement data for “ground-truthing”.

6. There are a number of uncertainties in current atmospheric mercury models, but there are a number of steps that could be taken to reduce these uncertainties.

7. Due to the scarcity of available data, only limited model evaluation analyses can currently be carried out. Therefore, the accuracy of model results – and the significance of the uncertainties in introducing errors into the simulation – can only be roughly estimated.

8. Data exist that could be made available for more detailed model evaluation. Additional data could be collected for more targeted evaluations. The establishment of a nationwide monitoring network to provide measurement data for speciated ambient atmospheric concentrations of mercury would be extremely useful would allow atmospheric mercury models to be evaluated and improved.

9. In spite of the many uncertainties, most atmospheric mercury models – including the HYSPLIT-Hg model – are able to produce results reasonably consistent with ambient measurements.

10. Results to date suggest that coal-fired power plants in the U.S. contribute the most to atmospheric mercury deposition to the Great Lakes. This is consistent with their being

responsible for ~50 percent or more of the estimated ionic mercury emissions in the Great Lakes region.

11. A number of additional modeling analyses using the HYSPLIT-Hg model could be undertaken to provide more and better information regarding the transport and deposition of mercury to the Great Lakes.

4. Trends in Great Lakes Mercury

An attempt is made in the following section to provide illustrative data on Great Lakes mercury trends. It must be noted that a comprehensive treatment of this issue is beyond the scope of this report. Nevertheless, a limited attempt has been made to assemble available literature data regarding trends.

The fate and cycling of mercury within the Great Lakes ecosystem is highly complex and is influenced by a number of watershed and lake processes (e.g., Mason and Sullivan, 1997; Sullivan and Mason, 1998; Sunderland and Foley, 2003; Chen *et al*., 2005; Shanley *et al*., 2005; Kamman *et al*., 2005; Dennis *et al*., 2005; Perry *et al*., 2005; Booty *et al*., 2005, Rolphus *et al*., 2003). Mercury in Great Lakes watersheds – some of which comes from atmospheric deposition – can be delivered to the Great Lakes in inorganic and organic forms (e.g., methylation can occur in the watersheds and this can be a source of methylmercury to the lakes). Mercury can also be deposited directly to the lakes. Once inorganic or organic mercury is introduced to a lake, a number of processes influence its behavior, including the following:

- partitioning of mercury between the dissolved phase and suspended particles;
- settling of suspended particles, ultimately to the sediment layer at the bottom of the lake;
- interconversion of different mercury forms in the water column and the sediment, including oxidation/reduction reactions and methylation/demethylation processes;
- volatilization of mercury from the lake;
- discharge of mercury from the lake through its outflow.

Sediments are continuously covered over with new material, and thus mercury in the sediments is slowly being buried. There are a number of factors that affect the bioavailability of mercury, but all things being equal, it likely becomes less bioavailable as it gets buried deeper and deeper. The depth of the bioavailable surficial sediment layer with respect to mercury may be on the order of 2.5 cm – i.e., below this depth, the mercury can be considered to unavailable – but this estimate is highly uncertain (Sunderland and Foley, 2003). Sedimentation rates are highly variable within and among the Great Lakes, but 2.5 cm represents on the order of 2-20 years of sedimentation, based on typical sedimentation rates (e.g., Robbins and Edgington, 1975; Farmer, 1978; Rossman, 1999; Mortimer, 1987; Warren et al., 1996)

While there are many uncertainties in current understanding, it is not expected that there will be a direct correspondence between mercury loading, concentrations of mercury in sediments, and the concentrations of mercury in fish. The historical record of mercury introduced to the Great Lakes through atmospheric and other loading pathways is not known precisely, although broad outlines can be surmised. It is likely that trends in sediment and fish concentrations have lagged behind trends in loadings, due at least to the following factors: (a) it takes time for mercury introduced to the Great Lakes to be transported to the active sediment layer in which much of the methylation and introduction into the food chain occurs, and during this time, internal mixing within the lakes occurs; (b) the bioaccumulation process takes place over the lifetimes of organisms – e.g., fish accumulate mercury over the course of their lifetime and thus reflect conditions over many years. As a corollary to the above, the response of the Great Lake system to changes in mercury loading will not be instantaneous, but is more likely to be on ~decadal (or even longer) time scales (e.g., Sunderland and Foley, 2003; Pirrone *et al*., 1998). The time scale of the response will likely vary from lake to lake, and will most likely even vary from one region to another within any given lake. Thus, the interpretation of trend data is very complicated.

A multimedia modeling project is underway for the Great Lakes (IJC, 2006), extending the Sunderland and Foley (2003) analysis. It is anticipated that this project will eventually provide results estimating the time course of fish concentrations in response to different future loading scenarios.

A. Mercury Emissions

Pirrone *et al*. (1998) have estimated anthropogenic mercury emissions for 1800-1990 from sources in North America and the Great Lakes region. The figure summarizing their estimates is reproduced below (Figure 75). Analysis of dated sediment cores from the Great Lakes showed very little mercury deposition until ~1920 suggesting that the large emissions from gold and silver mining from 1850 to 1920 did not result in significant atmospheric deposition to the Great Lakes. Mercury emissions from these activities are believed to have largely been in the form of elemental mercury. As discussed above (e.g., Figure 27, page 43), the deposition impacts of elemental mercury emissions are relatively insignificant compared to other forms of mercury. This may explain the lack of any significant impact from these gold and silver mining activities.

There are detailed estimates of historical U.S. emissions for a few pollutants (e.g., USEPA, 2000b); however, the earliest available estimates for U.S. mercury emissions are for 1990. Thus, there is a limited data record to examine detailed emissions trends. Figure 76 shows estimates of 1990 and 1999 U.S. atmospheric mercury emissions (USEPA, 2005e). There are two important features seen in this figure. First, emissions from coal-fired power plants do not appear to have changed significantly over this period. Second, emissions from medical waste incinerators and municipal waste incinerators appear to have decreased significantly. The decrease is due to a number of factors, including:

(a) Installation of additional pollution control equipment at some facilities, e.g., activated carbon injection installed at many municipal waste incinerators;

(b) Closure of some facilities, a factor particularly important for medical waste incinerators;

(c) Reduction of mercury in the waste stream through pollution prevention methods. For municipal waste, an example includes the reduction of mercury content of batteries. For medical waste, many health care providers have introduced measures to reduce the entry of health-care related mercury – in thermometers, manometers, laboratory reagents, etc. – into the medical waste stream.

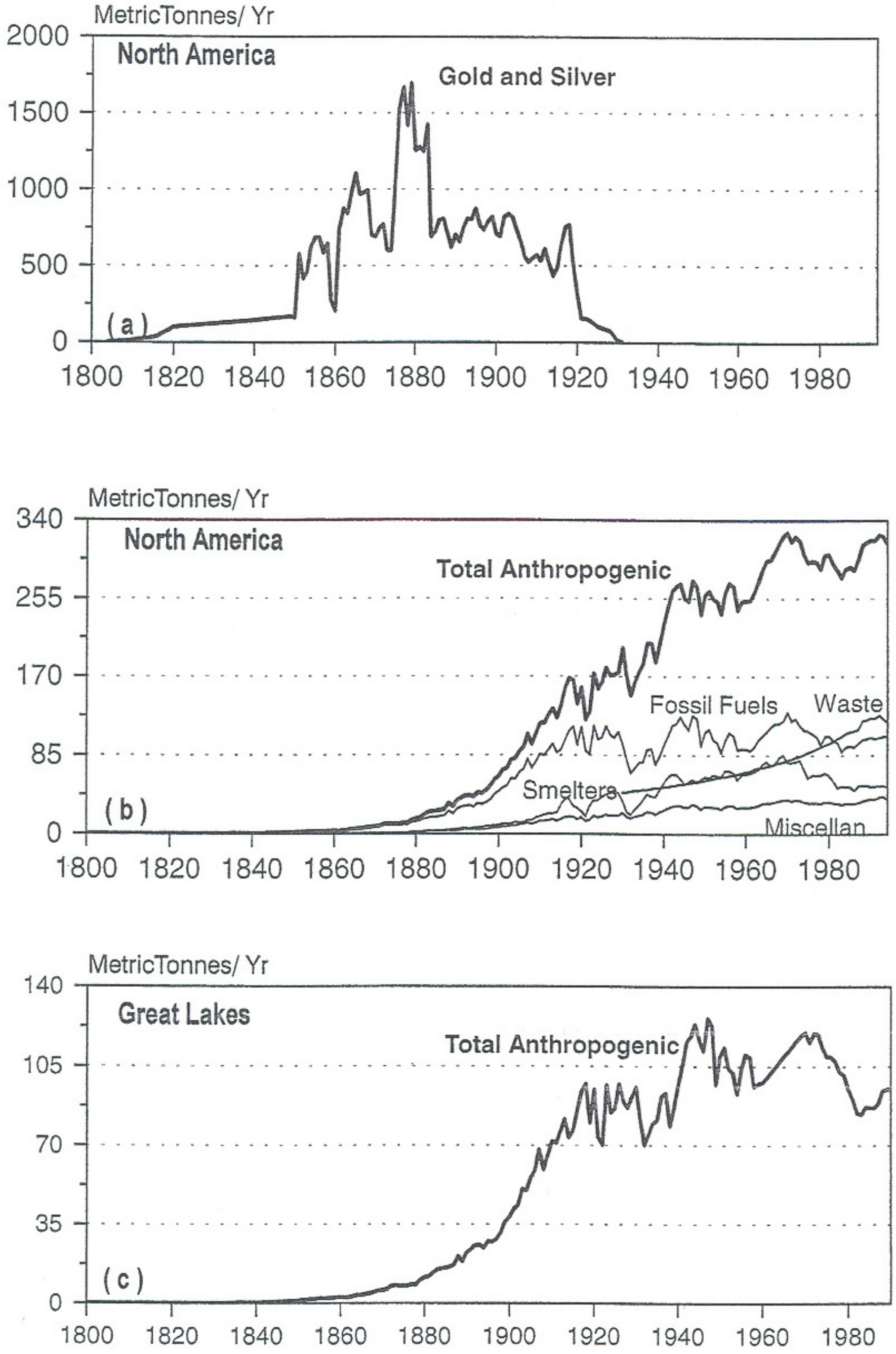
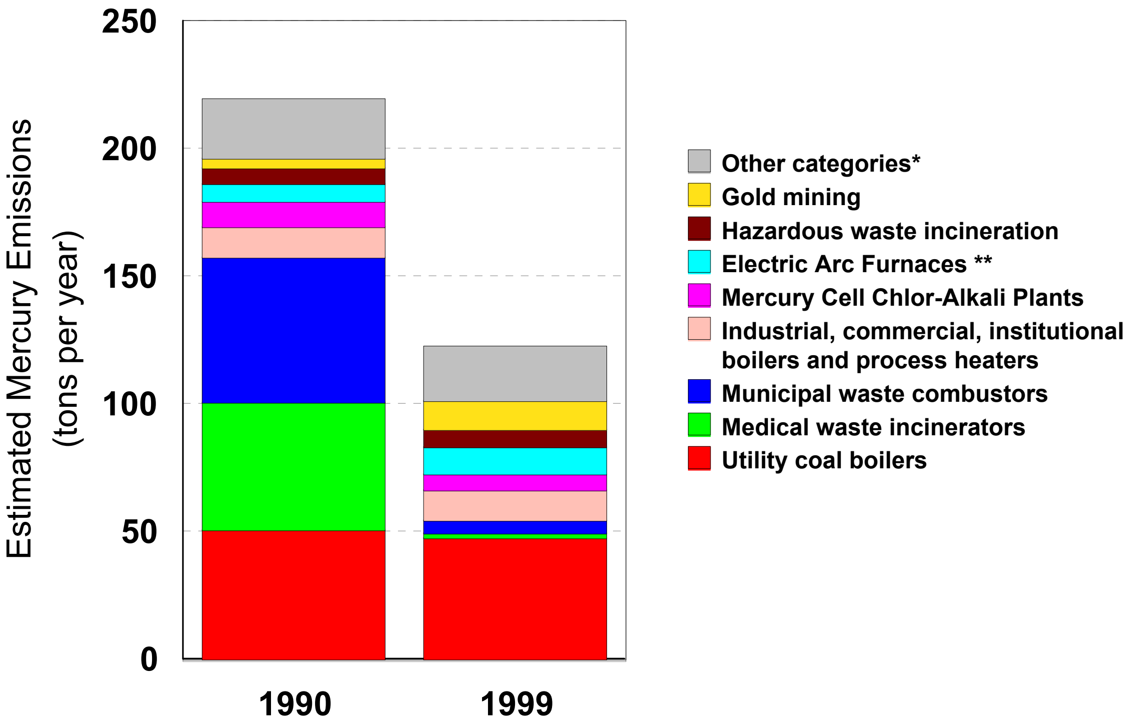


Figure 75. Mercury emissions in North America and the Great Lakes region (1800-1990). Atmospheric mercury emissions from (a) gold and silver mining in North America; (b) *modern* anthropogenic sources in North America; and (c) *modern* anthropogenic sources in the Great Lakes region (including the 8 Great Lakes U.S. states and the province of Ontario).
[a reproduction of Figure 2 from Pirrone *et al.* (1998).]



* Data for Lime Manufacturing are not available for 1990.
** Data for Electric Arc Furnaces are not available for 1999. The 2002 estimate (10.5 tons) is shown here.

Figure 76. Mercury emissions trend data from the U.S. EPA.

As noted above, however, the precise timing of the reductions in emissions from municipal and medical waste incineration has not been well characterized. It is very likely that the significant reductions have occurred between ~1990 and ~2001, but, it is not known with any certainty how fast those reductions occurred at any given facility. In order to use these emissions inventories with trends in monitoring data, it would be extremely useful if an accurate historical record of emissions could be assembled, particularly for large sources that have changed significantly. It is anticipated that significant reductions in emissions from U.S. coal-fired power plants will occur as a result of the Clean Air Interstate Rule (CAIR) and the Clean Air Mercury Rule (CAMR).

Data regarding trends in Canadian emissions are available from Environment Canada (2005). They report that until the 1980's, the largest source of anthropogenic mercury emissions was the chlor-alkali industry (15 facilities were reported to be in operation in the 1970's). Emissions have been dramatically reduced in this sector, through pollution control measures, process changes (to non-mercury-based manufacturing methods), and facility closure. At present, only one Canadian facility remains in operation in Canada. Total inventoried anthropogenic emissions in Canada are reported to have been 32 metric tons/year in 1990. The total emissions dropped to 11 metric tons/year by 1995, largely due to process changes in metal smelting operations. In 1995, this source sector still accounted for ~40 percent of Canadian emissions. By 2000, the total emissions are reported to have dropped to ~8 metric tons/year, with electricity generation and metal smelting each contributing about 25 percent of the total.

The most detailed historical emissions data found were those of Sunderland and Chmura (2000a,b) for Maritime Canada. If comparable data were available for the Great Lakes and other regions, trends in monitoring data could be interpreted much more reliably, and model-based estimates of historical loadings to the Great Lakes could be made.

B. Mercury Deposition

1) Wet deposition measurements in the Great Lakes region

As discussed above (in Section 3), the Mercury Deposition Network (MDN) is a collection of sites at which mercury wet deposition is measured. A map of all of the current sites was shown above (Figure 4, page 19). The objective of the MDN is to measure regional background mercury levels. Accordingly, the sites are generally located in areas that not strongly influenced by any one source or sources in the region. As a result, if mercury emissions increased or decreased in a given region – especially changes in emissions of ionic mercury, which can have the most significant local and regional effects – the MDN sites in the region might not reflect the change; the sources whose emissions changed are not likely to have (or have had) large impacts at the sampling sites – indeed, the MDN is designed specifically to avoid such impacts.

Nevertheless, the data records for all of the MDN sites in the Great Lakes region were examined, and it was found that five sites have the longest records of available data: a total of eight years, from 1996-2003[12]. These five sites are highlighted in Figure 77.

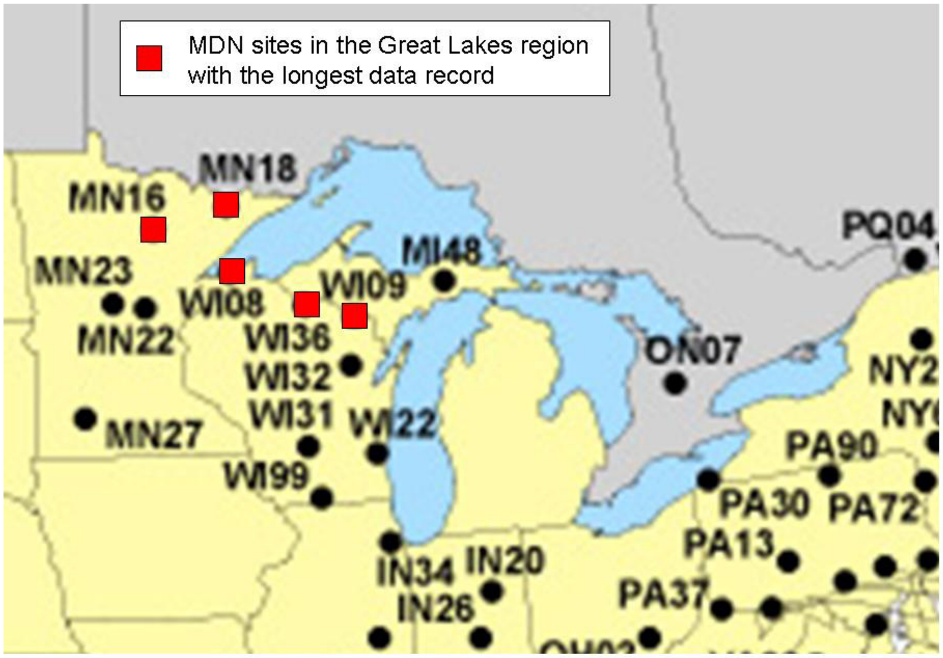


Figure 77. Great Lakes MDN sites with the longest measurement record.

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[12] The five sites are currently operating, but complete data for 2004 and 2005 are not yet available. Therefore, only the period from 1996-2003 is examined here.

Precipitation totals can be quite variable from year to year. Observed trends in wet deposition will be strongly influenced by these yearly variations. Since the dataset is very limited (only an 8-year record), the most useful way to evaluate trends may be to examine trends in the volume-weighted average concentration of mercury in the precipitation collected at each site. To obtain these concentrations, the annual total measured mercury wet deposition was divided by the annual total precipitation measured at each of the five sites for each year of available data. The resulting trend data are presented in Figure 78 through Figure 82. There does not appear to be any consistent trend at the sites. At two of the sites (MN16 and WI36) the yearly volume-weighted mean concentrations are relatively constant throughout the period. At WI08, there appears to be an increase from 1996 to 2000, with a significant drop to ~1996 levels starting in 2001. At WI09, a small peak in concentrations may have occurred in 1999-2000. At MN18, the concentration is highly variable, but there may be an overall decrease in concentration from 1996-2003, even though any individual year does not necessarily follow this pattern. Figure 83 combines all the data into one graph, showing the overall trend in the combined precipitation concentration at the five sites.

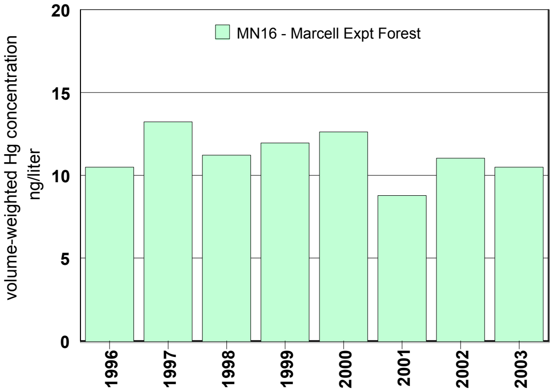

Figure 78. Mercury concentration in precipitation at MN16.

