2.0 SOURCES AND PATHWAYS OF MERCURY

2.1 Sources

2.1.1 Overview

Mercury can be emitted into the atmosphere from natural or anthropogenic (associated with human activity) sources. Natural sources are mainly associated with volcanic emissions, volatilization from marine and aquatic environments, releases associated with wind-blown dust and the weathering of rock formations. Anthropogenic releases can be due to intentional or incidental human use and are associated with both point sources or diffuse areal releases.

In North America combustion point sources are the largest source of mercury to the atmosphere, with stationary combustion of fuels being the main contributor. There are four significant categories of combustion sources: municipal and medical waste incineration, coal-fired electrical utilities, commercial and industrial boilers, and metallurgical processes. The coal-fired electric utilities are currently the principal contributor of atmospheric mercury emissions in the United States. In Canada emissions are dominated by primary metal production (Figures 2 and 3).

Incidental use of mercury describes the release in the environment of mercury when other raw feed material is being processed and mercury does not play a substantive role in the process. Energy production (utilities) and manufacturing are considered activities associated with incidental releases of mercury. Intentional use of mercury in production processes or consumer products result in mercury emissions when such products or byproducts are ultimately managed as waste (Ref. 5). Thus, incinerators and waste disposal facilities are considered as contributing to intentional releases.

2.1.2 Estimated Global Emission of Mercury

During the workshop, Luke Trip, of the Environmental Protection Service of Environment Canada, presented a global overview of the emission sources of mercury, based on estimates prepared by J.M. Pacyna and E.G. Pacyna. These estimates were based on the collection of emission data at a country level; in cases where no official estimates were available, they were determined on the basis of emissions factors and statistical data on the production of industrial goods and/or the consumption of raw materials. National estimates were provided from 17 countries and checked for completeness and comparability. The authors noted that it was very difficult to entirely verify the data obtained.

During the year 1995 the total mercury released to the atmosphere from anthropogenic sources was estimated to be approximately 1,900 tonnes (~ 2,094 tons), compared to about 2,100 tonnes (~ 2,314 tons) during the year 1990. These data suggest that there has not been a significant change in total mercury released annually to the atmosphere over that five-year period. The authors acknowledged that the year 1995 data do not contain emissions of mercury from gold production processes because of the highly speculative nature of such releases. These can however be substantial and it is thought that as much as 325 tonnes (~ 358 tons) can be emitted from this process annually, half of it from Africa. While the total emissions did not significantly change, the authors nevertheless observed a change in the dominant sources and their geographic locations.

In the year 1995, stationary combustion of fuel represented 77 percent of total emissions of mercury, an increase of 17 percent since the year 1990 (Table 3), due to the increased combustion of coal to produce electricity and heat over the five year period. The use of mercury in battery production and chlor-alkali cell processes to produce chlorine gas has significantly decreased. No major changes in the emissions of mercury from pig iron and steel production have been observed between the years 1990 and 1995. With the exception of uses in gold refining, noted above, emissions of mercury resulting directly from its various applications or uses were believed to be insignificant on a global scale in the year 1995 although its presence in the waste stream resulted in significant releases.
There have been two major changes with respect to the geographic distribution of major emission regions:

- A decrease in mercury emissions in Europe and North America. This can be explained by pollution prevention activities, further installation of emission and other control equipment and procedures, and a decrease of emissions from combustion sources, mostly in Europe. In Central Europe this decrease appears to be correlated to a decrease in industrial activities, but this statement needs to be verified.
- The Asian contribution to global emissions of total mercury has increased by over 25 percent, primarily due to the increase in combustion of coal in China. In fact, Asia now dominates the emissions from stationary combustion sources. Figure 4 indicates that, along with South Africa, Asia contains areas with among the highest total mercury emissions (from all sources) in the world.

2.1.3 United States

Mercury is used in industrial processes because of its distinctive physio-chemical properties (i.e. conducts electricity, acts as a biocide, is useful in the measurement of temperature and pressure, and forms alloys with almost all other metals). Mercury is widely used in metallurgy, manufacturing and dentistry, with chlorine production as the major user of mercury in the United States. The annual U.S. demand for mercury has decreased from 554 tonnes (~ 611 tons) in the year 1991 to 436 tonnes (~ 481 tons) in the year 1995 (Ref. 6). The most significant changes in reported mercury consumption are the dramatic reduction in use in paints and batteries. In addition, since the 1980s and 1990s there have been significant reductions in the use of mercury in laboratories, wiring devices and switches, and measuring and control instruments.

