



**SCOPING STUDY FOR MERCURY DEPOSITION
IN THE UPPER MIDWEST**

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Prepared for the

Midwest Regional Planning Organization
Des Plaines, IL

Document CP149-03-01a

June 2003

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EXECUTIVE SUMMARY

Mercury (Hg) is emitted into the atmosphere as gaseous (elemental, Hg(0), or divalent, Hg(II)) or particulate species (Hg(p)). Gaseous mercury can also adsorb to particulate matter (PM). In the atmosphere, mercury species can be converted from Hg(0) to Hg(II) and vice-versa. Most atmospheric Hg(II) is inorganic while organic Hg(II) is mostly present in water bodies.

Mercury is removed from the atmosphere via precipitation and dry deposition processes to the Earth's surface. Due to its higher solubility, Hg(II) is removed much more rapidly than Hg(0). Once deposited to the Earth's surface, mercury can enter the aquatic food chain in surface water bodies where it becomes methylated and bioaccumulates as methylmercury in fish. Sensitive human populations and wildlife that consume large amounts of fish may then be exposed to mercury concentrations that are potentially harmful to their health.

We present here a review of the current state of knowledge of atmospheric mercury with particular emphasis on the midwestern and northeastern United States.

Experimental Data from Monitoring Networks

The Mercury Deposition Network (MDN) includes a large number of sites where wet deposition of mercury is measured. Most of the sites are located in the eastern United States (i.e., east of the 100° longitude). This network provides useful information on the spatial and temporal variability of mercury wet deposition in the eastern United States. It has been used extensively for the performance evaluation of mercury atmospheric deposition models.

The MDN data show some patterns that can be explained with our current understanding of the atmospheric fate and transport of mercury. For example, an urban area such as Chicago, which has a variety of mercury emission sources (mobile sources, medical waste incinerators, municipal waste incinerators, etc.), seems to have some influence on mercury wet deposition. High concentrations of oxidants and PM that are typically associated with large urban areas may also contribute to the conversion of a small fraction of Hg(0) to Hg(II). On the other hand, some of the patterns that appear in the MDN data seem counter-intuitive. For example, it is not clear why northern Minnesota shows mercury wet deposition fluxes that exceed not only those of northern New York and Maine but also those of Pennsylvania. Most Pennsylvania sites are located downwind of an industrial area, the Ohio Valley, which includes large emissions of sulfur dioxide (SO₂) and mercury. The influence of this SO₂ source area on sulfate deposition appears clearly. However, the influence of the mercury sources in the Ohio Valley fails to appear in the mercury wet deposition measurements in Pennsylvania. Possible explanations for this Pennsylvania "anomaly" include the following:

- Underestimation of mercury emissions in the upper Midwest (e.g., taconite facilities)
- Reduction of Hg(II) to Hg(0) in the plumes of the major sources upwind of Pennsylvania
- Rapid local dry deposition of Hg(II) in the vicinity of the major sources upwind of Pennsylvania

Most MDN sites show a strong temporal variation throughout the year with higher deposition during spring and summer and lower deposition during winter in most cases. This pattern is more pronounced in the upper Midwest than in the Northeast.

Municipal incinerator mercury emissions have decreased by 12 Mg y⁻¹ from 1998 to 2000 due to the installation of Maximum Available Control Technology (MACT). This corresponds to 9% of the estimated U.S. anthropogenic emissions. In the same period, medical waste incinerator emissions have also decreased. However, only one region (northern New York and Maine) shows a decreasing trend in mercury deposition. All the other regions show decreases and increases that vary from year to year. It seems that this year-to-year variability masks the potential effect of the emission reduction from incinerators. As the MDN database grows, more meaningful long-term trend analyses can be carried out. It will be useful to compare such trends with the contemporaneous trends in mercury emissions to elucidate whether there is a discernible relationship between the levels of anthropogenic mercury emissions and mercury deposition.

The Lake Michigan Mass Balance Study (LMMBS) was conducted in the Lake Michigan region from July 1994 to October 1995. It included meteorological measurements over water with high spatial resolution as well as mercury concentration and wet deposition measurements at four sites located on the lake-shore. The seasonal variability of wet deposition during the LMMBS is consistent with the seasonal variability observed in the Mercury Deposition Network (see above). The most important aspect of the LMMBS is perhaps the strong decreasing spatial gradients from the southern part of the lake (i.e., near Chicago) to the northern part of the lake that were observed for both mercury wet deposition and ambient concentrations of Hg(p). This result suggests that an urban area such as Chicago has a significant effect on local and regional mercury deposition. For example, the Chicago urban area was estimated to contribute 14% of wet deposition to Lake Michigan. This conclusion is qualitatively consistent with the analysis of the MDN data presented above.

Emissions

There are significant uncertainties in the emission inventories of mercury species. These uncertainties fall into four major categories: (1) emissions of total mercury from specific anthropogenic source categories and individual sources, (2) natural emissions of mercury from land and oceans, (3) re-emissions of deposited mercury from land and oceans and (4) speciation of those emissions (i.e., relative fractions of Hg(0), Hg(II) and Hg(p)).

Anthropogenic emissions of mercury originate from a variety of sources including coal-fired power plants, municipal waste incinerators, medical waste incinerators, chlor-alkali plants, mobile sources, taconite facilities, cement plants, coal combustion from non-utility sources and numerous other industrial, residential and commercial sources.

Among these sources, coal-fired power plants are the best characterized sources in terms of both emission rate and speciation of mercury because of the Information Collection Request (ICR) program that was implemented by the U.S. Environmental Protection Agency (EPA). This program required, starting in 1999, that all power plants provide information on the mercury content of their coal and that stack emission measurements be conducted to characterize speciated mercury emissions at eighty power plants. No such comprehensive emission measurement program has been conducted for the other source categories. The Toxics Release Inventory (TRI) program of EPA provides quantitative information on the annual amounts of toxic compounds released to the various media, including the atmosphere. However, TRI reporting is not subject to the same scrutiny as more focused programs such as ICR. As a result, the amount reported may be inaccurate or even not reported. Moreover, TRI reporting does not provide any information regarding mercury speciation.

In the absence of facility specific information on the speciation of the mercury emissions, one must rely on other sources of data, such as source sampling conducted at another similar facility. Unfortunately, there is a paucity of such data and one must, in most cases, rely on a single facility to characterize the mercury speciation of an entire source category. However, there is a fair amount of variability within a source category that is not represented when using data from a single facility.

Natural emissions and re-emission of mercury occur from mercuriferous land areas, other land areas and water bodies including the oceans. Uncertainties in these emissions affect the relative contributions of anthropogenic and natural emissions to the global mercury cycle and, consequently, to mercury deposition.

The chemical speciation of mercury emissions is of utmost importance because Hg(0) will enter the global background due to its long atmospheric lifetime whereas Hg(II) and Hg(p) may deposit locally or regionally.

Atmospheric Transformations

Known transformations among inorganic mercury species include the gas-phase oxidation of Hg(0) to Hg(II), the aqueous-phase oxidation of Hg(0) to Hg(II), the aqueous-phase reduction of Hg(II) to Hg(0), various aqueous-phase equilibria of Hg(II) species and the aqueous-phase adsorption of Hg(II) to PM. However, it should be noted that our knowledge of mercury chemistry continues to evolve as new laboratory data become available, and the chemical kinetic mechanisms currently used in models may need to be revised accordingly.

There seems to be some circumstantial evidence of reduction of Hg(II) to Hg(0) in power plant plumes from various experimental studies including dilution chamber experiments, data from MDN (see above) and continuous ambient measurements of speciated mercury downwind of power plants. Some aircraft measurement campaigns are being performed to elucidate whether such conversion of Hg(II) to Hg(0) indeed takes place in power plant plumes. Results are not yet available from these aircraft campaigns. If the reduction of Hg(II) to Hg(0) in plumes is confirmed by field data, the processes that govern such reaction(s) will then need to be identified and the models of the atmospheric fate and transport of mercury will need to be revised accordingly.

Deposition

The removal of mercury from the atmosphere occurs via dry deposition and wet deposition.

Hg(0) is sparingly soluble and is not removed significantly by wet deposition; its dry deposition velocity is also believed to be low. As a result, Hg(0) has a long atmospheric lifetime, on the order of several months, that is governed by its oxidation to Hg(II).

On the other hand, Hg(II) is quite soluble and can adsorb to PM and surfaces; it is consequently removed rapidly by wet and dry deposition processes. Data collected at two rural sites in Indiana and Tennessee show that Hg(II) has a relatively high dry deposition velocity (0.4 cm s^{-1} over grass and 5.1 to 5.9 cm s^{-1} over the forest canopy for the conditions of the measurements). Measurements of mercury concentrations in the ambient air before and after rain events showed that Hg(II) was significantly depleted (by about 50%) whereas Hg(0) was not significantly depleted (10% or less).

Particulate mercury, Hg(p), is mostly present in the fine fraction of particulate matter (PM_{2.5}), although some Hg(p) may be present in coarse PM. Because fine PM has a low dry deposition velocity, one expects the atmospheric lifetime of Hg(p) in the absence of precipitation to be on the order of several days.

Recommendations

As discussed above, there are still significant uncertainties in our understanding of the atmospheric fate and transport of mercury. Many of those uncertainties can be minimized by obtaining experimental data on the emissions, transformations and deposition of mercury species.

Improving emission inventories for mercury will require additional experimental field programs that can fall into the following categories:

- Characterization of anthropogenic mercury emissions (including chemical speciation) at selected facilities

- Characterization of background emissions (i.e., natural emissions and re-emissions) of mercury
- Reconciliation of mercury emission factors and emission speciation with ambient measurements

There are few data currently available on the chemical speciation of mercury in the atmosphere. For example, the measurements conducted during the Lake Michigan Mass Balance Study did not include any Hg(II) measurements despite the fact that Hg(II) is the mercury species that contributes the most to mercury deposition. Instruments are now available to measure mercury continuously with mercury speciation (i.e., Hg(0), Hg(II) and Hg(p)). Consequently, we recommend that such measurements be conducted to develop a comprehensive database of speciated mercury ambient concentrations in a variety of environments (e.g., urban, suburban, rural and remote sites). Such speciated mercury data can be used to

- Evaluate models of the atmospheric fate and transport of mercury
- Reconcile the ambient speciation of mercury with source-specific emission speciation (see above)
- Estimate dry deposition fluxes

The Mercury Deposition Network (MDN) provides a reasonably comprehensive network for characterizing mercury wet deposition. The collection of mercury wet deposition data on an event basis will be a useful addition because such data can be used in combination with other information on meteorology and ambient chemistry to investigate the possible causes of high mercury wet deposition events.

There is currently a paucity of data on the dry deposition of mercury species. Dry deposition of mercury is commensurate with wet deposition. It is, therefore, essential to properly characterize the dry deposition flux of mercury to obtain an accurate estimate of the total deposition of mercury to the Earth's surface. To that end, we recommend that dry deposition flux measurements be conducted over a variety of surface areas (e.g., urban, agricultural, forest and surface water).