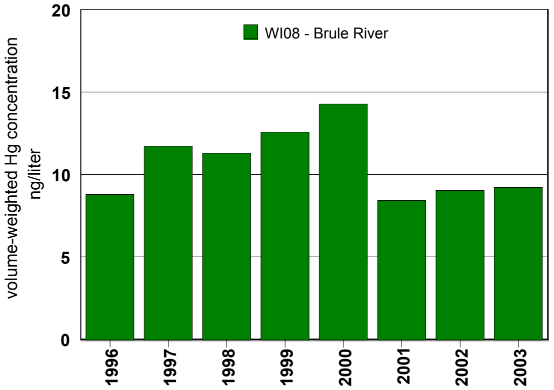

Figure 79. Mercury concentration in precipitation at WI08.

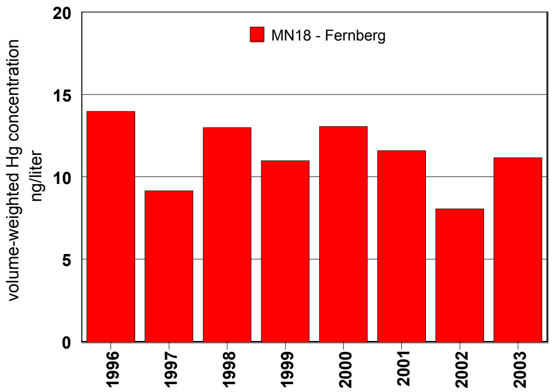

Figure 80. Mercury concentration in precipitation at MN18.

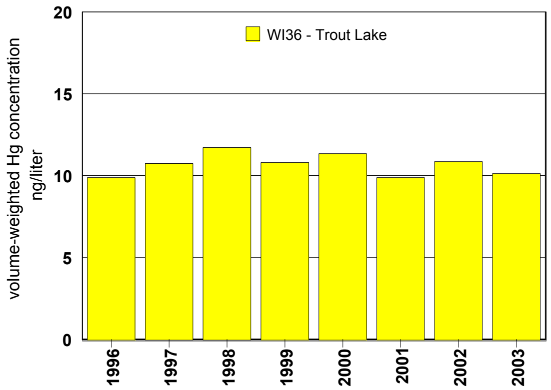

Figure 81. Mercury concentration in precipitation at WI36.

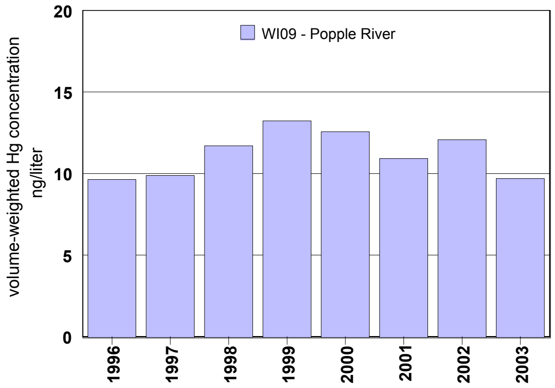

Figure 82. Mercury concentration in precipitation at WI09.

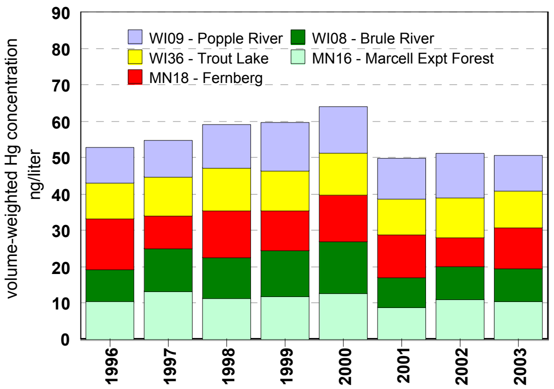

Figure 83. Mercury conc. in precip. at long-term MDN sites near the Great Lakes.

In Figure 84 and Figure 85 these five sites are shown along with estimated emissions of ionic mercury (RGM). Figure 84 shows the RGM emissions inventory used in Cohen et al. (2004), believed to represent conditions in ~1995-1996, and Figure 85 shows the RGM emissions from the 1999 U.S.EPA National Emissions Inventory, which is believed to represent emissions somewhere in the 1999-2001 period. The timing of the reduction in emissions from municipal and medical waste incinerators between these two inventories is not well known; EPA has not provided data for any given facility that purports to accurately characterize the time course of emissions in the ~10 year period starting in the early 1990's.

Ionic mercury was chosen for these maps because it is the form that is believed to be most readily wet-deposited. It can be seen from these two figures that while there were reported changes in emissions of ionic mercury between 1995-1996 and 1999-2001, there were only a few changes in the vicinity of the 5 sites discussed above. In addition, it must be noted that the MDN sites are chosen so that they are *not* strongly impacted by any large mercury sources. Thus, the network is not designed to pick up temporal trends in local, source-impacted deposition impacts. Nevertheless, the EPA has reported that required emissions reductions at large municipal waste incinerators were completed by 2000 (USEPA, 2005b), and so, it is possible that the reduced mercury concentrations in precipitation that occurred between 2000 and 2001 are due to these decreases. Detailed atmospheric fate and transport modeling could be done to investigate this issue. However, an accurate, time-resolved emissions inventory for each of the large emissions sources in the region would be required.

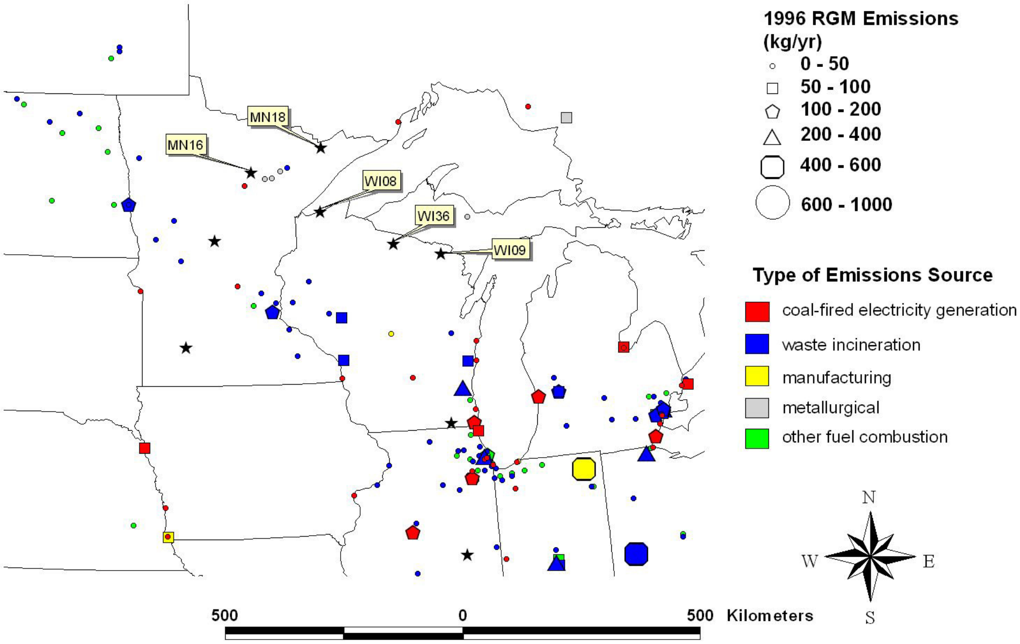

Figure 84. MDN sites and 1995-1996 RGM emissions.

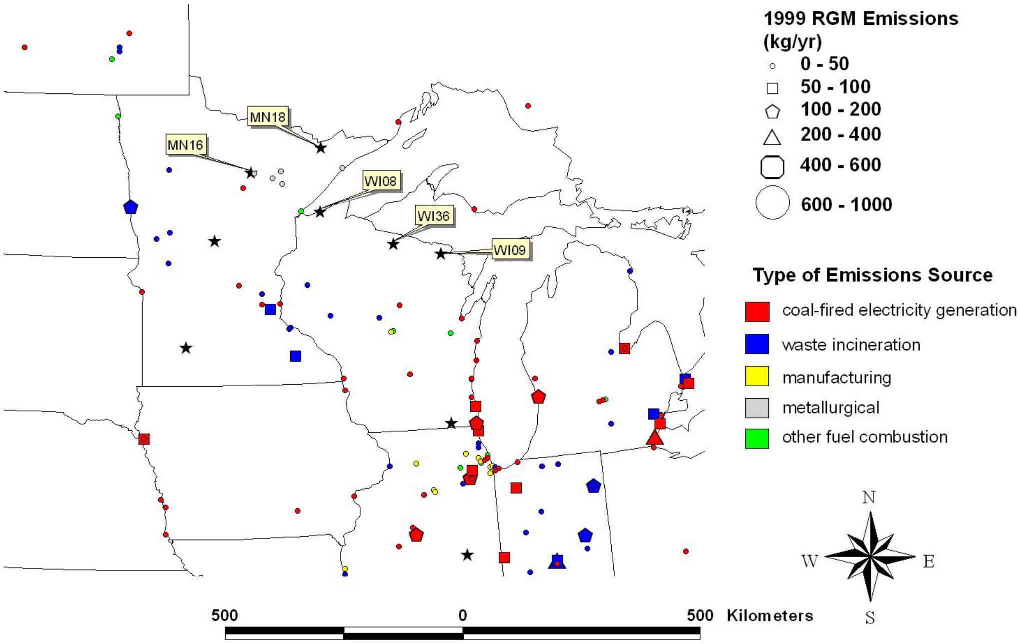

Figure 85. MDN sites and 1999-2001 RGM emissions.

2) Other mercury wet deposition measurements

Glass and Sorenson (1999) reported mercury wet deposition measurements for 1990-1995 at six sites in the Upper Midwest. One of the sites – at Lamberton, MN, in south-western Minnesota – became a Mercury Deposition Network site (MN27). The first year of complete Mercury Deposition Network data at the site was 1997. The site is still operating, and the last full year of complete data presently available is for 2003. The site is several hundred miles farther from the Great Lakes than the five sites discussed above (see Figure 77, above), and so it is perhaps less representative of the Great Lakes region. Nevertheless, the two data sets provide almost a complete record of mercury wet deposition from 1990-2003.

Figure 86. Mercury Deposition Network site (MN27) at Lamberton, MN.
The first picture shows the view from the collector towards the south-west, and the second picture shows the view towards the north-east.
Additional pictures and information regarding this site can be found at:
http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=MDN&id=MN27

1990-2003 data for mercury concentration in precipitation, precipitation amount, and wet deposition of mercury are shown in Figure 87, Figure 88, and Figure 89. The annual variability in the data is relatively large, and there does not appear to be a clear trend. In considering these data, it must be noted that different methodologies were used in the two measurement programs. Glass and Sorenson (1999) report on ~1-year intercomparison at two sites with a methodology similar to the MDN. Differences on the order of ~5-15 percent between the two methodologies were found with co-located measurements.

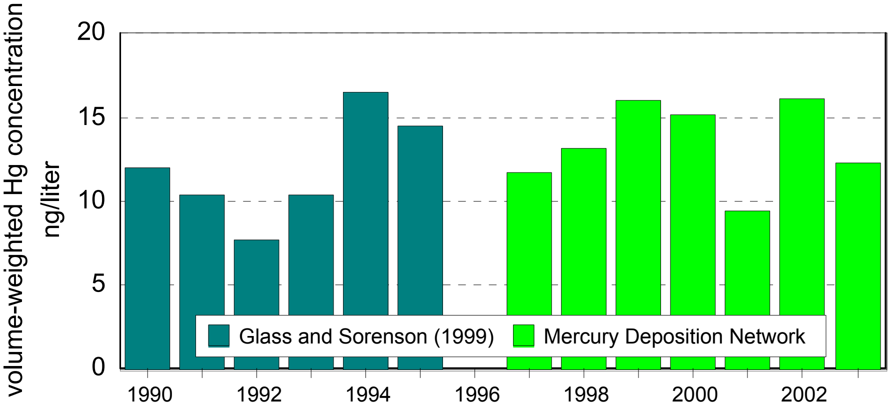

Figure 87. Mercury concentration in precipitation at Lamberton, MN (1990-2003)

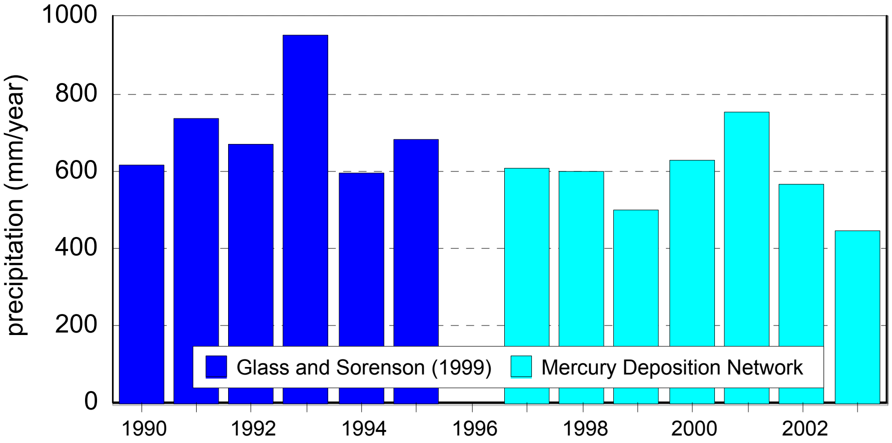

Figure 88. Precipitation at Lamberton, MN (1990-2003)

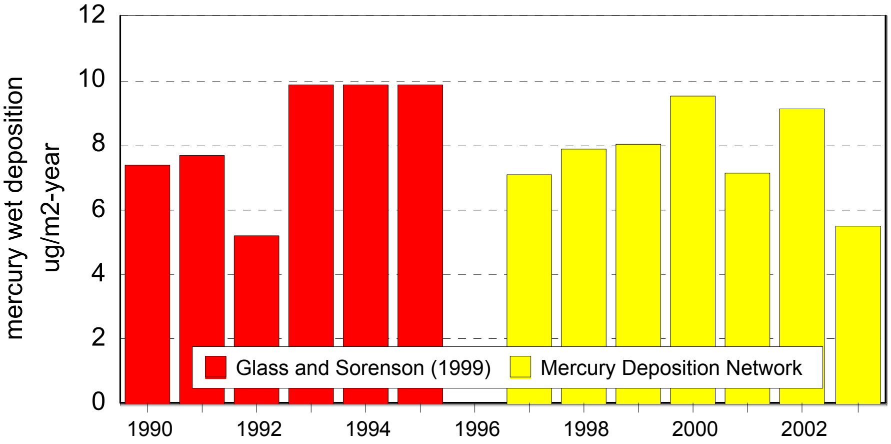

Figure 89. Mercury wet deposition at Lamberton, MN (1990-2003)

An analysis of 13 MDN sites and one additional site (at Underhill, VT) has recently been completed, for deposition and concentrations in the Northeast over 1996-2002 (Van Arsdale *et al*., 2005). In this analysis, it was concluded that wet mercury deposition at the sites did not reflect reported emissions reductions in the region. However, as noted above, MDN sites are typically sited in locations without strong source influences. Thus, MDN sites will not necessarily reflect the trend in regional emissions. This is particularly true if the overall regional changes in emissions are primarily due to large changes at a few facilities, and the MDN sites do not happen to be strongly influenced by the emissions from those facilities. This phenomenon was discussed above in relation to the five MDN sites near the Great Lakes with the longest data record (e.g., see Figure 84 and Figure 85, above).

Keeler *et al*. (2005) have recently published the results of a long-running wet deposition monitoring program near Lake Champlain at Underhill Center, Vermont. Data for 1993-2003 were analyzed, and it was reported that a clear trend in the annual wet deposition totals was not observed. However, a significant decrease in the magnitude of peak wet deposition events was observed, leading the authors to suggest that a major source influence was controlled during the period.

An overall summary of trend information for the Mercury Deposition Network is shown in Figure 90. In the MDN, samples of mercury wet deposition are nominally collected weekly, so there are on the order of ~50 samples per site per year. Over the years, the number of sites has grown steadily, and thus, the total number of samples per year has grown, from less than 700 in 1996 to more than 4000 in 2003. The reason for the apparent decline in the number of samples for 2004 is that the data record for that year is not yet complete. The annual average wet deposition per sample and the annual average mercury concentration in each sample are shown. Note that the concentration values (in units of ng/liter) have been multiplied by 10 so that they can be seen easily on the graph. That is, the ~100 ng/liter values shown on the graph correspond to actual measured sample concentrations of ~10 ng/liter.

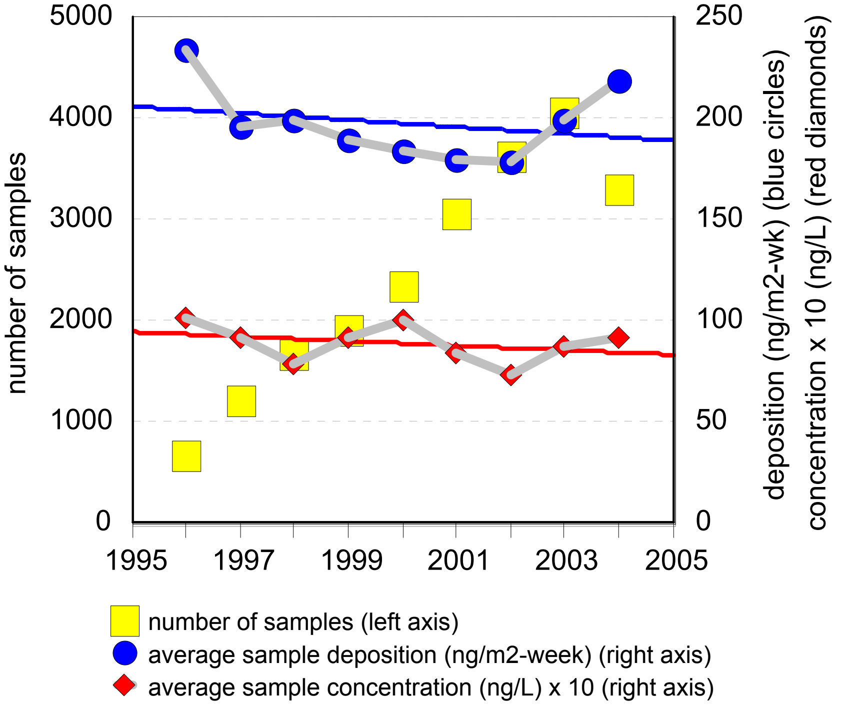

Figure 90. Overall trends in Mercury Deposition Network measurements.

In examining the data shown in Figure 90, there do not appear to be strong trends present in either mercury deposition amount or concentration. For the deposition averages, this treatment of the data appears to show a slight decreasing trend from 1996 through 2002, with a potential increase in 2003-2004. The concentration data show a more complicated pattern. Best-fit lines have been drawn through the data, showing that both concentration and deposition may have decreasing trends.

While interesting, one must be careful not to place too much emphasis on any conclusions that might be drawn from this simple treatment of the MDN data for the following reasons. First throughout the period, sites have been added and some sites have been discontinued. Thus, each year, the averages are for a different set of sites. Year to year differences are no doubt partly due simply to the changing universe of MDN sites. Second, sample collection did not occur for the entire year for each site for each year, as sites were established or discontinued at different times of the year. So, seasonal influences on wet deposition could be contributing to any year-to-year differences in the overall averages. This seasonal factor is particularly true for the data shown for 2004. At the time of this writing, the data record for this year is only complete through ~September. Deposition and concentrations at many MDN sites shows significant seasonal variations, with both being highest in summer, lowest in winter, and at intermediate values in spring and fall. Thus, the apparent increase in average deposition shown in the 2004 data may be due simply to the fact that the lower deposition expected in the late fall has not yet been factored into the average. Taking the above into account, it is not clear if there is any real significance in any of the year-to-year changes in the MDN data, or any trends that might appear to exist due to these changes.

