## Chapter-25

# ATMOSPHERIC MERCURY: A DECADE OF OBSERVATIONS IN THE GREAT LAKES

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## INTRODUCTION

The Great Lakes contain approximately 20 percent of the world's surface freshwater and are one of the world's most precious resources. While the Great Lakes are cleaner today than they have been since the 1950s, many factors continue to threaten their health. Contaminant levels remain a concern, especially those that are bioaccumulative, and fish consumption advisories continue to be issued for all of the Great Lakes States and for the Province of Ontario. Environmental threats to the Great Lakes ecosystems extend far outside the region and for many these threats are global in nature.

Mercury (Hg) is one of these persistent, bioaccumulative toxic pollutants of concern. Once mercury is released into the environment it can be converted to an extremely persistent, bioaccumulative organic form, methylmercury. Methylmercury can then build up in organisms high within the food chain, such as fish, posing a risk to wildlife and humans that consume these fish. Mercury continues to be targeted as a pollutant of concern for source identification, reduction and/or elimination through a variety of state, federal and international efforts. Recently, the Great Lakes Governors identified reducing the input of toxic substances to the lakes and reducing human health impacts as major priorities for restoration efforts in the Great Lakes. The atmosphere has been determined to be the most significant source of Hg to Michigan's inland lakes and for some of the

Great Lakes (Fitzgerald et al., 1991; Landis et al., 2002a). Mercury monitoring was identified by the Great Lakes Commission in 2003 as one of the most urgent priority among the air toxic programs in the Great Lakes.

On a global basis, it is estimated that between 50 to 75% of total atmospheric Hg emissions are of anthropogenic origin (Pirrone et al., 1996). Natural emissions are typically assumed to be elemental gaseous $Hg^0$ (Pacyna and Pacyna, 2002), however, a lack of measurement data make this assumption highly uncertain. Anthropogenic emissions are primarily $Hg^0$, divalent reactive gaseous mercury (RGM), and particulate Hg (Hg(p)). The dominant form of Hg in the atmosphere is $Hg^0$. Because it's relatively insoluble and deposits very inefficiently, the mean residence time for $Hg^0$ in the atmosphere is estimated to be approximately one year (Schroeder and Munthe, 1998) allowing for global redistribution. However, this lifetime was recently challenged due to new insights on the atmospheric chemistry of Hg, and these studies suggest the lifetime of Hg will likely be much shorter. RGM directly emitted to the atmosphere is expected to deposit efficiently on a local or regional scale near major sources largely because of its solubility, as is the case for $Hg_p$. Atmospheric deposition at any particular location can, therefore, be a complex combination of local, regional, and global emissions and transport/ transformation processes (EPMAP, 1994).

Major anthropogenic Hg sources in the Great Lakes Region and preliminary estimates of their annual emissions into the atmosphere have been reported (Pirrone et al., 1996; USEPA, 1994). Sources include: fossil fuel utility boilers, municipal and hospital waste incinerators, iron and steel production, coke production, lime production, hazardous waste recycling facilities, and secondary copper, petroleum refining, and mobile sources. However, the sources of Hg are numerous and many are not well characterized. It appears that an accurate emissions inventory that includes speciated anthropogenic as well as natural Hg sources is still years away.

Research aimed at understanding atmospheric mercury concentrations, chemistry, and deposition in the Great Lakes Region has been carried out at the University of Michigan Air Quality Laboratory (UMAQL) since 1990. Early studies focused on the relative importance of urban/source areas like Detroit and the Chicago/Gary area on loadings to the Great Lakes. These large-scale collaborative efforts included the Lake Michigan Mass Balance Study (LMMBS) and the Atmospheric Exchange Over Lakes and Oceans Study (AEOLOS). These early investigations required the development and refinement of methods for the measurement and analysis of samples collected in networks. The Great Lakes Atmospheric Mercury Assessment Project (GLAMAP) was such a network and provided the first comprehensive regional atmospheric mercury measurements in the Great Lakes Region. This international study showed the importance of a regional approach to understanding mercury sources and transport. The research to develop and refine measurement methods for automated wet and dry deposition which began with these early studies continues to this day. In the mid to late 1990s it became clear that methods were needed for speciated gaseous mercury and for the accurate determination of mercury associated with particulates. These efforts as well as intensive studies carried out in the Great Lakes to investigate the atmospheric processes that control the transport and fate of mercury are discussed and the major conclusions from our efforts are presented.

Here we report on studies performed in the Great Lakes Region over the past decade and the insights gained from this work into the sources, transport, chemistry, and deposition of atmospheric mercury. A summary of the major findings from this work are presented and implications discussed.