1. INTRODUCTION

Mercury (Hg) is emitted into the atmosphere as gaseous or particulate species. Gaseous mercury can be either elemental, Hg(0), or divalent, Hg(II). Gaseous mercury can also adsorb to particulate matter (PM). In the atmosphere, mercury species can be converted from Hg(0) to Hg(II) and vice-versa. Most atmospheric Hg(II) is inorganic and organic Hg(II) is mostly present in water bodies.

Mercury is removed from the atmosphere via precipitation and dry deposition processes to the Earth's surface. The atmospheric lifetime of Hg(0) is believed to be on the order of a few months. Hg(0) is not deposited rapidly to the Earth's surface and its atmospheric lifetime is, therefore, governed by oxidation to Hg(II). Gaseous Hg(II) species tend to have an atmospheric lifetime of several hours to a few days because of their high solubility that favors their removal by wet and dry deposition. Particulate mercury is present mostly in fine particles and, in the absence of precipitation, it can remain in the atmosphere for several days.

Once deposited to the Earth's surface, mercury can enter the aquatic food chain in surface water bodies where it becomes methylated and bioaccumulates as methylmercury in fish. Sensitive human populations and wildlife that consume large amounts of fish may then be exposed to mercury concentrations that are potentially harmful to their health.

We present here a review of the current state of knowledge of atmospheric mercury with particular emphasis on the midwestern and northeastern United States. First, we review existing data on the atmospheric deposition and ambient concentrations of mercury. We review data from the Mercury Deposition Network (MDN) in Section 2 and data from the Lake Michigan Mass Balance Study in Section 3. Next we review the current knowledge of the emissions (Section 4), transformations (Section 5) and deposition processes (Section 6) of mercury. In addition, we discuss the major sources of uncertainties for each of those areas. Recommendations for conducting specific studies that would help in reducing the major sources of uncertainties are provided in Section 7.

2. MERCURY DEPOSITION NETWORK DATA

2.1. The Mercury Deposition Network

The Mercury Deposition Network (MDN) (NADP/MDN, 2003) includes a large number of sites where wet deposition of mercury is measured. As shown in Figure 2-1, most of the sites are located in the eastern United States (i.e., east of the 100° longitude). This network provides useful information on the spatial and temporal variability of mercury wet deposition in the eastern United States. It has been used extensively for the performance evaluation of mercury atmospheric deposition models (e.g., Pai et al., 1997; Bullock et al., 1997; Seigneur et al., 2001a, 2003a, 2003b; Bullock and Brehme, 2002). We are using the MDN database here to develop some understanding of the spatial and temporal patterns in mercury wet deposition.

2.2. Spatial Patterns

Figures 2-2 through 2-5 show the annual mercury deposition wet fluxes measured by MDN over the past four years for which data are available (i.e., 1998 through 2001). Some general spatial patterns emerge from those data.

We see from the MDN data that mercury wet deposition fluxes in the southeastern United States are greater than in the northeastern United States. In 2001, for example, mercury wet deposition in Florida exceeds $14 \mu\text{g m}^{-2} \text{y}^{-1}$; it is in the range of 6 to $10 \mu\text{g m}^{-2} \text{y}^{-1}$ in the Carolinas and in the range of 4 to $6 \mu\text{g m}^{-2} \text{y}^{-1}$ in Maine.

The spatial patterns in the northern part of the eastern United States are, however, more complex. For this analysis, we grouped the MDN sites according to the following regions: northern Minnesota; central and southern Minnesota; northern Wisconsin; southern Wisconsin, Illinois and Indiana; Pennsylvania; and northern New York and Maine. The sites located in northern Minnesota, northern Wisconsin, northern New York and Maine are distant from major anthropogenic emission sources of mercury. The sites in southern Minnesota, southern Wisconsin, Illinois, Indiana and Pennsylvania are more likely to be influenced by local or regional anthropogenic emission sources.

Table 2-1 summarizes the annual mercury wet deposition fluxes for these six regions. Clearly, there are large overlaps in the values of the mercury deposition fluxes among these regions. Nevertheless, some patterns emerge when we compare the mean values and/or eliminate the outliers. The northeastern region (northern New York and Maine) has the lowest mercury wet deposition with a mean value of $7.0 \mu\text{g m}^{-2} \text{y}^{-1}$. The region around Chicago (i.e., southern Wisconsin, Illinois and Indiana) shows the largest mercury wet deposition with a mean value of $11.3 \mu\text{g m}^{-2} \text{y}^{-1}$. As expected, the northern Minnesota sites (mean wet deposition of mercury of $8.9 \mu\text{g m}^{-2} \text{y}^{-1}$) and northern Wisconsin (mean wet deposition of mercury of $8.6 \mu\text{g m}^{-2} \text{y}^{-1}$) show similar results that are lower than those observed in the region surrounding Chicago. The central/southern

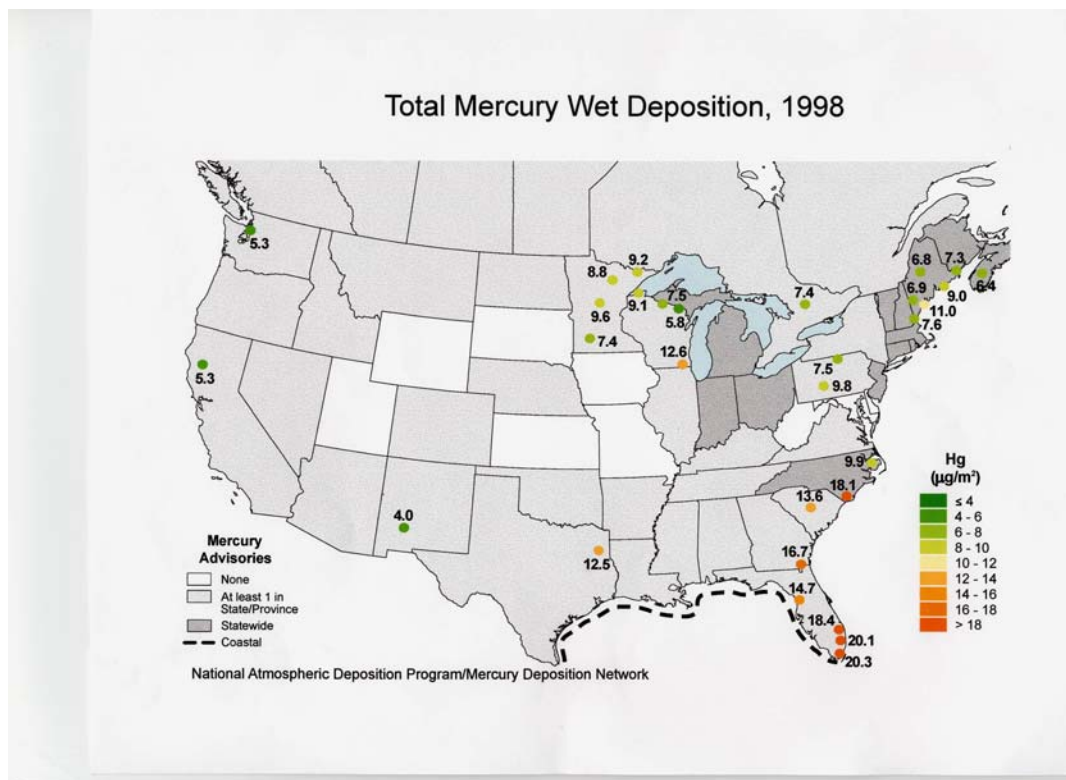


Figure 2-2. Annual mercury wet deposition fluxes ($\mu\text{g}/\text{m}^2\text{-y}$) at MDN sites in 1998 (NADP/MDN, 2003).

Table 2-1. Summary of MDN annual wet deposition fluxes ($\mu\text{g m}^{-2} \text{y}^{-1}$) for the midwestern and northeastern United States (the ranges at individual MDN sites are shown in parentheses).

Region	1998	1999	2000	2001	Average
Northern Minnesota	9.0 (8.8-9.2)	9.5 (8.0-11.0)	9.0 (8.6-9.5)	8.2 (7.2-9.3)	8.9
Central & southern Minnesota	8.5 (7.4-9.6)	9.5 (6.7-12.4)	8.5 (7.6-9.5)	9.6 (7.2-12.1)	9.1
Northern Wisconsin	7.5 (5.8-9.1)	10.5 (9.0-13.3)	8.6 (7.5-9.2)	7.9 (7.7-8.0)	8.6
Southern Wisconsin, Illinois and Indiana	12.6 (12.6)	9.1 (9.0-9.2)	12.0 (9.6-14.5)	11.7 (9.0-13.0)	11.4
Pennsylvania	8.6 (7.5-9.8)	7.3 (5.6-9.1)	9.4 (7.0-12.5)	8.1 (4.9-11.4)	8.4
Northern New York and Maine	8.4 (6.8-11.0)	7.5 (6.9-8.4)	7.3 (5.2-8.7)	5.1 (4.0-6.3)	7.1

Minnesota region shows a mean mercury wet deposition value ($9.0 \mu\text{g m}^{-2} \text{y}^{-1}$) that is quite similar to that of northern Minnesota. However, while the two northern Minnesota sites show values that are within $3 \mu\text{g m}^{-2} \text{y}^{-1}$ of each other, the central and southern Minnesota sites show much greater differences (up to $5.7 \mu\text{g m}^{-2} \text{y}^{-1}$). The central Minnesota site shows greater mercury wet deposition than the southern Minnesota site in 1998, 1999 and 2001 but the reverse is true in 2000. The Pennsylvania region shows relatively low mercury wet deposition (mean value of $8.3 \mu\text{g m}^{-2} \text{y}^{-1}$) compared to the other regions except the Northeast. This result appears counter-intuitive because Pennsylvania is located downwind of the Ohio Valley, a region that includes large mercury emission sources.

Figure 2-6 shows a recent inventory of mercury anthropogenic emissions for the United States. It is clear that mercury anthropogenic emissions are greater in the eastern United States than in the Midwest, in part because of the greater density of coal-fired power plants in the Ohio Valley. Comparing this emission map with the MDN mercury wet deposition maps, we see that there is no obvious correspondence between the emission source regions (e.g., the Ohio Valley) and the mercury deposition regions (e.g., Pennsylvania). Figure 2-7 shows the sulfate annual deposition fluxes measured at the National Acid Deposition Program (NADP) sites in 2001. The sulfate deposition patterns are consistent with greater deposition around and downwind of the Ohio Valley. Therefore, the sulfate deposition patterns suggest that mercury transformations and deposition follow different patterns than those of sulfur species.