It must be noted that meteorological conditions can vary widely over the short time periods discussed above (~10 years and less) and these variations complicate the interpretation of any trend data. Ideally, one would want to use much longer data records to investigate trends in any parameters – like wet deposition – that are intimately connected with the weather.

3) Modeled deposition to the Great Lakes from U.S. and Canadian sources

Overall modeled mercury deposition to the Great Lakes for 1996 arising from U.S. and Canadian anthropogenic sources was reported by Cohen et al. (2004). These estimates used a 1995-1996 emissions inventory for the U.S. and Canada. As noted above, the modeling results presented in this report use the same 1996 meteorology but use more recent emissions inventory data (1999-2001 for the U.S.; 2000 for Canada). Figure 91 and Figure 92 present the overall Great Lakes model results for the two different analyses. Since the same meteorological data was used for both estimates, the changes in deposition due to different weather have been factored out. In essence, the comparison shows an estimate of the differences in deposition that would arise solely as a result of changes in reported emissions. It can be seen that the model-estimated deposition (kg/year, Figure 91 and flux (µg/m^2-year, Figure 92) between 1995-1996 and 1999-2001 decreases significantly for each of the Great Lakes. This difference is almost entirely due to reduced emissions from municipal and medical waste incinerators in the U.S. It is also noted that in both periods, the model estimates show that the U.S. far more mercury through atmospheric deposition than does Canada.

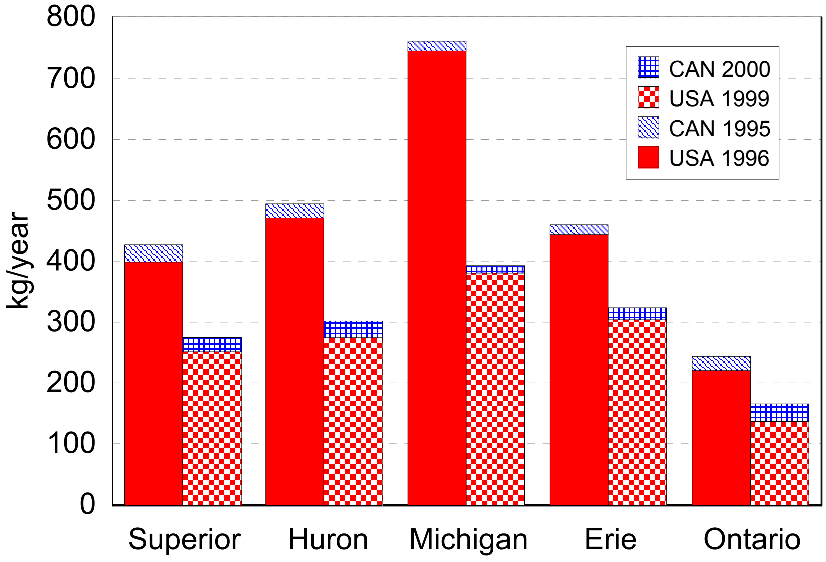

Figure 91. Modeled mercury deposition to the Great Lakes (1995-1996 vs. 1999-2001).
(arising from anthropogenic mercury air emissions sources in the United States and Canada)

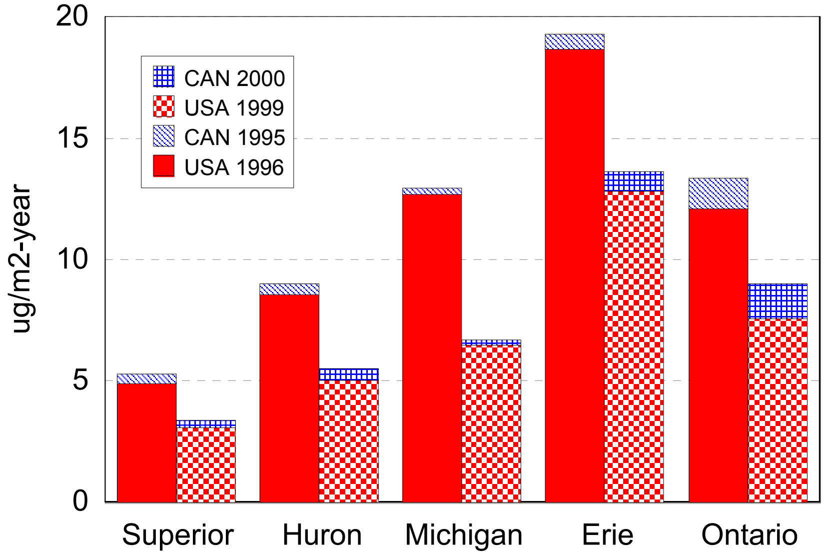

Figure 92. Modeled mercury flux to the Great Lakes (1995-1996 vs. 1999-2001).
(arising from anthropogenic mercury air emissions sources in the United States and Canada)

C. Mercury Concentrations in Sediments

Sediments can be a useful data source for discerning trends in contaminant loading. However, any given sediment core only represents the trend in sediment loading at the particular sampling site at which the sediment core was taken. Mercury contamination can occur via a number of activities – e.g., atmospheric emissions (and subsequent deposition), effluent discharge, and waste dumping – and there can be significant spatial variations in these loading rates. Moreover, there can be significant spatial differences in sedimentation rates and sediment *focusing* (i.e., areas to which sediments tend to preferentially collect, relative to surrounding regions). In large systems such as the Great Lakes, there can therefore be large spatial variations in sediment concentrations and loading rates for mercury [e.g. Forsythe *et al*. (2004), Kerfoot *et al.* (1999), Marvin *et al*. (2002, 2004a), Painter *et al*. (2001), and Rossman (1999)]; this is illustrated for the Great Lakes in Figure 93 from Marvin *et al.* (2004b). Thus, the extent to which any given core represents the overall mercury loading to a given lake or more local loading histories is generally not known.

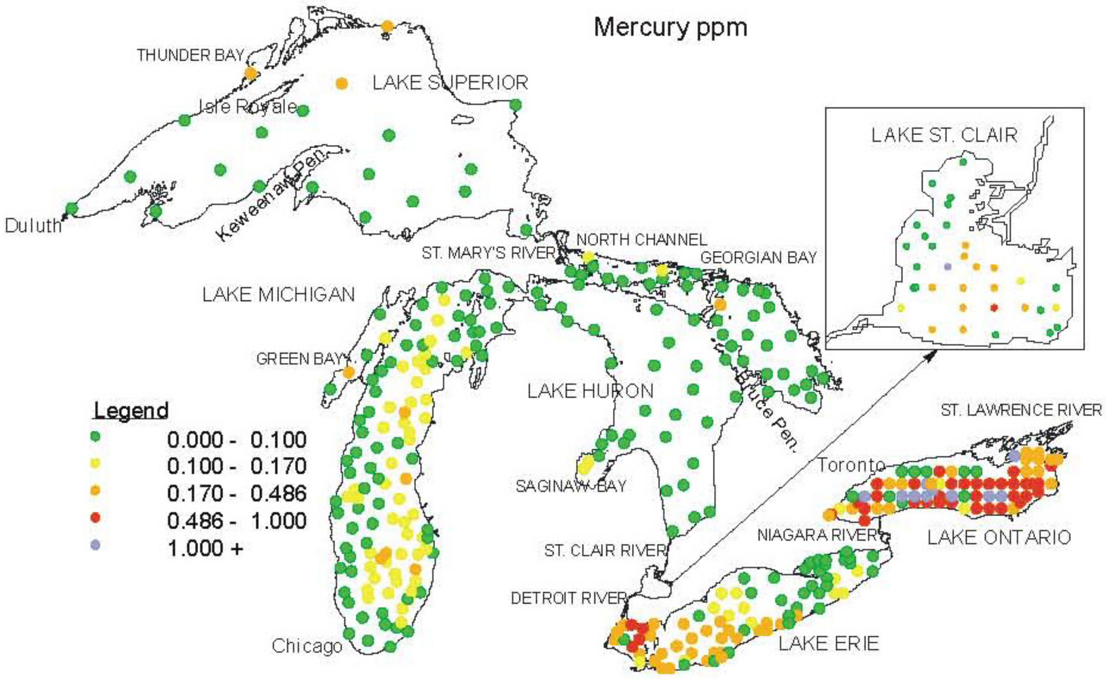

Figure 93. Spatial distribution of total mercury in Great Lakes surficial sediments. From Marvin *et al.* (2004b). Total mercury (ug/g dry weight) in the top 1-3 cm of the sediment layer, based on data collected in Lake Superior (2000), Lake Huron (2002), Lake Michigan (1994-95), Lake Erie (1997) and Lake Ontario (1998).

Lake Michigan

Long-term trends in sediment accumulation rates of mercury in Lake Michigan have been estimated by Pirrone *et al*. (1998), Rossman (2002), and Marvin *et al.* (2004b) on the basis of dated sediment cores.

The data presented by Pirrone *et al*., shown in Figure 94, indicate that there appeared to be a gradual increase in loadings starting in ~1880, leading to peaks in ~1930 and ~1940. From 1940 to 1980, the loading appears to have decreased. However, the level in 1980 is still significantly higher than the pre-industrial level. The data presented by Marvin *et al.* (2004b), shown in Figure 95, shows a similar trend.

Rossman (2002) reported that mercury concentrations in surface sediments at a site in the south-eastern portion of the lake decreased from 300 ng/g in 1969 to 100 ng/g in 1994, and the flux of mercury to the sediments at the site decreased from 13 ng/cm^2/yr in 1981 to 4.1 ng/cm^2/yr in 1994. This decrease is reasonably consistent with that shown in Figure 95 for the same period.

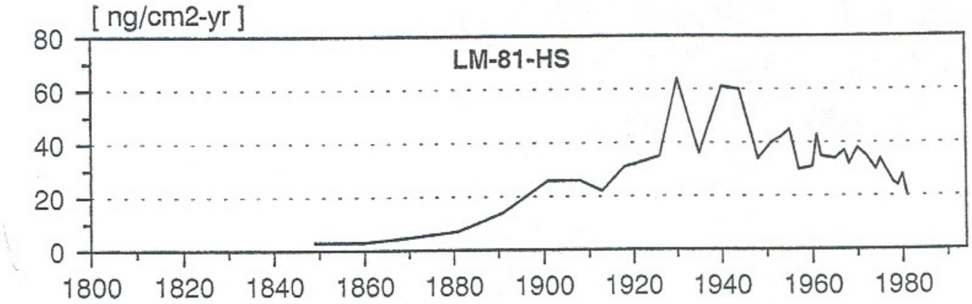

Figure 94. Mercury accumulation rates in Lake Michigan (1850-1980). From Pirrone *et al.* (1998).

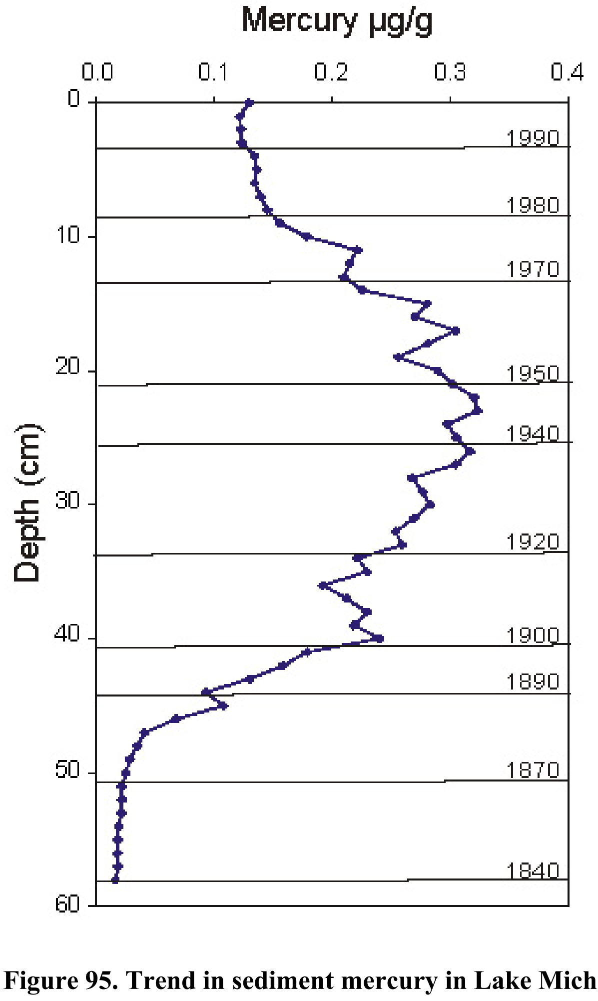

Figure 95. Trend in sediment mercury in Lake Michigan. Profile of total mercury (ug/g dry weight) levels in a core sample from Lake Michigan (from Marvin et al., 2004b).

Lake Superior

Rossman (1999) has summarized mercury trend data in Lake Superior sediments. Sediment samples at many sites showed fairly low and constant mercury concentrations from ~1500-1900, with concentrations increasing significantly from 1900 to the 1970's. Examples of these data are shown in Figure 96. At some sites, a clear, localized signal from anthropogenic activities was found (e.g., from taconite ore dumping). Comparable, point-source-influenced sediment mercury data were found by Kerfoot *et al*. (1999).

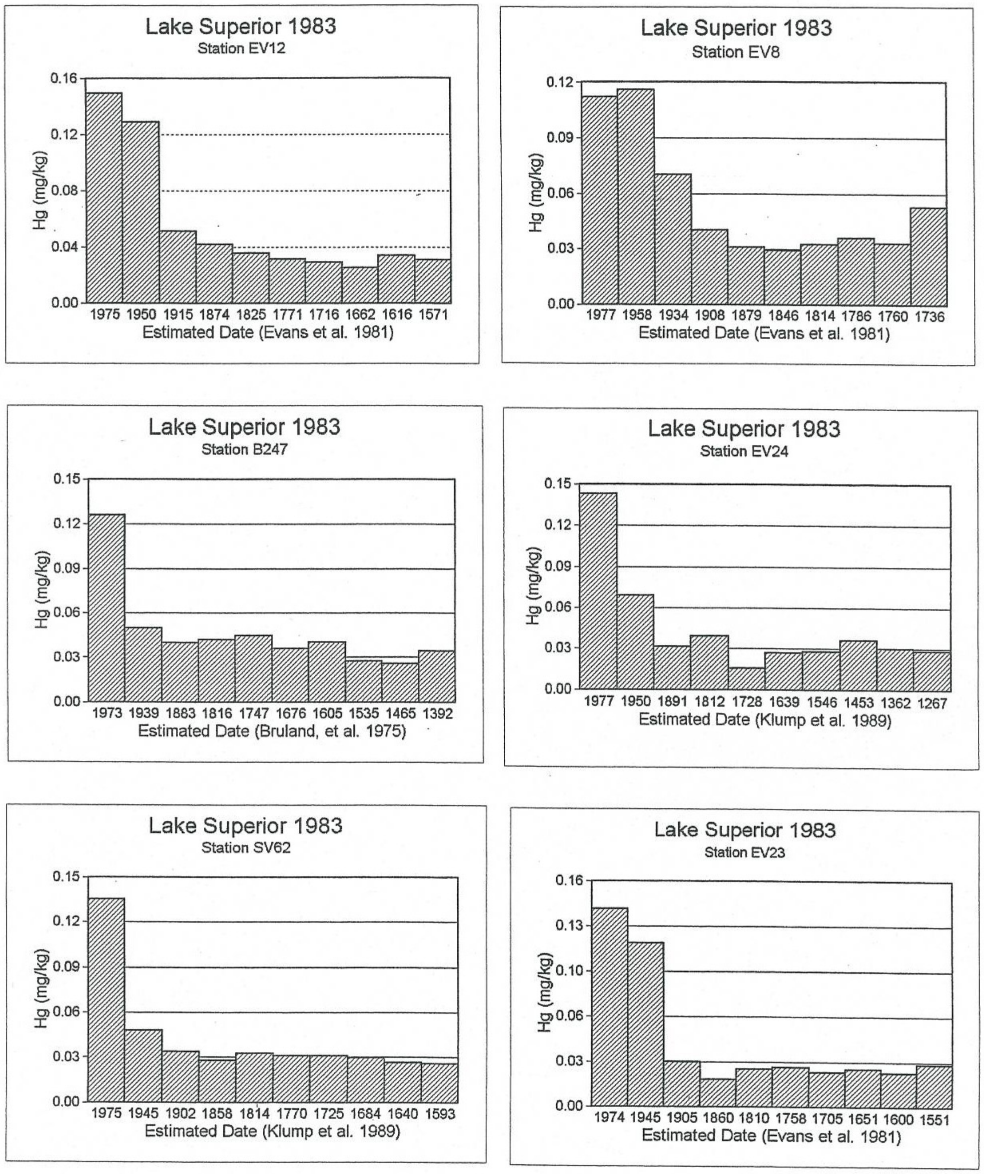

Figure 96. Mercury time trend data from Lake Superior sediments. From Rossman, R. (1999) [Figure 3], showing examples of sediment records less noticeably impacted by point sources.

Lake Erie

Pirrone et al. (1998) presented 1890-1990 data for a Lake Erie sediment core, shown below in Figure 97. These data generally show an increase in mercury loading from 1890 up to 1945, a decrease from 1945 to 1950, and several subsequent peaks in the early 1950's and the 1965-1980 period. There appears to have been a decrease from 1980 to 1990.

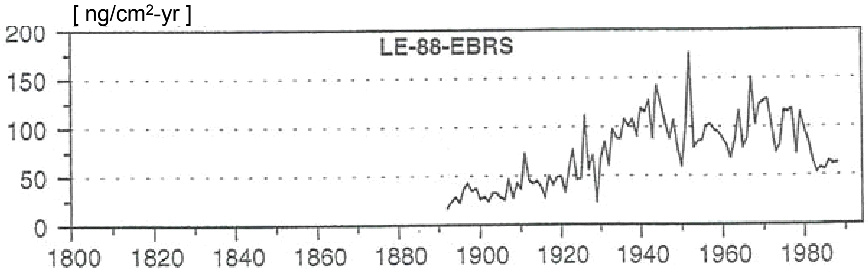

Figure 97. Mercury in a Lake Erie sediment core.
From Pirrone et al. (1998)

Temporal trend data for three different sediment cores (Figure 98) collected in 1997-98 in Lake Erie have been presented by Painter et al. (2001). The core sampling sites were chosen from the three main sediment deposition basins in Lake Erie. The western basin core, most reflecting the influence of inputs from the Detroit River, has generally higher mercury concentrations than the other areas of Lake Erie. The sediment records at these sites are complex and reflect the complex history of mercury loading. The western basin core in particular appears to show rather dramatic variations. Exact dates are not provided for the cores, but it is stated that for the western basin core, the 20 cm depth represents sediments from 1960-65. There is a sharp peak before and after this period, and another sharp peak at the 10 cm depth. The date corresponding to this 10 cm depth is not given, but it would be some period between 1965 and 1997 (perhaps ~1980). Mercury concentrations in the other basins – while much lower than those in the western basin – showed somewhat similar patterns.