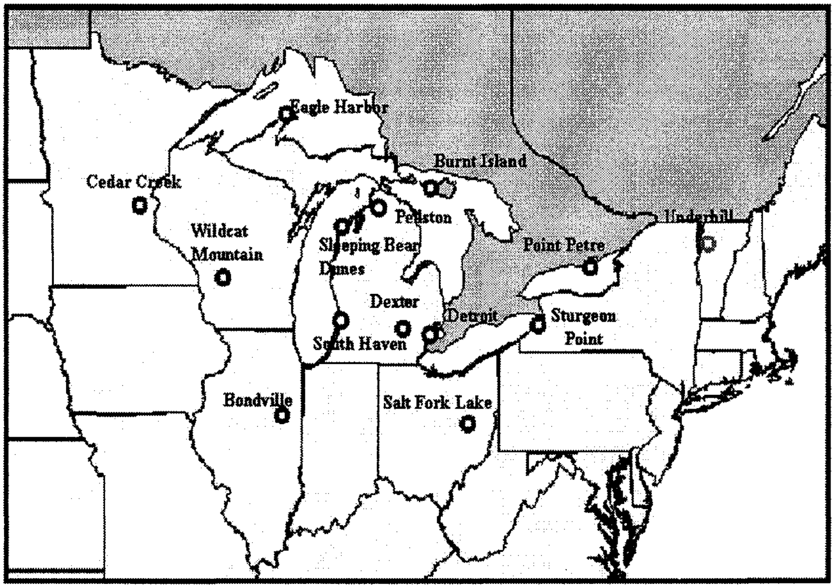

*Figure 1.* Great Lakes Atmospheric Mercury Monitoring Sites.

# METHODS

## Sampling Sites

The atmospheric measurements discussed in this chapter were collected at multiple sites in the Great Lakes Region as part of a number of mercury studies with different objectives and goals. The characteristics of each of the monitoring sites established and utilized have varied from urban, suburban, rural, lakeshore, upwind, downwind, etc. The sites are shown in Figure 1 and complete site descriptions are provided in the references cited in the text.

## Ambient Mercury –Development of USEPA IO-5

Sampling and analysis of vapor and particulate phase Hg in the atmosphere was not routinely performed in the early 1990's. Techniques employed at this time included the use of Au-coated sand traps for the collection of vapor phase Hg followed by Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) for analysis (Fitzgerald and Gill, 1979). The high pressure drop induced by the Au-coated sand led to the development of Au-coated bead traps which were shown to be ideal for ambient sampling of total vapor phase Hg. Particulate-phase Hg sampling and analysis were also not well developed at that time, and were prone to many sampling biases and artifacts. The importance of well-tested methods that could be employed in a network led to the development of new and refined techniques (Keeler et al., 1995). The new vapor and particulate phase sampling and analysis procedures were included in the USEPA Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air (IO-5) that was published in 1999 (USEPA, 1999).

## Automated Speciation Systems

Semi-continuous sampling of speciated Hg in the atmosphere has been carried out using the Tekran (Toronto, Canada) mercury speciation units as described by Landis et al., 2004. Measurements of $Hg^0$, $Hg_p$, and RGM were performed using an integrated Tekran®, Inc. 2537A, 1130, 1135-P automated mercury measurement system. This system measured the three Hg species in a semi-continuous fashion, for twelve sample cycles performed over a 24-hour period. A complete single operation cycle consisted of a 1-hr sampling period and a 1-hr desorption period. During the sampling period, ambient air drawn at a rate of 10 L $min^{-1}$ first passed through a KCl-coated denuder housed in the Model 1130. The air then flowed into the Regenerable Particulate Filter (RPF) assembly located within the Model 1135-P. RGM in the air stream was collected by the KCl-coated denuder followed by the capture of $Hg_p$ (<2.5μm) by a quartz filter disk inside the RPF assembly. $Hg^0$ which remained in the air stream was then directed into 2537A at a flow rate of 1 L $min^{-1}$. The Model 2537A was equipped with a pair of matched gold cartridges which allow alternate sampling and desorption. The adsorbent trap thermally desorbs and detects $Hg^0$ using Cold Vapor Atomic Florescence Spectrometry (CVAFS). During the sampling hour, $Hg^0$ was measured and detected at a 5-min resolution while the RGM and $Hg_p$ were collected. During desorption, zero air generated by the Model 1130 replaced the ambient air stream into the 2537A at a flow rate of 7 L $min^{-1}$. The previously sampled $Hg_p$ and RGM were thermally desorbed and converted to elemental mercury at 800 °C and at 500 °C respectively. The Model 2537A sequentially detects the amount of $Hg_p$ and RGM.

Freshly coated denuders were replaced on a weekly basis. Internal calibrations were performed on a daily basis using an internal permeation tube. Calibration of the permeation tube was carried out prior to each intensive campaign. The detection limit for RGM and $Hg_p$ was 4 pg $m^{-3}$, which was calculated as three times the standard deviation of the blank.

The automated mercury methods were compared against the manual methods developed by the UM for the USEPA IO-5. Table 1 shows a comparison of the total gaseous Hg concentration collected in both urban and rural locations using the manual and automated systems.