The Chicago urban area may explain some of the high mercury deposition observed in southern Wisconsin and northern Indiana (see Section 3). The Pennsylvania sites near Pittsburgh show greater mercury wet deposition than the other Pennsylvania sites in 1998, 1999 and 2001 (but not in 2000). The site in southeastern Pennsylvania near Philadelphia shows the highest (in 2000) or third highest (after the two sites near Pittsburgh in 2001) mercury wet deposition among the Pennsylvania sites. There are no MDN sites located near other major eastern cities such as Washington, New York and Boston. This slight association between some urban areas and their corresponding MDN sites suggests that urban areas may be significant contributors to mercury wet deposition. The contribution of urban areas to mercury deposition may be due to their mercury emissions as well as to the high concentrations of oxidants (e.g., ozone and OH radicals) and PM that may be conducive to the oxidation of a small fraction of Hg(0) to Hg(II) (see Section 5).

Mercury wet deposition is, of course, affected by the amount of precipitation. It is, therefore, important to assess whether the patterns that we identified above are a result of precipitation amount and/or mercury atmospheric concentrations. To that end, we present in Table 2-2 the mercury annual concentrations in rain for the same regions as those used in Table 2-1. The lowest mercury concentrations in precipitation occur in northern New York and in Maine. This is consistent with the results presented above that showed that this region had the lowest mercury wet deposition fluxes. The next lowest mercury concentrations occur in Pennsylvania. As a matter of fact, from 1998 to 2000,

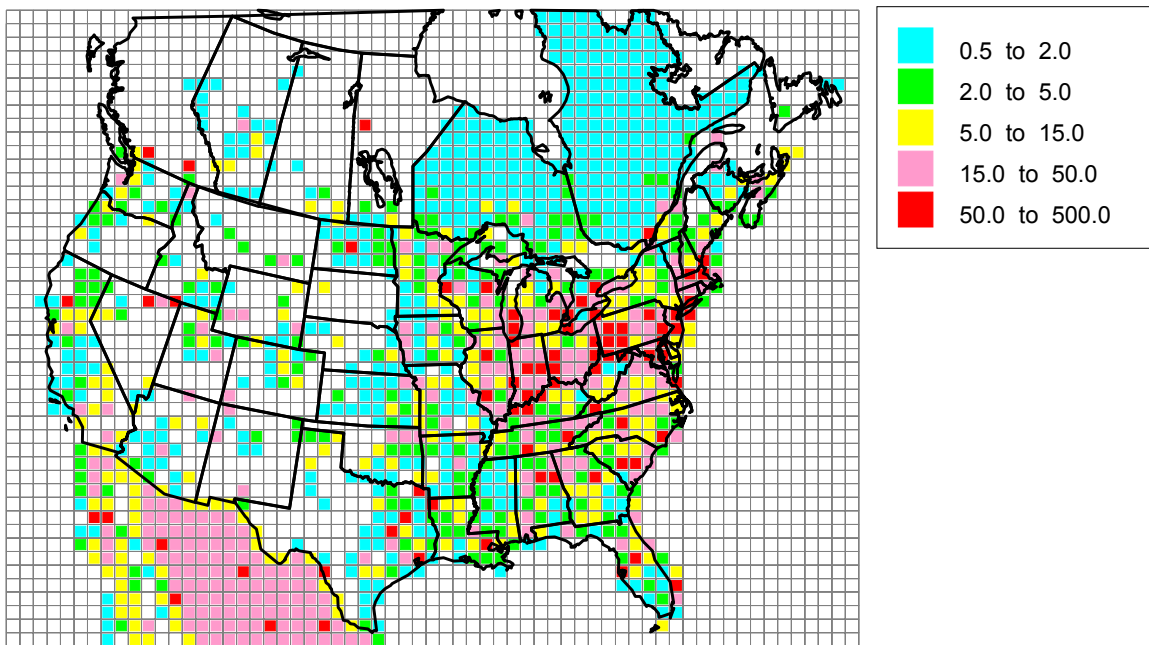


Figure 2-6. Example of an anthropogenic mercury emissions inventory for North America ($\mu\text{g m}^{-2} \text{y}^{-1}$) (based on Seigneur et al., 2003b).

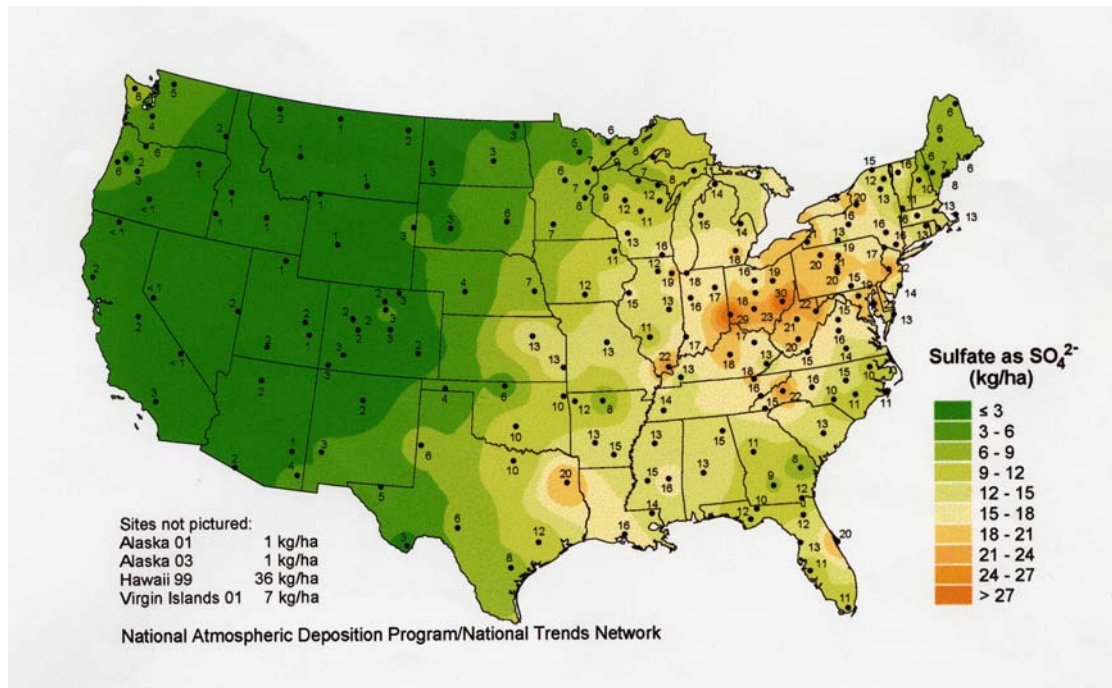


Figure 2-7. Annual sulfate wet deposition fluxes (kg/ha-y) at NADP sites in 2001 (NADP, 2003).

Table 2-2. Summary of MDN annual mercury concentrations in precipitation (ng l⁻¹) for the midwestern and northeastern United States (the ranges at individual MDN sites are shown in parentheses).

Region	1998	1999	2000	2001	Average
Northern Minnesota	12.7 (11.3-14.1)	12.0 (11.3-12.7)	13.5 (12.5-14.5)	11.3 (9.3-13.3)	12.4
Central & southern Minnesota	13.0 (12.5-13.6)	16.1 (15.2-17.0)	13.5 (11.8-15.2)	11.6 (9.7-13.6)	13.5
Northern Wisconsin	11.6 (11.3-11.9)	12.4 (10.9-13.7)	12.2 (10.6-14.4)	10.1 (9.3-11.0)	11.6
Southern Wisconsin, Illinois and Indiana	12.4 (12.4)	10.3 (10.0-10.6)	12.5 (11.6-13.4)	11.9 (10.2-13.4)	11.8
Pennsylvania	9.5 (8.9-10.2)	8.1 (7.0-9.3)	10.1 (9.0-11.2)	10.4 (6.6-14.3)	9.5
Northern New York and Maine	6.8 (6.1-8.6)	6.4 (5.5-7.3)	6.4 (5.1-7.0)	6.9 (6.2-8.0)	6.6

the highest mercury concentration measured in Pennsylvania was lower than all mercury concentrations measured in Minnesota and Wisconsin. Therefore, the fact that the mercury deposition fluxes in Pennsylvania are lower on average than those observed in Minnesota and Wisconsin is not due to lower precipitation but to lower mercury concentrations in precipitation. In fact, there is more precipitation in Pennsylvania than in Minnesota or Wisconsin on average (see Table 2-3).

In summary, the mercury wet deposition measurements show some spatial patterns that can be explained with our current understanding of the atmospheric fate and transport of mercury. For example, an urban area such as Chicago, which has a variety of mercury emission sources (mobile sources, medical waste incinerators, municipal waste incinerators, etc.), seems to have some influence on the wet deposition flux of atmospheric mercury. On the other hand, some of the spatial patterns that appear in the MDN data seem counter-intuitive. For example, it is not clear why northern Minnesota shows mercury wet deposition fluxes that exceed not only those of northern New York and Maine but also those of many areas in Pennsylvania. As mentioned above, most Pennsylvania sites are located downwind of an industrial area, the Ohio Valley, which includes large emissions of sulfur dioxide (SO₂) and mercury. The influence of this SO₂ source area on sulfate deposition appears clearly (see Figure 2-7 and Table 2-4). Yet, the influence of this mercury source area fails to appear in the mercury wet deposition measurements. As a result, simulations conducted with models that contain our current understanding of mercury physics and chemistry tend to overpredict mercury wet deposition in Pennsylvania (e.g., Seigneur et al., 2003a). Possible explanations for this Pennsylvania “anomaly” include the following:

- Underestimation of mercury emissions in the upper Midwest (e.g., taconite facilities)
- Reduction of Hg(II) in the plumes of the major sources upwind of Pennsylvania
- Rapid local dry deposition of Hg(II) in the vicinity of the major sources upwind of Pennsylvania

We will discuss these possibilities further in Sections 4, 5 and 6, respectively.

Another hypothesis is that a large fraction of Hg(II) would adsorb onto PM (because of a greater availability of PM); therefore, a smaller fraction of Hg(II) would be available for precipitation scavenging. However, most of the PM surface area that is available for adsorption is in the fine mode, and the removal of sulfate by precipitation (see Figure 2-7) suggests that fine PM is removed to a large extent by precipitation. Therefore, it is unlikely that the adsorption of mercury to PM could explain the differences observed in mercury deposition between Pennsylvania and Minnesota.

Table 2-3. Summary of annual precipitation amounts (cm y⁻¹) for the midwestern and northeastern United States (the ranges at individual MDN sites are shown in parentheses).

Region	1998	1999	2000	2001	Average
Northern Minnesota	71 (62-80)	83 (76-91)	68 (64-73)	78 (76-81)	75
Central & southern Minnesota	64 (60-69)	75 (50-74)	67 (62-72)	82 (75-89)	72
Northern Wisconsin	59 (53-66)	77 (71-84)	79 (79)	76 (71-82)	73
Southern Wisconsin, Illinois and Indiana	103 (94-113)	85 (75-95)	98 (87-110)	93 (82-104)	95
Pennsylvania	110 (110)	97 (82-113)	62 (109-124)	76 (63-89)	86
Northern New York and Maine	121 (110-147)	113 (99-128)	117 (109-122)	75 (63-96)	106

Table 2-4. Summary of annual sulfate deposition fluxes ($\text{kg ha}^{-1} \text{y}^{-1}$) for the midwestern and northeastern United States (the ranges at individual MDN sites are shown in parentheses).

