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Modeling the atmospheric transport and deposition of mercury to the Great Lakes ☆

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Abstract

A special version of the NOAA HYSPLIT_4 model has been developed and used to estimate the atmospheric fate and transport of mercury in a North American modeling domain. Spatial and chemical interpolation procedures were used to expand the modeling results and provide estimates of the contribution of each source in a 1996 anthropogenic US/Canadian emissions inventory to atmospheric mercury deposition to the Great Lakes. While there are uncertainties in the emissions inventories and ambient data suitable for model evaluation are scarce, model results were found to be reasonably consistent with wet deposition measurements in the Great Lakes region and with independent measurement-based estimates of deposition to Lake Michigan. Sources up to 2000 km from the Great Lakes contributed significant amounts of mercury through atmospheric transport and deposition. While there were significant contributions from incineration and metallurgical sources, coal combustion was generally found to be the largest contributor to atmospheric mercury deposition to the Great Lakes.
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Mercury contamination in the Great Lakes and many other ecosystems is increasingly being recognized as a serious environmental concern. The dominant route of human exposure to mercury is through fish consumption, and significant portions of the general population are believed to be consuming toxicologically significant levels of mercury (e.g., National Research Council, 2000). Historical discharges—e.g., from chlor-alkali production using the mercury-cell process—are believed to have caused large accumulations of mercury in sediments in Lake Erie and Lake Ontario (Marvin et al., 2004). As these discharges have been substantially reduced, atmospheric deposition is now believed to be a more significant loading pathway for these lakes. Mass balance calculations for Lake Michigan (Mason and Sullivan, 1997) and Lake Superior (Dolan et al., 1993) indicate that atmospheric deposition accounts for approximately 75% of the overall mercury loading to these lakes.

While there have been several mercury modeling efforts in North America (Bullock et al., 1998; Bullock and Brehme, 2002; Dvonch et al., 1998; Lin et al., 2001; Pai et al., 1997; Seigneur et al., 2000, 2001, 2003a, b; Shannon and Voldner, 1995; Xu et al., 2000a-c), none has developed detailed source–receptor relationships for the Great Lakes, as advocated in Annex 15 of the Great

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Lakes Water Quality Agreement (International Joint Commission (IJC), 1987) and the Clean Air Act (US EPA, 1990). To effectively address mercury issues in the Great Lakes, it is important to know the relative importance of sources of the contamination. This paper provides estimates of such *source–receptor* information.

The atmospheric forms and behavior of mercury are complex (Lin and Pehkonen, 1999; Schroeder and Munthe, 1998; Lindqvist et al., 1991). Mercury exists in both elemental and oxidized chemical forms in the atmosphere. The predominant form in the atmosphere is generally elemental mercury (Hg^0). Its limited solubility results in only small amounts being dissolved in atmospheric water droplets and its relative volatility means that little will be adsorbed onto the surface of aerosol particles; thus, it exists primarily in the gas phase in the atmosphere.

Oxidized mercury species can be found in all phases in the atmosphere (vapor, aqueous droplets, and particulate) and are often defined operationally by measurement devices. One class of oxidized species is very water soluble, is less volatile than Hg^0, and is relatively "sticky" to many surfaces. In this paper, we will refer to these species as *soluble* Hg(II) or simply Hg(II). When in the gas phase, these species are often called *reactive gaseous mercury* (RGM). Due to their water solubility, these same species can exist dissolved in aqueous droplets when this phase is present in the atmosphere. Little about the actual species in this class of mercury is known, but one species believed to be significant is mercuric chloride ($HgCl_2$). These Hg(II) species have an affinity for and can be reversibly adsorbed to soot in the atmosphere, particularly within aqueous droplets.

Another class of atmospheric mercury species is relatively insoluble, even less volatile, and exists associated with atmospheric particulate matter. This class is operationally defined as the mercury collected in particulate measurement devices (e.g., filters). Mercuric oxide (HgO)—formed through oxidation of Hg^0 in combustion systems and in the ambient atmosphere—may be one of the most important species of this *particulate mercury* [Hg(p)]. Compounds with mercury in oxidation states other than [2^+] may also comprise a portion of Hg(p) but little about the precise speciation of this atmospheric mercury form is known. Due to its limited solubility, Hg(p) may be less bioavailable than Hg(II) after being deposited to ecosystems.

In most locations, the great majority of the mercury in the atmosphere ($\sim$95%) is in the elemental form. However, this is not always true. For example, during polar sunrise mercury-depletion events, the majority of atmospheric mercury occurs as RGM (Lindberg et al., 2002). As discussed below (see Atmospheric chemistry of mercury), each of the above forms of mercury can be transformed into the other in the atmosphere. Because these chemical transformations are relatively slow, and given that wet and dry deposition of elemental mercury is a relatively inefficient process, the "average" atmospheric lifetime of Hg^0 is believed to be on the order of 0.5–1 year (e.g., Tokos et al., 1998), allowing for the wide distribution of this mercury species. Well-mixed background concentrations of approximately 1.5–2.5 ng/m^3 are found throughout the northern hemisphere, even in the absence of local sources, while background concentrations on the order of 1.0–1.5 ng/m^3 are found in the southern hemisphere (e.g., Temme et al., 2003). The other forms of mercury are more readily deposited by wet and dry processes and likely have typical atmospheric lifetimes of a few days to a few weeks. Thus, these forms typically have more local and regional impacts.

A conceptual model for atmospheric mercury deposition to the Great Lakes (and many other water bodies) can be summarized as follows (see for example Vette et al., 2002). First, the dry and wet downward deposition flux of mercury to the Lakes is generally dominated by the Hg(II) and Hg(p) forms. A portion of the mercury deposited onto a lake's watershed can also be subsequently transported to the lake. Because their watersheds are smaller relative to their size than many other lakes, the Great Lakes probably receive proportionally less mercury from this indirect route than many other water bodies. Mercury can also be contributed through direct discharge into the lake or its tributaries from polluting facilities. Once in the lake, mercury can undergo a number of conversion processes, including the formation of methylmercury and reduction of Hg(II) to Hg^0. Methylmercury is the most important species, due to its toxic and bioaccumulative properties. In the lake, some of the mercury resides in the water column in dissolved form or associated with suspended sediments. Some of the mercury in the lake is incorporated into the sediments; it may reside there, be resuspended, or be incorporated, after conversion to methylmercury by bacteria in the sediments and elsewhere, into the food chain. Some of the elemental mercury in the lake—and potentially a small amount of the methylmercury (Rolfhus et al., 2003)—will volatilize from the lake surface for transport via the atmosphere to other locales, representing a loss of mercury from that particular water body.

This volatilization or surface exchange process of Hg^0 across the lake's surface is comparable to that for PCBs and other similar semivolatile pollutants. The direction and magnitude of the net flux will vary with time and will depend on the water and air temperatures, the wind speed, other meteorological and aquatic variables, and the relative concentrations of mercury in the lake and in the air above the lake. Estimates for Lake Michigan (Vette et al., 2002; Landis and Keeler, 2002) based on measurements made in the 1994–1995 Lake Michigan Mass Balance Study (LMMBS) suggest that the average net direction of the elemental mercury Hg^0 flux during that study was upward (i.e., out of the lake); this may also be the case for Lake Michigan currently. Overall, mercury can be considered dry and wet deposited to the lakes in the form of Hg(II) and Hg(p), and some portion of it revolatilized in the form of Hg^0; if more is deposited than revolatilized, then the mercury concentrations in the lake ecosystem will increase and vice versa.

1. Methodology

1.1. Mercury emissions inventory

A mercury emissions inventory for the United States was obtained from the US EPA (Ryan, 2001). The inventory contained annual emissions estimates for most anthropogenic sources of mercury. For coal-fired electricity generation, municipal waste incinerators, and medical waste incinerators, the estimates in this inventory were for 1999, while the remainder were reported to be representative of 1996 emissions.

Ideally, in any analysis such as this, all critical information—including the emissions inventory, meteorological data, and ambient monitoring data for model evaluation—would be referenced to the same time period. Unfortunately, there was no single year for which comparable emissions inventories for the United States and Canada existed. As the best compromise, the nominal year for this analysis was chosen to be 1996; i.e., 1996 meteorological data were used to drive the model, and 1996 ambient data were used for model evaluation. Therefore, the goal was to utilize emissions inventory data representative of 1996 to the greatest extent possible.

The US inventory was modified in recognition that one source category (coal combustion in commercial, industrial, and institutional boilers and process heaters) appeared to be underrepresented in this inventory, and so data from an alternative 1995–1996 US EPA inventory (Bullock, 2000; US EPA, 1997) were utilized for this source type. This alternative inventory was also used for US municipal waste incinerators and medical waste incinerators, because significant reductions in emissions from these source categories occurred between 1996 and 1999 (Mobley, 2003).

The coal-fired electricity generation emissions estimates for 1999 were retained because they were based on a significant amount of source testing and were estimated with a much more sophisticated approach than used in previous inventories. Emissions from this source category appear to have been fairly similar in 1996 and 1999, at least in total (Mobley, 2003).