*Table 1.* Comparison of Vapor Phase Hg Measurement Techniques: Au-Coated Glass Beads vs. Tekran 2537 Continuous Hg Vapor Analyzer.

| **Location** | **Dates** | **N** | **Mean Conc. ($ng/m^3$)** | **Mean % Diff.** |
|---|---|---|---|---|
| Chicago, IL | Jan. 15 - 22, '95 | 14 | 4.2 | 4.4 |
| Davie, FL | Aug. 27 - Sep. 7, '95 | 21 | 2.6 | 5.7 |
| Dexter, MI | Oct. 16 - 30, '95 | 22 | 1.6 | 6.1 |

The mean absolute percent difference calculated between the daily Au-coated bead method employed in USEPA IO-5 and the 24-hour average of the 5-minute concentrations collected using the Tekran 2537 ranged from 4.4-6.1%. The difference in the two methods is within the analytical and sampling uncertainties of the methods used. The Tekran 1130/1135 automated sampling systems for RGM and $Hg_p$ were also compared against manual methods and the results are reported in Landis et al (2002b) and Lynam and Keeler (2004).

## Event Precipitation System

The importance of collecting wet deposition on an event basis for receptor modelling and meteorological analysis has been established (Burke et al., 1995; Hoyer et al., 1995; Dvonch et al., 1999; Landis and Keeler, 1997). The first event-based network in the Great Lakes basin was operated at four sites in Michigan from 1992-1994 (Hoyer et al., 1995). Mercury wet deposition was collected using a MIC-B (MIC Co., Thornhill Ontario) following the design of Merle et al., 1990. This collector was a wet-only automated design which collected the precipitation into a large Teflon-coated funnel which was attached to a 10-L borosilicate glass bottle (Keeler et al., 1994). The desire for a more discrete sampling system that could collect event samples into individual sample bottles without pouring off from a larger collection bottle led to the UM Modified MIC-B sampler described by Landis and Keeler 1997.

The UM sampler allows for the automated collection of up to four different samples using independent sampling trains. The Hg sampling train is composed of glass and Teflon and samples were collected into acid-cleaned Teflon sampling bottles. A separate sampling train was used for trace elements and a third was used for major ions. Precipitation samples were analyzed for total Hg using (CVAFS) and a suite of trace elements (Fe, As, Cd, Pb, V, Cr, Ni, Mn, Zn, etc.) using a Finnigan MAT "Element" magnetic sector (high-resolution) ICP-MS. Analyses of major ions were performed using ion chromatography (Dionex 600) and provides excellent MDLs for the major ions (sulfate MDL ~0.04 mg $L^{-1}$). All sample handling, processing, and analysis methods employed ultra-clean techniques (Landis and Keeler, 1997; Hoyer et al., 1995).

## Dry Deposition

Atmospheric dry deposition remains one of the most difficult measurements to perform for Hg as well other pollutants. Techniques used to estimate the dry deposition flux include micrometeorological approaches, throughfall collection, ambient measurements used in inferential models, and direct measurements using surrogate surfaces. Throughfall measurements, foliar washing, and surrogate surface techniques were employed in the Great Lakes and were described by Rea et al. (2000; 2001; 2002).

Two types of surrogate surfaces were used to directly measure the dry deposition flux of atmospheric mercury. The first was a novel water surface sampler developed concurrently with researchers developing a water surface sampler for nitrogen and sulfur compounds, under a cooperative agreement with the USEPA (Yi et al. 2002). The UM Mercury Water Surface Sampler (MWSS) sampler allowed the collection of both reactive gaseous Hg and particulate Hg forms. The second type of surrogate sampler, described below, used a low-Hg blank, greased surface for the collection of particulate bound Hg. A brief description of the techniques are provided.

## Mercury Water Surface Sampler (MWSS)

Total (particulate + gas phase) Hg fluxes were measured using an aerodynamically smooth, Frisbee shaped, recirculating water collection surface during the Atmospheric Exchange Over Lakes and Oceans Study (AEOLOS). The MWSS used in these studies contained a rigorously acid-cleaned glass insert that fit into the center of the aerodynamic surface that was filled with MQ water before each sampling period. The water surface developed by the UMAQL and used in the Lake Michigan studies was patterned after the symmetric low speed airfoil used at Carnegie Melon University (Wu et al., 1992). The airfoil has a sharp leading edge to minimize airflow disruptions caused by collector geometry. The airfoil was constructed of plastic and acid cleaned before the start of the intensive sampling campaign. The expense and difficulties associated with properly cleaning the sampler before each sampling period led to the development of a simpler water surface sampler described below.

The simpler MWSS used in subsequent studies was similar to the recirculating water surface sampler described above except a static water surface was employed. Eliminating the recirculating sampling stream prevented the loss of particulate Hg in the sampler and simplified the cleaning procedures. The static sampler contained a rigorously acid-cleaned Teflon insert that fit into the center of the aerodynamic surface that was filled with MQ water before each sampling period. The water surface plate (39.4 cm diameter, 0.65 cm depth) was made of Teflon, and was replaced with a new acid cleaned plate before each sample. The Teflon plate was placed inside the center area of the aerodynamic surface holder so that the water surface is level with the top of the Frisbee. All fittings downstream of the collection surface were made of Teflon or plastic to minimize adsorption. The dry deposition flux (ng $m^{-2}$ $h^{-1}$) for Hg collected with the water surface sampler represents the combined RGM and particulate-bound Hg mass in the solution divided by the duration of the sampling period (nominally 24-h). The dry deposition samplers were covered at the onset of any precipitation and uncovered immediately following the rain.