Region	1998	1999	2000	2001	Average
Northern Minnesota	7 (7-7)	7 (7-8)	5 (5-6)	5 (5-6)	6
Central & southern Minnesota	8 (8-8)	6 (5-8)	6 (6-6)	6 (6-7)	7
Northern Wisconsin	6 (6-7)	7 (7-8)	7 (7)	7 (7-8)	7
Southern Wisconsin, Illinois and Indiana	23 (18-26)	18 (15-20)	16 (14-19)	16 (13-18)	18
Pennsylvania	20 (20)	18 (16-21)	22 (22-23)	16 (15-17)	19
Northern New York and Maine	14 (10-18)	10 (9-11)	11 (8-15)	8 (6-13)	11

2.3. Temporal Patterns

Table 2-5 shows the mercury wet deposition fluxes by quarter for 2001. Most sites show a strong temporal variation throughout the year.

The Minnesota and Wisconsin sites show higher deposition (more than 40% of annual deposition) during April-June (Site MN18 is an exception but it is missing data from April 1 to 16). The second highest (or highest for Site MN18) mercury deposition occurs during July-September. At most sites, January-March shows the lowest deposition (1 to 13% of annual deposition).

The temporal pattern is different in the other regions. In Illinois and Indiana, January-March still shows the lowest deposition (6 to 15% of annual deposition); however, the period with the highest deposition is more evenly distributed across April-June, July-September and, for some sites, October-December.

In Pennsylvania, five sites show the highest deposition during April-June (37 to 67% of annual deposition), one site in July-September (38%) and one during July-September and October-December (28%). This latter site (PA30) shows mercury deposition that is fairly well distributed through the year (quarterly deposition is 22 to 28% of annual deposition). At the other six sites, the lowest deposition occurs in January-March for three sites and in October-December for the other three sites.

The greater deposition of mercury during the warmer months may result from a variety of causes including (1) greater concentrations of oxidants (ozone and OH radicals) that oxidize Hg(0) to Hg(II) and would lead to greater concentrations of Hg(II), (2) greater emissions of mercury from some source categories during the warmer months (e.g., greater use of power plants during summer due to an increase use of air conditioning), (3) greater scavenging of atmospheric mercury by summer storms than by precipitation during other seasons, or (4) a combination of those factors. A better understanding of the seasonal variability of mercury emissions, atmospheric chemistry and precipitation scavenging is needed to diagnose the reasons for the seasonal variation observed in mercury wet deposition.

It is also of interest to note the year-to-year variability in mercury deposition. Municipal incinerator mercury emissions have decreased by 12 Mg y⁻¹ from 1998 to 2000 due to the installation of Maximum Available Control Technology (MACT) (see Section 4.4). This corresponds to 9% of the estimated U.S. anthropogenic emissions. In the same period, medical waste incinerator emissions have also decreased. However, only one region (northern New York and Maine) shows a decreasing trend. All the other regions show decreases and increases that vary from year to year. Such a year-to-year variability masks the potential effect of the emission reduction from incinerators.

As the MDN database grows, more meaningful long-term trend analyses can be carried out. It will be useful to compare such trends with the contemporaneous trends in

Table 2-5. Seasonal distribution of wet deposition of mercury in 2001 (Source: NADP/MDN, 2003)

Site	Annual Total ($\mu\text{g m}^{-2} \text{y}^{-1}$)	Jan-Mar (%) ^a	Apr-Jun (%) ^a	Jul-Sep (%) ^a	Oct-Dec (%) ^a
MN16	7.2	13	44	29	14
MN18	9.3	3	19	46	32
MN23	12.1	1	57	35	7
MN27	7.2	7	47	39	6
WI08	7.7	10	51	29	11
WI09	7.9	4	52	31	12
WI31	12.3	6	47	34	13
WI36	8	4	54	24	18
WI99	13	8	45	33	14
IL11	9	15	36	34	15
IN20	12.1	8	36	40	16
IN21	12.6	11	25	28	36
IN28	11.9	6	30	44	20
IN34	11	13	30	29	27
PA00	6.8	22	41	21	15
PA13	11.4	7	67	15	11
PA30	7.4	23	22	28	28
PA37	9.5	12	37	34	16
PA60	8.3	33	40	20	8
PA72	8.5	17	41	30	12
PA90	4.9	10	34	38	18

a. Percent values may not add to 100 due to round-off error

mercury emissions to elucidate whether there is a discernible relationship between the levels of anthropogenic mercury emissions and mercury deposition. For example, the effect of the implementation of MACT standards on incinerators from 1998 to 2000 on mercury deposition in the United States could be investigated.

3. LAKE MICHIGAN MASS BALANCE STUDY

The Lake Michigan Mass Balance Study (LMMBS) was conducted in the Lake Michigan region from July 1994 to October 1995. It included meteorological measurements over water with high spatial resolution as well as mercury concentration and wet deposition measurements at several sites. Mercury measurements were conducted at four sites on the lake-shore: Kenosha, WI at the border between Wisconsin and Illinois; Chicago, IL; Sleeping Bear Dunes, MI in the northern part of Lake Michigan; and South Haven, MI in the southern part of Lake Michigan.

Landis and Keeler (2002) used these measurements to develop estimates of mercury deposition over Lake Michigan. For wet deposition, they used the precipitation data and mercury concentrations in precipitation available at the four measurement sites to develop estimates of precipitation and mercury concentrations in precipitation over the entire area of Lake Michigan using an advanced interpolation technique referred to as “kriging”. Then, mercury wet deposition was calculated as the product of precipitation and mercury concentration in precipitation. For dry deposition, they first estimated the meteorological variables (wind speed, temperature, relative humidity) and concentrations of gaseous and particulate mercury over the entire area of Lake Michigan using the same interpolation technique (kriging). Next, they used a mathematical model of dry deposition that includes the effects of meteorology and land cover on dry deposition velocities as well as the effect of the particle size distribution for particulate mercury.

Wet deposition of mercury over the 16-month period and spatially averaged over the Lake Michigan area was $15.5 \mu\text{g m}^{-2}$. This corresponds to a total atmospheric input of 895 kg for Lake Michigan for the 16-month period. The corresponding annualized values are $10.6 \mu\text{g m}^{-2}$ and 614 kg. There is, however, significant temporal and spatial variability in the mercury wet deposition fluxes over Lake Michigan. Wet deposition is more important during summer months (July and August) with monthly values of 1.78 and $1.79 \mu\text{g m}^{-2}$ (i.e., about 38% greater than the mean). This greater wet deposition is due to greater precipitation amounts as well as greater mercury concentrations. Wet deposition is lowest in February with a monthly value of $0.18 \mu\text{g m}^{-2}$ (i.e., about 14% of the mean). Thus, monthly mercury wet deposition values cover a range with an order of magnitude difference between the highest and lowest values. The spatial variability of mercury wet deposition shows a strong south-to-north gradient with greater wet deposition in the southern part of Lake Michigan. This greater wet deposition is due to both greater precipitation amounts and greater mercury concentrations near Chicago.

Dry deposition of mercury was calculated for Hg(p) and gaseous Hg(II) (Hg(0) is sparingly soluble and, therefore, its dry deposition to a water body is negligible). Over the 16-month period, the spatially averaged dry deposition flux of Hg(p) was calculated to be $1.6 \mu\text{g m}^{-2}$, which corresponds to 92 kg for the total loading to Lake Michigan. The corresponding annualized values are $1.2 \mu\text{g m}^{-2}$ and 69 kg. No clear temporal trend appeared for Hg(p) dry deposition but there was significant variability from month to

month (lowest value of $0.06 \mu\text{g m}^{-2}$ in April, June and August 1995 and highest values of 0.15 and $0.14 \mu\text{g m}^{-2}$ in September and February 1995 and November 1994). The dry deposition flux of Hg(p) was nearly one order of magnitude greater in the southern part of Lake Michigan (i.e., near Chicago) than in the northern part because of greater Hg(p) concentrations in the southern part. No gaseous Hg(II) measurements were performed; this is a major source of uncertainty in the LMMBS because gaseous Hg(II) dominates dry deposition. To estimate the dry deposition of Hg(II), the assumption was made that Hg(II) constituted 1 to 5% of total gaseous mercury (TGM) (Vette et al., 2002). This assumption is based on data collected by Lindberg and Stratton (1998) at different locations (in rural Indiana and Tennessee); it includes seasonal and diurnal profiles. Clearly, this Hg(II)/TGM ratio is an approximation of the actual ratio over Lake Michigan and a major source of uncertainty in the deposition estimates. The dry deposition flux of gaseous Hg(II) over the 16-month period was calculated to be $11.7 \mu\text{g m}^{-2}$, which corresponds to 676 kg for the entire lake area. The corresponding annualized values are $8.5 \mu\text{g m}^{-2}$ and 490 kg. Temporal and spatial variability of Hg(II) dry deposition was not reported.

The emission of dissolved mercury from Lake Michigan to the atmosphere was found to be commensurate with dry deposition of gaseous mercury to the lake. The annualized emission flux of dissolved mercury was calculated to be $7.8 \mu\text{g m}^{-2}$, which corresponds to a total amount of 453 kg for Lake Michigan. For comparison, the total (i.e., dry and wet) estimated deposition flux to Lake Michigan was $20.3 \mu\text{g m}^{-2}$. Thus, only about 60% of mercury deposited to Lake Michigan remains in the lake and about 40% is re-emitted to the atmosphere. Wet deposition and dry deposition were estimated to contribute about half each to total deposition to Lake Michigan.

It is important to note that there are large uncertainties in the dry deposition estimates because those are not direct measurements. Overall uncertainties in dry deposition values arise from (1) uncertainties in the algorithms used to calculate the dry deposition fluxes (which depend on Hg(p) particle size, gaseous Hg(II) deposition characteristics and meteorological data), (2) uncertainties in the Hg(p) and Hg(II) ambient concentrations (which show significant spatial and temporal variability and were measured with limited spatial and temporal resolution in the case of Hg(p) and estimated in the case of Hg(II)), and (3) uncertainties in the spatial interpolation of a sparse monitoring network over the entire lake.

The seasonal variability of wet deposition during the LMMBS is consistent with the seasonal variability observed in the Mercury Deposition Network (see above). The most important aspect of the LMMBS is perhaps the strong decreasing spatial gradients from the southern part of the lake (i.e., near Chicago) to the northern part of the lake that were observed for both mercury wet deposition and ambient concentrations of Hg(p). This suggests that an urban area such as Chicago has a significant effect on local and regional mercury deposition. For example, the Chicago urban area was estimated to contribute 14% of wet deposition to Lake Michigan. This conclusion is qualitatively consistent with the analysis of the MDN data presented in Section 2.