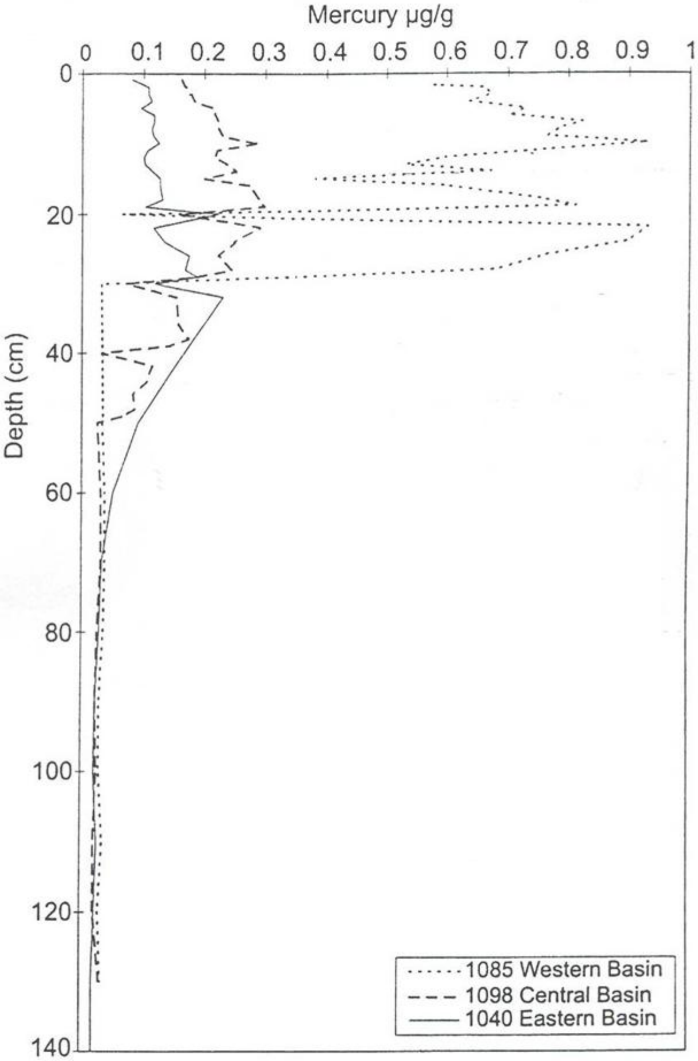

Figure 98. Mercury in Lake Erie sediments.
Profiles of total mercury concentrations (ug/g) in core samples from each of the three major Lake Erie sediment deposition basins collected in 1997-98 [Figure 2 in Painter *et al.*, 2001]. The exact dates corresponding to each depth were not determined, but the 20 cm depth was estimated to correspond to 1960-65 in the western basin core, 1965-1970 in the eastern basin core, and 1955-60 in the central basin core.

Lake Ontario

Pirrone et al. (1998) presented 1830-1980 data for a Lake Erie sediment core, shown below in Figure 99. These data generally show an increase in mercury loading from 1830 up to 1945, a broad peak from 1945-1960, and a decrease from 1960 to 1980.

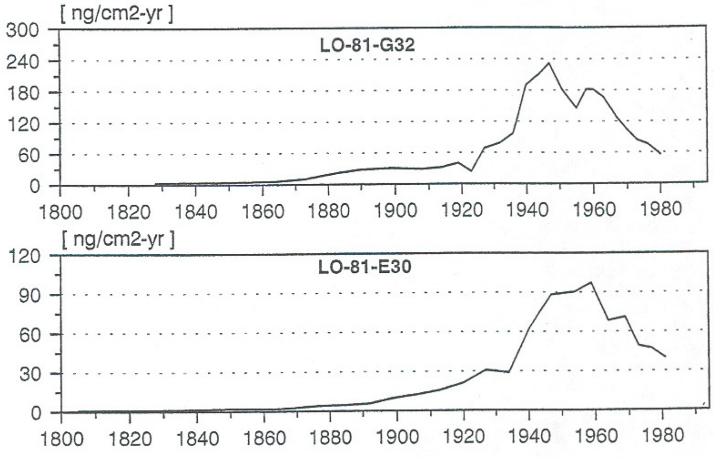

Figure 99. Mercury accumulation rates in Lake Ontario sediment cores (1830-1980). From Pirrone *et al.* (1998).

Spatial and temporal trends in sediment mercury concentrations in Lake Ontario have also been reported by Marvin *et al* (2003). A total of 66 sites were sampled in 1998. Almost all of the sediment samples (~97 percent) showed elevated mercury levels relative to the background. Sediment core analysis revealed trend information over the previous century. Mercury temporal trend data for one site is presented in the paper – and is reproduced here as Figure 100. It can be seen that the levels gradually increased to about 4-5 ug/g (dry weight) until 1940-50. A large peak appeared to exist for the next core segment corresponding to ~1955-60, in which the sediment mercury concentration rose to ~12 ug/g. The concentrations reduced significantly in the next core segment, corresponding to ~1960-65, back down to the 5 ug/g level. The concentrations dropped somewhat in ~1970, rose during the 1970's and dropped to 2 ug/g from 1980 till about ~1995. The concentration in the most recent layer (~1996-98) appears to increase again to the 5 ug/g level.

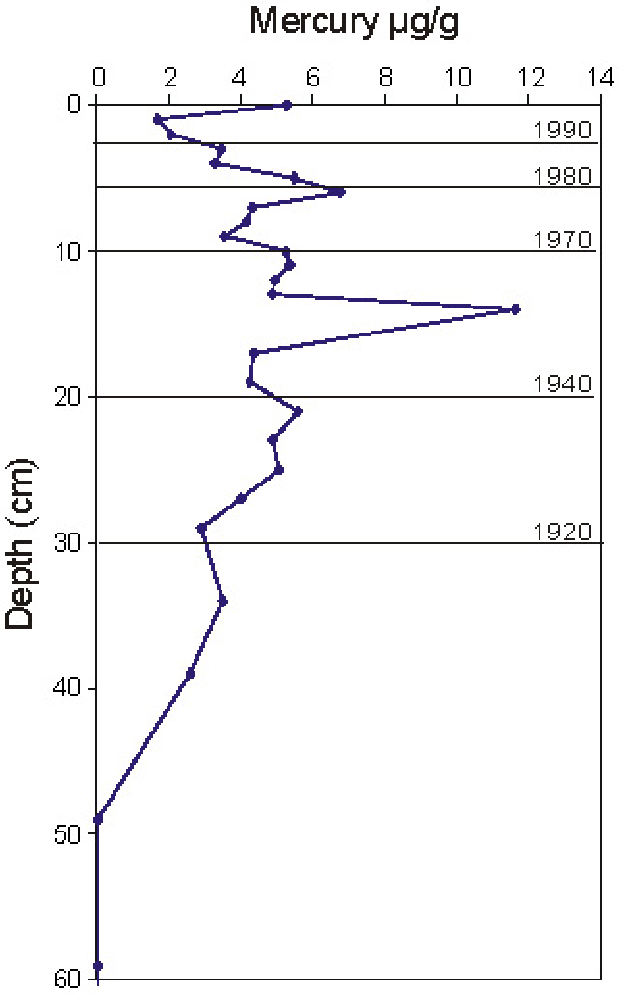

Figure 100. Trend in sediment mercury in Lake Ontario.
Profile of total mercury (ug/g dry weight) levels in a core sample from station 1034 in the Mississauga basin of Lake Ontario (from Marvin et al., 2003).

Lake Huron

Illustrations of detailed time trend sediment mercury data could not be found for Lake Huron. However, Marvin et al. (2004b) reported estimates of pre-industrial background concentrations and concentrations found during a 1969 and 2002 survey of Lake Huron sediments. Marvin and colleagues report an estimate of pre-industrial background mercury concentrations of ~0.026 µg/g. In the 1969 survey there appeared to be several areas that appeared to show anthropogenic influence, and the mean surficial sediment concentration was 0.220 µg/g. In contrast, the mean surficial sediment concentration found in the 2002 survey was 0.043 µg/g – very similar to the estimated pre-industrial background -- and far less evidence of sites with anthropogenic influence were found. Thus, there appears to have been a general decrease in the concentrations of mercury in surficial sediments in Lake Huron between 1969 and 2002.

D. Mercury Concentrations in Biota

Illustrative trend data on mercury concentrations in Great Lakes biota are presented in this section. Mercury trend data were found for several species of fish, Herring Gull eggs, and mussels.

Data on trends in Great Lakes fish have been collected and assembled by the Ontario Ministry of the Environment, the Canadian Department of Fisheries and Oceans, and Environment Canada. These Canadian agencies have assembled data only for the four Canadian Great Lakes (i.e., all lakes except Lake Michigan).

Mercury was added only recently (2001) to the routine analyte list for EPA's Great Lakes Fish Monitoring Program, and so mercury-in-fish long-term trend data for Lake Michigan – the one Great Lake with only U.S. borders – could not be found. Data on mercury *trends* in Lake Michigan fish were not found in any of the Lake Michigan LaMP documents (2000, 2002, 2004), in SOLEC documents, or in searches of the scientific literature and agency websites. It might be possible to compare fish mercury concentration data collected in the 1994-1995 Lake Michigan Mass Balance Study with recent data from the EPA's Great Lakes Fish Monitoring Program (e.g., Carlson and Swackhamer, 2006), but assembling this comparison – attempting to account for methodological and locational differences – is beyond the scope of this report.

Data on chemical contaminants – including mercury -- in Herring Gull eggs in the Great Lakes region have been collected since 1971 by the Canadian Wildlife Service (Weseloh et al., 2006; Weseloh, 2006; Koster et al., 1996).

The NOAA National Status and Trends Mussel Watch Program has monitored pollutants at over 250 sites in U.S. coastal waters, including the Great Lakes, since 1986 (Lauenstein and Cantillo, 1993a,c, 1998; O'Connor, 1996, 1998, 2002). In this program, mussels are collected and analyzed for a number of trace chemical contaminants. There are 25 sites in the Great Lakes region, and the data for these sites were obtained from the NOAA Center for Coastal Monitoring and Assessment (2006). For these Great Lakes sites, data on mercury concentrations in mussels are available for 1992-2004.

Mercury concentration data for 45-cm walleye in Lakes Superior, Huron, Ontario, and Erie are presented in Figure 101, based on data from the Ontario Ministry of the Environment (2006b) and Environment Canada (2006).

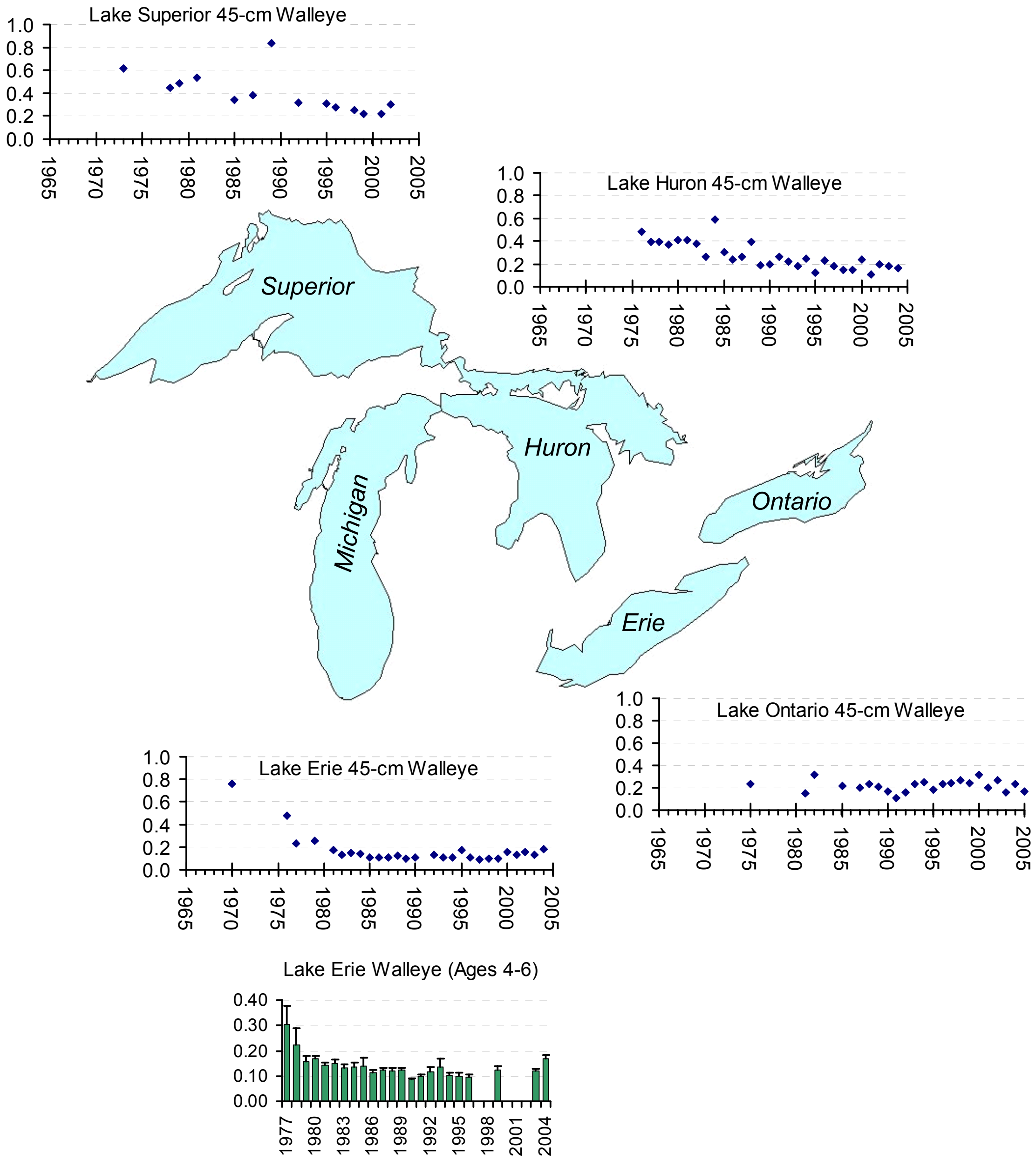

Figure 101. Mercury concentration trends Great Lakes Walleye. Total mercury concentrations (ppm or ug Hg/g). Sources of data: Ontario Ministry of the Environment (2006b), for 45-cm Walleye data, and Environment Canada (2006), for data on Lake Erie Walleye ages 4-6.

Available data for 1977-2003 on mercury concentrations in Great Lakes rainbow smelt are summarized in Figure 102 for four Great Lakes (Environment Canada, 2006). It appears that the mercury concentrations in smelt have generally decreased over this period, although the trends are not simple (e.g., Lake Erie).

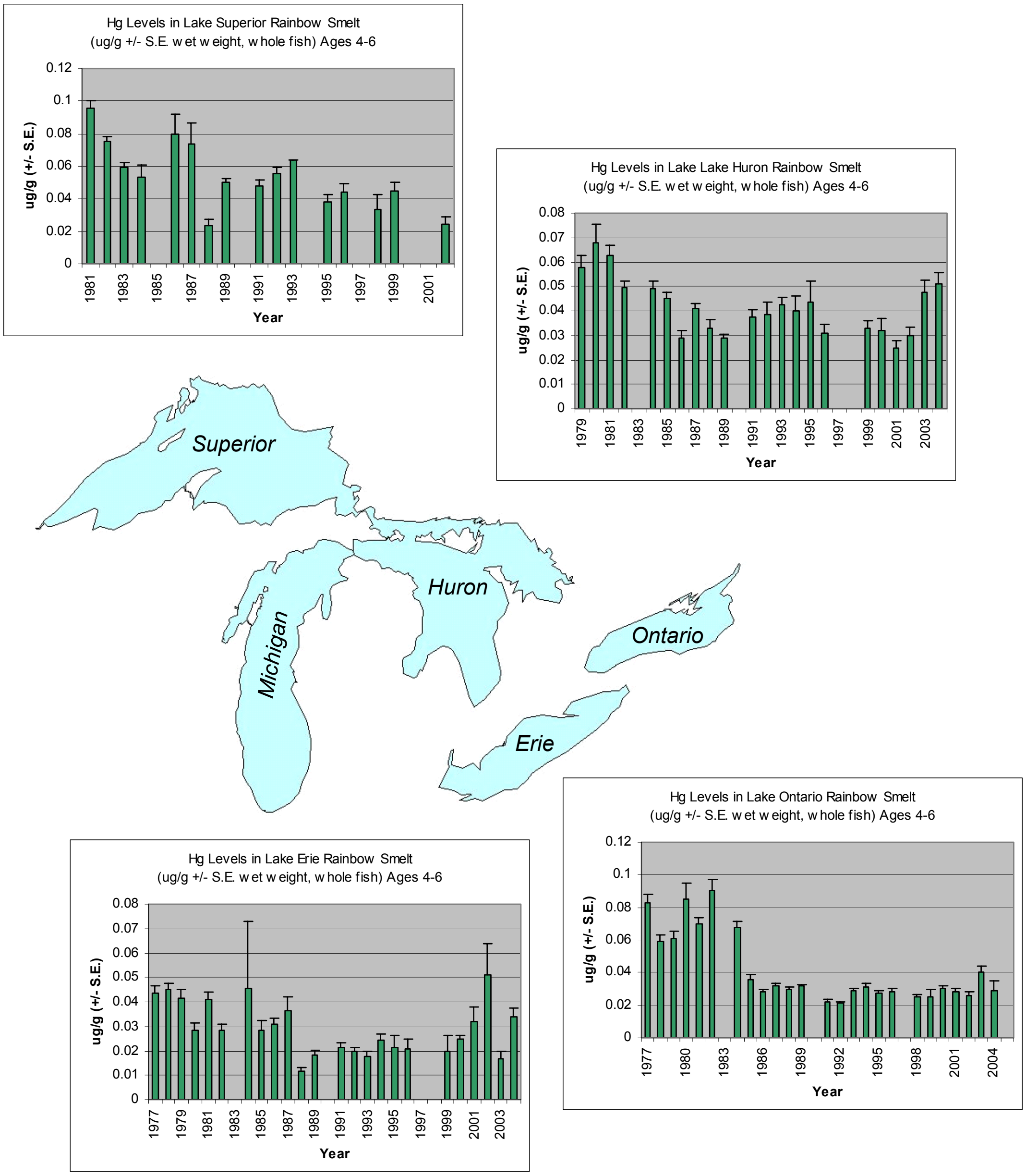

Figure 102. Total mercury levels in Great Lakes Rainbow Smelt, 1977-2004.
Source of data: Environment Canada (2006). Note that the scales for the lakes are different.

Data for mercury concentrations in Great Lakes lake trout, generally for the period from ~1980 to ~1995 smelt are summarized in Figure 103 for four Great Lakes (Environment Canada, 2006). It appears that the mercury concentrations in lake trout have generally decreased over this period, although again, the trends are not simple (e.g., Lake Superior).

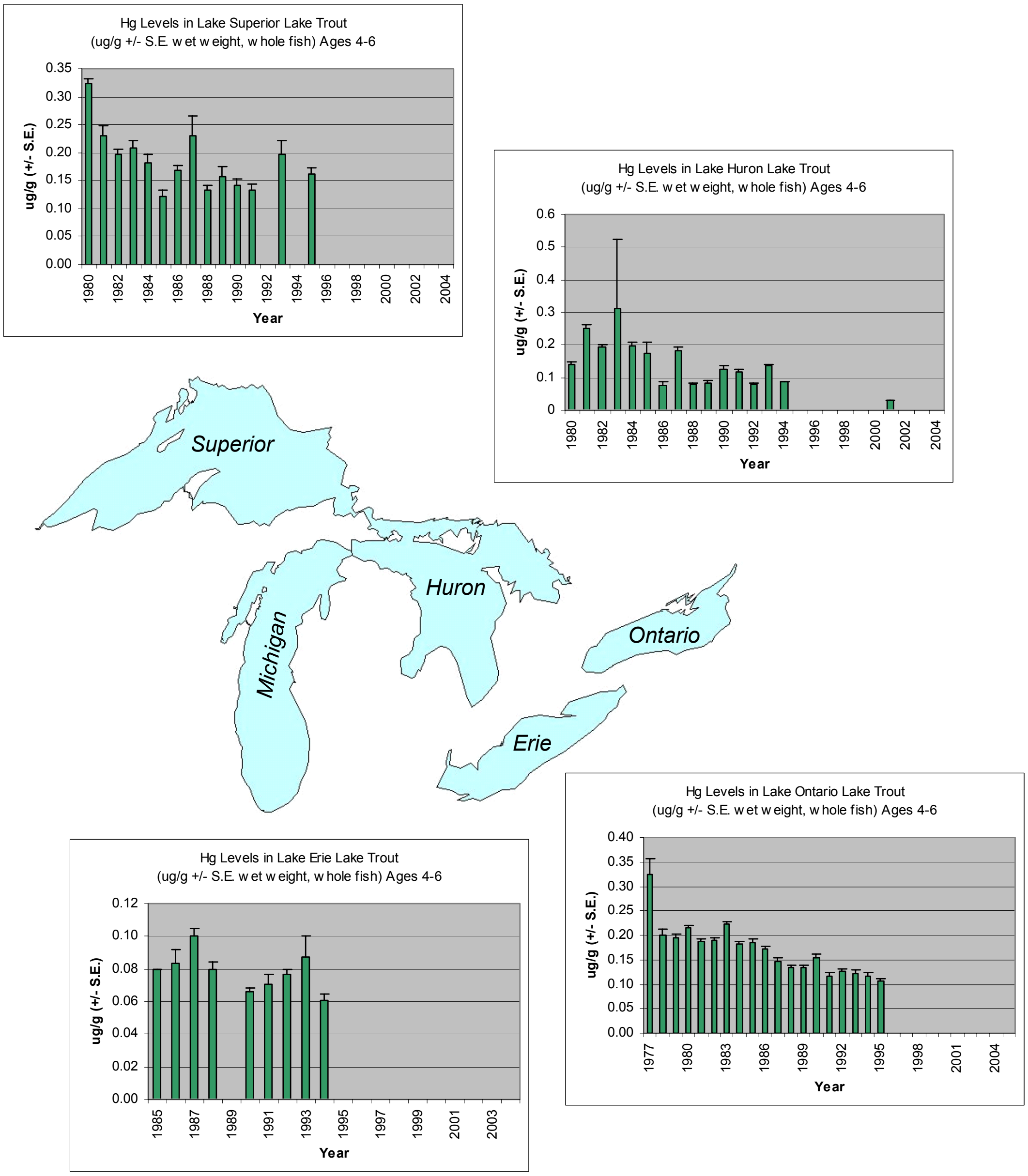

Figure 103. Mercury concentration trends in Lake Trout in the Great Lakes. Data from Environment Canada (2006). Note that for Lake Huron, there was an average of 25 fish sampled each year from 1980 to 1994, but that the data shown for 2001 represents only 1 fish.