Anne Pope of the Emissions, Monitoring and Analysis Division of the USEPA reviewed the years 1996 and 1999 inventory of sources of mercury to the atmosphere in the United States. She emphasized that modelers using emission estimates in their models should first understand how the data were compiled. She then presented the methodology behind the emission estimates. The U.S. National Emission Inventory (NEI) is an annual national repository of emissions data for the 188 hazardous air pollutants (HAPs) and Criteria air pollutants identified in the U.S. Clean Air Act. It is assembled by the USEPA to support policy making and regulatory impact studies and will be available to the public on the EPA website in the summer of 2002, when it will replace the National Toxic Inventory (NTI).

<table>
<thead>
<tr>
<th>Continent</th>
<th>Stationary combustion</th>
<th>Non-ferrous metal production</th>
<th>Pig Iron and steel production</th>
<th>Cement production</th>
<th>Waste disposal</th>
<th>Total</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Europe</td>
<td>185.5 (204)</td>
<td>15.4 (17)</td>
<td>10.2 (11)</td>
<td>26.2 (29)</td>
<td>12.4 (14)</td>
<td>249.7 (275)</td>
<td>13.1</td>
</tr>
<tr>
<td>Africa</td>
<td>197 (217)</td>
<td>7.9 (9)</td>
<td>0.5 (0.6)</td>
<td>5.2 (6)</td>
<td></td>
<td>210.6 (232)</td>
<td>11</td>
</tr>
<tr>
<td>Asia</td>
<td>860.4 (948)</td>
<td>87.4 (96)</td>
<td>12.1 (13)</td>
<td>81.8 (90)</td>
<td>32.6 (36)</td>
<td>1074.3 (1184)</td>
<td>56.1</td>
</tr>
<tr>
<td>North America</td>
<td>104.8 (116)</td>
<td>25.1 (28)</td>
<td>4.6 (5)</td>
<td>12.9 (13)</td>
<td>66.1 (73)</td>
<td>213.5 (235)</td>
<td>11.2</td>
</tr>
<tr>
<td>South America</td>
<td>2.9 (30)</td>
<td>25.4 (28)</td>
<td>1.4 (2)</td>
<td>5.5 (6)</td>
<td></td>
<td>59.2 (65)</td>
<td>3.1</td>
</tr>
<tr>
<td>Australia &amp; Oceania</td>
<td>99.9 (110)</td>
<td>4.4 (5)</td>
<td>0.3 (0.3)</td>
<td>0.8 (0.9)</td>
<td>0.1 (0.1)</td>
<td>105.5 (116)</td>
<td>5.5</td>
</tr>
<tr>
<td><strong>TOTAL The year 1995</strong></td>
<td><strong>1474.5 (1625)</strong></td>
<td><strong>165.6 (183)</strong></td>
<td><strong>29.1 (32)</strong></td>
<td><strong>132.4 (146)</strong></td>
<td><strong>111.2 (123)</strong></td>
<td><strong>1912.8 (2108)</strong></td>
<td></td>
</tr>
<tr>
<td><strong>TOTAL The year 1990</strong></td>
<td><strong>1295.1 (1428)</strong></td>
<td><strong>394.4 (435)</strong></td>
<td><strong>28.4 (31)</strong></td>
<td><strong>114.5 (126)</strong></td>
<td><strong>139 (153)</strong></td>
<td><strong>2143.1 (2362)</strong></td>
<td></td>
</tr>
</tbody>
</table>

*1. Estimates of maximum values, which are regarded as close to the best estimate value.  
*2. The total emission estimates for the year 1990 include also 171.1 tonnes (189 tons) of mercury emission from chlor-alkali production and other less significant sources.
The current inventory includes both stationary sources and mobile sources. Stationary sources of HAPs include both major point and area designations. Major sources, as defined in the Clean Air Act, are facilities that have the potential to emit 10 tons per year of a single HAP or 25 tons of multiple HAPs. Area sources of HAPs are defined as those facilities that have the potential to emit less than 10 tons (nine tonnes) of a single HAP or 25 tons (22.5 tonnes) per year of a combination of HAPs. For HAPs, all major sources are inventoried as point sources; area sources are inventoried either as point or nonpoint sources depending on the availability of facility-specific information. Nonpoint and mobile source data are aggregated at the county level. Point sources or facility entries are allocated at the individual stack level (Ref. 9).