4. EMISSIONS

4.1. Current Emission Inventories

As pointed out by GEIA (2003) and Seigneur et al. (2001a), there are significant uncertainties in the emission inventories of mercury species. These uncertainties fall into four major categories: (1) emissions of total mercury from specific anthropogenic source categories and individual sources, (2) natural emissions of mercury from land and oceans, (3) re-emissions of mercury from land and oceans and (4) speciation of those emissions (i.e., relative fractions of Hg(0), Hg(II) and Hg(p)).

Anthropogenic emissions of mercury originate from a variety of sources including coal-fired power plants, municipal waste incinerators, medical waste incinerators, chlor-alkali plants, taconite facilities, mobile sources, cement plants, coal combustion from non-utility sources and numerous other industrial, residential and commercial sources. We discuss below the first five of these source categories in more detail. Table 4-1 presents an inventory of those sources that was developed for North America for the years 1998/1999 (Seigneur et al., 2001a).

Among the above sources, coal-fired power plants are the best characterized sources in terms of both emissions and speciation of mercury because of the Information Collection Request (ICR) program that was implemented by the U.S. Environmental Protection Agency (EPA). This program required, starting in 1999, that all power plants provide information on the mercury content of their coal and that stack emission measurements be conducted to characterize speciated mercury emissions at eighty power plants.

No such comprehensive mercury emission measurement program has been conducted for the other source categories. The Toxics Release Inventory (TRI) program of EPA provides quantitative information on the annual amounts of toxic compounds released to the various media, including the atmosphere. However, TRI reporting is not subject to the same scrutiny as more focused programs such as ICR. As a result, the amount reported may be inaccurate or even not reported. For example, a chlor-alkali plant in Wisconsin did not report any TRI mercury emissions for 1998 whereas that plant was still in operation. Moreover, TRI reporting does not provide any information regarding mercury speciation.

In the absence of facility specific information on the speciation of the mercury emissions, one must rely on other sources of data, such as source sampling conducted at another similar facility. Unfortunately, there is a paucity of such data and one must in most cases rely on a single facility to characterize the mercury speciation of an entire source category. For example, Dvonch et al. (1999) sampled municipal waste incinerators, medical waste incinerators and cement plants in Florida. Their speciated

Table 4-1. Example of an inventory of anthropogenic mercury emissions for North America (Mg y^{-1}) (Source: Seigneur et al., 2001a, 2003b).

Source Category	United States	Southern Canada	Northern Mexico	Total
Electric utilities	41.5	1.3	9.9	52.7
Waste incineration	28.8	3.4	(a)	32.2
Non-utility coal burning	12.8	(a)	(a)	12.8
Mining	6.4	0.3	(a)	6.7
Chlor-alkali facilities	6.7	.05	(a)	6.8
Mobile sources	6.2	(a)	(a)	6.2
Other sources	30.6	9.6	23.6	63.8
Total	133.0	14.7	33.5	181.2

(a) included under “other sources”

emissions can be used for those source categories. However, there is a fair amount of variability within a source category that is not represented when using data from a few facilities.

To illustrate the current uncertainties in mercury emission inventories, we present in Table 4-2 a comparison of two inventories developed for Wisconsin. The AER/EPRI inventory corresponds to the North American inventory that was published by Seigneur et al. (2001a) and later updated by Seigneur et al. (2003b) (see Figure 2-6). It corresponds to 1998 for all source categories except power plants that are for 1999. The Wisconsin inventory is based on an inventory for 1999 provided by the Wisconsin Department of Natural Resources. The two inventories differ by 176 kg y^{-1} , which is about 6%.

Some source categories, such as coal-fired power plants, chlor-alkali plants and mobile sources, are in good agreement. However, there are some significant differences in emission estimates for many of the other source categories. Some differences, such as the larger emission rates for lamp breakage in the AER inventory are due to different emission factors being used in the preparation of the two inventories. Other differences, such as other point sources and other area sources, result from differences in inventories of sources (e.g., different thresholds for mercury emissions reporting). Note that this comparison only addresses the emissions of total mercury. Uncertainties also reside in the chemical speciation of those mercury emissions, as discussed below.

4.2. Mercury Speciation

Table 4-3 presents some mercury speciation profiles used by the State of Wisconsin and/or AER for several source categories. It appears that both inventories use the same speciation for many source categories. The reason for such agreement is to a certain extent due to the fact that the mercury speciation data are few and that only one reference data set is available for many source categories. For example, both groups use the data obtained by Dvonch et al. (1999) in Florida at four municipal waste incinerators, four medical waste incinerators and two cement plants. Therefore, such agreement does not properly reflect the uncertainties associated with those data. As shown by the ICR data, there is considerable variability in the speciation of mercury emissions of coal-fired power plants of a given type. Similarly, one would not expect all municipal waste incinerators, medical waste incinerators and cement plants to have the same speciation as the ones sampled for three days in Florida.

A source that includes a large fraction of Hg(II) is more likely to have a local impact compared to a source with similar emissions of total mercury but a lower fraction of Hg(II). Therefore, municipal waste incinerators and medical waste incinerators should have their emissions deposited closer to their source than mobile sources. This reasoning, however, assumes that there are no chemical transformations of mercury species after their release from the stack. As discussed in Section 5, there is some circumstantial evidence that such transformations may occur in some cases.

Table 4-2. Comparison of two emission inventories by source category (kg y⁻¹) for Wisconsin.

Source Type	AER / EPRI Inventory ^a	WDNR Inventory ^b
Coal-fired power plants	940	1036
Other coal combustion	417	101
Non-utility petroleum product combustion	32	27
Wood burning	7	25
Municipal waste incineration	78	88
Medical waste incineration	439	0 ^c
Pulp & paper	52	22
Lamp breakage	95	14
Lime manufacturing	3	6
Human cremation	9	2
Chlor-alkali facilities	491	491
Mobile sources	608	554
Other point sources	0	604
Other area sources	0	28
Total	3171	2995^d

^(a) 1998/1999 inventory of Seigneur et al. (2001a) updated by Seigneur et al. (2003b)

^(b) 1999 inventory of the Wisconsin Department of Natural Resources

^(c) listed under other point sources

^(d) difference with the sum of individual source categories is due to round-off

Table 4-3. Examples of mercury speciation (%) for emissions from selected source categories.

Source category	Hg(0)	Hg(II)	Hg(p)	Reference
Coal-fired power plants	3-99	1-97	0-2	ICR, 1999
Municipal waste incinerators	24	75	1	Dvonch et al., 1999
Medical waste incinerators	4	95	1	Dvonch et al., 1999
Cement plants	74	25	1	Dvonch et al., 1999
Mobile sources	90	10	0	EPA OTAQ, 2003

Emissions of Hg(0) will primarily enter the global background because of the low solubility and low dry deposition velocity of Hg(0). Those emissions can be partially deposited in the United States as part of the global contribution to mercury deposition. However, model simulations (e.g., Seigneur et al., 2003c) have shown that this contribution to mercury deposition in the United States from U.S. sources is small because U.S. anthropogenic sources constitute a small fraction (about 3%) of total global mercury emissions.

4.3. Coal-Fired Power Plants

Coal-fired power plants are currently the largest anthropogenic source of mercury in the United States (see Table 4-1). As mentioned above, their emissions are the best characterized among all source categories because the EPRI Field Chemical Emission Measurement (FCEM) program and Department of Energy (DOE) sampling program conducted in the 90's (EPRI, 1994) and the recent ICR program implemented by EPA in 1999 have provided a large amount of data on mercury emissions (including chemical speciation) on this source category.

Average mercury speciation ($\text{Hg}^0/\text{Hg}^{\text{II}}/\text{Hg}^{\text{P}}$) as a function of coal type is 54/44/2 for bituminous coal, 56/42/2 for anthracite coal and 75/24/1 for lignite coal. However, there is huge variability, even within a given category of power plants. For example, power plants burning bituminous coal with a wall-fired boiler and cold-side electrostatic precipitators for particulate control have an average speciation of 46/53/1; however, the range for Hg(0) is from 17 to 90%. The average speciation for power plants burning subbituminous coal with a wall-fired boiler and cold-side electrostatic precipitators for particulate control and a scrubber for SO_2 control is 93/6/1; however, the range for Hg(0) is from 88 to 98%.

Emission control devices for particulate matter reduce mercury emissions by 20 to 40% (EPRI, 1994). In the absence of a Selective Catalytic Reduction (SCR) system, flue gas desulfurization (FGD) systems (i.e., scrubbers) reduce mercury emissions significantly (e.g., by about 43 to 51% according to Chu et al., 2003) and modify the mercury emission speciation because Hg(II), which is quite soluble, is preferentially removed by scrubbing. For example, the installation of a FGD system at a coal-fired power plant in the Northeast reduced mercury emissions by 66% and modified the chemical speciation from 86% Hg(II) to 21% Hg(II) (Mitchell et al., 1997). Some of the Hg(II) removed by the FGD system may be reduced and released as Hg(0); however, this potential partial "re-emission" has not yet been well quantified. SCR systems that control NO_x emissions have been shown to oxidize Hg(0) to Hg(II). For example, recent data show an increase in the fraction of the latter by about 10 to 70 percentage points (Chu et al., 2003). The extent of the oxidation depends on the coal type, the coal chloride content, the Hg(II) fraction at the SCR inlet, other flue gas constituents and the characteristics of the SCR system (e.g., space velocity, catalyst type). Placing an SCR system before an FGD system can, therefore, improve mercury removal efficiency because the SCR system increases the fraction of Hg(II) that is later scrubbed efficiently

by the FGD system. According to recent results, an FGD system placed downstream of an SCR system can remove from 84 to 92% of mercury (Chu et al., 2003).

Although a consistent set of information has emerged from these field programs, it is important to note that there is large variability in the chemical speciation of mercury emissions among power plants, even among a specific category of power plants (i.e., those burning the same type of coal and with the same type of boiler and emission control equipment).

4.4. Incinerators

Municipal waste incinerators and medical waste incinerators have historically been major source categories for mercury emissions. The chemical speciation was studied, for example, by Dvonch et al. (1999) and was found to be dominated by Hg(II) (Hg(p) was not measured and was assumed to represent only 1% of the emissions). Since the chemical speciation is likely to be predominantly Hg(II), emissions from those sources should tend to deposit locally. However, the installation of emission control equipment (e.g., through the implementation of Maximum Available Control Technology, MACT) has significantly reduced their emissions in the United States. For example, emissions from municipal waste incinerators were estimated to be 14 Mg y⁻¹ in 1998 (Seigneur et al., 2001a). According to EPA (2002), their emissions were 41 Mg y⁻¹ in 1990 and have decreased to 2 Mg y⁻¹ in 2000.