The Lake Erie LaMP (2002) reports that mercury concentrations in Lake Erie sports fish have declined over the past 25 years. Figure 104 shows trend data in Lake Erie white bass. The majority of the decrease appears to have occurred between the 1976-80 data and the 1981-85 data. There appears to have been little change since 1981-85.

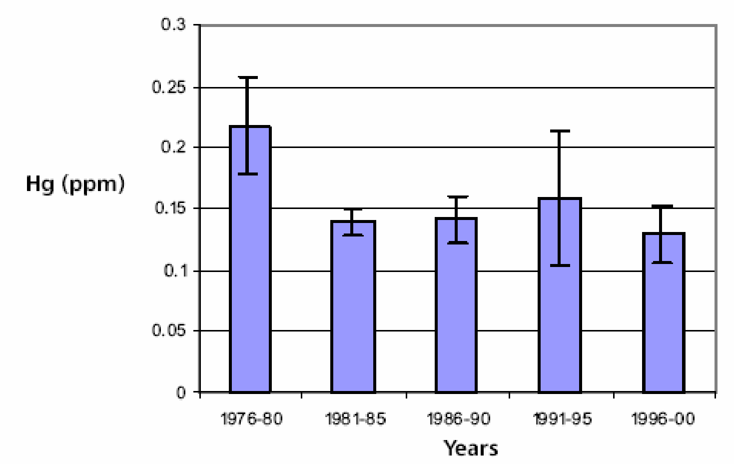

Figure 104. Trend in mercury concentrations in Lake Erie White Bass. From the Lake Erie LaMP (2002) for 30 cm (12 inch) White Bass in Lake Erie Block 1.

The Lake Ontario LaMP (2004) reports trend data in mercury concentrations in Coho salmon, collected by the Ontario Ministry of the Environment. Figure 105, taken from this document, shows the trend from 1978-2001. There appears to have been a moderate decrease over this period in mercury concentrations.

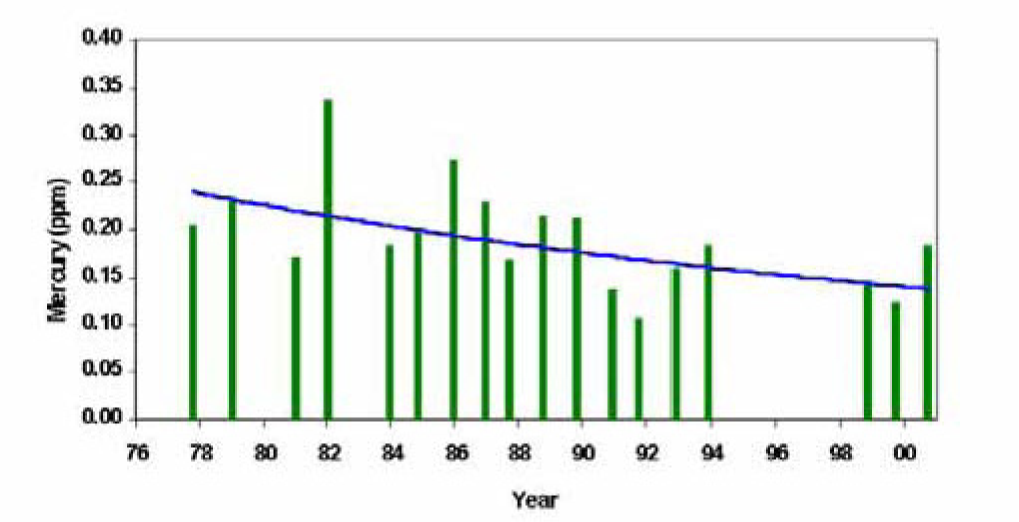

Figure 105. Mercury trend in 50-cm Lake Ontario Coho Salmon. From the Lake Ontario LaMP (2004), citing data from the Ontario Ministry of the Environment, for the Credit River spawning run.

Trends in mercury concentrations in Herring Gull eggs based on annual monitoring conducted at 15 colonies in the Great Lakes region are shown in Figure 106. It can be seen that for most of the colonies, there appears to have been a decrease in concentrations from the 1970's through the mid 1980's. For most of the colonies, the concentrations appear to have been relatively constant from the mid-1980's to 2005, the latest data available.

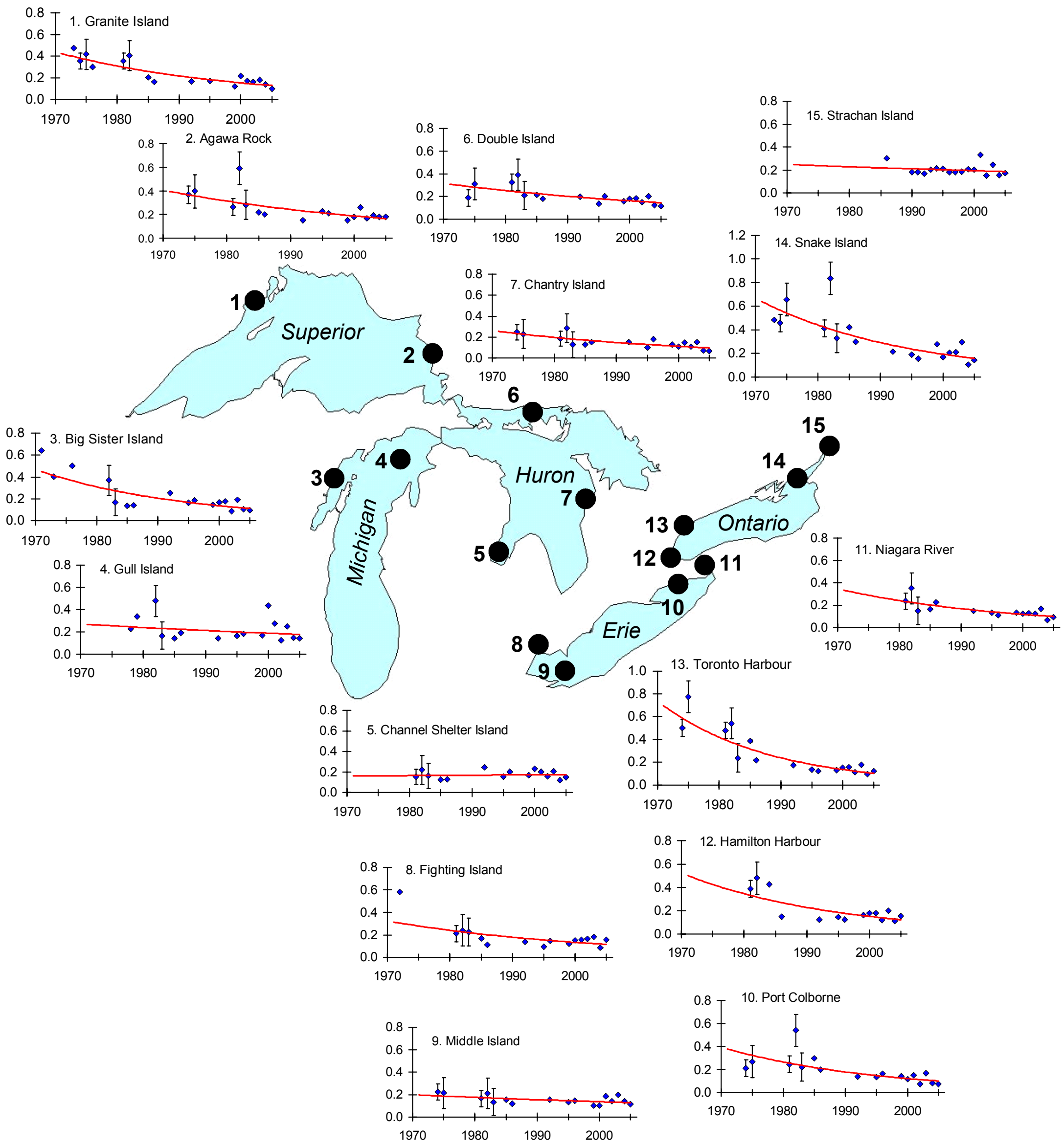

Figure 106. Trends in Herring Gull Egg Hg concentrations.
Source of data – Canadian Wildlife Service. Total mercury concentrations in eggs from colonies in the Great Lakes region expressed in units of ug Hg/g (wet weight). From 1971 – 1985, analysis was generally conducted on individual eggs (~10) from a given colony, and the standard deviation in concentrations is shown on the graphs. From 1986 to the present, analysis was generally conducted on a composite sample for a given colony. The trend lines shown are for illustration purposes only; they were created by fitting the data to a function of the form $y = cx^b$.

Trends in mercury concentrations in mussels from 1992-2004 at 25 Great Lakes region sites are presented in Figure 107, based on data from the NOAA Mussel Watch Program. There does not appear to be any consistent trend in these data. The lack of any significant trend from 1992-2004 is generally consistent with the data in other biota presented above, in which there is typically little change in concentrations from the mid-1980's to the present.

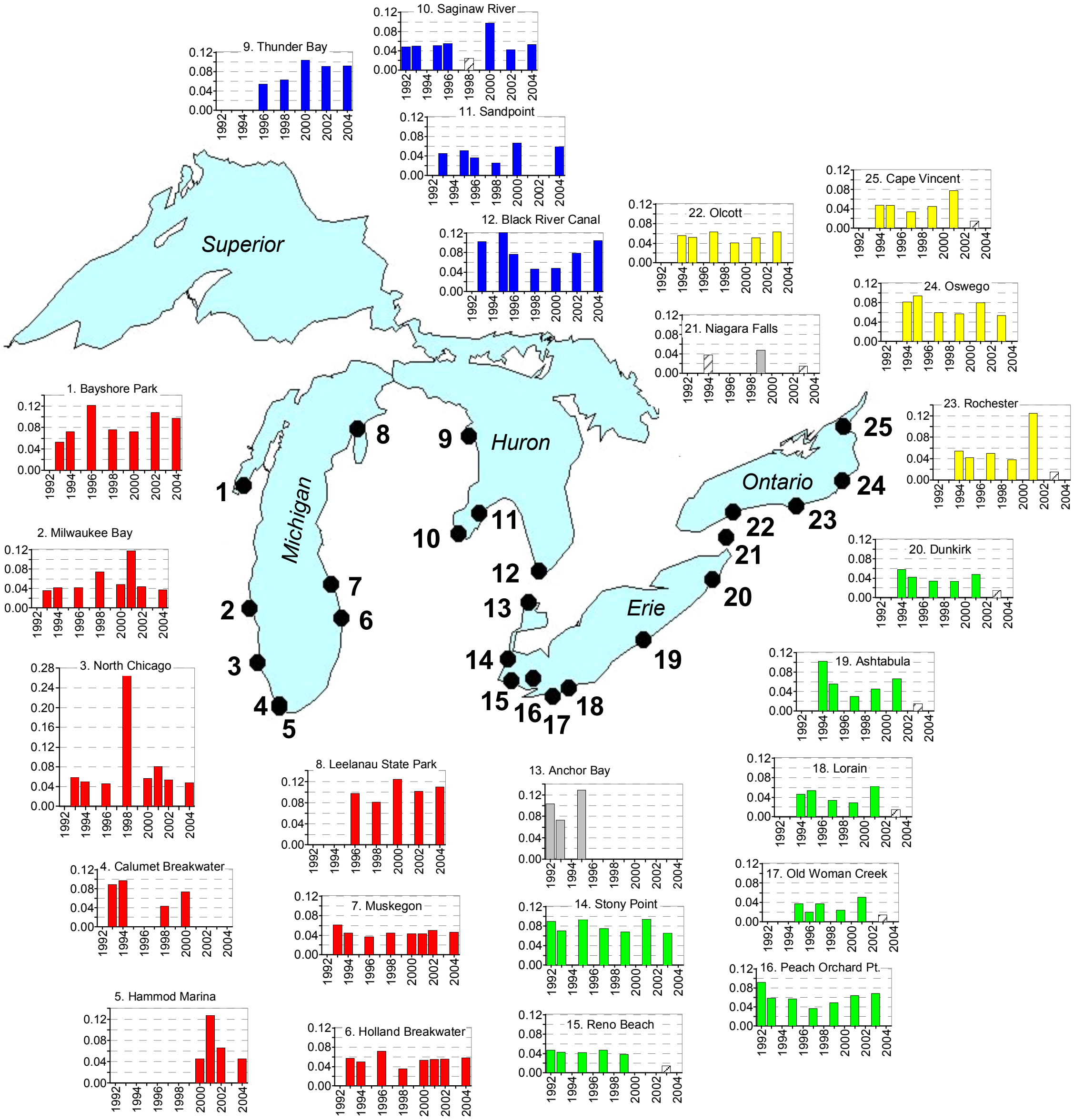

Figure 107. Mercury concentration in Great Lakes region mussels (1992-2004).
Total mercury in mussels (ug/g, on a dry weight basis). In a few cases (e.g. for several sites in 2003), mercury concentrations were below the detection limit. In these cases the concentrations are shown with a white cross-hatched bar at a value of one-half the detection limit; in reality, the mercury concentration could have been anywhere between zero and the detection limit. Source of data: NOAA Center for Coastal Monitoring and Assessment (CCMA) (2006) and "Monitoring Data - Mussel Watch" website: http://www8.nos.noaa.gov/cit/nsandt/download/mw_monitoring.aspx

E. Summary of Great Lakes Mercury Trend Data

Relevant temporal trend data for mercury in the Great Lakes region was assembled from the literature for the following: (a) emissions to the air; (b) atmospheric deposition; (c) concentrations in sediments; and (d) concentrations in fish and other biota.

Historical data on atmospheric mercury emissions in the Great Lakes region are scarce and uncertain, but it appears that they rose sharply until ~1945, were approximately level from 1945-1970, and decreased between 1970-1980. Temporal trend data for U.S. air emissions indicate a significant decrease in emissions from municipal and medical waste incinerators sometime between the early 1990's and ~2001. Over the same period emissions from coal-fired electricity generation and other source categories were relatively constant. From 1990-2000, Canadian emissions are reported to have decreased by ~75 percent, largely due to process changes at metal smelting facilities.

The longest available wet deposition data records in the Great Lakes region are for 1996-2003 at five Mercury Deposition Network sites. There were only moderate changes in estimated ionic mercury emissions in the vicinity of these sites between 1995-1996 and 1999-2001, but the precise timing of these changes is not known. Thus, it is difficult to determine if the trends in precipitation mercury concentrations are related to these reductions. Overall, there may have been a decrease in concentration between 2000 and 2001, and this may have been related to decreases in regional mercury emissions from waste incinerators (i.e., if the emissions reductions at the relevant incinerators occurred at this time). Detailed atmospheric fate and transport modeling could be done to investigate this issue. However, an accurate, time-resolved emissions inventory for each of the large emissions sources in the region would be required.

Model-estimated deposition to the Great Lakes decreased significantly between 1995-1996 and 1999-2001, primarily due to decreases in mercury emissions from U.S. municipal and medical waste incinerators. In both periods, the model results suggest that U.S. sources contributed much more to Great Lakes atmospheric mercury deposition than Canadian sources.

Examples of sediment mercury trend data were found for each of the Great Lakes except for Lake Huron. The data typically show a 1940-1960 peak in sediment mercury, and in some cases there are also secondary peaks in the 1970's. Since the 1970's sediment mercury concentrations appear to have generally been decreasing in the Great Lakes.

Data on mercury levels in Great Lakes fish and Herring Gull eggs are generally available starting in the 1970's, while data on levels in mussels are available beginning in 1992. While there are variations among species and among lakes, the data generally seem to show a reduction from 1970 to the mid-1980's, with little change since the mid-1980's. This is most likely due to the significant reduction that occurred in the 1970's in effluent discharges to the Great Lakes (and their tributaries) from a number of sources (e.g., chlor-alkali plants).

5. Appendices

Appendix A.

EPA Clean Air Mercury Rule: Air Quality Modeling and Deposition Results

The U.S. Environmental Protection Agency (EPA)
authored this Appendix and requested that
it be included in this Report to Congress.

Appendix A.
EPA Clean Air Mercury Rule: Air Quality Modeling and Deposition Results

This chapter summarizes the air quality modeling conducted by the U.S. Environmental Protection Agency in support of the Clean Air Mercury Rule (CAMR) promulgated in March 2005 (U.S. EPA, 2005a). EPA used a sophisticated photochemical air quality model to predict the levels of mercury deposition for a 2001 base year and a 2020 projection reflecting co-control of mercury from implementation of the Clean Air Interstate Rule (CAIR) and CAMR. We estimated utility attributable deposition of mercury based on zero-out modeling for both the 2001 and 2020 baselines. In addition, as part of the Regulatory Impact Analysis (RIA) for the final rule, the estimated changes in mercury deposition associated with the control options were then combined with fish tissue data for use in estimating health and welfare effects of CAMR (U.S. EPA, 2005c and U.S. EPA, 2005d).

The Agency views the application of a robust and sophisticated modeling approach as critical and required for assessing the mercury deposition associated with CAMR because of the density and properties of mercury and its complex transport and reactions in the atmosphere. The Community Multiscale Air Quality (CMAQ) modeling system best met EPA's requirements and the recommendations of the 1997 Mercury Study Report to Congress for a "single air quality model" to address mercury deposition. CMAQ is a three-dimensional grid-based Eulerian air quality model designed to estimate pollutant concentrations and depositions over large spatial scales (e.g., over the contiguous United States). It accounts for spatial and temporal variations as well as differences in the reactivity of mercury emissions. In addition, the boundary and initial species concentrations are provided by a three-dimensional global atmospheric chemistry and transport model, i.e., Harvard's GEOS-CHEM model. The model simulations are performed based on power plant-specific emissions of mercury by species as provided by the Integrated Planning Model (IPM) and similar projections for other sources (U.S. EPA, 2005b and U.S. EPA 2005d).

Section I provides a summary of the emissions inventories that were modeled for this assessment. Section II discusses the model and its configuration and inputs for this application. Section III summarizes the model performance based on available 2001 monitoring data. Section IV summarizes the results of estimating mercury depositions for the 2001 and 2020 scenarios modeled. Section V provides the references for this chapter.