The NEI blends and merges different sources of data, beginning with available EPA data, then information from state and local agencies, which represent 90 percent of the data set. If necessary, Toxic Release Inventory (TRI) data are used but their use is minimal, representing only one percent of the data set. TRI is not a suitable input for models because it does not include all the sources (13,000 facilities are reported instead of the 19,000 reported through EPA and the States and local agencies). There are concerns about the quality of emission inventories for individual sources in the TRI databases as well, as it is largely self-reported information.

The final version of the year 1999 NEI currently under preparation is to contain estimates of process level emissions within a facility and the source-specific parameters necessary for modeling, such as precise location and detailed emission data. Location data and emission parameters are crucial for an accurate inventory and this segment of the inventory still needs improvement. In the year 1999, 10 percent of data did not include accurate information. Location errors, including incorrect or missing latitude/longitude and incorrect or missing county Federal Information Processing Standards (FIPS) codes, require resolution for modeling. Obviously if the location of a facility is reported incorrectly or is missing, estimating release, transport, exposures and ultimately risks with any accuracy is very difficult (Ref. 10).

The data presented by Anne Pope show a decrease in emissions of mercury largely due to the introduction of controls on municipal waste combustion and medical waste incineration from the years 1990 to 1999. This can be attributed to more stringent emission standards and improved sorting and control at such facilities. However, mercury emission maps of the United States continue to show high levels in some individual counties due to current municipal waste combustion. This trend is especially apparent in Florida, the West Coast and the Great Lakes region. Furthermore, utility boilers do not follow a decreasing trend; there is only a four ton difference between the years 1990 and 1999 inventory for this category (Figure 5).

The issue of speciation of mercury in the inventory was also addressed. It was noted that very little testing data are available on emissions of elemental gaseous, gaseous divalent and particulate divalent species of mercury except for coal-fired electric utility boilers. For utility coal boilers, the type of coal influences speciation. While individual sources will vary, generally ionic mercury represents 40 percent of the emissions of utility boilers, particulate less than five per-
cent and elemental 55 percent. Table 4 shows the emissions profiles of mercury releases, illustrating the different speciations possible, depending on the source.

Ms. Pope emphasized the need for improved measurements of both speciation and associated stack parameters. Modelers need to recognize and consider the uncertainty of inventories when using data in models. Furthermore, the diurnal and monthly variation of mercury emissions need more study. Also the inventories are only for anthropogenic sources and do not estimate emissions from natural sources, which could be comparable or greater. Other sources estimate that global natural emission rates are in the vicinity of 1,000 tonnes/year (~ 1,102 tons/year) (Ref. 11). Although these estimates are highly uncertain, it appears that natural emissions could account for about 50 percent of the total global emissions.

In a recent study (Ref. 12), the relative contribution of natural and anthropogenic sources to the deposition of atmospheric mercury over several centuries was examined. A mercury deposition record over the last 270 years was established from ice cores collected in Wyoming at the Upper Fremont Glacier, which allowed estimation of the impact of atmospheric releases of mercury from both natural and anthropogenic regional and global sources.

Preindustrial (before the year 1840) measurements of mercury were used to extrapolate a background value of three nanograms per litre (3 ng/L) throughout the ice-core record. Since that time, anthropogenic inputs were associated with 52 percent of the total deposition, while background concentrations contributed to 42 percent of the total mercury in the ice core, with volcanic events (including three major eruptions at Tambora, Krakatau, and Mount St Helens) contributing a further six percent of the total. These values are in agreement with the aforementioned estimate of global natural emissions accounting for about 50 percent of total emissions; however, the study notes that, in the past 100 year period, the estimated contribution to mercury deposition from anthropogenic sources was 70 percent.

### 2.1.4 Canada

In Canada, mercury is not commercially produced; the last Canadian mercury mine closed in the year 1975. Demand for mercury is largely met by imports from the United States and was estimated at 2.8 tonnes (~ 3.08 tons) in the year 1999 (Ref. 13). The major uses of mercury are in electrical apparatus, industrial applications, and control instruments. The use of mercury in the electrolytic preparation of chlorine is less widespread than in the United States. While there were 15 active chlor-alkali plants in Canada in the 1970s, only one now currently remains in operation. Consumption for applications such as gold recovery, industrial chemicals, and paints and pigments has been phased out.

Marc Deslauriers of the Pollution Data Branch of Environment Canada discussed the methodology behind the Canadian mercury emission inventory. Data estimates are assembled from a number of sources, including the National Pollutant Release Inventory (NPRI, 73 percent of data, based on mandatory reporting), the Criteria Air Contaminants emissions inventory (CAC, 16 percent of data), Accelerated Reduction/Elimination of Toxics Program (ARET, five percent (5%) of data, voluntary reporting), industry supplied estimates (five percent (5%)) and further consultation with the industry (one percent (1%)).