4.5. Mobile Sources

Emissions of mercury from mobile sources may be a major source of uncertainty in current emission inventories. The early EPA emission factors (mass of mercury emitted per mile travel by vehicle type) were set to zero for many vehicle categories (light-duty gasoline vehicles, light-duty gasoline trucks and heavy-duty diesel vehicles). The corresponding nationwide mercury emission estimate of the National Toxics Inventory (NTI) of the U.S. Environmental Protection Agency (EPA) was 6.2 Mg y⁻¹. The emission factors with zero values corresponded to cases where the measurements were below the detection limit. The current EPA inventory uses half-the-detection-limit for those cases where the measurements were below the detection limit. As a result, the new nationwide mercury emission estimate for mobile sources is 27 Mg y⁻¹.

Edgerton (2003; private communication) performed continuous measurements of nitrogen oxides (NO_x), sulfur dioxide (SO₂), carbon monoxide (CO) and speciated mercury at a site in Atlanta, GA. These measurements can be used to identify the influence of certain source categories on mercury ambient concentrations. For example, high CO concentrations are indicative of an urban plume with mobile source emissions. If one assumes that all CO is attributable to mobile sources, then an empirical emission factor can be deduced by relating the CO and mercury concentrations. Preliminary results suggest a CO/Hg mass ratio of 0.7 x 10⁶ to 2.6 x 10⁶. Using a CO emission estimate of 8.5 x 10⁷ Mg y⁻¹ for the United States in 1999, we obtain a corresponding mercury emission estimate of 33 to 121 Mg y⁻¹. This result suggests that mercury

emissions from mobile sources may be underestimated by a factor of 1.2 to 4.5. Note, however, that the upper bound of the ambient estimate may reflect other mercury sources such as evasion from soils.

4.6. Chlor-Alkali Plants

Emissions of mercury from chlor-alkali plants can be obtained from the corresponding Toxics Release Inventory (TRI) reports. However, TRI data are highly uncertain and in certain cases incorrect. For example, the 1998 TRI did not include any emissions from a chlor-alkali plant in Wisconsin whereas that plant was still in operation and was estimated to emit about 500 kg y⁻¹ of mercury (i.e. about 17% of statewide emissions of anthropogenic mercury). Moreover, TRI emissions of mercury may be underestimated. The amounts of mercury used by the chlor-alkali industry were 136 Mg y⁻¹ in 1996 and 160 Mg y⁻¹ in 1997. These amounts exceed the amounts of mercury reported to be released to the atmosphere and other media in TRI which were 21 Mg y⁻¹ for 1996 and 14 Mg y⁻¹ for 1997 (i.e., 9 to 15% of the amount used). Thus, there is a need to reconcile those two quantities.

EPA conducted a comprehensive field program at a chlor-alkali plant to attempt to better characterize the emissions from such facilities. As such data become available, the emissions of chlor-alkali plants may need to be revised.

4.7 Taconite Facilities

There is a large uncertainty associated with the emissions of mercury from the taconite industry. The original estimate for this industry in the AER inventory was 15 Mg/y (Pai et al., 2000). These mercury emissions from iron ore roasting were estimated by assuming that the pellet firing process in the production of taconite is most likely to release mercury to the atmosphere. A midrange value of 0.25 ppm (Morey and Morey, 1990) was used for mercury concentrations in iron ore and it was estimated that 56 x 10⁶ Mg of iron ore are processed for taconite production, mostly in Minnesota. State measurements have been conducted at a taconite facility in Minnesota (Jiant et al., 2000). The current AER inventory (Seigneur et al., 2001) uses the results from those stack measurements, which lead to a mercury emission estimate of 0.43 Mg/y (i.e., a factor of 35 lower than the earlier estimate). Because the earlier estimate corresponds to more than 10% of the U.S. anthropogenic mercury inventory, it is important to assess whether the more recent estimate properly represents mercury emissions from taconite facilities. Data on the speciation of those mercury emissions are also needed. Clearly, emissions from those facilities could have a significant impact on mercury concentrations and, depending on the emission speciation, deposition in the upper Midwest.

4.8 Other Anthropogenic Sources

There are several categories of other anthropogenic sources that are currently poorly understood and need further characterization. Examples include electric arc furnaces, medical waste sterilizers, landfills, car shredders, waste transfer stations and

lamp breakage. Some of those sources may not be significant whereas others may represent a significant fraction of the U.S. anthropogenic emissions. For example, electric arc furnaces emissions are currently estimated to be low (0.015 Mg/y in the EPA inventory). On the other hand, mercury emissions from lamp breakage are potentially significant and are currently uncertain: they differ significantly between the AER inventory (7.7 Mg/y for the contiguous United States; Pai et al., 2000) and the EPA inventory (1.4 Mg/y).

4.9 Natural Emissions

Natural emissions of mercury occur from land and water surfaces. It must be noted, however, that emissions of mercury from land and water surfaces also include the re-emission of previously deposited mercury from both anthropogenic and natural sources.

Natural emissions of mercury from land are most important in mercuriferous areas that have soils and rocks that are naturally enriched in mercury. Such areas exist, for example, in the western parts of the American continents, southern England, the northern Mediterranean basin, some parts of East Asia and the eastern coast of Australia. Such natural emissions have been estimated at about 500 Mg y⁻¹. However, a detailed inventory is only available to date for Nevada with natural emissions estimated at about 10 Mg y⁻¹ (Zehner and Gustin, 2002) and more work is needed to extrapolate site specific measurements to a global inventory.

Mercury emissions from volcanoes are also important on a global scale with emissions estimated to be in the range of 7 to 200 Mg y⁻¹ (e.g., Nriagu and Becker, 2003). The variability of volcano activities makes such emission estimates difficult.

Natural emissions from the oceans are considerable with current estimates at about 2000 Mg y⁻¹ (i.e., about one third of the total global mercury emission budget). Emission fluxes from the oceans are believed to be greater near the equator and to decrease toward the poles (Kim and Fitzgerald, 1986).

Emissions of mercury from biomass burning (forest and grass fires) have been estimated to be significant on a global scale with a range of 100 to 1000 Mg y⁻¹ (Friedli et al., 2003). However, such estimates are extrapolated from data on forest fires that may not apply to savanna grass fires. Catastrophic (wild) fires may emit more mercury than prescribed fires (Sams, 2003). One should note that mercury released during fires is part of the mercury global cycle and is likely to be mostly re-emitted mercury rather than natural mercury.

The chemical speciation of natural mercury emissions is believed to be dominated by Hg(0) (Schroeder and Munthe, 1998; Gustin et al, 1999) although emissions of inorganic Hg(II) from soils (Zhang and Lindberg, 1999) and of dimethylmercury from the oceans (Schroeder and Munthe, 1998) are possible.

5. ATMOSPHERIC TRANSFORMATIONS OF MERCURY

5.1. Current Knowledge

Mercury exists in the atmosphere as elemental mercury, Hg(0), and oxidized mercury, Hg(II) (Schroeder and Munthe, 1998). Hg(II) can be inorganic (e.g., mercuric chloride, HgCl₂) or organic (e.g., methyl mercury, MeHg). It can also be present as particulate mercury (e.g., mercuric oxide, HgO, or mercury sulfide, HgS). In the atmosphere, Hg(0) is the dominant form. Hg(II) typically constitutes a few percent of total atmospheric mercury and is predominantly in the gas phase. MeHg concentrations in the atmosphere are negligible; however, Hg(II) becomes methylated in water bodies where it can bioaccumulate in the food chain. Hg(0) is sparingly soluble and is not removed significantly by wet deposition; its dry deposition velocity is also believed to be low. As a result, Hg(0) has a long atmospheric lifetime, on the order of a few months, that is governed by its oxidation to Hg(II). On the other hand, Hg(II) is quite soluble; it is consequently removed rapidly by wet and dry deposition processes. Particulate mercury, Hg(p), is mostly present in the fine fraction of particulate matter (PM_{2.5}), although some Hg(p) may be present in coarse PM (e.g., Landis and Keeler, 2002).

Table 5-1 presents the transformations among inorganic mercury species that are currently simulated in models. These transformations represent the current state of the science (Ryaboshapko et al., 2002; Seigneur et al., 2001a, 2003b). They include the gas-phase oxidation of Hg(0) to Hg(II), the aqueous-phase oxidation of Hg(0) to Hg(II), the aqueous-phase reduction of Hg(II) to Hg(0), various aqueous-phase equilibria of Hg(II) species and the aqueous-phase adsorption of Hg(II) to PM.

Our knowledge of the atmospheric reactions of organic mercury is limited to the oxidation of dimethylmercury by OH (Niki et al., 1983a), Cl (Niki et al., 1983b), O(³P) (Lund-Thomsen and Egsgaard, 1986) and NO₃ (Sommar et al., 1996). The first two reactions lead to the formation of monomethylmercury whereas the latter one leads to the formation of inorganic mercury. Atmospheric dimethylmercury, which originates primarily from the oceans (see Section 4), is rapidly converted to other species and, therefore, is not a major component of the global mercury cycle.

The atmospheric chemistry of mercury presented in Table 5-1 shows that aqueous reactions (that occur in clouds and fogs) can lead to either oxidation of Hg(0) to Hg(II) or reduction of Hg(II) to Hg(0). Such reduction-oxidation cycles affect the overall atmospheric lifetime of mercury. As mentioned above, the chemical atmospheric lifetime of Hg(0) is currently believed to be a few months. However, in non-precipitating clouds, Hg(II) may be reduced back to Hg(0), thereby extending the lifetime of mercury in the atmosphere. It is, therefore, important to differentiate between the chemical lifetime of a mercury species, which may range from several days to several hours for Hg(II) and Hg(p) and is a few months for Hg(0), and the overall atmospheric lifetime of mercury

Table 5-1. Equilibria and reactions of atmospheric mercury.