I. 2001 and 2020 Emissions Inventories

This section summarizes the emissions inventories that serve as the inputs to the air quality model used for the Clean Air Mercury Rule. The CAMR Emissions Inventory Technical Support Document (TSD) discusses the development of the 2001 and 2020 emissions inventories for input to the air quality modeling of this final rule in greater detail (U.S. EPA, 2005b). Table 1 provides the emission sources and the basis for current and future-year inventories, while Table 2 summarizes the mercury emissions by species from utilities, also known as Electric Generating Units (EGUs), and other sources that were used in modeling of mercury deposition.

As Table 2 demonstrates, a total of almost 115 tons of mercury were emitted by all US sources in 2001. EGUs emitted a total of 48.6 tons, or 42.3 percent of mercury emissions from US sources during this base year. Almost 21 tons of the most readily deposited form of mercury, i.e., reactive gaseous mercury (RGM), were emitted by these utilities and therefore comprised 42.4 percent of their mercury emissions.

The 2020 baseline emissions shown in Table 2 accounts for increases in economic activity and population growth between 2001 and 2020 that lead to increased production in the utility and manufacturing sectors and hence increases in emissions over time, as well as the implementation of regulatory policies from MACT standards (primarily on non-EGU sources) and the CAIR controls (as applied to EGUs in the eastern U.S.) which decreases emissions over this time period. Total mercury emissions in 2020 are roughly 87 tons, reflecting a net reduction of almost 28 tons (or 24 percent) from 2001 levels. As shown, the 2020 baseline with CAIR shows net reductions in mercury emissions for EGUs of 14.2 tons, or a 29.1 percent reduction, from 2001 levels. Utility emissions are expected to account for 39.5 percent of total mercury emissions in 2020, which is only slightly lower than their share in 2001. However, the reductions associated with CAIR co-control show a large reduction of 61.8 percent in their emissions of reactive gaseous mercury relative to their 2001 level of emissions, i.e., 20.58 tons in 2001 to only 7.87 tons in 2020.

Table 3 shows the reductions in mercury emissions associated with the CAMR in 2020. The 2020 EGU emissions are reduced by approximately 10 tons to a total of 25 tons, representing a 11 percent reduction from total baseline emissions in 2020 (with CAIR), or a 27 percent reduction from the EGU sector alone. In comparison to current mercury emissions (i.e., the 2001 base year scenario), the total reduction in EGU emissions under the CAIR and CAMR is approximately 24 tons (or 48 percent).

Table 1. Summary of Emissions Sources for 2001 and 2020 Mercury Emissions Inventories

Sector	Emissions Source	2001 Base Year	2020 Base Case Projections
Utilities - Electric Generating Units (EGU)	Power industry electric generating units (EGUs)	1999 National Emission Inventory (NEI) data	Integrated Planning Model (IPM) reflecting growth in Btu demand as well as regulatory policies implemented through 2020, such as the Clean Air Interstate Rule
Non-EGU point sources	Non-Utility Point	1999 NEI, with medical waste incinerator sources replaced with draft 2002 NEI	(1) Department of Energy (DOE) fuel use projections, (2) Regional Economic Model, Inc. (REMI) Policy Insight® model, (3) decreases to REMI results based on trade associations, Bureau of Labor Statistics (BLS) projections and Bureau of Economic Analysis (BEA) historical growth from 1987 to 2002, (4) Maximum Achievable Control Technology category growth and control assumptions
Non-point sources	All other stationary sources inventoried at the county level	1999 NEI, with medical waste incinerator sources replaced with draft 2002 NEI	same as above

[a] This table documents only the sources of data for the U.S. inventory. The sources of data used for Canada and Mexico are explained in the technical support memorandum and were held constant from the base year to the future years.

Table 2. Summary of Mercury Emissions by Species: 2001 and 2020 (with CAIR) Baselines

Emissions Source	Mercury Emissions Species (tons)			Total Mercury Emissions (tons)
	Elemental	Reactive Gaseous	Particulate	
2001 Base Year				
EGUs	26.26	20.58	1.73	48.57
Non-EGU Point	37.85	13.33	7.60	58.78
Non-point	5.05	1.53	0.96	7.54
Total, All Sources	69.16	35.44	10.29	114.89
2020 (with CAIR) Baseline				
EGUs	25.72	7.87	0.83	34.42
Non-EGU Point	28.03	10.37	6.61	45.01
Non-point	5.69	1.30	0.77	7.76
Total, All Sources	59.44	19.54	8.21	87.19

Table 3. Summary of Changes in Mercury Emissions Associated with CAMR: 2020

Emissions Source	Change in Mercury Emissions Species (tons)			Total Change in Mercury Emissions (tons)
	Elemental	Reactive Gaseous	Particulate	
EGUs	8.07 (31.4%)	1.30 (16.5%)	0.00 (0.0%)	9.37 (27.2%)
Non-EGU Point	n/a	n/a	n/a	n/a
Non-point	n/a	n/a	n/a	n/a
Total, All Sources	8.07 (13.6%)	1.30 (6.7%)	0.00 (0.0%)	9.37 (10.7%)

Note: n/a is not applicable.

II. CMAQ Model Overview, Inputs, and Application

The Community Multiscale Air Quality (CMAQ) modeling system is a comprehensive three-dimensional grid-based Eulerian air quality model designed to estimate pollutant concentrations and depositions over large spatial scales (Dennis et al., 1996; Byun and Ching, 1999; Byun and Schere, 2004). The CMAQ model is a publically available, peer-reviewed, state-of-the-science model consisting of a number of science attributes that are critical for simulating the oxidant precursors and non-linear chemical relationships associated with the formation of mercury. Version 4.3 of CMAQ (Byun and Schere, 2004, Bullock and Brehme, 2002) was used for CAMR. This version reflects updates to earlier versions in a number of areas to improve the underlying science and address comments from peer review. This model is fully described in the Air Quality Modeling Technical Support Document for the Final Clean Air Interstate Rule (Docket #OAR-2003-0053-2151).

The updates in mercury chemistry used for CAMR from that described in (Bullock and Brehme 2002) are as follows:

- the elemental mercury (Hg0) reaction with H_2O_2 assumes the formation of 100 percent reactive gaseous mercury (RGM) rather than 100 percent particulate mercury (HgP)
- the Hg0 reaction with ozone assumes the formation of 50 percent RGM and 50 percent HgP rather than 100 percent HgP
- the Hg0 reaction with OH assumes the formation of 50 percent RGM and 50 percent HgP rather than 100 percent HgP,
- the rate constant for the Hg0 + OH reaction was lowered from 8.7 to 7.7 $\times 10^{-14} cm^3 molecules^{-1} s^{-1}$

CMAQ simulates every hour of every day of the year and requires a variety of input files that contain information pertaining to the modeling domain and simulation period. These include hourly emissions estimates and meteorological data in every grid cell as well as a set of pollutant concentrations to initialize the model and to specify concentrations along the modeling domain boundaries. These initial and boundary concentrations were obtained from output of a global chemistry model. We use the model predictions in a relative sense by first determining the ratio of mercury deposition predictions. The calculated relative change is then combined with the corresponding fish tissue concentration data to project fish tissue concentrations for the future case scenarios. The following sections provide a more detailed discussion of the modeling and a summary of the results.

Key science aspects of CMAQ as applied for CAMR include:

- Gas-Phase Chemical Solver: Euler Backward Iterative (EBI) scheme
- Advection Scheme (vertical and horizontal): Piecewise Parabolic Method (PPM) scheme
- Vertical Diffusion: K-theory eddy diffusivity scheme; minimum diffusivity is 1 m^2/sec
- Dry Deposition: M3DRY module, modified RADM scheme with Pleim-Xiu land surface model
- Aqueous Chemistry: RADM Bulk scheme
- Cloud Scheme: RADM Cloud scheme
- Vertical Coordinate: Terrain-following Sigma coordinate

II.A CMAQ Modeling Domain and Configuration

As shown below in Figure 1, the CMAQ modeling domain encompasses all of the lower 48 States and extends from 126 degrees west longitude to 66 degrees west longitude and from 24 degrees north latitude to 52 degrees north latitude. The modeling domain is segmented into rectangular blocks referred to as grid squares. The model predicts pollutant concentrations and depositions for each of these grid cells. For this application the horizontal domain consisted of 16,576 grid cells that are roughly 36 km by 36 km. The modeling domain contains 14 vertical layers with the top of the modeling domain at about 16,200 meters, or 100 millibar. The height of the surface layer is 38 meters. More information on the vertical layer structure for CMAQ that was used for the CAMR applications can be found in the Air Quality Modeling for CAMR Technical Support Document (U.S. EPA 2005a).

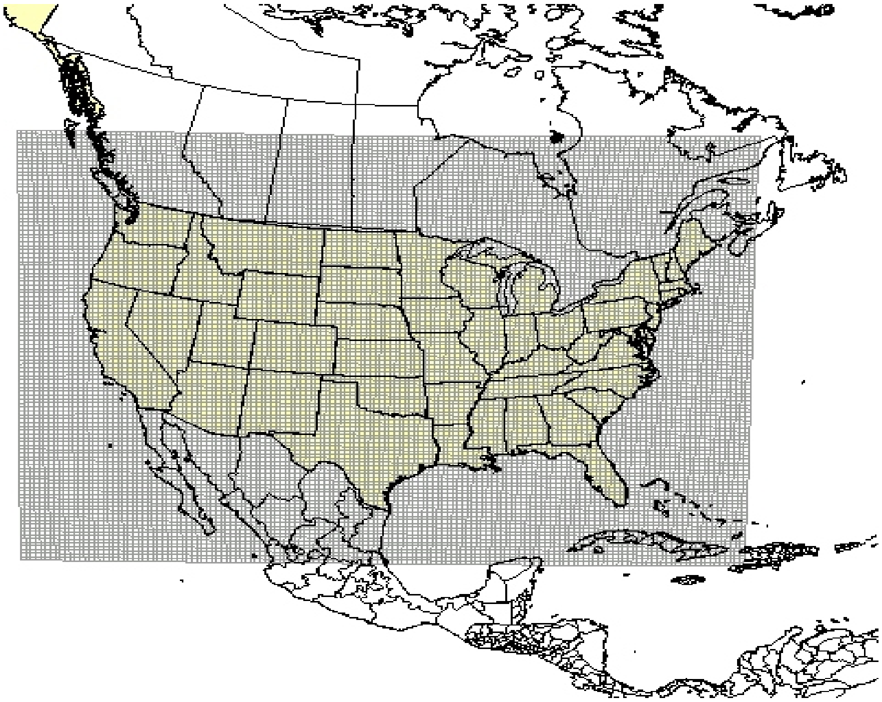

Figure 1. CMAQ Modeling Domain

II.B Time Period Modeled For Mercury Deposition

CMAQ was run for a full year for each emissions scenario modeled under CAMR. The overall model run time for completing an annual simulation was reduced by dividing the year into two six-month periods which were run in parallel on different computer processors. That is, the annual simulation was performed as two separate six month model runs. One run was for January through June and the other run was for July through December. Each six-month runs included a 10-day ramp-up (i.e., "spin-up") period designed to minimize the influence of the initial concentration fields (i.e., initial conditions) used at the start of the model run. The development of initial condition concentrations is described in Section D below. The ramp-up periods used for the CAMR CMAQ applications are as follows:

- first six-month ramp-up period is December 22 - 31, 2000
- second six-month ramp-up period is June 21 - 30, 2001

Model predictions from these ramp-up periods were discarded and not used in analyses of the modeling results. The meteorological conditions, initial conditions and boundary conditions were held constant for each of the emissions scenarios modeled and are described below in sections II.C and II.D.

II.C Meteorological Inputs to CMAQ

Meteorological data, such as temperature, wind, stability parameters, and atmospheric moisture contents influence the formation, transport, and removal of air pollution. The CMAQ model requires a specific suite of meteorological input files in order to simulate these physical and chemical processes. For the CAMR CMAQ modeling, meteorological input files were derived from a simulation of the Pennsylvania State University / National Center for Atmospheric Research Mesoscale Model (Grell et al., 1994) for the entire year of 2001. These data inputs and model preprocessor code are available as part of the public docket for EPA's Clean Air Interstate Rule (CAIR) (Docket #OAR-2003-0053-1688). This model, commonly referred to as MM5, is a limited-area, nonhydrostatic, terrain-following system that solves for the full set of physical and thermodynamic equations which govern atmospheric motions. For this analysis, version 3.6.1 of MM5 was used. The MM5 horizontal domain consisted of a single 36 x 36 km grid with 165 by 129 cells, selected to maximize the coverage of the Eta model analysis region and completely cover the CMAQ modeling domain with some buffer to avoid boundary effects. The MM5 was run on the same map projection as CMAQ. The 2001 meteorological modeling utilized 34 vertical layers with a surface layer of approximately 38 meters.

A complete description of the configuration and evaluation of the 2001 meteorological modeling is contained in McNally (2003), however some of the key model physics options are as follows:

- Cumulus Parameterization: Kain-Fritsch
- Planetary Boundary Layer Scheme: Pleim-Chang
- Explicit Moisture Scheme: Reisner 2
- Radiation Scheme: RRTM longwave scheme
- Land Surface Model: Pleim-Xiu
- Four-Dimensional Data Assimilation (FDDA): analysis nudging only

The annual MM5 simulation was divided into four separate periods: 12/16/00 to 4/05/01, 3/16/01 to 7/05/01, 6/14/01 to 10/02/01, and 9/17/01 to 2/04/02. Within each of these periods the model was run for 5 ½ days blocks with a restart occurring at 1200 UTC every fifth day. To assure continuity in the surface moisture, the model initial conditions were updated with the soil conditions from the end of the previous 5 ½ day period using the EPA "INTERPX" processor.

In terms of the 2001 MM5 model performance evaluation, we used an approach which included a combination of qualitative and quantitative analyses to assess the adequacy of the

MM5 simulated fields. The qualitative aspects involved comparisons of the model estimated sea level pressure and radar reflectivity fields against observed values of the same parameters from historical weather chart archives. The statistical portion of the evaluation examined the model bias and error for temperature, water vapor mixing ratio, and the index of agreement for the wind fields. These statistical values were calculated on a regional basis. The results of the evaluation indicate that the 2001 model data had a bias in surface temperature of -0.6 degrees Celsius and the error averaged 2.1 degrees C. The humidity fields had a bias of -0.2 g/kg and an error of 1.0 g/kg. The wind speed index of agreement averaged 0.86. The model was found to overestimate precipitation, on average by about 1.6 cm. The precipitation bias was strongest in the summer. Qualitatively, the model fields closely matched the observed synoptic patterns, which is expected given the use of FDDA. In general, the bias and error values associated with the 2001 data are in the range of model performance found from other non-EPA regional meteorological model applications (Environ, 2001).

The MM5 outputs were processed to create model-ready inputs for CMAQ using the Meteorology-Chemistry Interface Processor (MCIP) as described in U.S. EPA (1999). MCIP version 2.2gvm was used to convert the MM5 output to CMAQ meteorological input. This version contained two differences from the main MCIP version 2.2 in that: 1) it allowed for treatment of the graupel associated with the Reisner 2 microphysics scheme and 2) it included a patch to compensate for a minor error in MM5 associated with vegetation fractions.

II.D Initial and Boundary Condition Inputs to CMAQ

In this section we describe the approach used to provide the boundary conditions (BCs) and the concentrations used to initialize the model runs for the CAMR CMAQ modeling. Non-episodic national modeling, such as the CAMR annual mercury modeling, requires the prescription of BC's to account for the influx of pollutants and precursors from the upwind source areas outside the modeling domain. The pollutant influxes from the upwind boundaries, which are often dynamic in nature, can affect pollutant concentrations within the modeling domain. For example, a number of recent studies show that long-range, intercontinental transport of pollutants is important for simulating seasonal/annual ozone, PM and mercury (Jacob, et al., 1999; Jaffe et al., 2003; Fiore, et al., 2003, Selin 2005). A scientifically sound approach to estimate incoming pollutant concentrations associated with intercontinental transport is to use a global chemistry model to provide dynamic BCs for the regional model simulations**.**

For the CAMR annual mercury modeling, we used the predictions from a global three-dimensional chemistry model, the GEOS-CHEM model (Yantosca, 2004), to provide the BCs and initial concentrations. The global GEOS-CHEM model simulates atmospheric chemical and physical processes driven by assimilated meteorological observations from the NASA's Goddard Earth Observing System (GEOS). This model was run for 2001 with a grid resolution of 2 degree x 2.5 degree (latitude-longitude) and 20 vertical layers. The predictions were used to provide one-way dynamic BCs at 3-hour intervals and initial concentration field for the CMAQ simulations. We used an interface utility tool developed at the University of Houston (Byun and Moon, 2004; Moon and Byun, 2004) to link the GOES-CHEM with CMAQ. The scale, chemical, and dynamic linking between the two models are needed since the horizontal and vertical coordinates, chemical species representations, and model output time are different. A detailed description of how the GEOS-CHEM model outputs were used to develop inputs to CMAQ including the data preparation, spatial and temporal conversion procedures, and species mapping tables are given in Moon and Byun (2004).

II.E CMAQ Model Applications

For the air quality modeling in support of CAMR, CMAQ was run for a number of emissions scenarios including:

- a 2001 base year,
- a 2001 base year with utility mercury emissions zeroed-out,
- a 2020 projection with CAIR incorporated,
- a 2020 projection with utility mercury emissions zeroed-out, and
- a 2020 projection with CAIR and CAMR incorporated.

These scenarios allowed for determination of the US utility contribution to total mercury deposition across the nation as well as the incremental future impact of CAIR and CAMR in reducing utility attributable mercury deposition.

III. CMAQ Model Performance Evaluation

At this point in time, it is difficult to assess model performance for total mercury deposition. Scientist currently believe through analysis of very limited measurements that wet and dry deposition are approximately equal in magnitude. There currently is no measurement network to evaluate the performance of models in estimating dry deposition of mercury. Thus, we are not able to evaluate the performance of air quality models in predicting dry deposition. There is a network of mercury wet deposition monitors, which are scattered throughout remote locations in the United States and Canada, mostly in the east. Thus, model predictions of wet deposition can be evaluated by a monitoring network.

An operational model performance evaluation for mercury wet deposition for 2001 was performed to estimate the ability of the CMAQ modeling system to replicate base-year wet depositions of mercury. The wet deposition evaluation principally comprises statistical assessments of model versus observed pairs that were matched in time and space on a seasonal and annual basis. The statistics are presented separately for the entire domain, the East, and the West (using the 100th meridian to divide the eastern and western United States).

III.A Results of CMAQ Model Performance Evaluation

For mercury wet deposition, this evaluation includes comparisons of model predictions to the corresponding measurements from the Mercury Deposition Network (MDN). The statistics were calculated using the predicted-observed pairs for the full year of 2001 and for each season, separately. Only sites where data was available more than half the weeks in a season were utilized for the seasonal performance evaluation and only sites that had four seasons meeting this data completeness requirement were utilized for the annual performance evaluation. There were 52 MDN sites in 2001 that meet the annual data completeness requirements, of those sites 48 were located in the east and 4 were located in the west. The results for the annual performance evaluation are shown below in Table 4. The format of all the statistics is such that negative bias values indicate model predictions that were less than their observed counterparts. Positive bias values indicate model overestimation of observed counterparts.

Table 4. CMAQ Performance Statistics for Mercury Wet Deposition: 2001

Area	**No. of MDN Sites**	**Mean CMAQ Predictions (ug/m^2)**	**Mean Observations (ug/m^2)**	**Ratio of Means (pred/obs)**	**Bias (ug/m^2)**	**Fractional Bias (%)**	**Fractional Error (%)**
Entire Domain	**52**	**7.29**	**9.46**	**0.77**	**-2.17**	**-23.2**	**30.2**
East	**48**	**7.25**	**9.79**	**0..74**	**-2.55**	**-27.0**	**30.2**
West	**4**	**7.76**	**5.41**	**1.43**	**2.34**	**21.7**	**30.5**

The results contained in Table 4 shows that averaged annually over all MDN monitoring sites, CMAQ underestimates mercury wet deposition by approximately 23 percent with an fractional error of approximately 30 percent. The 4 MDN sites in the west do not provide an adequate or representative basis for inferring model performance.