The US inventory contained a total of 17,513 discrete point sources with specific locations. As is common practice in emissions inventories, certain source categories (e.g., mobile sources, residential fuel consumption, flourescent lamp breakage) were not estimated at precise locations but were estimated at the county level. There were 17 such source categories (on average) specified in each of 3141 US counties. For the purposes of this modeling analysis, it was assumed that the location for each area source was the centroid of each county. For large receptors such as the Great Lakes, this assumption will not introduce any significant inaccuracy into the simulation.

For Canada, a 1995 inventory was the latest available comprehensive data compilation. In this inventory, there were 583 point sources. Area sources in this inventory were specified on a 50-km grid in the Great Lakes region and a 100-km grid in the remainder of the country. Within the 473 50-km grid-squares and 1140 100-km grid-squares, there was an average of approximately 22 area source categories per grid square. Analogous to the US inventory, area sources in the Canadian inventory were assumed to be located at the centroid of each grid square. It is believed that there were very few (if any) significant changes in Canadian emissions between 1995 and 1996 and so this 1995 inventory was assumed to be approximately representative of 1996 Canadian emissions. There were no estimates of emissions from mobile sources available for inclusion in the Canadian inventory.

To summarize the inventory used in this modeling analysis, Fig. 1 shows the geographical distribution of the total anthropogenic mercury emissions throughout the United States and Canada. The annual emissions in the two countries are broken down by source category on a *per capita* basis in Fig. 2. To form these per capita estimates, the United States population used was 265,179,411 and the Canadian population used was 29,992,000. The relative importance of coal combustion in the United States and metallurgical processes (e.g., smelting) in Canada is apparent. It should be noted that mercury emissions from Canadian metallurgical processes and from US medical and municipal waste incinerators have been significantly reduced since the date of this inventory.

Most natural emissions or reemissions of previously deposited mercury are believed to be in the elemental form (e.g., Schroeder and Munthe, 1998; Scholtz et al., 2003; Gustin, 2003). However, emissions from many significant current anthropogenic sources, such as coal-fired electrical utilities or municipal or medical waste incinerators, are often mixtures of Hg^0, Hg(II), and Hg(p). Because of the distinct atmospheric deposition behavior of these different forms, estimates of the amounts of each form emitted from each source is needed. The US inventory contained such information, albeit on a fairly approximate basis, as the estimates were based on very few measurements for most source categories. Analogous speciation data for the Canadian

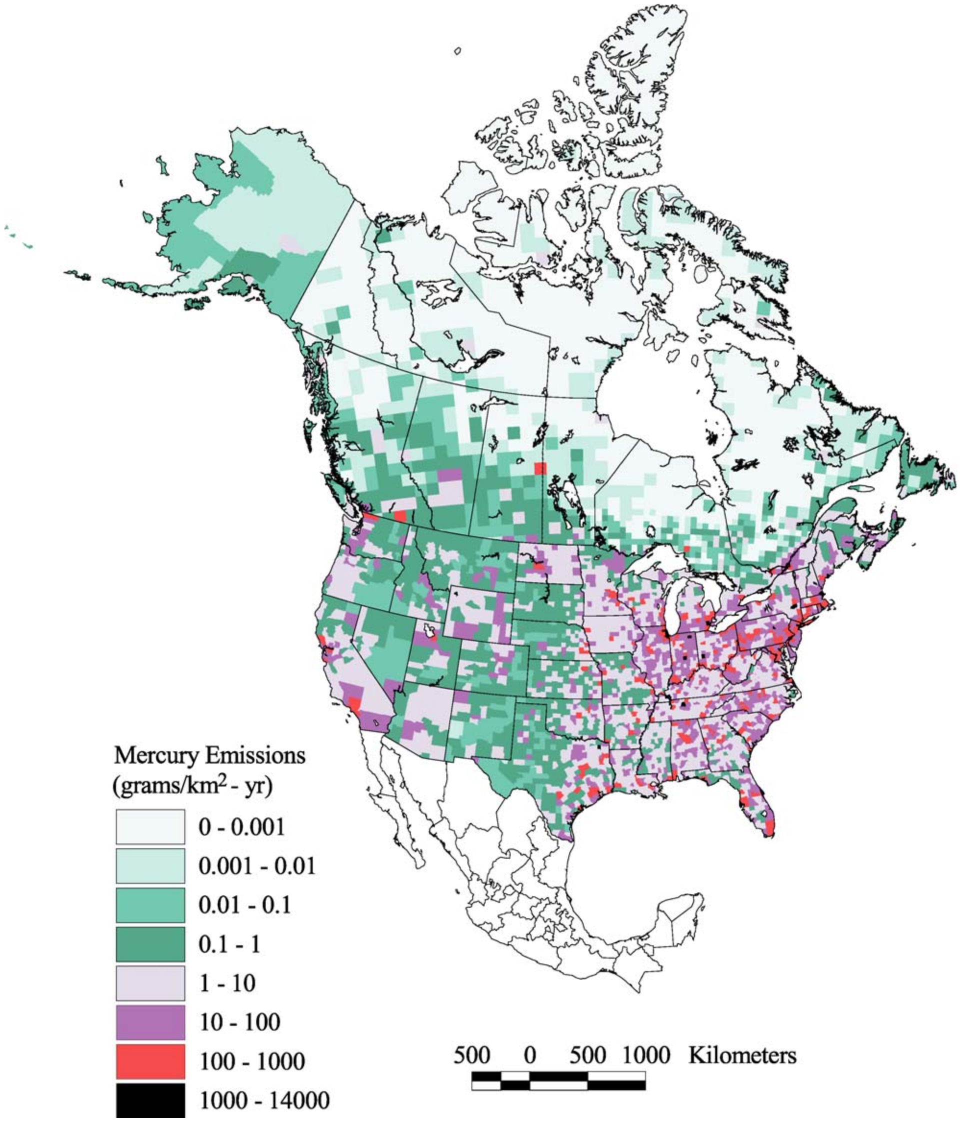

Fig. 1. Geographic distribution of total mercury emissions to the atmosphere from US and Canadian anthropogenic sources (1995/1996).

emissions were not available. Therefore, estimates for the proportions of the different mercury forms emitted from Canadian sources were made by assuming that they were similar to the corresponding source categories in the United States. Fig. 3 shows the average emissions profile for different source categories; the combined United States/Canada annual emissions of each form of mercury from each source category are shown in Fig. 4.

Only *direct anthropogenic* emissions for the reference year(s) have been explicitly included in this analysis. As discussed below, *natural* and *reemissions* of mercury were approximately accounted for by assuming that they roughly balanced the deposition of *elemental* mercury from direct anthropogenic emissions. In addition, only sources in the United States and Canada were included. Other modeling exercises have suggested that the contribution of sources outside the United States and Canada to atmospheric deposition to the Great Lakes accounts for ~13% (Shannon and Voldner, 1995) to ~20% (Dastoor, 2003, personal communication) of the total deposition. Inclusion of emissions from Mexico, Europe, Asia, and the rest of the world in this HYSPLIT_4-based modeling methodology is planned for the future.

There are many uncertainties in both the US and the Canadian inventories and in the application of such inventories in this modeling analysis. 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 discussed throughout this paper, 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, some potentially significant sources (e.g., electric arc furnaces) were not included. Third, while emissions from some source

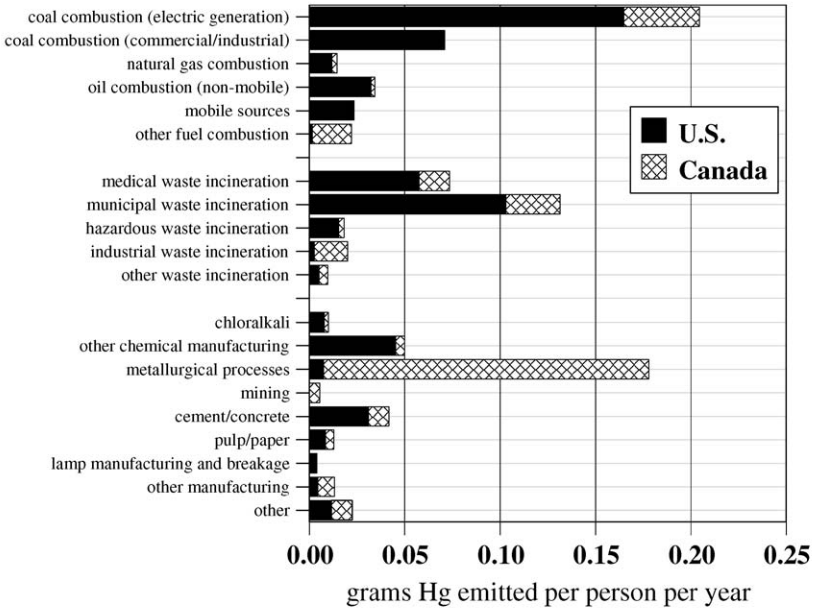

Fig. 2. Annual per-capita mercury emissions from US and Canadian sources.