### TABLE 4. Emission Profiles of Mercury Releases – tons per year 1999 (Anne Pope USEPA, 1999 U.S. NEI Draft)

<table>
<thead>
<tr>
<th>Source</th>
<th>Ionic (tpy)</th>
<th>Ionic (%)</th>
<th>Particulate (tpy)</th>
<th>Particulate (%)</th>
<th>Elemental (tpy)</th>
<th>Elemental (%)</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal-Fired Electric Utility Boilers</td>
<td>20.4</td>
<td>40%</td>
<td>1.5</td>
<td>&lt;5%</td>
<td>26.1</td>
<td>5%</td>
<td>48</td>
</tr>
<tr>
<td>Municipal Waste Combustors</td>
<td>8.8</td>
<td>58%</td>
<td>3.0</td>
<td>20%</td>
<td>3.3</td>
<td>22%</td>
<td>15.1</td>
</tr>
<tr>
<td>Medical Waste Incinerators</td>
<td>9.3</td>
<td>75%</td>
<td>2.5</td>
<td>20%</td>
<td>0.6</td>
<td>5%</td>
<td>12.4</td>
</tr>
<tr>
<td>Other</td>
<td>12.5</td>
<td>20%</td>
<td>8</td>
<td>13%</td>
<td>41</td>
<td>67%</td>
<td>61.5</td>
</tr>
<tr>
<td>Total</td>
<td>51</td>
<td>37%</td>
<td>15</td>
<td>11%</td>
<td>71</td>
<td>52%</td>
<td>137</td>
</tr>
</tbody>
</table>
The Canadian National Pollutant Release Inventory (NPRI), created in the year 1992, is a multimedia database reporting on releases to water, air, and land (solid waste) of over 260 pollutants. Significant changes were made to the NPRI reporting requirements for the year 2000. In previous years, a facility was exempt from reporting to the NPRI if its employees worked less than 20,000 hours during the reporting year (equivalent to 10 full-time employees) (Ref. 14). Also, very limited, if any, mercury data were being reported at the original 10-tonnes (~ 11-tons) and one percent (1%) concentration reporting threshold.

Environment Canada has removed the 20,000-hour employee threshold as well as the one percent concentration exemption for mercury. Manufacturers processing or otherwise releasing five kg (~ 11 lbs) of mercury annually are now subject to reporting, with an exemption for dentists. As a result the data set has undergone some changes:

- 1000 percent increase in facilities reporting mercury releases (from 18 to 199)
- 350 percent increase in total releases reported (from 1.98 to 8.9 tonnes (~ 1.94 to 9.8 tons))
- 230 percent increase in atmospheric releases reported (from 1.76 to 5.82 tonnes (~ 1.94 to 6.42 tons))

Lower thresholds mean better data for specific facilities. In the new inventory, facilities must report emissions from their major stacks (stack height greater than 50 meters (~ 54.5 yds.)). The obligation to report improves the quality of stack parameters, which is especially critical for any modeling effort. With the new thresholds, NPRI now contains more information on air and land emission but water releases require further examination. NPRI year 2000 information accounts for 73 percent of the air releases, compared to 21 percent in the year 1995. The new inventory is the most comprehensive to date and is used by most modelers.

Deslauriers also presented trends regarding mercury emissions in Canada. Since the year 1970, emissions have been reduced by 90 percent (Figure 6). Major reductions have been achieved in:

- Base Metal Smelting (98 percent or 27 tonnes (~ 30 tons))
- Chlor-alkali Industry (99 percent or 23.9 tonnes (~ 26 tons) - largely through closure of facilities)
- Removal from Agriculture/Household Fungicides (100 percent or 6.5 tonnes (~7 tons))
- Incineration Sectors (80 percent or three tonnes (~3.3 tons))

Technological changes in the base metal smelting sector are a significant factor in the reduction of emissions. Smaller reductions were also achieved in many applications such as pharmaceutical products and fluorescent lamp manufacture.

Because of the observed reduction in the base metal smelting sector, power generation now has more relative importance in the emission inventory, accounting for 27 percent of the annual estimations (Figure 7). When asked if the decrease in mercury emissions in Canada over the past years was similar to the trend in the United States, Deslauriers pointed out that emissions have decreased in Canada largely due to reductions from mining and smelting activities. In the United States, the decreases have been largely associated with further control of municipal and medical waste incinerators (90 percent reduction). The main distinction between the United States and Canada is that emissions from the coal-fired utility sector have been relatively stable in the United States.