### Dry Deposition Greased Surface

The particulate phase dry deposition flux was measured using a smooth greased plate with a sharp leading edge ($<10^{\circ}$) mounted on a wind vane or using a symmetric low speed airfoil with a greased center section as described in Wu et al. (1992). The greased plate type of deposition system was used successfully to directly measure particulate dry deposition (Holsen et al. 1992; Sofuoglu et al. 1998; Gilemeister, 2001). The dimensions of the each greased strip used was 5.7 x 1.8 cm with five plates and 20 strips with a total collection area of 205.2 $cm^2$ exposed. All sample components of the surrogate surfaces were acid cleaned following the procedure defined in Landis and Keeler (1997). The dry deposition flux (ng $m^{-2}$ $h^{-1}$) for Hg collected with the greased surfaces was determined by measurement of the particulate-bound Hg mass on the surface divided by the area of each greased surface and the duration of the sampling period (nominally 24-h). Experiments were performed to show that $Hg^0$ did not significantly contribute to the mass of Hg collected by the water and the greased surrogate surfaces. These experiments were performed in the laboratory using the entire surrogate surface samplers under controlled conditions at ambient concentrations similar or greater than typical urban levels (5.5 – 8.7 ng $m^{-3}$).

## MERCURY LEVELS IN THE GREAT LAKES

### Ambient Mercury Measurements

The Lake Michigan Urban Air Toxics Study (LMUATS) provided new insight on the levels and behavior of atmospheric mercury and other hazardous air pollutants in the southern Lake Michigan Basin (Keeler, 1994; Holsen et al., 1992; Pirrone and Keeler, 1993; Pirrone et al., 1995). Total mercury measurements were performed simultaneously at three locations during the summer of 1991 as part of the month-long intensive study. The project was one of the first designed to observe the behavior of many different classes of compounds as they were advected from the urban/industrial source regions across Lake Michigan.

The LMUATS revealed that ambient mercury concentrations, both vapor and particulate phase, were significantly elevated in the Chicago urban/industrial area relative to the levels measured concurrently in surrounding areas. The levels of atmospheric mercury varied greatly from day to day at the urban Chicago location. In addition, the total vapor phase mercury concentrations varied diurnally with the highest concentrations observed during the daytime.

Measurements of particulate mercury provided new data on the levels, particle size, and form of this critical pollutant. The concentrations of particle phase mercury during LMUATS were significantly greater than those observed previously at rural sites in the Great Lakes Region, as much as 50 times greater. Particulate mercury was measured on coarse particles $>2.5$ µm in size as well as on fine particles $<2.5$ µm. Furthermore, coarse particle Hg was measured in both urban and rural locations, and that the chemical form and reactivity of the particulate Hg varied depending upon the source and meteorological conditions. Since the 1991 study on Lake Michigan, over-water measurements of mercury have been performed in the southern Lake Michigan Basin with levels exceeding those measured during LMUATS (particulate Hg concentrations $>1$ ng/m$^3$) (Keeler et al., 1994), and confirmed that particulate Hg was associated with both fine and coarse particulate matter. These findings suggested that dry deposition estimates for mercury had likely underestimated the mass loading of this toxic compound to both terrestrial and aquatic systems. The LMUATS and subsequent over-water cruise Hg data provided the impetus for the later Lake Michigan studies that followed, and made it clear that the factors controlling the transport and deposition of mercury from the atmosphere were not well-understood.

Some of the first long-term atmospheric Hg data in the region was collected as part of a Great Lakes Protection Fund sponsored project that commenced in 1992 (Hoyer et al., 1995). Daily total vapor and particulate phase Hg samples and event wet deposition (discussed later), were collected at three rural sites in Michigan (Pellston, South Haven and Dexter) over a two-year period. Extensive development studies provided sampling and analytical methods for routine atmospheric Hg determinations, and were designed to be robust under very harsh conditions experienced at sampling sites located in three different climatic regions within the Great Lakes Basin.

Regional and local–scale spatial gradients were reported for both the atmospheric concentrations and wet deposition of Hg. Meteorological analysis indicated that the elevated levels of Hg observed in the atmosphere were associated with transport from the urban/industrial area in Detroit as well as with transport from the Chicago/Gary corridor (Hoyer, 1995; Keeler and Hoyer, 1997). The findings demonstrated that source-receptor relationships for atmospheric Hg could be determined, and that short-duration ($\leq$ daily) ambient sampling and event-precipitation sampling were critical for this determination.