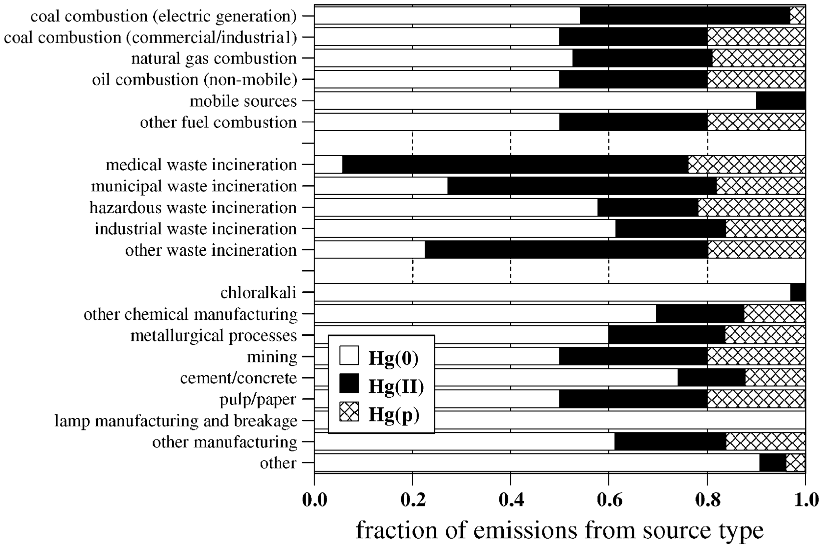

Fig. 3. Speciation profile of mercury emissions from US and Canadian anthropogenic sources.

categories (e.g., coal-fired power plants) have been measured with some regularity, other categories have been rarely measured. As a result, the annual emissions estimates are uncertain for many sources.

Finally, information on the temporal variation of emissions was not available, and so all emissions sources in the inventories were assumed to have been continuous and constant throughout the year. This is probably a reasonable assumption for coal-fired power plants (the largest-emitting source category in the inventory), but may be less appropriate for many other source categories. Even for sources that were relatively continuous, data for episodes such as maintenance or upset-related shut downs were not included in the inventory. Weather patterns can be highly episodic and significantly affect source–receptor relationships; thus, temporal emissions uncertainties will certainly compromise the accuracy of the estimated concentrations or deposition at any particular location and time. However, this analysis has been conducted over the course of an entire year (and primarily, annual estimates have been generated), and this will likely reduce the overall uncertainty introduced by this variability.

1.2. Atmospheric transport and dispersion model

The NOAA HYSPLIT_4 model (Hybrid single-particle Lagrangian integrated trajectory model, Version

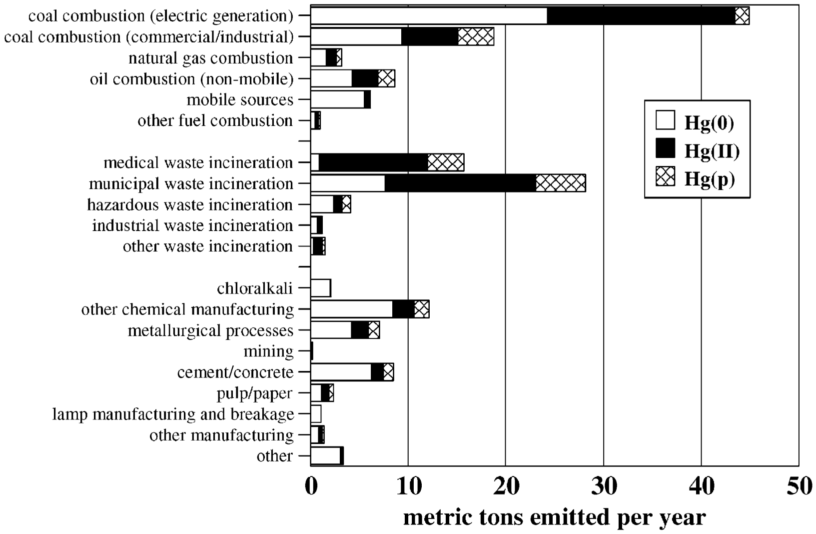

Fig. 4. Speciated annual mercury emissions from US and Canadian anthropogenic sources.

4) (Draxler and Hess, 1998), followed by a spatial and chemical interpolation procedure (Cohen et al., 2002), was used to estimate source–receptor relationships. In this application of the HYSPLIT model, hypothetical puffs of pollutant were considered to be emitted from each given source location. These puffs were released once every 7 h for an entire year; sensitivity analyses showed that the results with such a release frequency were not significantly different from results with a more frequent release. All puffs were released at a height of 50 m; sensitivity analyses showed that the results were not significantly affected by this particular choice of release height. The subsequent advection and dispersion of the pollutant puffs were then simulated using meteorological data supplied to the model. A full year of meteorological output from NOAA's Nested Grid Model (NGM) (Rolph, 1997) was used for the 1996 year-long simulations in this study. These data had a horizontal resolution of 180 km, 11 vertical levels up to 6000 m elevation, and a temporal resolution of 2 h. The NGM model was initialized with observations every 12 h, and the periods between initializations represent forecast data. All precipitation data in the NGM archive are 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 (e.g., in the model evaluation exercises described below). However, it is not likely that the overall deposition and the source–receptor relationships for the Great Lakes estimated here would be significantly affected.

The HYSPLIT_4 model has recently been used to simulate atmospheric fate and transport of dioxin to the Great Lakes (Cohen et al., 2002) and many of the model modifications made for that study have been retained in the present application. Several mercury-specific changes and additions were incorporated into the model for this analysis. The most significant of these concerned the treatment of atmospheric chemistry.

1.3. Atmospheric chemistry of mercury

In the aforementioned dioxin modeling, only a gas-phase reaction with the hydroxyl radical ($OH^{\bullet}$) and gas- and particle-phase photolysis were considered in the chemistry module, and it was assumed that no conversion from one congener to another occurred. However, the atmospheric chemistry of mercury is more complex (Schroeder et al., 1991; Lin and Pehkonen, 1999), involving many more reactions and interconversion of different mercury forms. The mercury chemical equilibrium and reaction scheme used in this analysis is similar to that currently being employed in other atmospheric mercury models (e.g., as summarized in Ryaboshapko et al., 2002, 2003).

Elemental mercury in the gas phase can be oxidized to Hg(II) by a number of agents, including ozone (Hall, 1995), hydrogen peroxide (Tokos et al., 1998), chlorine (Calhoun and Prestbo, 2001; Ariya et al., 2002), and hydroxyl radical (Sommar et al., 2001), and, in the aqueous phase (e.g., cloud droplets), by several different oxidizing species, including ozone (Munthe, 1992), hydroxyl radical (Lin and Pehkonen, 1997), hydrochlorous acid (HOCl), and hypochlorite ion (OCl^{-1}) (Lin and Pehkonen, 1998). Divalent mercury can be reduced to elemental mercury by sulfurous acid [HSO_3^{-1}] (Van Loon et al., 2000), formed in pH-dependent amounts from dissolved sulfur dioxide. Until recently, it was thought that the hydroperoxyl radical [HO_2] also reduced Hg(II), but recent determinations by Gardfeldt and Jonnson (2003) have indicated that this reaction may be of much less importance than it originally appeared to be. As described in the Supplementary Material, ambient concentrations of ozone, sulfur dioxide, and soot and the pH and aqueous chloride ion concentration were estimated from ambient data, and concentrations of other key reactants ($OH^\bullet$, Cl_2, etc.) were estimated using other empirically based procedures.

The physical–chemical behavior of Hg(p) is not well understood. For example, the extent to which it is dissolved whenever the particle that it is associated with becomes a droplet is uncertain, and assumptions with regard to this solubility vary among different atmospheric chemistry models. Moreover, while it is known that there is a reversible adsorption/desorption of dissolved Hg(II) to and from soot surfaces within a droplet (Seigneur et al., 1998), the relationship of adsorbed Hg(II) species and Hg(p) species has not been well characterized. In previous HYSPLIT mercury studies, it was found that model results were more consistent with ambient measurements when it was assumed that Hg(p) was insoluble (Ryaboshapko et al., 2003), and so this assumption was followed here. It was also assumed that Hg(II) formed reversible complexes with soot in aqueous droplets, and this *Hg(II)–soot* complex was considered a separate, fourth form of mercury in this modeling, in addition to Hg^0, Hg(p) (insoluble), and Hg(II) not associated with soot.

We note also that heterogeneous halogen-mediated oxidation reactions appear to play a very significant role in the "Arctic sunrise" mercury depletion events (Lindberg et al., 2002). Measurements of relatively elevated concentrations of Hg(II) at high altitudes (Landis, 2001) suggest that these or similar reactions may also be of significance in the upper troposphere and lower stratosphere. Their occurrence there may be due to low temperatures which lead to the formation of ice crystals, upon which these heterogeneous reactions might take place. Homogeneous gas-phase reactions may also play a role. It is hoped that the characterization of these reactions can eventually be improved to the point where they can be accurately included in future simulations. Additional details on the atmospheric chemistry simulation methodology are provided as Supplementary Material.

1.4. Dry and wet deposition of atmospheric mercury

As noted previously, Hg^0 is only sparingly soluble in water, and it is not efficiently incorporated into wet deposition. As a result, the preponderance of mercury in wet deposition is in the oxidized or particulate forms. Mercury, like other pollutants, is also subject to dry deposition phenomena, in which it is transported down to the Earth's surface by atmospheric dispersion and then some portion adheres to various surfaces (water, vegetation, soil, buildings, etc.). In addition to this downward dry deposition flux component, there is also generally an upward flux component of mercury from land and water arising from natural sources or reemission of previously deposited mercury from anthropogenic or natural sources. At any given location and time, the relative magnitudes of the downward and upward components will vary, and these magnitudes will generally be different for each form of mercury.