Equilibrium Process or Chemical Reaction	Equilibrium or Rate Parameter ^a	Reference
$\text{Hg}(0) (\text{g}) \rightleftharpoons \text{Hg}(0) (\text{aq})$	0.11 M atm^{-1}	Sanemasa, 1975; Clever et al., 1985
$\text{HgCl}_2 (\text{g}) \rightleftharpoons \text{HgCl}_2 (\text{aq})$	$1.4 \times 10^6 \text{ M atm}^{-1}$	Lindqvist and Rodhe, 1985
$\text{Hg}(\text{OH})_2 (\text{g}) \rightleftharpoons \text{Hg}(\text{OH})_2 (\text{aq})$	$1.2 \times 10^4 \text{ M atm}^{-1}$	Lindqvist and Rodhe, 1985
$\text{HgCl}_2 (\text{aq}) \rightleftharpoons \text{Hg}^{2+} + 2 \text{Cl}^-$	10^{-14} M^2	Sillen and Martell, 1964
$\text{Hg}(\text{OH})_2 (\text{aq}) \rightleftharpoons \text{Hg}^{2+} + 2 \text{OH}^-$	10^{-22} M^2	Sillen and Martell, 1964
$\text{Hg}^{2+} + \text{SO}_3^{2-} \rightleftharpoons \text{HgSO}_3$	$2.1 \times 10^{13} \text{ M}^{-1}$	van Loon et al., 2001
$\text{HgSO}_3 + \text{SO}_3^{2-} \rightleftharpoons \text{Hg}(\text{SO}_3)_2^{2-}$	$1.0 \times 10^{10} \text{ M}^{-1}$	van Loon et al., 2001
$\text{Hg}(\text{II}) (\text{aq}) \rightleftharpoons \text{Hg}(\text{II}) (\text{p})$	34 l/g	Seigneur et al., 1998
$\text{Hg}(0) (\text{g}) + \text{O}_3 (\text{g}) \longrightarrow \text{Hg}(\text{II}) (\text{g})$	$3 \times 10^{-20} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Hall, 1995
$\text{Hg}(0) (\text{g}) + \text{HCl}(\text{g}) \longrightarrow \text{HgCl}_2(\text{g})$	$10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Hall and Bloom, 1993
$\text{Hg}(0) (\text{g}) + \text{H}_2\text{O}_2 (\text{g}) \longrightarrow \text{Hg}(\text{OH})_2 (\text{g})$	$8.5 \times 10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Tokos et al., 1998
$\text{Hg}(0) (\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow \text{HgCl}_2(\text{g})$	$2.6 \times 10^{-18} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Ariya et al., 2002
$\text{Hg}(0) (\text{g}) + \text{OH}(\text{g}) \longrightarrow \text{Hg}(\text{OH})_2(\text{g})$	$8.0 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Sommar et al., 2001
$\text{Hg}(0) (\text{aq}) + \text{O}_3 (\text{aq}) \longrightarrow \text{Hg}^{2+}$	$4.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	Munthe, 1992
$\text{Hg}(0) (\text{aq}) + \text{OH} (\text{aq}) \longrightarrow \text{Hg}^{2+}$	$2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Lin and Pehkonen, 1997
$\text{HgSO}_3 (\text{aq}) \longrightarrow \text{Hg}(0) (\text{aq})$	0.0106 s^{-1}	van Loon et al., 2000
$\text{Hg}(\text{II}) (\text{aq}) + \text{HO}_2 (\text{aq}) \longrightarrow \text{Hg}(0) (\text{aq})$	$1.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	Pehkonen and Lin, 1998 ^b
$\text{Hg}(0) (\text{aq}) + \text{HOCl} (\text{aq}) \longrightarrow \text{Hg}^{2+}$	$2.09 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	Lin and Pehkonen, 1998
$\text{Hg}(0) (\text{aq}) + \text{OCl}^- \longrightarrow \text{Hg}^{2+}$	$1.99 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	Lin and Pehkonen, 1998

Hg(II) refers to divalent Hg species

^a The parameters are for temperatures in the range of 20 to 25°C, see references for exact temperature; temperature dependence information is available for the Henry's law parameter of Hg(0) and for the kinetic rate parameter of the HgSO₃ reaction.

^b This reaction was recently challenged by Gardfeldt and Johnson, 2003.

(that can cycle among the various species), that is presently estimated to be on the order of one year (e.g., Seigneur et al., 2001).

It should be noted that there are considerable uncertainties in the current chemical kinetic mechanisms of atmospheric mercury (e.g., Ryaboshapko et al., 2002) and that our knowledge of mercury chemistry continues to evolve. As new laboratory data become available, the chemical kinetic mechanism presented in Table 5-1 may need to be revised accordingly.

5.2. Mercury Transformations in Plumes

There seems to be some circumstantial evidence of reduction of Hg(II) to Hg(0) in power plant plumes from various experimental studies. We briefly discuss those studies below. First, the MDN data along a west-to-east transect from Minnesota to Pennsylvania show no significant spatial gradient in mercury annual wet deposition fluxes although the Ohio Valley includes several large mercury emission sources located, under prevailing wind conditions, upwind of Pennsylvania. As mentioned in Section 2, models of the atmospheric fate and transport of mercury tend to predict greater mercury deposition in Pennsylvania than in Minnesota because the emissions from the Ohio Valley affect mercury deposition downwind. This discrepancy between the model predictions and the observations suggests that some atmospheric processes are not correctly represented in the models. One possibility is that atmospheric transformations take place that convert Hg(II) to Hg(0), thereby reducing mercury deposition since Hg(0) has an atmospheric lifetime of a few months. Another possibility is that dry deposition predominates in Pennsylvania, thereby limiting wet deposition (see Section 6). Also, an underestimation of mercury emissions in the upper Midwest cannot be ruled out (e.g., taconite facilities, see Section 4).

Second, the University of North Dakota Energy and Environmental Research Center and Frontier Geosciences, Inc. conducted experiments where the exhaust flue gases from a coal-fired power plant stack were sampled, diluted and analyzed in a Teflon-lined dispersion chamber. These experiments showed a lower Hg(II)/Hg(0) ratio in the chamber than in the stack (Laudal, 2001). The interpretation of those results is complicated by the fact that some Hg(II) is scavenged by the walls of the chamber. Nevertheless, the discrepancy in mercury speciation between the stack and the chamber suggests that some reactions reducing Hg(II) to Hg(0) are taking place. If such reactions also take place in the power plant plume, they would limit mercury deposition downwind of the source.

Third, ambient sampling of Hg species (Hg(II), Hg(0), and Hg(p)), NO_x and SO₂ was conducted with continuous monitors downwind of coal-fired power plants in the Atlanta region (Edgerton et al., 2001). The SO₂/NO_x ratio can be used as a signature of individual power plants assuming that there is little oxidation and deposition of SO₂ and NO_x between the stacks and the sampling site. Then, the corresponding speciated mercury measurements can be compared with the mercury speciated emissions estimated from the Information Collection Request (ICR) program. The results from this study

suggest that the Hg(II)/Hg(0) ratio at the downwind location is lower than the Hg(II)/Hg(0) ratio estimated from the ICR data for the stack emissions. Furthermore, modeling of these power plant plumes indicates that current models do not account for this change in the Hg(II)/Hg(0) ratio in the plumes (Seigneur et al., 2001b).

Some aircraft measurement campaigns are being performed to elucidate whether such conversion of Hg(II) to Hg(0) indeed takes place in power plant plumes. Results are not yet available from those campaigns. If the reduction of Hg(II) to Hg(0) in plumes is confirmed by field data, the processes that govern such reaction(s) will then need to be identified and the models of the atmospheric fate and transport of mercury will need to be revised accordingly.

6. ATMOSPHERIC DEPOSITION

The removal of mercury from the atmosphere occurs via dry deposition and wet deposition. We review in this section the current state of knowledge of these two processes for the various mercury species.

There are very few data available on the dry deposition of mercury species. Lindberg and Stratton (1998) measured the deposition of Hg(II) at two rural sites in Indiana and Tennessee. Those measurements were conducted using the gradient method where Hg(II) concentrations were measured at two different heights (0.25 and 1 m over grass in Indiana and 20 and 40 m over a forest in Tennessee). These data show that Hg(II) has a relatively high dry deposition velocity (0.4 cm s^{-1} over grass and 5.1 to 5.9 cm s^{-1} over the forest canopy for the conditions of the measurements). Such data are consistent with the fact that Hg(II) is a fairly soluble species (deposition on wet surfaces) with strong adsorptive characteristics (adsorption on surfaces). Because its solubility is comparable to that of nitric acid (HNO_3), most models of the atmospheric fate and transport of mercury assume that Hg(II) species have the same dry deposition velocity as HNO_3 . For example, a continental simulation over North America showed a mean dry deposition velocity of Hg(II) over agricultural lands of 0.38 cm s^{-1} (Pai et al., 1997). Additional experimental data on Hg(II) dry deposition are needed in order to develop a better understanding of its dry deposition process and to remove the assumption that it behaves as HNO_3 . Because Hg(0) is not very soluble or reactive, its dry deposition velocity is considerably less than that of Hg(II). For example, a global simulation used a dry deposition velocity of 0.01 cm s^{-1} for Hg(0) over land areas (Seigneur et al., 2001a). Particulate mercury is present mostly in fine PM although a significant fraction has been measured in coarse PM (Landis and Keeler, 2002). Because fine PM has a low dry deposition velocity, one expects the atmospheric lifetime of Hg(p) in the absence of precipitation to be on the order of several days.

Wet deposition of mercury occurs via dissolution of the gaseous species into cloud droplets, activation of particles into cloud droplets, coalescence of particles with cloud droplets, and scavenging of gaseous species and particles by precipitation below the cloud base. Because Hg(II) is quite soluble, it is readily removed by wet deposition. Hg(0) has a very low solubility (Sanemasa, 1975) and is assumed to have a negligible contribution to mercury wet deposition. Hg(p) is removed via the activation, coalescence and scavenging processes mentioned above. Because Hg(II) species have solubilities similar to that of nitric acid (HNO_3), the HNO_3 scavenging coefficient is generally used for Hg(II). For example, a value of $0.0000476 \text{ h s}^{-1} \text{ mm}^{-1}$ (Seinfeld, 1986) can be used (scavenging of Hg(II) is a function of the precipitation intensity, expressed in mm/h). Measurements of mercury concentrations in the ambient air before and after rain events showed that Hg(II) was significantly depleted (by about 50%) whereas Hg(0) was not significantly depleted (10% or less) (Lindberg and Stratton, 1998). The relative contributions of rainout (in-cloud scavenging) and washout (below-cloud scavenging) to mercury wet deposition will vary depending on the types of clouds. Precipitation from stratiform clouds with little updraft may be dominated by washout whereas precipitation

from cumuliform clouds with strong updraft may be dominated by rainout; however, no quantitative assessment of the relative importance of washout versus rainout has been conducted to date for mercury wet deposition.

Wet and dry deposition fluxes of mercury have been shown to be interrelated (Pai et al., 1999). An increase in wet deposition (e.g., due to increased precipitation) leads to a decrease in dry deposition because of lower atmospheric mercury concentrations. Similarly, an increase in dry deposition (e.g., due to a land use category such as deciduous forest being more conducive to dry deposition) will lead to a decrease in wet deposition. It is interesting to investigate whether such a relationship between dry and wet deposition processes can explain the Pennsylvania “anomaly” described in Section 2. Figure 6-1 shows a map of vegetation in North and Central America. In general terms, the vegetation varies from coniferous forest in northern Minnesota to mixed forest in Wisconsin, agricultural land in Illinois and Indiana and deciduous forest in Ohio and Pennsylvania. Therefore, one may expect, for a given mercury ambient concentration, a greater dry deposition flux in Ohio (deciduous forest) than in Illinois (agricultural land). Conversely, there should be a lower wet deposition flux in Ohio than in Illinois. Model simulations that take into account dry deposition processes as a function of land use and meteorological conditions and wet deposition processes as a function of precipitation have not so far been able to reproduce this Pennsylvania “anomaly” (e.g., Bullock et al., 1997; Seigneur et al., 2003a). One possibility is that dry deposition is underestimated in those models. Since their parameterizations of dry deposition integrate the available information (e.g., the work of Lindberg and Stratton, 1998, see above), further investigation of this issue will require additional experimental data on dry deposition over a variety of land use categories and meteorological conditions. A sensitivity simulation recently conducted by AER suggests that an increase by a factor of two in the dry deposition velocity of Hg(II) leads to a decrease of about 10% in the wet deposition flux of mercury. Therefore, a significant underestimate in the dry deposition velocity of Hg(II) would be required to explain the Pennsylvania “anomaly”.