A scatter plot of the observed versus predicted annual mercury wet deposition for all the sites is shown below in Figure 2. It can be seen that although the CMAQ model tends to underpredict mercury wet deposition on average, the majority of predictions are within 30 percent of observed values. Most of the remaining sites have predictions that are within 50 percent of observations. There is one site in the west in British Columbia where the model overpredicts by greater than a factor of 2. However, the precipitation at this site was overpredicted by the meteorological input model by 55 percent.

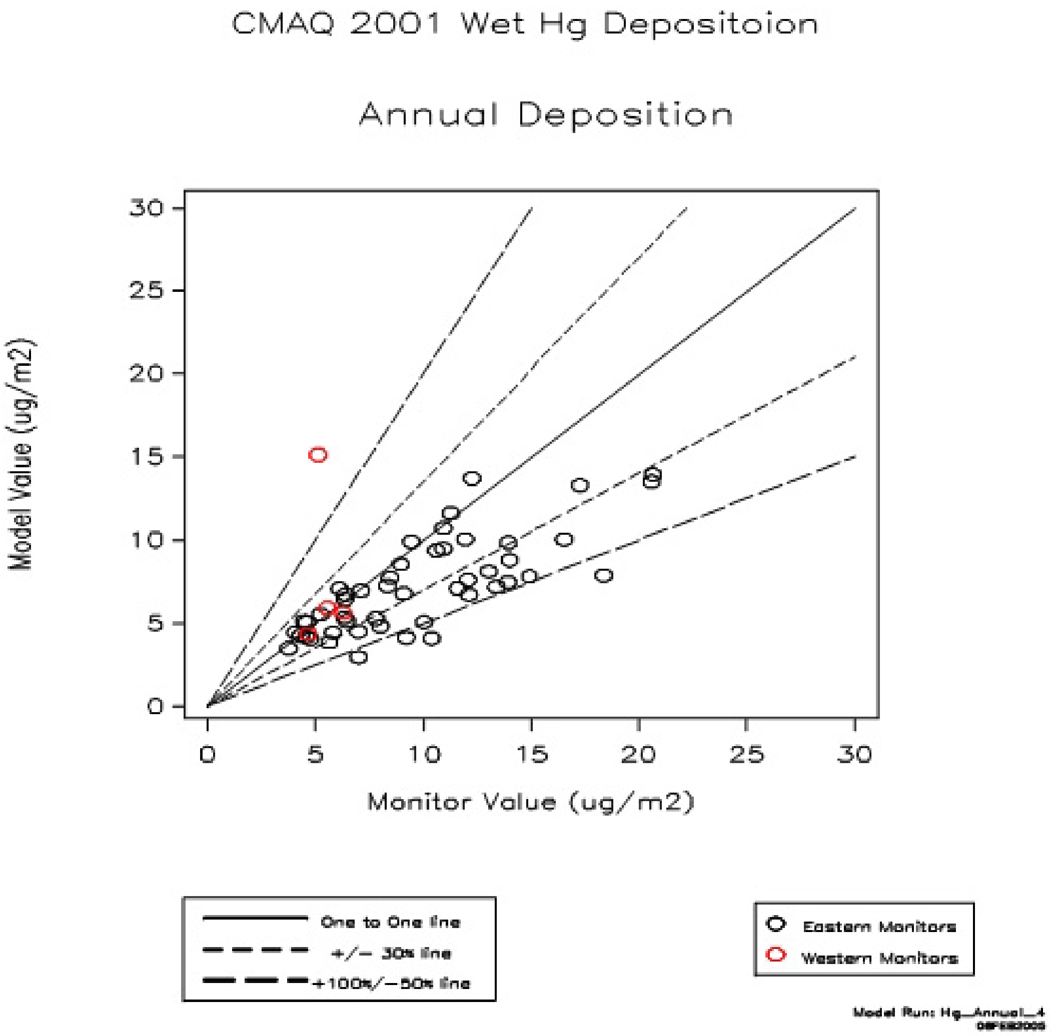

Figure 2. Scatter Plot of Modeled Versus Monitored Mercury Wet Deposition: 2001

IV. Impacts of CAMR on Mercury Depositions

Section IV.A discusses the results of the mercury deposition modeling for the 2001 base case, 2020 CAIR and 2020 CAMR modeling. Section IV.B provide results specific to the Great Lakes region for the purposes of this report.

IV.A Mercury Deposition for 2001 Base Case, 2020 CAIR and CAMR

Maps showing the mercury deposition results are provided below. The annual total mercury deposition predicted by CMAQ for the 2001 base case is shown in Figure 3. As shown, we observe higher predicted mercury deposition in the Ohio River Valley, along the Gulf Coast and Pacific West Coast, and Chicago area along Lake Michigan. Figure 4 provides the CMAQ predicted reduction in total mercury deposition that would result if all US power plant mercury emissions were zeroed-out. This figure identifies those areas of the US that are most influenced by mercury emissions from US power plants, which is concentrated in the eastern US along the Ohio River Valley.

Figure 5 provides the CMAQ predicted annual total mercury deposition for 2020 with CAIR, and Figure 6 provides the change in total mercury deposition in 2020 with CAIR relative to 2001 base case. As shown, the implementation of CAIR and other minor non-utility mercury emissions decreases in 2020 result in a similar reduction in total mercury deposition as completely eliminating power plant mercury emissions (from Figure 4). The main cause of this result is that CAIR results in a very large decrease in reactive gaseous mercury (RGM) emissions from US power plants through the implementation of scrubber control technology (see Table 2). RGM is the most readily deposited form of mercury. The change in total mercury deposition in 2020 with CAMR incremental to CAIR implementation is shown in Figure 7. As shown in Figure 7, the implementation of CAMR results in some scattered total mercury deposition reductions beyond CAIR in 2020 but, for the most part, these reductions are not large compared to those obtained by CAIR in 2020 relative to 2001 base case. Most of the mercury emissions reductions from CAMR are in the form of elemental mercury (Hg0). This form of mercury is not readily deposited, but enters the global pool of mercury. Thus, CAMR will result in a reduction of the transport of mercury to other places in the world.

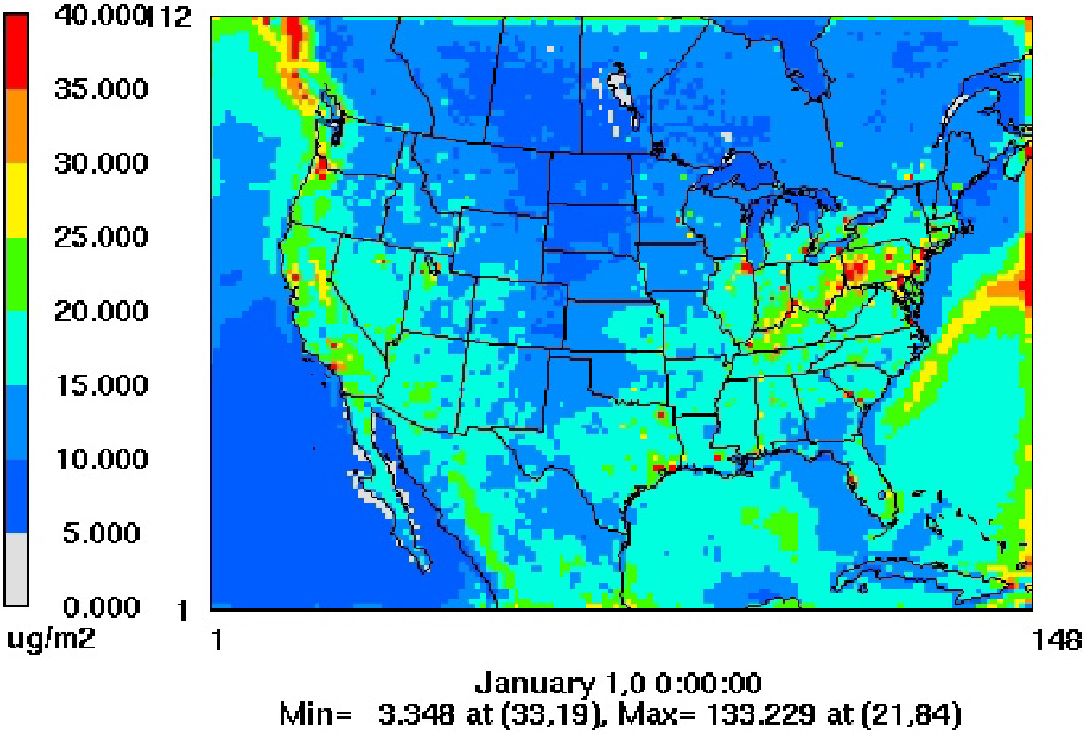

Figure 3. Base Case Total Mercury Deposition: 2001

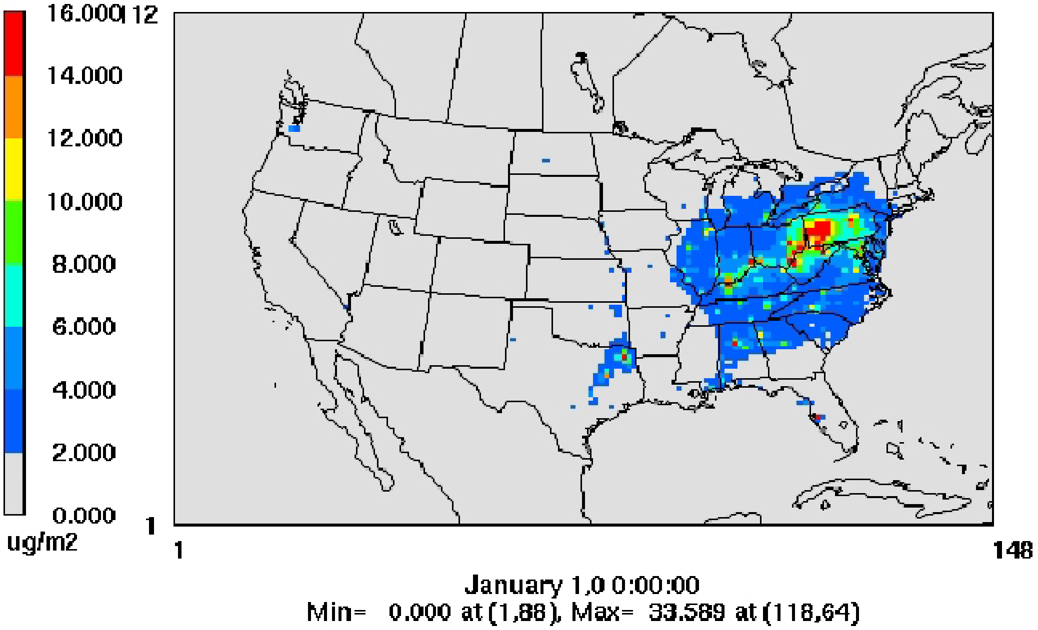

Figure 4. Decrease in Total Mercury Deposition with Power Plant Zero-Out Simulation: 2001

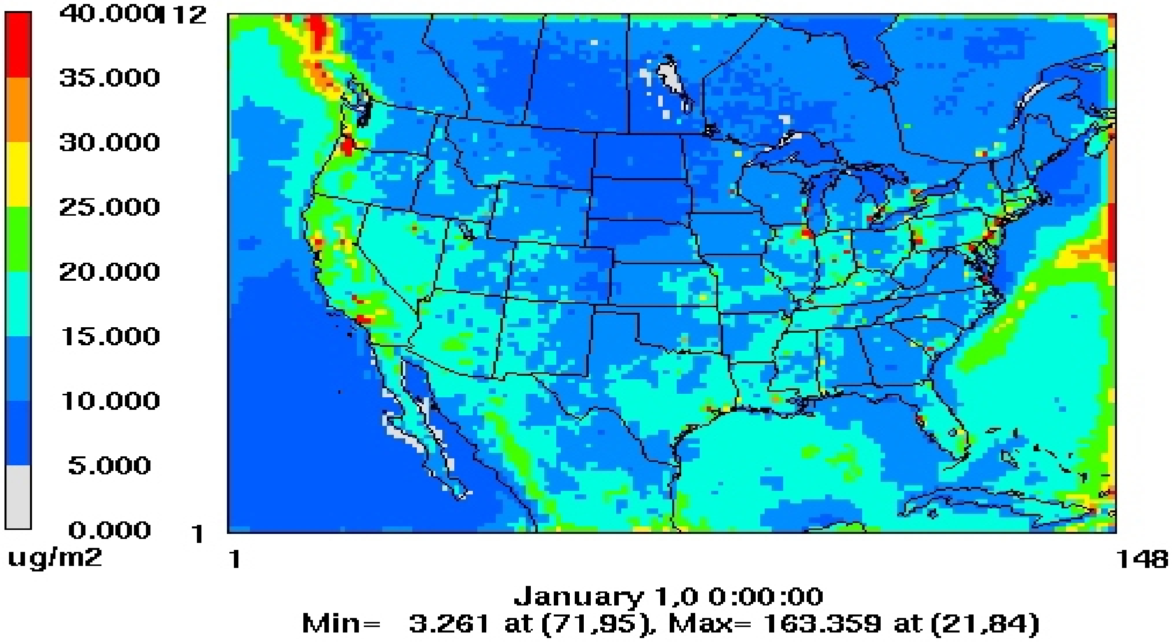

Figure 5. Total Mercury Deposition: 2020 with CAIR

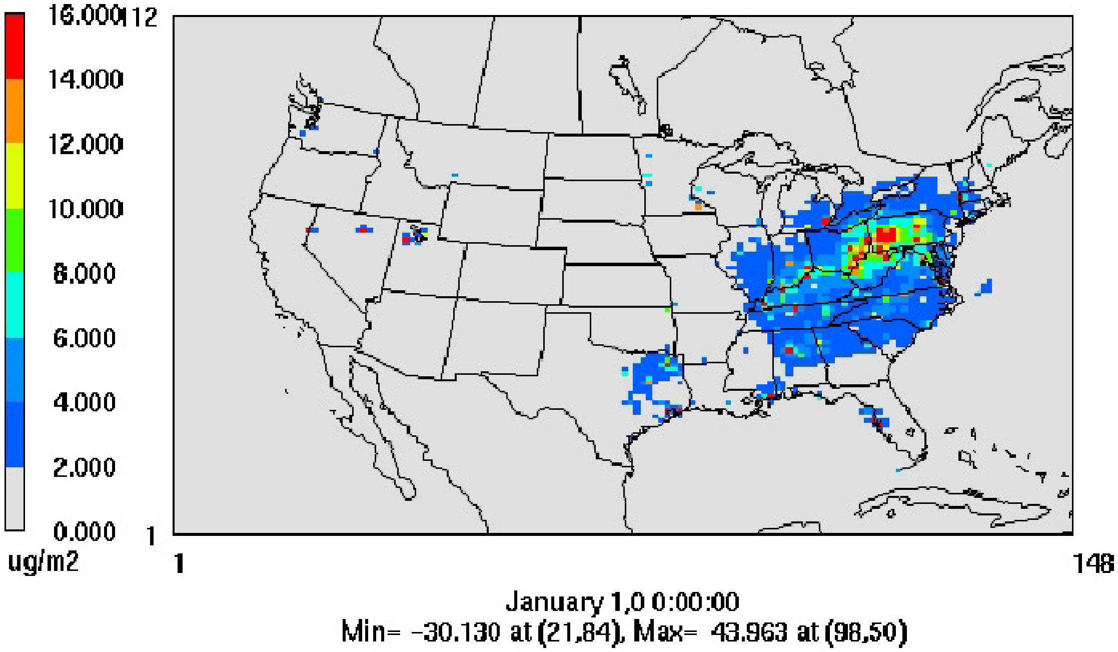

Figure 6. Change in Total Mercury Deposition for all Sources: 2020 with CAIR Relative to 2001

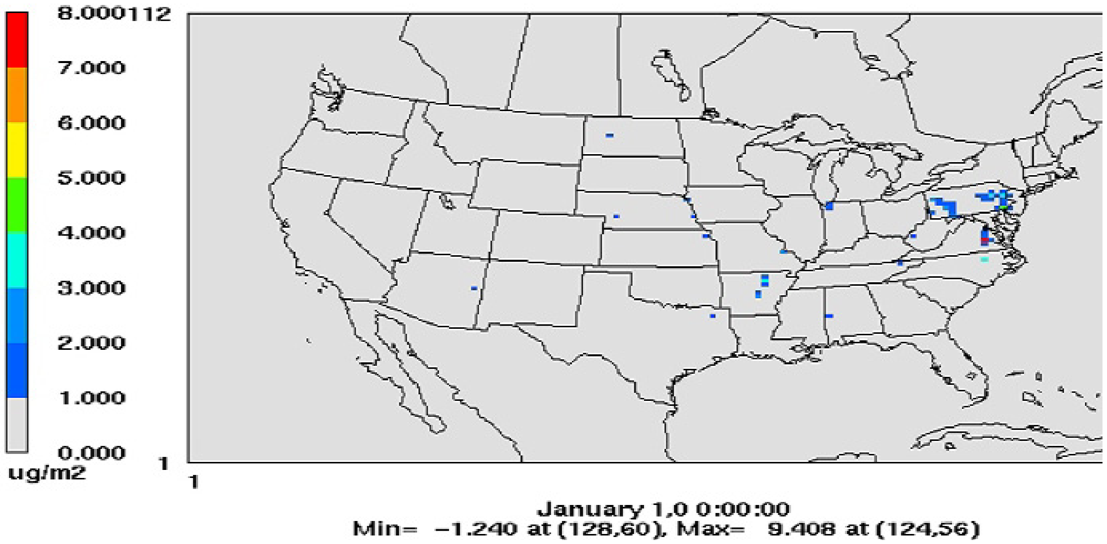

Figure 7. Change in Mercury Deposition from Power Plants Due to CAMR: 2020

IV.B Mercury Deposition for Great Lakes Region

This section provides a comparison of CMAQ and HYSPLIT mercury depositions from US utilities as well as CMAQ results specific to the Great Lakes region for the 2001 base year and 2020 with CAIR and CAMR. Table 5 and Figure 8 provide the average CMAQ predicted utility attributable mercury depositions to the Great Lakes and the corresponding HYSPLIT predictions. The resulting mercury depositions for each of the Great Lakes are similar for the two models, especially for Lake Erie, which had the highest mercury deposition. The average mercury deposition predicted by each model are within 1 ug/m^2 for each of the Great Lakes. These similar results occur even though the two modeling techniques are different and each model used a completely different meteorological year (HYSPLIT-1996 and CMAQ-2001). There also may be some differences in the utility mercury emissions and speciation input to the two models, although both inventories are based on the 1999 mercury utility emissions inventory.