Deslauriers envisioned additional reductions through the Canada Wide Standard (CWS) and the Multi-Pollutant Emission Reduction Strategies (MERS) under development by the Canadian government. The CWS addresses two specific sources of mercury: base metal smelting and incineration. Despite significant reductions from the base metal sector, more can be done by employing the “best available technologies” at all plants emitting less than two grams (~.07 ounces) of mercury per tonne (~ 1.1 tons) of product, which could reduce mercury emissions a further 800 kg/year (~ 0.9 tons/year) by the year 2008 (Ref. 15). Standards also address mercury from medical, hazardous, sludge and municipal waste incineration.
MERS is a national suite of sectorial emission reduction plans, to be built from jurisdictional plans on particulate matter, ozone, and national multi-pollutant analysis (Ref. 16). MERS affects several key sectors such as electric power generation, base metals, iron and steel, pulp and paper.

Relevant pending projects of the Pollution Data Branch of Environment Canada were also reviewed:

- publication of mercury trends in Canada from the years 1970 to 2000 in early 2002
- compilation of mercury emissions on an annual basis beginning in the year 2002
- provision of an enhanced data set for modelers in the year 2002
- a forecast for mercury emissions from mid-2002 up to the year 2015

Deslauriers also emphasized the need for research and data on speciation and the important effect the latter information has on modeling and policy development.

### 2.1.5 Mexico

In Mexico, the majority of mercury consumption, generally of secondary origin, is related to the manufacturing of chlorine, light bulbs, dental amalgams and instruments. Mercury consumption in Mexico in the year 1996 was estimated to be between 30 and 33 tons (~27 and 30 metric tonnes) (Ref. 17). It has been reported that mercury production has occurred in Mexico since the year 1891 and reached its peak in the mid 1940s. The declining price of mercury in the following years has depressed production. Between the years 1995 and 1999, no primary production was officially recorded for Mexico (Ref. 18).

Gildardo Acosta Ruiz from Acosta y Asociados reviewed the methodology behind the assembly of emission inventories in Mexico and the current level of knowledge regarding the major sources of mercury. The previous inventories for mercury compiled in Mexico by the Electric Power Research Institute (EPRI) included the six northernmost Mexican states. In the absence of emissions estimation methodologies developed specifically for Mexico, EPRI relied on estimates based on emission factors developed by the USEPA and Parcom-Atmos of the Netherlands. The results do not take into account Mexico’s technological context and the fact that the mercury content in extracted minerals has not yet been analyzed. In the year 2000, the Instituto National de Ecología (INE) identified the major sources of mercury and developed an approach to estimate usage, disposal and emission. For INE, consumption and usage estimates are taken as a surrogate for emissions. Regarding consumption data, these were estimated from official statistics and data provided by the various industries (Ref. 19).

The estimates presented by Acosta Ruiz were developed using two approaches drawn from the EPRI, INE and Parcom-Atmos inventories. The first one was to include the activity level of electrical facilities, mercury use in the chlor-alkali industry and mercury process characteristics and behavior. In a second step, data were compared with U.S. information. It was observed that the largest emissions are from gold mining and refining which represent 36 percent of total estimated emissions in the year 1999. Processing of this ore requires two thermal operations: the smelting and the roasting to eliminate organic matter and mercury sulfide during the refining of gold. During these processes mercury is being released and there are no data on recovery of such mercury. Thus it is assumed that the entire release goes into the atmosphere. Using data from 60 mines producing more than 14 kg (~31 lbs) of gold per day and comparing them to data from Nevada, Acosta Ruiz was able to produce the estimates shown in Figure 8.

Mercury mining in Mexico ceased in the year 1995. Secondary production occurs through reprocessing of old mine tailings at former metal processing plants (Ref. 20). This accounts for 31 percent of the known emissions. Chlor-alkali plants, with nearly 16 percent of the total emissions, are also an important source of mercury (Figure 8 and Table 5). Mercury consumption data were obtained from these facilities. USEPA in its Mercury Report to Congress estimates emitted losses of 3.5 grams per ton of mercury used in this process as an emission factor whereas INE uses 40 g of mercury emitted per ton of mercury used. In his study, Acosta Ruiz used a factor in between those two. Other contributions, such as the flux from old mercury mining and amalgamation sites and the absence of recycling of thermometers and devices that contain mercury, were not addressed in this study. Furthermore the open burning of refuse at dumps and landfill sites in Mexico may release significant amounts of mercury but there are no data available on such releases.