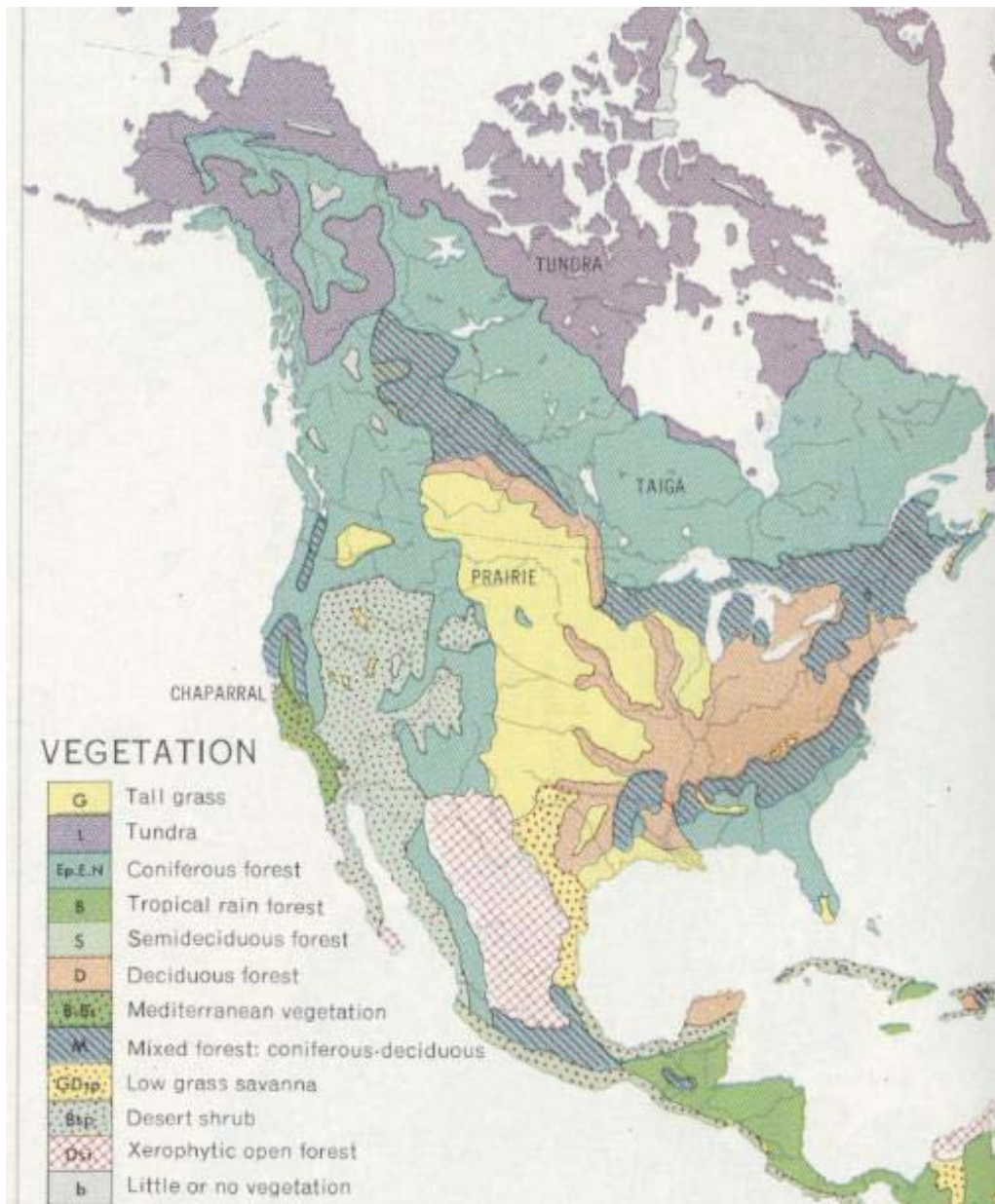


Figure 6-1. Map of vegetation in North and Central America (source: the World Book Atlas, World Book Encyclopedia, Inc., Chicago, IL).

7. RECOMMENDATIONS

As discussed above, there are still significant uncertainties in our understanding of the atmospheric fate and transport of mercury. Many of those uncertainties can be minimized by obtaining experimental data on the emissions, transformations and deposition of mercury species. We discuss such experimental studies below.

7.1. Emissions

A comparison of two emission inventories for Wisconsin showed an overall difference on the order of 6%. For all source categories except power plants, the speciation of those emissions is usually based on measurements conducted at a single facility. In addition, there are huge uncertainties regarding the natural emissions and re-emissions of mercury. Such background emissions are important because their magnitude affects our current estimates of the atmospheric lifetime of mercury and the relative contributions of natural and anthropogenic emissions to mercury deposition.

Improving emission inventories for mercury will require additional experimental field programs that can fall into the following categories:

- Characterization of anthropogenic mercury emissions (including chemical speciation) at selected facilities.
- Characterization of background emissions (i.e., natural emissions and re-emissions) of mercury.
- Reconciliation of mercury emission factors and emission speciation with ambient measurements

We discuss each of these categories below.

7.1.1. Characterization of anthropogenic mercury emissions at selected facilities

The ICR program implemented by EPA in 1999 to characterize the mercury emissions from coal-fired power plants represents the best example of the characterization of mercury emissions from an anthropogenic source category to date. Similar programs should focus on the other major source categories. The source categories that contribute most to mercury emissions in the atmosphere (particularly emissions of Hg(II) since Hg(II) is more susceptible to deposit locally than Hg(0)) should be studied in priority. Such categories may vary according to the region. Incinerators have seen their emissions decrease significantly because of the implementation of emission control measures such as MACT; nevertheless, they still constitute a non-negligible component of anthropogenic emissions of mercury in the United States.

Mobile sources and chlor-alkali facilities are significant sources of mercury. Their mercury speciation is believed to be primarily Hg(0), which tends to enter the global background rather than deposit locally; however, if a small but non-negligible fraction of those emissions consists of Hg(II) and/or Hg(p), their contribution will need to be addressed, particularly in light of the fact that many other source categories have decreasing emissions. Cement manufacturing plants and taconite facilities may also be significant sources in some areas and their emissions, including speciation, should be characterized.

7.1.2. Characterization of background emissions of mercury

Currently, some continental and regional models of mercury for North America do not include background mercury emissions under the assumption that they are balanced by the atmospheric deposition of Hg(0) to maintain global background concentrations of Hg(0). Although this assumption may be valid at continental scales and over long time periods, it may not apply at local and regional scales for short time periods because the deposition and emission fluxes may not always compensate each other at such smaller spatial and temporal scales. It may, therefore, be of interest to characterize the background emissions of mercury over land and surface waters.

Landis and Keeler (2002) characterized the emissions of mercury from Lake Michigan. Zehner and Gustin (2002) have characterized the emissions of mercury from mercuriferous soils. Similar measurements should be conducted for other areas (e.g., other Great Lakes and other types of land areas) to improve our estimates of background emissions.

7.1.3. Reconciliation of mercury emission factors and speciation with ambient measurements

Well-designed measurements of speciated ambient concentrations of mercury can provide valuable information that can be used to test our current understanding of the emissions and transformations of mercury species. A good example of such a measurement program is the set of continuous measurements conducted by Edgerton et al. (2001) in Atlanta. Collocated measurements of Hg(0), Hg(II), Hg(p), SO₂, NO_x and CO have provided some information on the speciation of Hg in power plant plumes and on the relative concentrations of CO and Hg. The Hg speciation in power plant plumes differed from that used in the ICR database which, therefore, raises some questions regarding the possible transformation of mercury in power plant plumes. The CO/Hg ambient ratio showed a value smaller than the one expected from the mobile source emission factors of CO and mercury. Such a difference may be due to either another source of mercury or an underestimation of the mercury emission factor for mobile sources. Ambient measurements should not be substituted for source emission characterization because other processes (transformation, other emissions and deposition) besides transport may occur between the source and the measurement site. Ambient measurements are very useful, however, to check our current knowledge and help design or refine experiments to better characterize the emissions of mercury in the atmosphere.

7.2. Ambient Mercury Concentrations

There are few data currently available on the chemical speciation of mercury in the atmosphere. For example, the measurements conducted during the Lake Michigan Mass Balance Study (see Section 3) did not include any Hg(II) measurements despite the fact that Hg(II) is the mercury species that contributes the most to mercury deposition. Instruments are now available to measure mercury continuously with mercury speciation (i.e., Hg(0), Hg(II) and Hg(p)). Consequently, we recommend that such measurements be conducted to develop a comprehensive database of speciated mercury ambient concentrations in a variety of environments (e.g., urban, suburban, rural and remote sites).

Such speciated mercury data can be used to

- Evaluate models of the atmospheric fate and transport of mercury
- Reconcile the ambient speciation of mercury with source-specific emission speciation (see Section 7.1.1)
- Estimate dry deposition fluxes (see Section 7.3)

7.3. Mercury Deposition Fluxes

7.3.1. Wet deposition

The Mercury Deposition Network (MDN) provides a reasonably comprehensive network for characterizing mercury wet deposition. Although additional data on wet deposition will always be useful, resources should be directed preferentially toward dry deposition measurements as discussed below.

The collection of mercury wet deposition data on an event basis will be a useful addition because such data can be used in combination with other information on meteorology and ambient chemistry to investigate the possible causes of high mercury wet deposition events.

Analysis of wet deposition data over long periods that were characterized by significant changes in mercury emissions may help unravel the relative importance of the local, regional and global components to mercury deposition. For example, the effect of the implementation of MACT standards on incinerators from 1998 to 2000 on mercury deposition in the United States could be investigated.

7.3.2. Dry deposition

There is currently a paucity of data on the dry deposition of mercury species. The data from Lindberg and Stratton (1998) constitute the only data set that is currently available for the continental United States. Dry deposition of mercury is commensurate with wet deposition. It is, therefore, essential to properly characterize the dry deposition flux of mercury to obtain an accurate estimate of the total deposition of mercury to the

Earth's surface. To that end, we recommend that dry deposition flux measurements be conducted over a variety of surface areas (e.g., urban, agricultural, forest and surface water).

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