The upward component of the surface-exchange flux of Hg(II) and Hg(p) at most locations is relatively insignificant; i.e., for these two forms, the net flux is almost always in the direction of deposition (down), and, as a reasonable, simplifying assumption, the upward flux phenomena for these two species is generally ignored. This approach has been taken in the atmospheric mercury modeling analysis discussed here; that is, only the downward flux of Hg(II) and Hg(p) has been modeled.

In addition, as a simplification of the deposition process, the approach of Bullock and Brehme (2002) and others was followed, in which it was assumed that the total dry deposition of *elemental* mercury from direct anthropogenic emissions was roughly balanced by the sum of the emissions of *elemental* mercury from natural sources and previously deposited anthropogenic emissions. That is, the net dry deposition of *elemental* mercury was assumed to be zero. A more sophisticated treatment of this phenomenon would no doubt be beneficial, but the limited understanding of the relevant processes and a lack of measurement data to evaluate estimates made their inclusion in the present study somewhat impractical. New approaches that may allow such processes to be included more realistically in simulations have been developed (e.g., Scholtz et al., 2003). Nevertheless, the ability of this model (see below) and other models to satisfactorily explain ambient mercury concentrations and deposition provides evidence that this simplified approach is somewhat consistent with the overall net cycling of elemental mercury between the atmosphere and the earth's surface.

Only the *direct* deposition to the lake surfaces has been estimated in this modeling analysis. *Indirect* atmospheric contributions, resulting from deposition to a lake's watershed and subsequent transfer to the lake, have not been estimated as part of this modeling. As noted above, 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 this 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% of the total loading to the lake, based on measurements made in 2000. Landis and Keeler (2002) estimate that tributary inputs account for approximately 16% of the loading to Lake Michigan, based on 1994–1995 measurements. Indirect atmospheric deposition would account for a portion of these contributions, but the fraction is unknown.

1.5. Source–receptor relationships

A procedure to establish linkages between significant point and area sources of mercury throughout the United States and Canada and the subsequent deposition of this contaminant to the Great Lakes basin was developed. In this technique (described for dioxin in Cohen et al., 2002) an interpolation procedure is used to estimate detailed source–receptor relationships. To conduct the analysis, explicit HYSPLIT modeling of emissions was 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 four explicitly modeled *standard source locations* nearest to that given source.

To account for the varying proportions of different mercury forms being emitted from different sources, separate unit-emission simulations of Hg^0, Hg(II), 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. 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 believed to be generally valid, based on the following arguments:

- Mercury is present at extremely trace levels in the atmosphere. As a consequence, it will not affect meteorology. Thus, meteorological parameters (wind speed and direction, temperature, humidity, precipitation, etc.) can be estimated independently and provided to the model.
- Most species that react with mercury compounds (e.g., O_3, SO_2, H_2O_2) are generally present at much higher concentrations than the mercury compounds. For example, O_3 is found in the atmosphere at concentrations on the order of 10–100 ppb, while Hg^0 is found at concentrations of 0.0001–0.001 ppb (~1–10 ng/m^3). Other species (e.g., $OH^\bullet$) generally react with many other compounds in addition to mercury, so, while present in trace quantities, their concentrations cannot be strongly influenced by their interactions with mercury.
- Wet and dry deposition processes themselves are not fundamentally affected by the presence of mercury and are generally considered to be *first order* with respect to mercury concentrations. In this context, *first order* means that the process rate is estimated with an expression of the form $rate = k \cdot c$, where k is a parameter which may depend on a number of factors, but which does not depend on the concentration of mercury, c.
- The current understanding of mercury's atmospheric chemistry does not include any chemical reactions or equilibrium relations that are not *first order* with respect to mercury.
- Finally, vapor/particle, vapor/droplet, and droplet/soot equilibrium relations can all be expressed as a ratio of the concentrations in different phases. A reasonable assumption can then be made that every mercury-containing compound has the same proportional chance (governed by this equilibrium ratio) of being in any given phase. Thus, the presence of mercury from one source is not expected to significantly affect the interphase distribution of mercury from any other source.

In light of the above factors, the emissions of mercury from one source are considered to be independent of mercury emissions from other sources. This assumed independence is likely to be valid for many other trace pollutants in the atmosphere, but is certainly not valid, for example, for emissions of volatile organic compounds (VOCs) and nitrogen oxides (NO_x).

As noted above, concentrations of key reactants influencing the atmospheric chemistry of mercury (e.g., O_3, $OH^\bullet$, SO_2, Cl_2) were estimated using a variety of empirical methods. We note that if this same overall modeling system were used to investigate different mercury emissions scenarios, emissions of VOCs, NO_x, SO_x and other species affecting the concentrations of these key reactants might change in these scenarios. In that situation, adjustments to the estimation methodology for these key reactants would need to be made if the changed emissions regime resulted in significant changes in these key reactants. In other words, while the emissions of mercury from sources are believed to be independent, emissions of many other species from these or other sources are not. However, in the results presented here, the simulations are for the same actual "real" situation, i.e., emissions and ambient conditions during 1996, and so this potential complication does not arise.

1.6. Results of the interpolation procedures: transfer coefficients

To illustrate some of the basic results of the fate and transport modeling and the spatial interpolation procedure, Fig. 5 shows the geographical distribution of model-estimated *transfer coefficients* to Lake Superior for emissions of Hg^0, Hg(II), and Hg(p). The standard source locations used for the interpolation are also shown. These maps show the *ratio* between the *deposition flux* to Lake Superior (micrograms of mercury (of all forms) deposited per year per square kilometer of lake surface) and the *hypothetical continuous emissions* (grams of mercury emitted per year from a given location) of the given form of mercury over the entire year 1996 from any given location throughout the modeling domain. It is important to stress that these maps do not incorporate emissions data. They simply represent the relative propensity of emissions from any given location to deposit in Lake Superior, based on the simulated atmospheric transport and fate of mercury. From these maps, it can be seen that, for essentially any given source location within the modeling domain, emissions of Hg(II) would result in the highest deposition in the lake, followed by emissions of Hg(p). In contrast, emissions of Hg^0 are predicted to result in significantly less relative deposition.

These results are consistent with the general understanding of the relative atmospheric behavior and fate of these different forms of mercury. Hg(II) is very water soluble, with relatively strong surface adhesion properties, and is therefore much more likely to be subject to wet and dry deposition. For example, Hg(II) can be

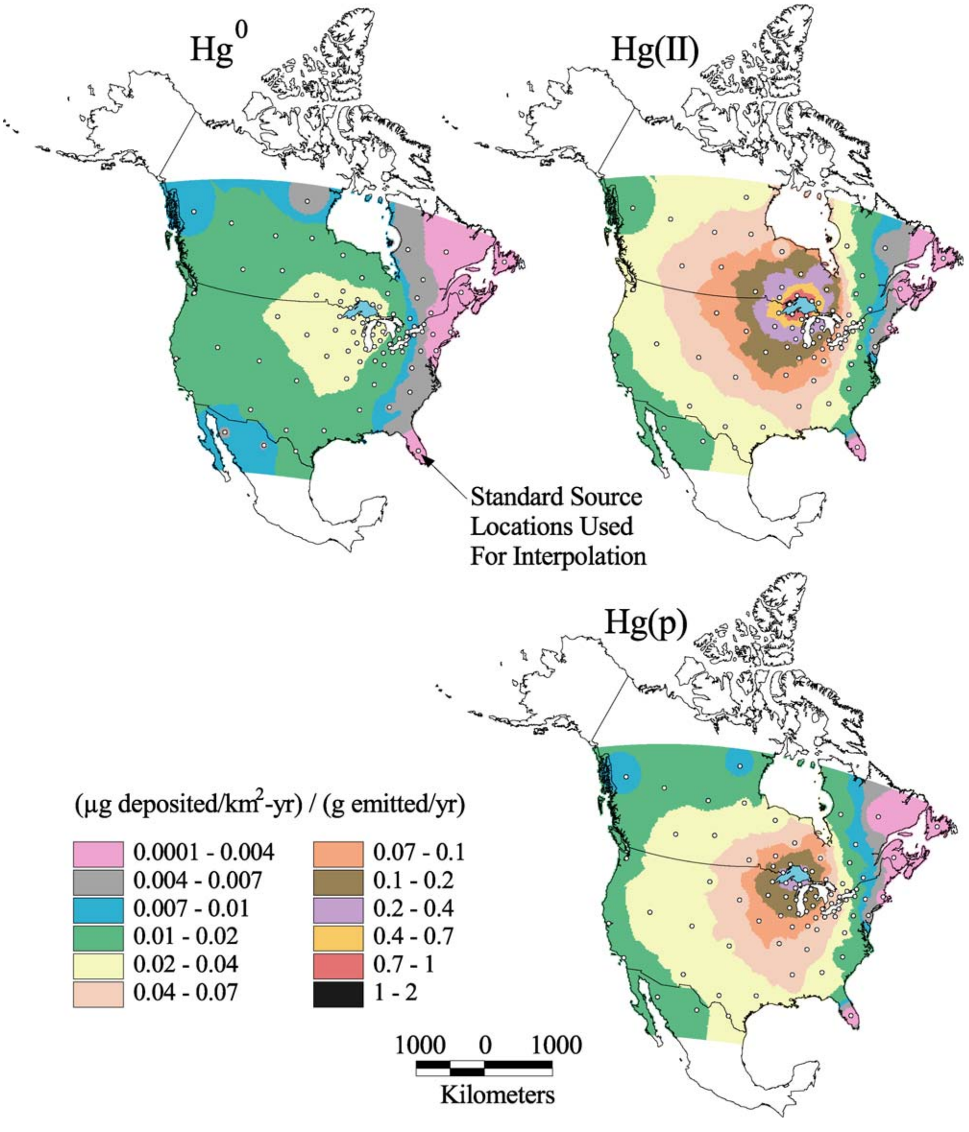

Fig. 5. Overall transfer coefficients for mercury to Lake Superior during 1996 for Hg^0, Hg(II), and Hg(p).