The Great Lakes Atmospheric Mercury Assessment Project (GLAMAP) extended the Hg measurements performed in Michigan to a region-wide network of ambient sites in the Great Lakes Region aimed to determine the influence of the large anthropogenic source areas on mercury levels. The GLAMAP commenced in 1994 to address the dearth of atmospheric mercury data for most of the Great Lakes region, and provided a unique database for investigating source-receptor relationships for atmospheric mercury. Measurements performed included gas- and particle-phase mercury, as well as particulate trace elements, from 11 rural monitoring locations across the entire region (Burke, 1998). A total of more than 1,300 sets of 24-hour measurements were collected from the 11 sites over a two-year period from December 1994 through December 1996. Atmospheric mercury concentrations measured during GLAMAP were typical of rural locations, with daily mean concentrations ranging from 1.0 to 3.5 ng $m^{-3}$ for gas-phase mercury and from 1 to 100 pg $m^{-3}$ for particle-phase mercury.

Statistically significant spatial and seasonal differences were observed for both gas- and particle-phase mercury measured across the Great Lakes region. Sub-regions were identified within the region where the GLAMAP sites had similar trends in atmospheric mercury levels. These trends are discussed in terms of their spatial and temporal trends.

## Spatial and temporal trends for atmospheric mercury

Atmospheric mercury concentrations measured during GLAMAP were statistically different across the Great Lakes region. Average gas-phase mercury concentrations for the two-year study period differed by as much as 25% between GLAMAP sites (1.63 - 2.03 ng $m^{-3}$), while average particle-phase mercury levels differed by nearly a factor of three (8.7 - 24.5 pg $m^{-3}$). These differences were greater than previously reported spatial gradients for atmospheric mercury across smaller geographic scales (Keeler and Hoyer, 1997; Olmez et al., 1996; Keeler et al., 1995; Iverfeldt and Lindquist, 1986). Concentrations of both gas- and particle-phase mercury were consistently higher at the sites in the *east* and *south* sub-regions compared to the sites in the *north* and *west* sub-regions. This spatial trend reflected the proximity of the sites to anthropogenic source areas for atmospheric mercury within the Great Lakes region.

Although concentrations for both gas- and particle-phase mercury were not statistically different between the two sampling years at any of the GLAMAP sites, seasonal differences were statistically significant. Additionally, the observed seasonal trends differed for the two forms of atmospheric mercury. Seasonally averaged gas-phase mercury concentrations were typically highest for the spring seasons and lowest for the autumn seasons during the study. This seasonal trend was consistent across most of the GLAMAP sites, indicating that regional-scale (or larger scale) processes were important for gas-phase mercury. In addition, the magnitude of these seasonal differences was significantly greater at the sites in the east and south parts of the Great Lakes region. Seasonally averaged particle-phase mercury concentrations were significantly higher for the winter season during GLAMAP, but only at the sites in the east and south. Particle-phase mercury concentrations were not statistically different between other seasons at these sites, or between all seasons at the sites to the north and west in the region.

Meteorological factors clearly played a significant role in the seasonal trends for both gas- and particle-phase mercury. For example, specific synoptic-scale meteorological conditions were consistently associated with both above and below average concentrations of particle-phase mercury at the sites in the eastern and southern portions of the Great Lakes region. Periods with elevated atmospheric pressure ($\geq$ 1020 mbar) across the region during the winter and autumn months with lower mixed-layer heights ($\leq$ 800 m) were associated with above average particle-phase mercury concentrations (30-50 pg $m^{-3}$). The highest concentrations of particle-phase mercury were observed during wintertime high pressure conditions with air mass transport from known anthropogenic source areas. Spatial differences in the seasonal behavior indicated that source influences also contributed to these trends.

Spatial differences in particle-phase mercury concentrations across the Great Lakes region were influenced by proximity to known anthropogenic source areas within the region, since synoptic conditions conducive to air mass transport from these areas were associated with the highest particle-phase mercury concentrations. Distance from the major source areas for the region likely influenced the lower range of concentrations at the sites in the north sub-region compared to the other GLAMAP sites.

Synoptic-scale meteorological features also influenced gas-phase mercury levels in the region but the significance of these relationships was not as strong as observed for particle-phase mercury. Periods with lower atmospheric pressure (daily mean sea-level pressure $\leq$ 1015 mbar) during the spring and summer seasons were associated with above average gas-phase mercury concentrations ($\geq$ 2.0 ng $m^{-3}$) at the sites in the east and south sub-regions. Precipitation ahead of the frontal boundary typically associated with low pressure systems also occurred with above average concentrations at these sites. Below average gas-phase mercury concentrations (1.4-1.6 ng $m^{-3}$) occurred during the autumn season with strong pressure gradients between high and low pressure systems, and fast transport across the region (daily mean wind speeds $\geq$ 6 m $sec^{-1}$). The highest concentrations of gas-phase mercury were observed with low pressure conditions and air mass transport from known source areas. Thus, it was shown that source-receptor relationships for ambient Hg were strongly influenced by the distance from anthropogenic source regions and atmospheric transport that was controlled by synoptic-scale meteorology.