There is very limited official information available on mercury emissions and mercury content in feedstock or waste streams. This is partly due to the embryonic nature of mercury regulation. Only two types of activity are regulated: ce-
ment production and burning of waste fuels. Standards for incinerators, hazardous waste and pharmaceuticals are currently proposed and are not yet promulgated and enforced. This inventory is a first step toward a better data set.

### 2.2 Transport and Deposition

#### 2.2.1 Transport of Mercury

##### 2.2.1.1 Florida Everglades Study

The atmosphere is the dominant transport vector of mercury to most ecosystems, particularly those that are remote from mercury point sources. As mentioned earlier, mercury residence time in the atmosphere is related to its speciation. Long-range transport of mercury is often associated with elemental mercury, while transport on a regional and or local scale is mostly due to Hg(II) and Hg(p) or particulate mercury.

Before presenting his results from the aircraft measurement campaign in Coral Springs Florida, located north of Ft. Lauderdale, and mercury speciation experiments in Point Barrow Alaska, (this latter in cooperation with Dr. Steve Lindberg and others), Dr. Matt Landis of the National Exposure Research Laboratory (NERL) USEPA noted several needs in the study of mercury transport and deposition. Specifically, continued support for improved emissions inventories, methodology to further determine ambient speciation of mercury, a further determination of defined impacts from specific source types, and linkage to aquatic modeling to allow for bioaccumulation estimates and potential exposure risk assessments were all seen as crucial.

The Florida study was an attempt to identify the sources responsible for the relatively high levels of mercury found in fish in the Everglades, on the southeastern coast of Florida. An aircraft containing sampling equipment able to measure various species of mercury, as well as particulates, NO\textsubscript{x}, CO\textsubscript{2}, and other parameters necessary to assist in the identification of the sources of prevailing ambient mercury concentrations was used in the study. Supportive measurements were also taken at ground based sites.

Specifically, the objectives of the aircraft sampling were to:

1. Obtain vertical atmospheric profiles (60 - 3500 meters (~ 65 - 3,800 yards)) of speciated ambient mercury off the South Florida coast;
2. Identify any vertical mercury gradients that might indicate the presence of rapid mercury chemical reactions in air or in cloud water; and
3. Investigate the role of long-range transport of RGM (Reactive Gaseous Mercury) in the marine troposphere.

Aircraft samples taken in January 2000, with prevailing winds from west to east, showed that concentrations of elemental mercury were in the vicinity of 2.25 to 2.5 ng/m\textsuperscript{3} at ground level—above the global background—and decreased with increasing altitude, while reactive gaseous mercury (RGM) increased with altitude (Figure 9). In June 2000, with the prevailing wind now from east to west, similar trends occurred.

Thus far, aircraft studies have generated some preliminary conclusions.

1. No evidence supporting the hypothesis that the Atlantic Ocean as a source of RGM was found; however, further sampling above the ocean should allow for more definitive comment.
2. Elevated levels of RGM, accompanied by high sulfur oxide concentrations, were observed at the surface in Coral Springs, Florida, suggesting an association with anthropogenic sources, possibly in Fort Lauderdale and Miami.
3. Elevated concentrations of RGM observed in the marine free troposphere suggest an elemental mercury oxidation mechanism aloft—a reaction with relatively rapid kinetics.

The study of dry deposition of mercury in the form of RGM is important to the evaluation of regional and global mercury budgets. By attempting to determine the forms of mer-

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<table>
<thead>
<tr>
<th>Table 5. Estimated Mercury Emissions by Sector – Mexico Year 1999 (Adapted from Gildardo Acosta Ruiz)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Source of Emission</strong></td>
</tr>
<tr>
<td>Gold mining and refining</td>
</tr>
<tr>
<td>Mercury mining/refining</td>
</tr>
<tr>
<td>Chlor-alkali plants</td>
</tr>
<tr>
<td>Copper smelters</td>
</tr>
<tr>
<td>Residential Wood Combustion</td>
</tr>
<tr>
<td>Carboelectric plants</td>
</tr>
<tr>
<td>Oil refineries</td>
</tr>
<tr>
<td>Amalgams</td>
</tr>
<tr>
<td>Fluorescent lamps</td>
</tr>
<tr>
<td>Primary Lead and Zinc smelters</td>
</tr>
<tr>
<td>Thermoelectric plants</td>
</tr>
<tr>
<td>Industrial commercial boilers</td>
</tr>
<tr>
<td>Other</td>
</tr>
<tr>
<td><strong>Total mercury emissions estimated</strong></td>
</tr>
</tbody>
</table>
cury present in the Florida skies that could be subsequently deposited on land and water, identification of possible mercury sources and associated transport mechanisms should be improved. The data from this study imply that regional transport of mercury, combined with oxidation mechanisms in the atmosphere, explain the high levels of RGM in the Everglades.