Table 5. Average US Utility Attributable Total Mercury Deposition to the Great Lakes Region (ug/m2): Current Baseline

Lake	HYSPLIT Model (1996 MET/1999 Emissions)	CMAQ Model (2001 MET/1999 Emissions)
Michigan	3.2	2.2
Erie	5.2	5.4
Superior	1.3	0.3
Huron	2.5	1.5
Ontario	3.6	2.6

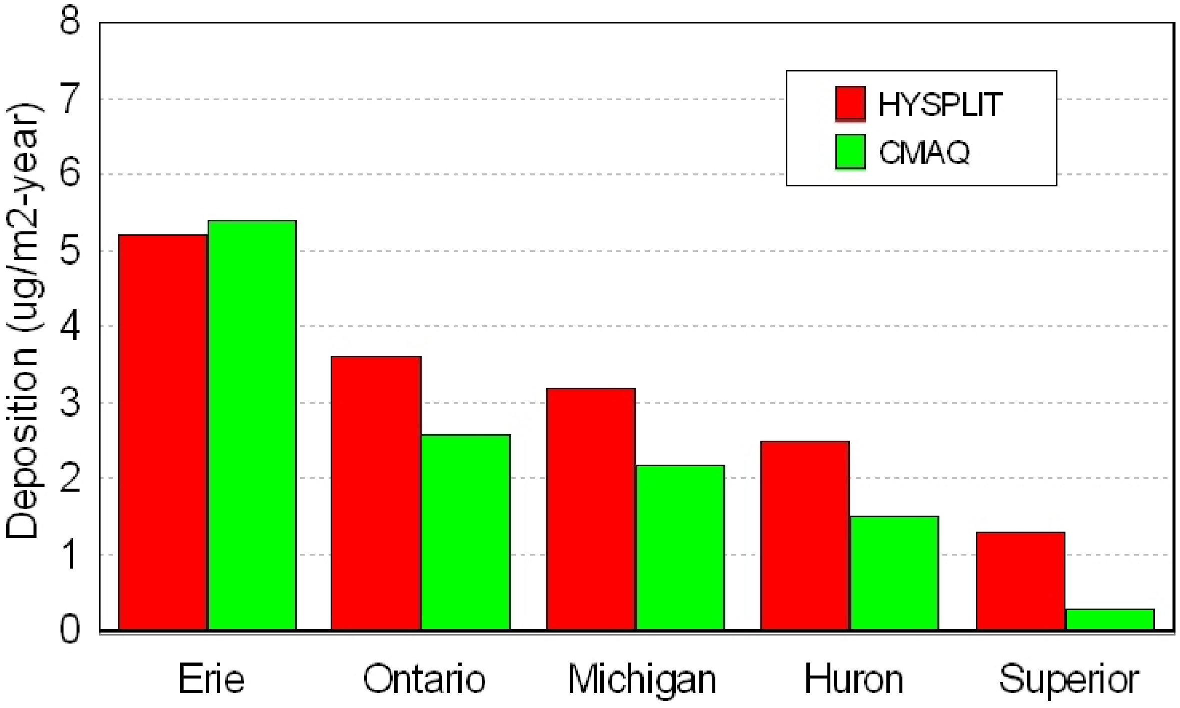

Figure 8. HYSPLIT and CMAQ Annual Average Mercury Deposition to the Great Lakes

Figure 9 provides the CMAQ modeled US utility attributable mercury deposition for 2001 to the Great Lakes region, while Figure 10 provides the corresponding 2001 mercury deposition for all sources. As shown in these figures, a large portion of the total mercury deposition to the Great Lakes region results from sources other than US utilities. Note that the scientific understanding of mercury atmospheric chemistry and deposition is still evolving, and changes in the current scientific understanding could necessitate changes to mercury air quality and deposition models. The existing uncertainties associated with modeled mercury deposition source impacts are described in more detail in the main body of this report (Section 3-F).

Figure 11 provides the CMAQ modeled total mercury deposition for 2020 with CAIR and CAMR from all sources, while Figure 12 provides the corresponding US utility attributable mercury deposition for the Great Lakes region. As shown in these figures, similar to the 2001 base case, a large portion of the total mercury deposition to the Great Lakes region results from sources other than US utilities. Comparing Figure 9 (i.e., 2001 base case) and Figure 12 (i.e., 2020 with CAIR and CAMR) shows a substantial reduction in the utility attributable mercury deposition to the Great Lakes. To this point, Table 6 provides the US utility attributable mercury deposition to each of the Great Lakes for 2001 and 2020 with CAIR and CAMR and the percent change over this time period. As shown, the reduction in utility attributable mercury deposition varies from 38 to 77 percent across the individual lakes.

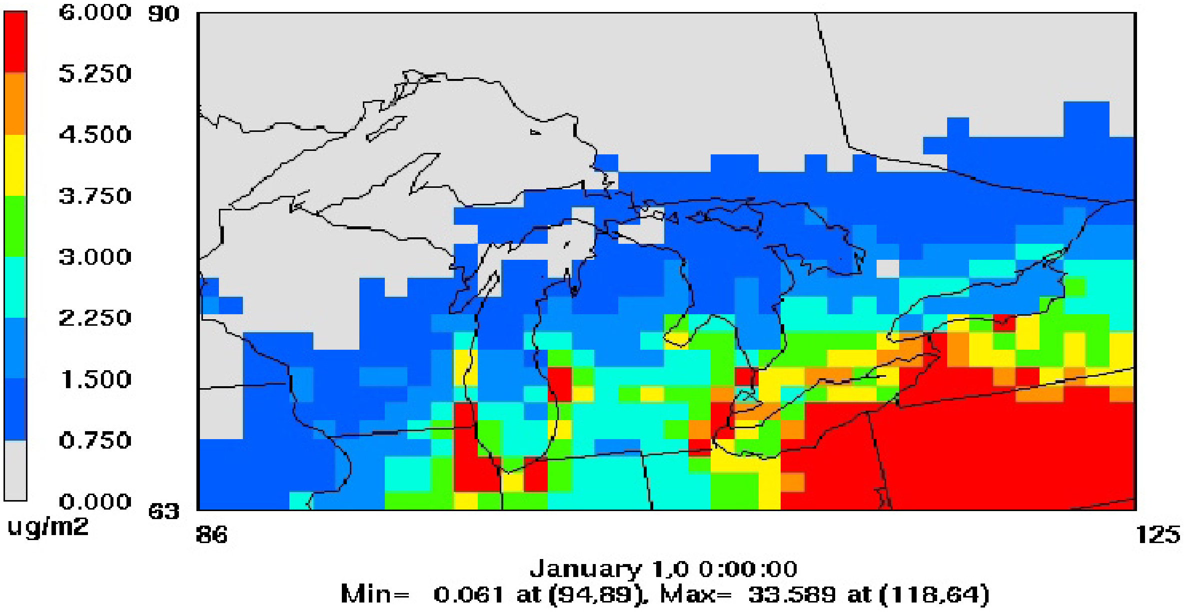

Figure 9. Total US Utility Attibutable Mercury Deposition to the Great Lakes Region: 2001

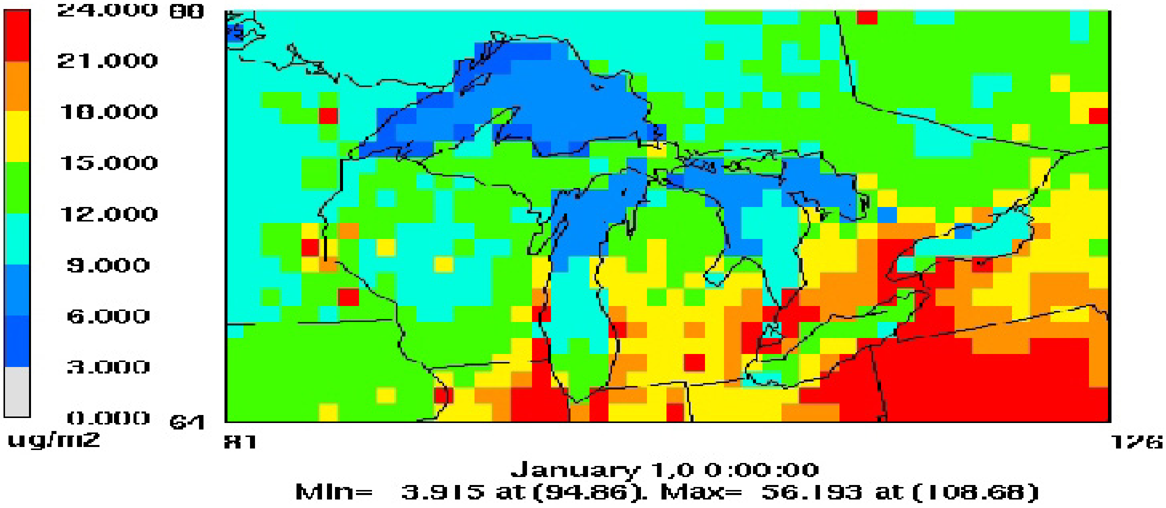

Figure 10. Total Mercury to the Great Lakes Region from All Sources: 2001

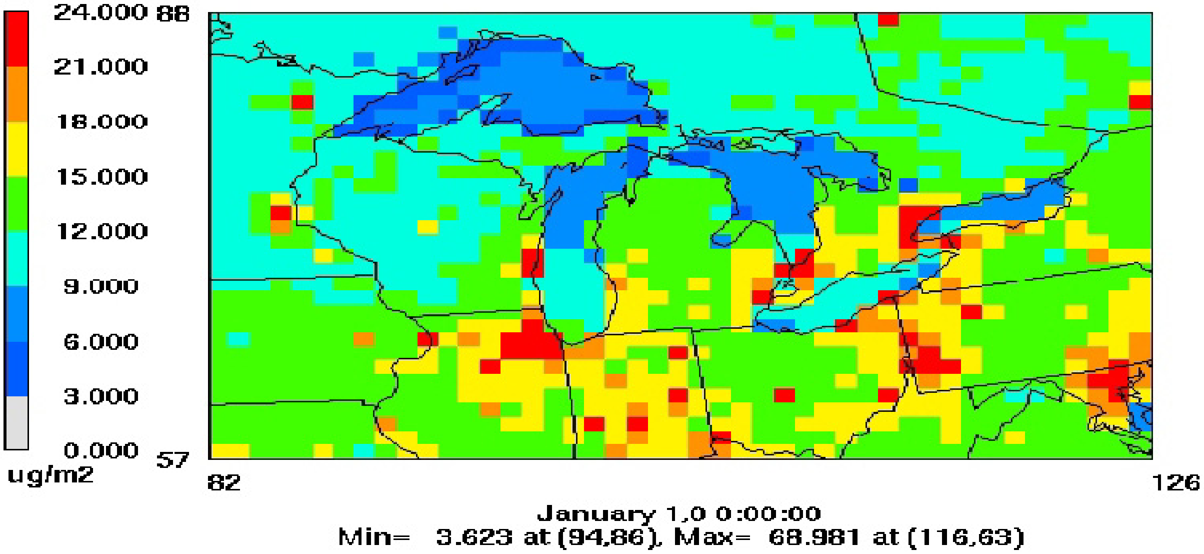

Figure 11. Total Mercury Deposition from All Sources to the Great Lakes Region: 2020 with CAIR and CAMR

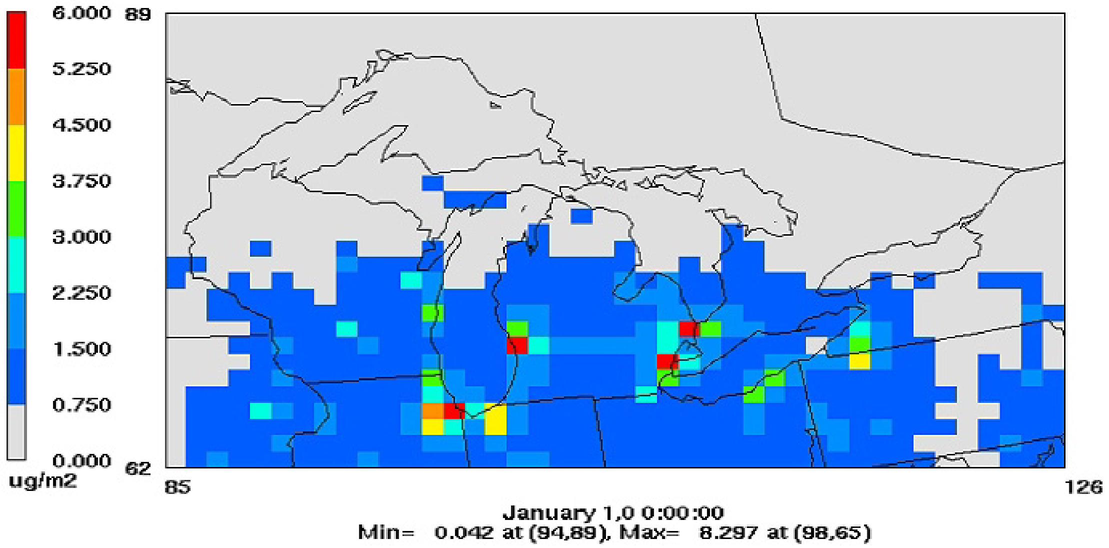

Figure 12. Total US Utility Attributable Mercury Deposition on to the Great Lakes Region: 2020 with CAIR and CAMR

Table 6. CMAQ Predicted Utility Attributable Mercury Deposition Estimates to the Great Lakes

Lake	2001 Basecase (ug/m2)	2020 w/ CAIR & CAMR (ug/m2)	Percent Change (%)
Michigan	2.1	1.3	-38.1%
Erie	5.4	1.6	-70.4%
Superior	0.3	0.2	-33.3%
Huron	1.5	0.7	-53.3%
Ontario	2.6	0.6	-76.9%

V. References

[for the reader’s convenience, references for this EPA Appendix have been integrated by NOAA into the references section for the entire report, beginning on page 146.]

Appendix B. Great Lakes Water Quality Agreement (Annex 15)

Revised
Great Lakes Water Quality Agreement of 1978
Agreement, with Annexes and Terms of Reference, between the United States and Canada
signed at Ottawa November 22, 1978 and
Phosphorus Load Reduction Supplement signed October 16, 1983
as amended by Protocol signed November 18, 1987
Office Consolidation
INTERNATIONAL JOINT COMMISSION UNITED STATES AND CANADA
September, 1989

ANNEX 15 - AIRBORNE TOXIC SUBSTANCES

http://www.ijc.org/rel/agree/quality.html#ann15

1. Purpose. The Parties, in cooperation with State and Provincial Governments, shall conduct research, surveillance and monitoring and implement pollution control measures for the purpose of reducing atmospheric deposition of toxic substances, particularly persistent toxic substances, to the Great Lakes Basin Ecosystem.

2. Research. Research activities shall be conducted to determine pathways, fate and effects of such toxic substances for the protection of the Great Lakes System. In particular, research shall be conducted to:

(a) understand the processes of wet and dry deposition and those associated with the vapor exchange of toxic substances;

(b) understand the effects of persistent toxic substances, singly or in synergistic or additive combination with other substances, through aquatic exposure routes on the health of humans and the quality and health of aquatic life where a significant source of these substances is the atmosphere, in accordance with sub-paragraph 4(b) of Annex 12; and

(c) develop models of the intermediate and long-range movement and transformation of toxic substances to determine;

(i) the significance of atmospheric loadings to the Great Lakes System relative to other pathways; and

(ii) the sources of such substances from outside the Great Lakes System.

3. Surveillance and Monitoring. The Parties shall:

(a) establish, as part of the Great Lakes International Surveillance Plan (GLISP) instituted under Annex 11, an Integrated Atmospheric Deposition Network in accordance with paragraph 4 below;

(b) identify, by means of this Network, toxic substances and, in particular, persistent toxic substances, appearing on List No. 1 described in Annex 1, of those designated as Critical Pollutants pursuant to Annex 2 and their significant sources in accordance with sub-paragraph 4(c) of Annex 12, and to track their movements; and

(c) utilize this Network in order to:

(i) determine atmospheric loadings of toxic substances to the Great Lakes System by quantifying the total and net atmospheric input of these same contaminants, pursuant to sub-paragraph 3(a) of Annex 11;

(ii) define the temporal and spatial trends in the atmospheric deposition of such toxic substances in accordance with sub-paragraph 4(a) of Annex 12; and

(iii) develop Remedial Action Plans and Lakewide Management Plans pursuant to Annex 2.

4. Components of the Integrated Atmospheric Deposition Network. The Parties shall confer on or before October 1, 1988, regarding;

(a) the identity of the toxic substances to be monitored; (b) the number of monitoring and surveillance stations; (c) the locations of such stations; (d) the equipment at such stations; (e) quality control and quality assurance procedures; and (f) a schedule for the construction and commencement of the operation of the stations.

5. Pollution Control Measures.

(a) The Parties, in cooperation with State and Provincial Governments, shall develop, adopt and implement measures for the control of the sources of emissions of toxic substances and the elimination of the sources of emissions of persistent toxic substances in cases where atmospheric deposition of these substances, singly or in synergistic or additive combination with other substances, significantly contributes to pollution of the Great Lakes System. Where such contributions arise from sources beyond the jurisdiction of the Parties, the Parties shall notify the responsible jurisdiction and the Commission of the problem and seek a suitable response.

(b) The Parties shall also assess and encourage the development of pollution control technologies and alternative products to reduce the effect of airborne toxic substances on the Great Lakes System.

6. Reporting. The Parties shall report their progress in implementing this Annex to the Commission biennially, commencing with a report no later than December 31, 1988.

Appendix C. Clean Air Act 1990 (excerpts)

TITLE I - AIR POLLUTION PREVENTION AND CONTROL

Part A - Air Quality and Emission Limitations

http://www.epa.gov/oar/caa/caa102.txt
Sec. 103. Research, investigation, training, and other activities.

(e) Ecosystem Research.- In carrying out subsection (a), the Administrator, in cooperation, where appropriate, with the Under Secretary of Commerce for Oceans and Atmosphere, the Director of the Fish and Wildlife Service, and the Secretary of Agriculture, shall conduct a research program to improve understanding of the short-term and long-term causes, effects, and trends of ecosystems damage from air pollutants on ecosystems. Such program shall include the following elements:

(1) Identification of regionally representative and critical ecosystems for research.

(2) Evaluation of risks to ecosystems exposed to air pollutants, including characterization of the causes and effects of chronic and episodic exposures to air pollutants and determination of the reversibility of those effects.

(3) Development of improved atmospheric dispersion models and monitoring systems and networks for evaluating and quantifying exposure to and effects of multiple environmental stresses associated with air pollution.

(4) Evaluation of the effects of air pollution on water quality, including assessments of the short-term and long- term ecological effects of acid deposition and other atmospherically derived pollutants on surface water (including wetlands and estuaries) and groundwater.

(5) Evaluation of the effects of air pollution on forests, materials, crops, biological diversity, soils, and other terrestrial and aquatic systems exposed to air pollutants.

(6) Estimation of the associated economic costs of ecological damage which have occurred as a result of exposure to air pollutants. Consistent with the purpose of this program, the Administrator may use the estuarine research reserves established pursuant to section 315 of the Coastal Zone Management Act of 1972 (16 U.S.C. 1461) to carry out this research.

Section 112 (m) Atmospheric Deposition to Great Lakes and Coastal Waters.

(1) Deposition assessment.- The Administrator, in cooperation with the Under Secretary of Commerce for Oceans and Atmosphere, shall conduct a program to identify and assess the extent of atmospheric deposition of hazardous air pollutants (and in the discretion of the Administrator, other air pollutants) to the Great Lakes, the Chesapeake Bay, Lake Champlain and coastal waters. As part of such program, the Administrator shall –

> (A) monitor the Great Lakes, the Chesapeake Bay, Lake Champlain and coastal waters, including monitoring of the Great Lakes through the monitoring network established pursuant to paragraph (2) of this subsection and designing and deploying an atmospheric monitoring network for coastal waters pursuant to paragraph (4);
>
> (B) investigate the sources and deposition rates of atmospheric deposition of air pollutants (and their atmospheric transformation precursors);
>
> (C) conduct research to develop and improve monitoring methods and to determine the relative contribution of atmospheric pollutants to total pollution loadings to the Great Lakes, the Chesapeake Bay, Lake Champlain, and coastal waters;
>
> (D) evaluate any adverse effects to public health or the environment caused by such deposition (including effects resulting from indirect exposure pathways) and assess the contribution of such deposition to violations of water quality standards established pursuant to the Federal Water Pollution Control Act and drinking water standards established pursuant to the Safe Drinking Water Act; and
>
> (E) sample for such pollutants in biota, fish, and wildlife of the Great Lakes, the Chesapeake Bay, Lake Champlain and coastal waters and characterize the sources of such pollutants.

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