## ATMOSPHERIC DEPOSITION PROCESSES

### Wet Deposition

From 1992-1994 the UMAQL operated the first Hg event precipitation network in the Great Lakes, which included 3 sites: Dexter, South Haven, and Pellston, MI (see Figure 1). This two-year record of data clearly indicated a strong gradient in the wet deposition of Hg from the elevated levels in the south to the lower levels observed at the Pellston site (Hoyer et al, 1995). This study also found that air mass transport from source regions in summer often led to highly elevated Hg concentrations in precipitation, whereas in winter, a similar air mass trajectory resulted in extremely low levels of Hg in precipitation (~1.5 ng $L^{-1}$) if the precipitation was snow. This was explained based on the difference in formation of rain droplets versus ice crystals, their different growth processes in-cloud with a potential influence on difference in below-cloud processes during deposition. The cloud microphysical processes, together with the atmospheric Hg speciation, were thought to be responsible for the strong seasonal variations that were observed in the event Hg concentrations and deposition.

The Lake Michigan Mass Balance Study (LMMBS) was performed from July 1994 through October 1995 at five sites (Bondville, IL, Chicago, IL, Kenosha, WI, South Haven, MI, and Sleeping Bear Dunes, MI). Similar to the earlier Michigan network, elevated concentrations of Hg in precipitation were observed at the southern lake sites when compared to the northern site at Sleeping Bear Dunes (Landis et al. 2002a). These observed gradients for Hg in wet deposition were also similar to the gradients observed in ambient gas and particle phase Hg from the GLAMAP project, which were largely the result of anthropogenic point source emissions in the southern Great Lakes region (Landis and Keeler, 2002a). The annual wet deposition of Hg to Lake Michigan averaged over the entire lake was 10.6 μg $m^{-2}$, or 895 kg to the lake. There was significant spatial and temporal variability in the mercury wet deposition flux over Lake Michigan. The summertime flux of Hg was much larger than the wintertime flux due to the higher concentrations of Hg in rain than in snow and the greater precipitation amounts observed in the summer.

The Atmospheric Exchange Over Lakes and Oceans Study (AEOLOS) conducted concurrently to the LMMBS added an over-water measurement component using the EPA research vessel *Lake Guardian* to the LMMBS network of land-based sites (Landis and Keeler, 2002). A meteorological cluster analysis was conducted which found the Chicago/Gary urban area had a significant impact on atmospheric Hg concentrations across the entire Lake Michigan Basin, and estimated that this area contributed almost 20% of the total deposition to Lake Michigan, and 14% to the wet deposition.

The total deposition due to the sources in the urban/industrial area would be even greater had RGM deposition been considered in that analysis, but due to the lack of a reliable method these measurements were not performed.

The importance of urban sources on deposition of Hg in the urban areas was also investigated in Detroit MI in 1996. Hg event precipitation was collected as part of a study to investigate the atmospheric contributions of Hg in urban runoff (Gildemeister et al., 2004). Mercury wet deposition measured in Detroit over the nine-month period was three times that measured at the Eagle Harbor site for the same period. At the conclusion of this study it was unclear how representative these findings were and whether this trend would continue after changes in Hg emissions.

Recognizing that long-term precipitation records are essential for establishing trends and understanding the impacts of changes in Hg emissions, a decade of event precipitation sampling has been conducted at three sites in Michigan (Dexter, Pellston, and Eagle Harbor, see site locations in Figure 1).

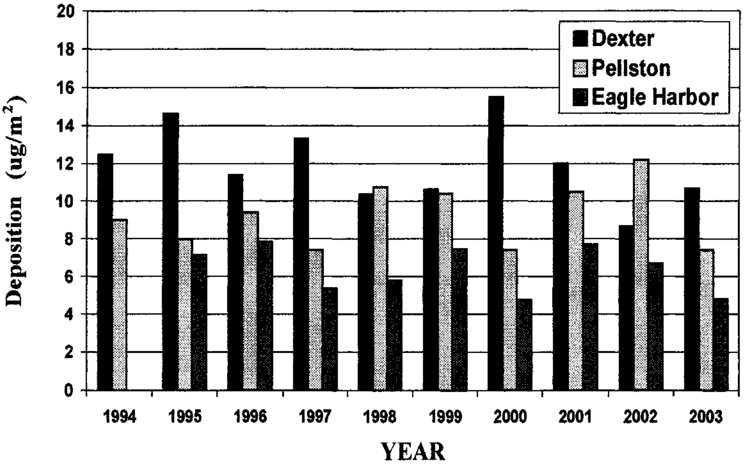

*Figure 2.* Annual Wet Deposition measured at Dexter, Pellston, and Eagle Harbor, Michigan 1994-2003.

Figure 2 displays the annual Hg wet deposition measured at these sites for the period 1994-2003. Over the 10-year deposition record, a clear decreasing gradient from south to north was observed. While the year-to-year variability in the deposition was on average 18% at each site, the 10-year total wet deposition sum at Dexter was 1.6 times the deposition collected at Pellston and 2.1 times that measured at the Eagle Harbor site. With the exception of the 2002 Hg deposition for Pellston (the maximum annual deposition over the 10 year record) the south to north decreasing gradient in deposition was observed each year. Futhermore, there was not an obvious trend in the deposition rates at the three sites over the decade of measurements. While there have been recent attempts to control Hg emissions within the region and nationally over the past decade, this data illustrates the consistent long-term impact that anthropogenic sources in the southern part of the Great Lakes region have had on Hg deposition across the Great Lakes Basin.