2.2.1.2 The Arctic Studies – Barrow Alaska

Mercury levels in Arctic wildlife are elevated above normal levels, notwithstanding some apparent reduction in global anthropogenic emissions over the last decade. Given there are few known mercury sources in the Arctic, an association with long-range transport must be considered (Ref. 21), including an exploration of possible mechanisms contributing to the accumulation of mercury from the global pool in the Arctic.

In the fall of 1998, Canadian researchers working at Alert Nunavut in the Arctic described what they referred to as Mercury Depletion Events (MDEs), during which concentrations of depositional elemental mercury dropped to very low levels, well below the global background concentrations. One hypothesis for this depletion was a transformation of the elemental mercury to reactive gaseous mercury, a much more soluble and thus bioavailable form of this contaminant. The presence of RGM could account for the relatively elevated levels of mercury seen in Arctic wildlife, a dietary staple of northern peoples.

Dr. Landis joined with Dr. Steve Lindberg of the Oak Ridge National Laboratory, Steve Brooks of NOAA and others to investigate the accumulation, speciation and cycling of mercury in the Arctic environment through an intensive sampling program at Barrow Alaska.

This program confirmed the occurrence of MDEs at the Barrow location, 1600 km (~ 994 mi) south of Alert, suggesting that this phenomenon could be widespread in the Arctic, and perhaps in Antarctica. The production of RGM during mercury depletion events was also confirmed.

The conversion of elemental mercury into reactive gaseous mercury appears to be associated with the arrival of the Arctic dawn. Depletion events begin with polar sunrise and persist until snow melt, which in Barrow is early to mid June. During the events, there is evidence of a strong correlation between elemental mercury and ozone, suggesting a link with chemical reactions driving ozone depletion, as the Canadians earlier suggested. No correlation between these two substances is apparent in the months prior to polar sunrise. The reactions with ozone likely also involve sunlight and reactive bromine, as both gaseous and aerosol bromide show strong seasonal peaks up to 100 ng/m$^3$ at Barrow, occurring midway between sunrise and snow melt. The bromide may originate in sea water, and the melting of the ice cap due to climate change may be further encouraging these interactions.

RGM concentrations at three Arctic locations can reach in excess of 300 pg/m$^3$, with occasional levels up to 900 pg/m$^3$, much in excess of measurements at rural sites in the eastern United States and comparable to levels of RGM normally seen near major mercury point sources.

The estimated resulting flux of mercury to the surface (principally by dry deposition) is in the vicinity of 40 µg/m$^2$ at peak times. By comparison, total (wet + dry) mercury depo-
sition in the northeastern United States has been estimated at 10 to 30 µg/m²/year.

These presentations reinforce the fact that a sophisticated knowledge of the chemistry of mercury in various media is vital to an understanding of its presence and impact in those media, including biota. This chemistry is complex, with many drivers and possible factors for consideration, including the significant transformation of a relatively unreactive and persistent form of mercury (elemental) to a highly reactive, transitory and available form (reactive gaseous mercury).

2.2.2 Putting Deposition in Context with Other Watersheds, and Pathways

Once deposited into bodies of water, inorganic mercury must be converted to toxic methylmercury by methylating bacteria before accumulation in fish and other biota can occur. Methylmercury is soluble, mobile, and is rapidly accumulated by aquatic organisms. Biomagnification associated with methylmercury in the foodchain results in significant mercury concentrations in fish, the main route for human exposure to this toxic compound. According to the Great Lakes Water Quality Board, this contaminant is subject to environmental cycling of mercury previously introduced into the environment (Ref. 22). Volatilization of mercury from land and water surfaces into the atmosphere can result in subsequent transport and deposition followed by revolatilization. Mercury contaminated sediments may resuspend mercury compounds in the water, allowing for bioaccumulation in the food web. In Maryland it was estimated that less than 20 percent of the mercury deposited in wet and dry deposition would be exported in streams and rivers (Ref. 23). Rather, there has been a buildup of mercury in soils and sediments.