wet-deposited from within precipitating clouds and even from below these clouds, due to its very high water solubility. Hg(p) can also be wet-deposited relatively efficiently if its host particles find themselves in precipitating clouds. In contrast to these forms, Hg^0 is only sparingly water soluble and relatively volatile—thus its potential for wet and dry deposition is comparatively limited. These considerations are the basis for the relatively long atmospheric lifetimes estimated for Hg^0, but relatively short atmospheric lifetimes for Hg(II) and Hg(p) (Schroeder and Munthe, 1998). Indeed, for emitted Hg^0, it is often the slow atmospheric conversion to Hg(II) and/or Hg(p) that is required as a step to eventual deposition.

As mentioned above, any given emissions source will generally emit a mixture of these different forms. For example, while there are significant variations based on the type of coal being burned, the type of pollution control equipment present, and other factors, on average, coal-fired power plants emit a mixture composed of approximately 50% Hg^0, 45% Hg(II), and 5% Hg(p). Fig. 6 shows the model-estimated transfer coefficients for this average coal-combustion emissions mixture for each of the Great Lakes. These results illustrate both the spatial and the chemical interpolation procedures. The patterns are similar for each of the Great Lakes and show that, as would be expected, the propensity for atmospheric deposition contributions is reduced substantially as the distance from the lake increases. Since the prevailing winds are from the west, potential contributions from regions west of a given lake tend to be greater than potential contributions from similar distances east of the lake. As another way of understanding this phenomena, the contribution potential falls off more steeply east of the lakes because winds that could transport mercury from sources in these regions occur less frequently.

As shown in Figs. 5 and 6, a total of 84 standard source locations were used, many of which were clustered around the Great Lakes basin. Analyses using approximately twice as many standard source locations were also performed, but the results did not vary significantly from this 84-location analysis. Therefore, as was found with the earlier dioxin analysis, it is believed that the interpolation procedure using these 84 locations is providing estimates of adequate accuracy.

In these transfer coefficient maps, it can be seen that there are small regions around a few of the standard source locations that appear to be artifacts of the interpolation procedure. For example, in the Hg(p) map in Fig. 5, there is a small circular region around the standard location in the northern, central portion of the map (in the Northwest Territories, about 500 km west of Hudson Bay). The fact that this small region surrounding the standard location appears to have a slightly lower potential for transport to the Lakes in comparison to the surrounding region is probably indicative of a slight loss of accuracy in the interpolation procedure. This is due to the fact that the standard locations are relatively sparsely distributed in this region and because the location is close to the edge of the modeling domain. To ameliorate this issue, more standard source locations in these regions could be added, and the modeling domain could be increased in size. However, it was not deemed necessary to expend the computational resources to accomplish this, as the contribution of mercury from these areas to the Great Lakes was inconsequential due to the fact that the transfer coefficients were relatively low and there were no significant sources in these regions.

1.7. Linking transfer coefficients and emissions data

Conceptually, to complete the modeling activity, the emissions inventory information is “multiplied” by the transfer coefficient information. In the map in Fig. 5 for Hg^0, it can be seen that there is, for example, a region that refers to transfer coefficient values in the range 0.01–0.02 (μg total Hg deposited/km^2-year)/(g Hg^0 emitted/year). Suppose that there was a mercury source emitting 1000 g of Hg^0 somewhere in that region. Using the model-estimated transfer coefficient, the estimated deposition flux of mercury resulting in Lake Superior from that source will be the following:

Deposition flux
= 1000 (g Hg^0 emitted/year) · 0.01–0.02 [(μg total Hg deposited/km^2-year)/(g Hg^0 emitted/year)]
= 10–20 (μg total Hg deposited/km^2-year).

To compute the actual amount of mercury contributed to the entire surface of Lake Superior from this hypothetical source through atmospheric deposition, one would multiply by the surface area of the lake, i.e.,

Deposition amount
= *flux · surface area*
= 10–20 (μg total Hg deposited/km^2-year) · 81,200 (km^2)
= 812,000–1,624,000 (μg total Hg deposited/year)
= 0.8–1.6 (g total Hg deposited/year).

Thus, the 1000 g of Hg^0 emitted from the hypothetical source over the year is estimated to result in a deposition to Lake Superior of 0.8–1.6 g of total mercury (i.e., mercury in all forms) or 0.08–0.16% of the emissions from this location.

The above is a simplified description of how the transfer coefficients and emissions data are combined in the model methodology. In practice, the multiplication of the emissions inventory map and the transfer coefficient map is done numerically, for each mercury form emitted by each source. This procedure results in

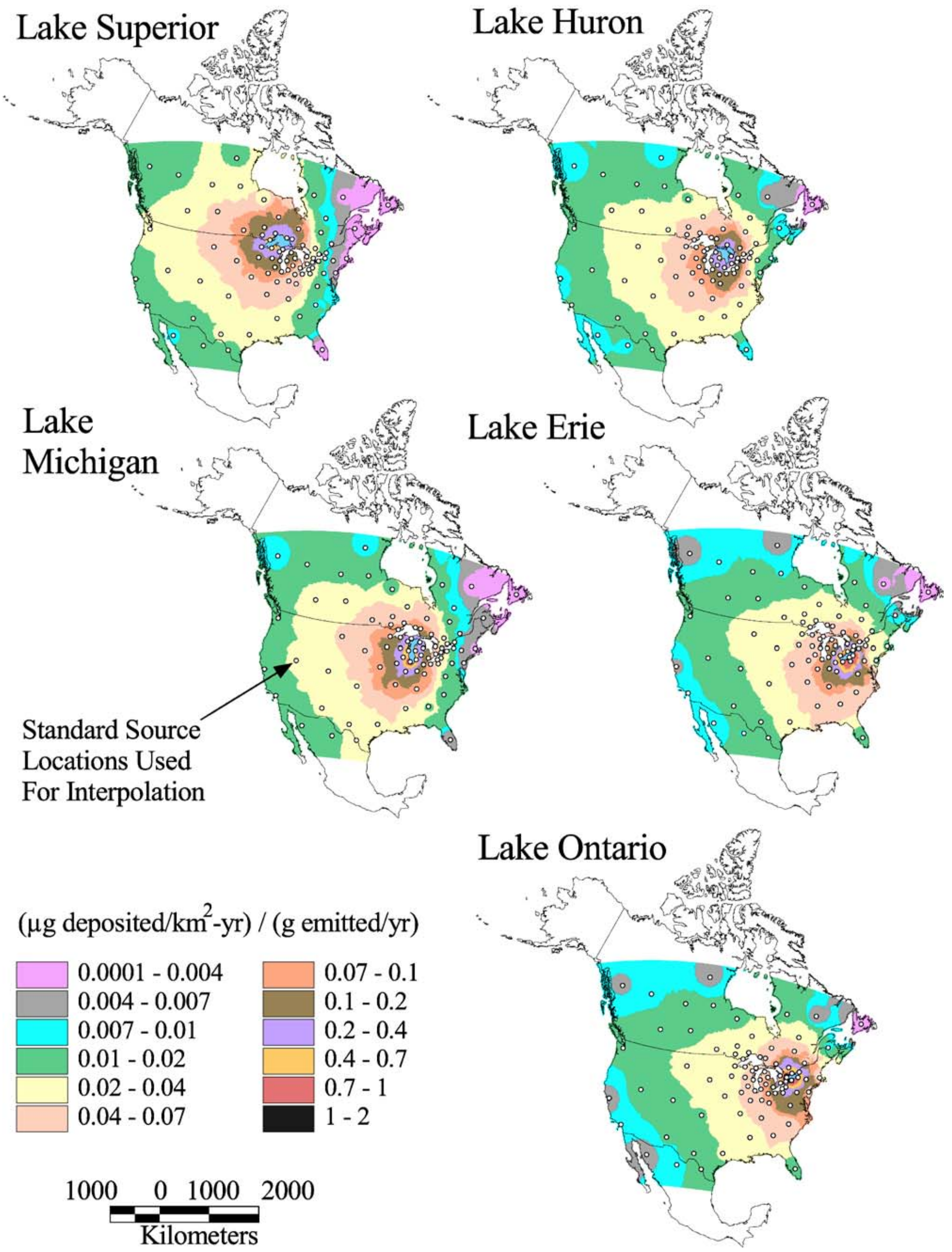

Fig. 6. Overall transfer coefficients for mercury to each of the Great Lakes during 1996 for an emissions profile typical of coal-fired utility boilers.

an estimate of the atmospheric deposition impact of *each* source in the emissions inventory to each of the Great Lakes. An analogous procedure is used to estimate source-by-source contributions to ambient concentrations and deposition at any location of interest in the modeling domain. A small fraction of the US and Canadian emissions lie outside of the modeling domain. Roughly approximated transfer coefficients were estimated for these sources, based on a consideration of the nearest explicitly estimated transfer coefficients. The impact of these sources on the Great Lakes will be insignificant, as there are few emissions ($<0.3\%$ of total emissions) and the transfer coefficients will be relatively small for transport to the Great Lakes. Thus, the use of approximate transfer coefficients for estimating these sources' contributions to Great Lakes deposition did not introduce any appreciable error into the analysis.