To date, only a limited number of studies have been performed simultaneously in urban areas and in downwind areas impacted by the sources. Studies in both Chicago and south Florida have found as much as 2/3 of the Hg wet deposition to be of local anthropogenic origin (Landis and

Keeler, 2002a; Dvonch et al., 1999). In light of this, the UMAQL has established a new urban Hg wet deposition network, which adds three urban sites, Detroit, Grand Rapids and Flint, to the long-term data collection at the three rural sites of Dexter, Pellston, and Eagle Harbor, in order to assess the long-term influence of urban sources relative to background regional sources through the central region of the Great Lakes. In addition, a new comprehensive monitoring site was established in Stuebenville, OH to specifically assess the impacts of coal-combustion emissions in the southern Great Lakes Region relative to other regional sources contributing to the Hg wet deposition at this site. Two additional years of data collection at the seven sites will allow for a full quantitative source apportionment and assessment of the role of urban anthropogenic sources on Hg wet deposition across the central Great Lakes Region.

## Dry Deposition

During periods without precipitation, Hg can be removed from the atmosphere by particle deposition and by gas exchange between the air, water, and earth's surface. The importance of dry deposition as a source of Hg to the Great Lakes and inland aquatic environments was the focus of several studies (Pirrone et al., 1993, 1995a,b; Rea et al., 2001, 2002; Landis et al., 2002a; Vette et al., 2002; Gildmeister et al., 2004). These studies have shown the importance of Hg speciation on the deposition to both urban and remote areas of the region.

Mercury dry deposition flux measurements were performed using surrogate surfaces techniques in Chicago, IL as part of the AEOLOS and LMMBS.

The dry deposition flux (ng $m^{-2}$ $h^{-1}$) for Hg collected with the water surface sampler represents the combined RGM and particulate-bound Hg mass in the solution, while the greased surface gives the particulate Hg flux only, thus providing a method to determine the RGM flux. The daily dry deposition fluxes measured in July 1994 are shown in Figure 3. The difference between the deposition measured with the two surrogate surfaces revealed that 52% of the dry deposition measured was due to particulate Hg and the remainder was due to RGM deposition.

As part of a whole-ecosystem Hg cycling study Rea et al. (2002) measured Hg in the foliage of deciduous trees in Pellston, MI over the course of the growing season and found that total foliar Hg accumulation was substantially less than vapor phase $Hg^0$ deposition estimated following Lindberg et al. (1992). It was determined that $Hg_p$ and RGM dry deposition were rapidly washed off foliar surfaces, and therefore foliar accumulation of

Hg most likely represents vapor phase $Hg^0$ assimilation Rea et al. (2001). In controlled pot and chamber studies with aspen, Ericksen et al. (2003) determined that all foliar accumulation of Hg was due to vapor uptake, regardless of soil Hg concentration.

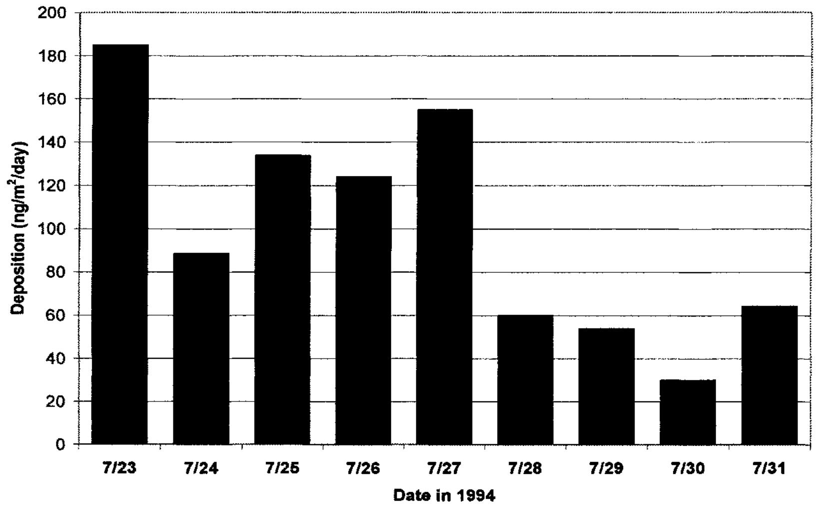

*Figure 3.* Mercury dry deposition flux measured in Chicago, Illinois using the UM aerodynamic mercury water surface sampler in 1994.