During the workshop Greg Mierle, from the Dorset Environmental Science Centre of the Ontario Ministry of the Environment, presented similar ideas. He argued that, despite the significant direct input of mercury to lake surfaces from the atmosphere, methylmercury in fish is derived either directly or indirectly from mercury in watersheds and that watersheds contain large pools of mercury accumulated over very long periods of time. Mierle pointed out that a study he conducted eleven years ago showed that, in an average lake, precipitation directly to the lake surface accounts for about half the total load of mercury deposition.

Several studies have attempted to explain where the mercury in streams originated. One interesting clue about the factors controlling mercury release from watersheds was the relationship between dissolved organic matter and mercury in stream water. A quantitative measure of colour was used as a surrogate for the presence of organic matter in waterbodies, and the trends in colour and mercury concentration in a typical stream very closely track each other over the two year monitoring period. It could then be concluded that bioavailability of mercury in the water column is influenced by dissolved organic carbon concentration. In the study, the colour in stream water was due to humic substances, and humic substances are associated with wetlands. This association suggested that the release of mercury could be associated with wetlands. John Rudd from the Experimental Lakes area in northwestern Ontario established in the early 1990s that wetlands are major sources of methylmercury which corroborates Mierle’s results. At the end of the study it was concluded that:

1. Wetlands are sources of methylmercury
   - Most methylmercury in lakes comes from either wetlands or in-lake production.
   - Current precipitation (wet deposition) is a minor source of this particular species (except for extreme scenarios of methylmercury in precipitation).
   - No assumptions are made about source of in-lake mercury.

2. Watersheds as sources of methylmercury
   - Total mercury inputs appear dependent on wetland area.
   - The in-lake production of methylmercury can be allocated based on loading of total mercury.
   - Watersheds, directly or indirectly, dominate methylmercury inputs to lakes.

Mierle noted that if these models and observations show that mercury found in fish is dominated, in most cases, by mercury exported from watersheds, one question remains: where does the mercury in watersheds come from?

In general, mercury in soil is stable for long periods of time, usually remaining on the surface of the sediment or soil, rather than moving through the soil to groundwater. Indeed, once incorporated into soils, mercury is tightly bound to organic matter and is not easily released. Thus, freshwater and marine sediments are important repositories for mercury. This strong adsorption of mercury to particulate matter also suggests that the transport of mercury-contaminated particles carried in surface runoff is an important mechanism for moving mercury from soil to water (Ref. 24).

Mierle presented a study done in Québec showing high concentrations of mercury at the surface of soils. This is consistent with the idea that watersheds store mercury deposited from the atmosphere. Studies related to mercury deposition patterns in soil in Québec and Ontario raised a number of uncertainties about mercury pools:

- Are the pools of mercury in soil active?
- Does the age of organic matter indicate the age of associated mercury?
How do soil disturbances (logging, fires, flooding) affect the pools?

How will climate change affect mercury pools in soil?

Mierle pointed out that the interaction between mercury in soils and incoming deposition was not well known. Climate change, with the increasing average ambient temperatures and dryness, might accelerate decomposition and promote mobilization of mercury in soils. Mierle concluded that the outcome of emission reductions on mercury in fish is quite uncertain. There are large pools of mercury in watersheds, and they may modulate the response to any changes in deposition. Furthermore, the existing pools may be susceptible to mobilization and ultimately further contamination of fish. There is a present need for models which elucidate the interactions of mercury in the watershed.

In his report, Robert Mason from the University of Maryland Center for Environmental Science expressed similar concerns and conclusions advanced by Mierle. “While current and pending legislation should lead to a decrease in anthropogenic input of mercury to the atmosphere, there will be a long legacy of mercury in watersheds where it is typically strongly retained. The mercury in soils will slowly be released to watersheds even after curtailment of anthropogenic sources, and could exacerbate the mercury problem for decades to come.” (Ref. 25) It will thus be more prudent to take into account existing pools of mercury in the development of programs and policies concerning mercury. When asked if he meant that efforts towards investing further in the abatement of mercury emissions were not appropriate, Mierle responded that investing in emission reduction should not cease. However, this investment should be balanced with more investments in research. Indeed, in the opinion of the presenter, more needs to be known about how mercury behaves before committing to further funding of control programs, to ensure that large investments for reduction of emissions yield the desired results. To some extent, the METAALICUS research project currently underway in the Experimental Lakes Area of northwest Ontario will respond to many of these research needs.