2. Model evaluation

In any modeling study, it is important to ground-truth the predictions to ensure that the simulations are providing reasonable results. The HYSPLIT model has been extensively evaluated in simulations of the transport and deposition of a variety of compounds and contaminants and has been shown to be capable of providing outputs and estimates that compare well with ambient measurements and other comparable data (Cohen et al., 1995, 1997, 2002; Draxler and Hess, 1998; Draxler, 1991, 2000; Stein et al., 2000; Rolph et al., 1992, 1993; McQueen and Draxler, 1994, Draxler et al., 1994).

This mercury modeling methodology has been applied in an ongoing mercury modeling intercomparison study organized by the Meteorological Synthesizing Centre-East [for the European Monitoring and Evaluation Program (EMEP)] over a European modeling domain, along with several other atmospheric mercury models from research groups around the world (Ryaboshapko et al., 2003). In this exercise, this HYSPLIT_4-based mercury-modeling methodology showed a very encouraging capacity to simulate atmospheric mercury and was comparable in its capabilities to the other models.

Because the science of atmospheric mercury modeling is evolving, and there are still significant uncertainties in the understanding of key processes, such model evaluation exercises are particularly critical. Unfortunately, uncertainties in emissions inventories greatly complicates any evaluation exercise. It is very difficult or impossible to determine whether inconsistencies between modeled and measured values are due to errors in the emissions inventory or errors in the chemistry and physics of the model. There are few data on the concentrations of different species or forms of mercury for model evaluation for the simulation year (1996). Two data sets have been chosen for initial model evaluation and are described below. Evaluation of the model is an ongoing process, and additional exercises will be discussed in forthcoming work.

Wet deposition measurements in the Great Lakes region. There are nine monitoring sites in the vicinity of the Great Lakes (within 250 km of any lake) at which mercury wet deposition samples were collected and for which data are available, including one site each in Illinois, Vermont, and Quebec and three sites each in Minnesota and Wisconsin (Fig. 7). The Minnesota, Wisconsin, and Illinois sites are part of the Mercury Deposition Network (2003) and represent weekly integrated samples. Data from the Underhill Center, Vermont (Burke et al., 1995; Gao, 2003) and St. Anicet, Quebec (Poissant and Pilote, 1998) sites represented event-based precipitation samples. Full-year 1996 data were available for all the sites with the following exceptions: (a) for the Illinois site, data for January through February only were available and (b) for one of the Minnesota sites (MDN_MN23), data from July through December only were available.

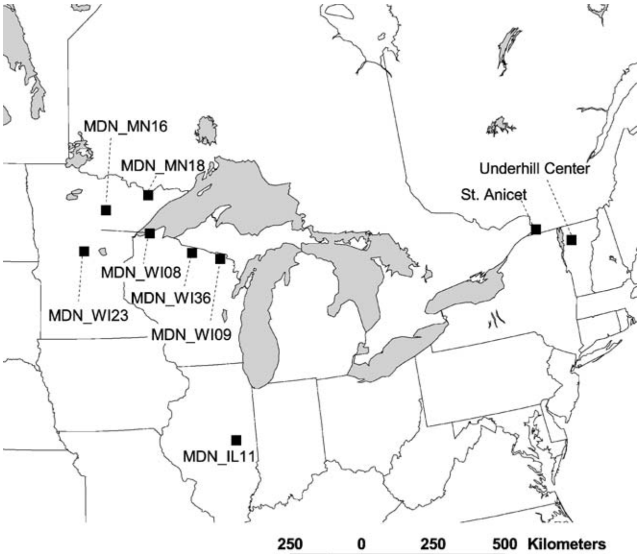

Fig. 7. Model evaluation sites for wet deposition fluxes within 250 km of any Great Lake with available data for 1996.

Precise agreement between measured and modeled values at any particular site is somewhat unlikely in the present analysis, given the coarse resolution of the meteorological data (180 km) and uncertainties in the amount, speciation, and temporal variation of emissions throughout the year. Moreover, the precipitation data from the NGM model represented *forecast*—not actual—precipitation at the sites and is known to be somewhat inaccurate. To approximately estimate the uncertainty associated with this aspect of the simulation, the wet deposition was estimated using *both* the NGM precipitation and the measured precipitation at the site. Despite all of the above, as the comparison in Fig. 8 shows, the model results are reasonably consistent with the measurements. In general, it can be seen that the model-predicted wet deposition flux tends to be lower than the measured fluxes. This result is not unexpected, given the omission of sources outside of the United States and Canada and all natural sources. Natural and global sources may affect wet deposition more strongly than dry deposition (Seigneur et al., 2003a), and so this systematic underprediction may be somewhat less for dry deposition.

Comparison with results from the Lake Michigan mass balance study. An additional evaluation exercise has been carried out by comparing the model-predicted deposition to Lake Michigan with measurement-based estimates obtained during the LMMBS (Landis and Keeler, 2002; Vette et al., 2002). An advantage of this comparison is that it is for an entire Great Lake (rather than a single location near a lake). This comparison is shown in Fig. 9 for estimated wet deposition of Hg(II) and Hg(p) (combined), dry deposition of Hg(II) and Hg(p), and total mercury deposition. The ranges shown for the LMMBS data are the reported standard

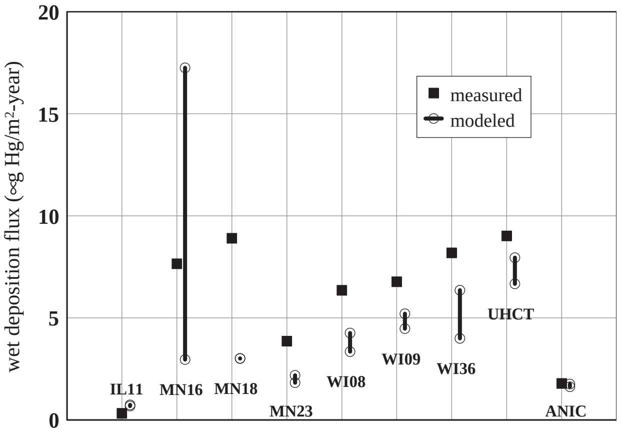

Fig. 8. Comparison of annual model-estimated wet deposition fluxes with measured values at sites within 250 km of the Great Lakes during 1996. The range of modeled estimates shown for each site represents the difference in estimated deposition in using the NGM-forecast *model* precipitation and the *actual* precipitation at the site.

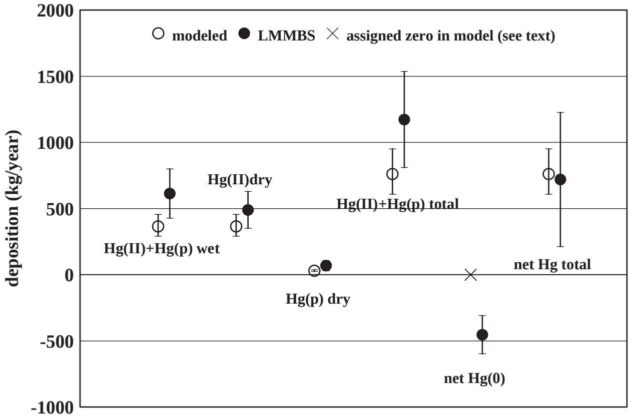

Fig. 9. Comparison of model-estimated deposition to Lake Michigan (1996) with that estimated in the LMMBS (1994–1995) (Landis and Keeler, 2002).

deviations (Landis and Keeler, 2002) for the estimates and are a measure of the uncertainty associated with these estimates. Analyses to estimate uncertainties in the HYSPLIT-based model estimates have not yet been carried out, but a rough estimate of the uncertainty (±25%) has been indicated for these data in Fig. 9.

The LMMBS measurement-based estimate of net Hg^0 deposition is also shown—actually a net evasion from the lake of 453±144 kg/year (thus, it is shown as a negative number, in contrast to the other values, which represent downward deposition to the lake). As discussed above, this quantity was not estimated in the modeling analysis, and so a comparison is not possible.

Precise agreement between the two sets of estimates would also not be anticipated, as the modeling results are for 1996, and the LMMBS measurements were carried out in 1994–1995. There were undoubtedly different weather patterns and precipitation amounts in these two periods, and perhaps even more importantly, mercury emissions during these two periods probably changed significantly. For example, during the 1994–1996 period, there were significant reductions in emissions from medical waste incinerators (due to the closure of many facilities) and municipal waste incinerators (due to closures, retrofits, and changes in waste stream composition). Moreover, the modeling analysis did not include contributions from sources outside the United States and Canada nor did it include the contribution of natural emissions. For all these reasons, one would expect that the model predictions would be somewhat less than the measurement-based deposition estimates. Nevertheless, it is encouraging to note that the model-predicted deposition amounts are the same order of magnitude as the measurement-based estimates and the difference between the two is in the expected direction.

3. Results and discussion

Given that the model appears to be providing results reasonably consistent with ambient measurements, we

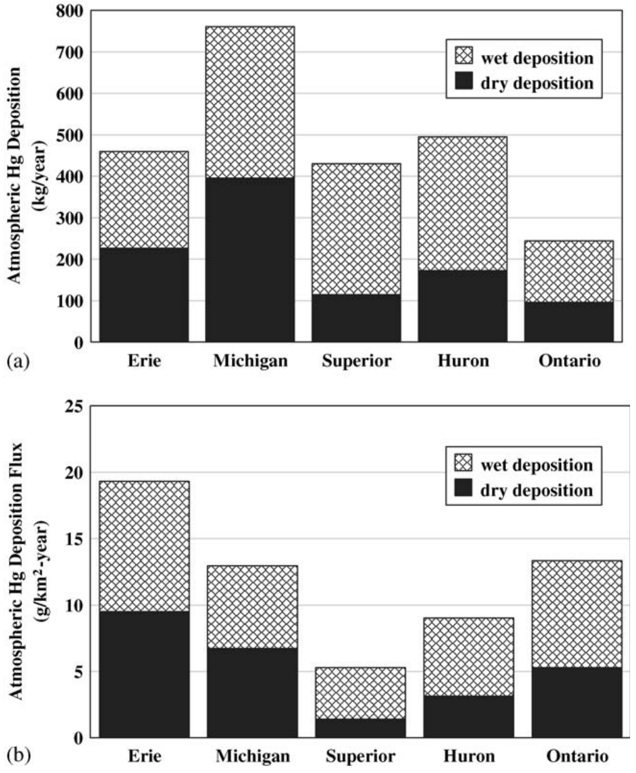

Fig. 10. Model-estimated annual atmospheric deposition amount (top) and flux (bottom) to the Great Lakes arising from anthropogenic sources in the United States and Canada.

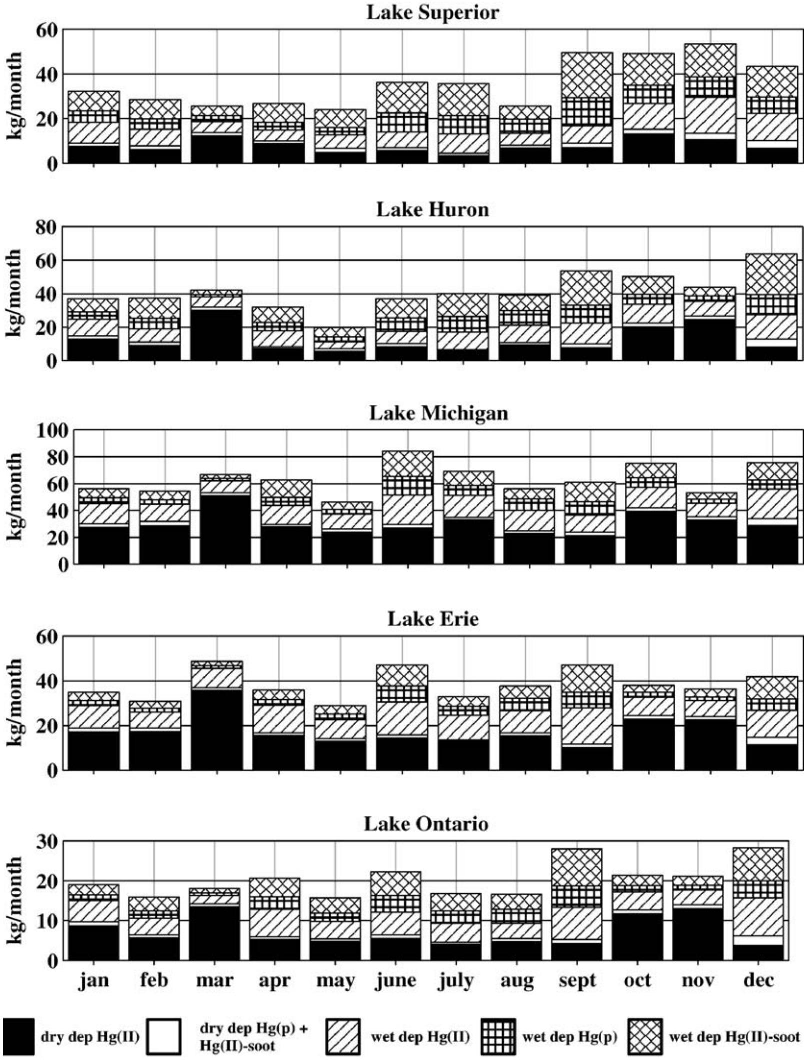

Fig. 11. Monthly model-predicted atmospheric wet and dry deposition of different forms of mercury to the Great Lakes during 1996.

can have some degree of confidence in the results of this source–receptor modeling methodology for mercury transport and deposition to the Great Lakes.

3.1. *Overall atmospheric deposition to the Great Lakes*

The overall model-estimated deposition amount (kg/year) and flux (g/km^2-year) of mercury to each of the Great Lakes is shown in Fig. 10 for both wet and dry deposition. It can be seen that both forms of deposition appear to be important. Lake Michigan is seen to have the greatest deposition amount, while Lake Erie appears to have the highest deposition flux.

Fig. 11 shows the monthly dry and wet deposition of the different forms of mercury to each of the Great Lakes. It can be seen that there is significant variation from month to month, and that while there is some similarity in the patterns among the different lakes, there are also significant differences.

3.2. *Geographical distribution of atmospheric deposition contributions of mercury*

As mentioned above, the modeling methodology described herein generates estimates of the contribution of *each* source in the emissions inventory (~106,000 discrete point and area source records) on *each* receptor of interest—representing unusually detailed source–receptor information. As a way of summarizing these results, Fig. 12 shows the geographical distributions of mercury source contributions to atmospheric deposition to Lake Superior. It can be seen that mercury deposition arises from throughout the region and that even distant sources can contribute significant amounts. For example, even sources in Florida appear to be able to contribute significant amounts of mercury to the lake.

Analogous maps for the other Great Lakes are provided as Supplementary Material. The geographical region of significant contributions is somewhat distinct

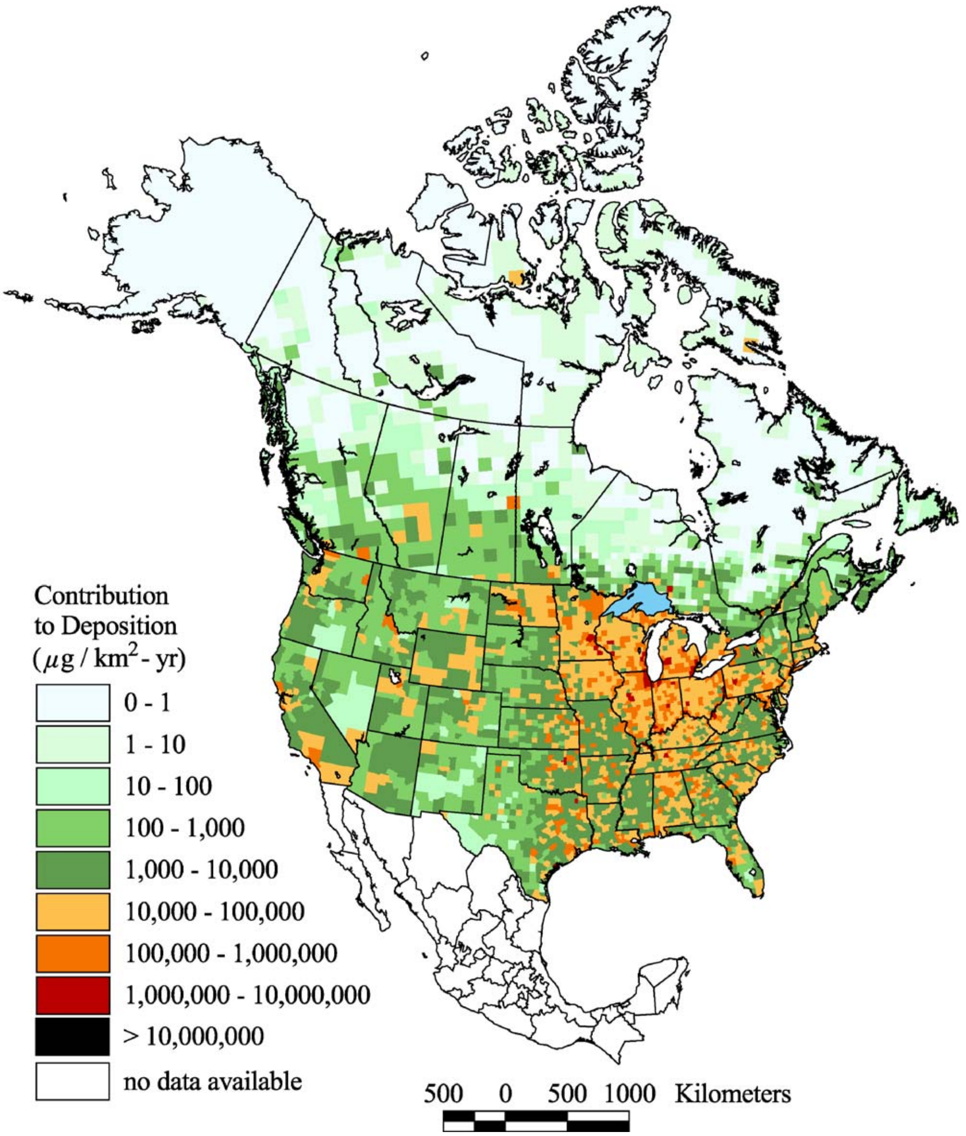

Fig. 12. Geographic distribution of contributions to atmospheric deposition of mercury to Lake Superior (μg/km^2-year).

for each lake, as would be expected given their different locations and the variations in the extent of industrialization and urbanization in each basin. For example, there are significant contributions to Lake Superior from the region within approximately 1000 km west of the lake, but the importance of this region to the other lakes is less, because the lakes are further away and have intense source regions nearby. For Lake Michigan, the contribution from the Chicago region stands out, due to its significant emissions and proximity to the lake; this particular region appears to be somewhat important for the other lakes also. For Lakes Erie and Ontario, contributions from the Ohio River Valley appear to be very significant, again, due to the high emissions in this region and the comparative proximity to these lakes. In general, for each of the lakes, contributions from the United States appear to be somewhat greater than contributions from Canada.

The geographical distribution of mercury contributions is illustrated in another manner in Fig. 13, where the emissions and contributions are shown as a function of distance from each lake. For Lake Superior and Lake Huron, significant deposition occurs from sources 200–1500 km from the lakes. For the other Great Lakes, there are more significant contributions from sources closer to the lakes, but, even for these lakes, the regional and long-range contributions are significant.

3.3. Atmospheric deposition contributions of mercury from different source types

In light of the limitations outlined in the discussion of emissions inventories earlier in this report, ascribing portions of the deposition to different source categories is an imprecise exercise. However, preliminary estimates of the impact of different source categories

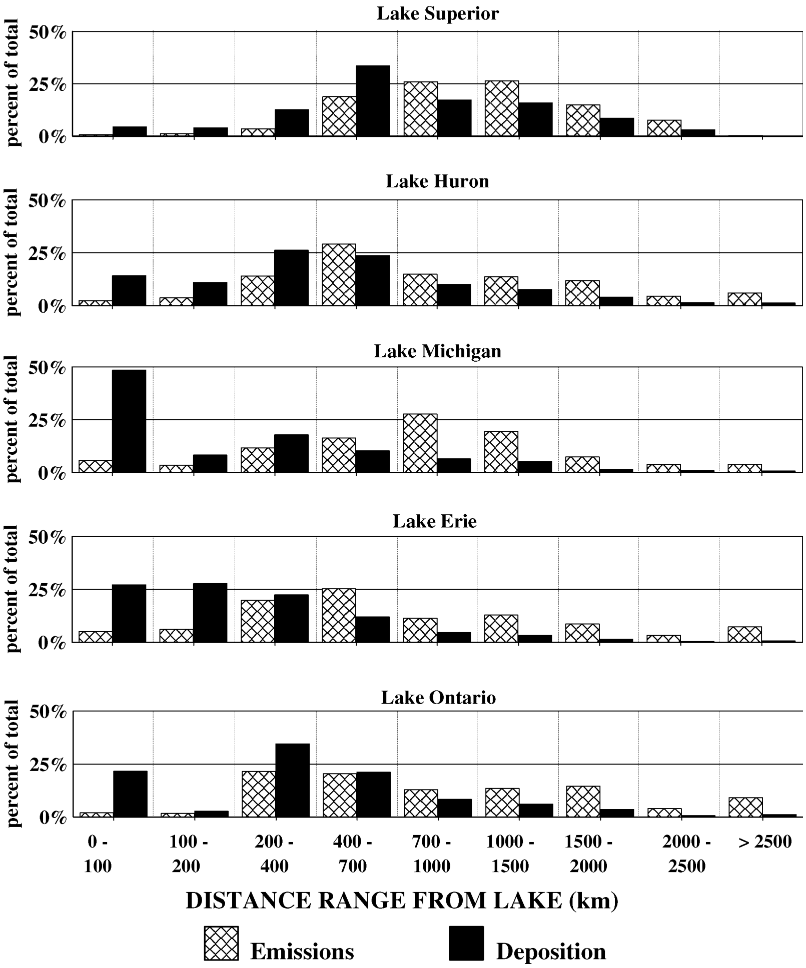

Fig. 13. Percentage of total estimated emissions and model-estimated deposition of mercury to the Great Lakes contributed from different distance ranges from each lake.

on deposition to the Great Lakes can be developed and are shown in Fig. 14.

This figure illustrates the *per capita* contribution from four broad source categories comprising the total inventory—fuel combustion, incineration, metallurgical operations, and manufacturing. This last category also includes emissions from a few non-manufacturing categories (e.g., fluorescent lamp breakage). One feature is the apparent relative importance of fuel combustion in the United States to mercury deposition in the Great Lakes. Most of the mercury emissions from this fuel combustion category come from various coal combustion activities (see Fig. 2), predominately the coal fired electrical utility sector. In Canada, by comparison on a *per capita* basis, metallurgical operations appear to have been the most important source sector in 1996 for most of the lakes.

As noted earlier, during and since the period under consideration in the model (1996) substantial reductions have been achieved in emissions from both municipal and medical waste incineration. The Canadian metallurgical operations have subsequently also lowered their mercury emissions. However, emissions from the coal-fired electrical utility sector have remained relatively stable up to the present.

4. Conclusions

The NOAA HYSPLIT_4 atmospheric fate and transport model has been used to generate the first detailed estimates of source–receptor relationships for atmospheric mercury deposition to the Great Lakes. While a number of uncertainties in emissions estimates, meteorological data, and the simulation of mercury's atmospheric chemistry were encountered, model results were consistent with ambient mercury measurements in the Great Lakes region. Long-range and regional transport was found to be very significant—at least 50% of the model-estimated deposition was contributed from sources 100–1500 km from each lake. Overall, coal combustion in the United States was found to be the most significant source category

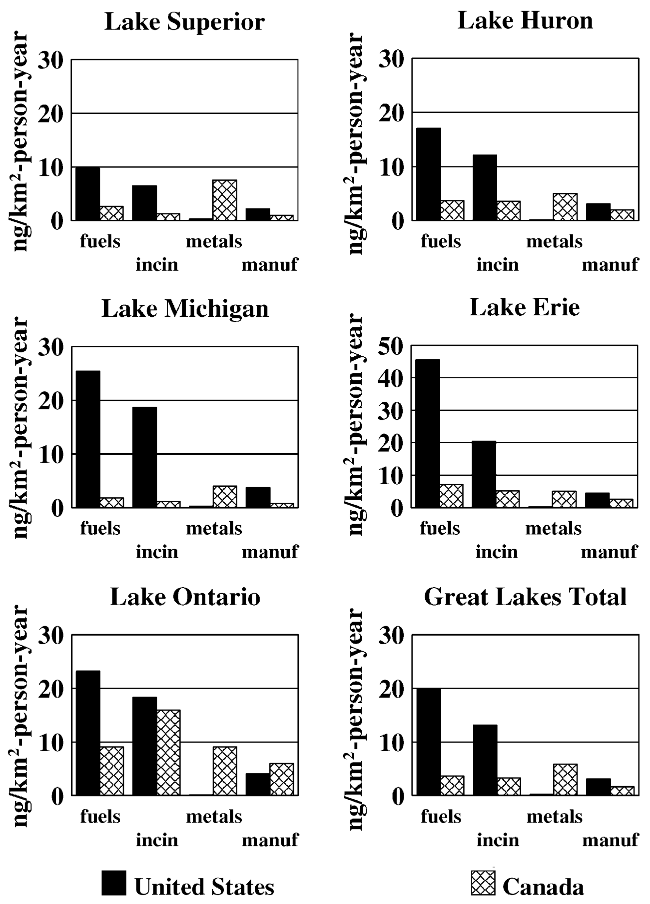

Fig. 14. Per capita mercury contributions to the Great Lakes from US and Canadian sources (ng Hg deposited per km^2 of lake surface per person per year); fuels, fuel combustion; incin, waste incineration; metals, metallurgical processes; manuf, includes other source types (e.g., lamp breakage) in addition to manufacturing processes (e.g., chloralkali production).

contributing mercury through atmospheric deposition to the Great Lakes.

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