The rate of Hg accumulation in foliage was linear with no significant difference between accumulation rates measured by Rea et al. (2002) in two different forests, with significantly different meteorological conditions and modeled vapor phase $Hg^0$ deposition velocities at each site. Miller et al. (2004) suggested that the lack of difference in foliar accumulation rates for the two sites studied by Rea et al. (2002) which indicated that foliar Hg accumulation was limited by biological processes mediating sequestration of the Hg. Since the annual transfer of Hg from foliage to forest floor via leaf fall represented the net vapor phase $Hg^0$ deposition (Rea et al., 2002; Ericksen et al., 2003), Miller et al (2004) developed an empirical method to estimate the accumulation of Hg in foliage of the study area, with the Hg content of deciduous foliage found to be a linear function of growing season length. To date, $Hg^0$ deposition and accumulation has not been adequately treated in Hg transport and deposition models and represents a significant source of uncertainty in our impact assessments.

In 1996, wet and dry deposition samples were collected at three sites in the City of Detroit to investigate the atmospheric contributions of Hg to urban runoff (Gildemeister, 2001; Gildemeister et al., 2004). The monthly dry particulate deposition flux for the April-October period was similar to the monthly wet deposition flux (10.2 μg $m^{-2}$ vs 14.8 μg $m^{-2}$, respectively) at the Livernois site in Detroit. It is anticipated that the total dry deposition flux due to both particulate and gaseous Hg would have been greater than the wet deposition flux, based upon the flux measurements performed in Chicago which suggested that the about 52% of the dry deposition was due to Hgp.

While it was evident that urban sources were impacting Hg deposition to downwind lakes and ecosystems, studies performed to date were limited by the lack of RGM measurements. The RGM data is essential for estimating the dry deposition of Hg and for identifying the source or sources of the Hg deposited.

## ATMOSPHERIC CHEMISTRY AND SPECIATION

Hg has been measured in the atmosphere in both gas and particle phases. While greater than 95% of global gaseous Hg is in the elemental state ($Hg^0$), it is the divalent gaseous form of Hg ($Hg^{2+}$), as well as particulate Hg, which are highly water soluble (Fitzgerald et al., 1991). It is this water solubility which makes $Hg^{2+}$ species the critical components in understanding Hg removal processes and deposition rates from the atmosphere (Lindberg et al., 1992). The fact that the gaseous forms of Hg interact in a complex way with particulate matter suggest that gas-particle partitioning of Hg also controlled the deposition from the atmosphere. A large fraction (as much as 95%) of the Hg emitted by various source types was in a water soluble, reactive gaseous form (Prestbo and Bloom 1995; Dvonch et al., 1999; Lindberg and Stratton, 1998). While much progress has been made in identifying and quantifying Hg emission sources, few field-based studies have attempted to identify the mechanisms and processes critical to enable predictive modelling of Hg transport, transformation, and deposition. These include the characterization of speciated Hg in emissions, ambient air, and ultimately deposition.

Beginning in 1998 the UMAQL, in collaboration with the USEPA-NERL and Florida DEP, performed a series of field-based evaluations of a prototype ambient Hg speciation instrument designed by Tekran Inc. (Model 1130P). In subsequent years, revisions of this prototype instrument were employed in several UMAQL studies of ambient mercury speciation in both urban and remote locations within and outside the Great Lakes region.

## Local Source Impacts in Urban Areas

Measurements of speciated gaseous Hg were made in Detroit, MI during each summer from 2000-2002. The sampling site was located in close proximity (within 4 km) to a large heavy industrial source complex (Dvonch et al 2004), which included coal combustion, oil refineries, coke ovens, iron/steel mills, and sewage sludge incineration. Strong local source impacts were observed at the site with the maximum hourly RGM value reached 208 pg/m$^3$ and the Hg$^0$ exceeded 14 ng/m$^3$ on July 17, 2001. An analysis of the surface meteorological data collected on-site indicated that winds were from the SW during this period, the direction of the nearby industrial source complex. These results provide evidence that Hg$^{2+}$ may remain in a divalent form downwind from the source. The maximum values observed in 2001 were quite similar to those measured in Detroit in 2000 and 2002 (Lynam and Keeler, 2002; Lynam and Keeler, 2004). The maximum RGM values in Detroit were also similar those previously measured by the UMAQL in Baltimore, MD in 1998, when levels reached 211 pg/m$^3$ after plume impaction at the measurement site by a nearby municipal waste incinerator (Dvonch et al., 2004). Elevated RGM may be expected immediately downwind of waste incinerators since previous in-stack measurements have shown that 75-95% of the Hg is emitted as RGM (Dvonch et al., 1999).

## Production of RGM in Ambient Air

Speciated measurements of gaseous Hg were made on the University of Michigan's North Campus in Ann Arbor, MI during the summer of 1999 (Dvonch et al., 2004). A clear diurnal pattern was observed in the RGM concentrations similar to that observed in Detroit. This pattern was particularly pronounced on certain days, such as those shown in June and July, 1999. The highest levels of RGM occurred during the daytime, after solar noon, as seen in Figure 4. A clear positive relationship between RGM and $O_3$ was also observed on these summer days, as RGM maximums exceeded 140 pg m$^{-3}$ on both June 22 and June 23, 1999. Overall for the 16-week sampling period at Ann Arbor, Dvonch et al. (2004) determined the diurnal patterns observed in RGM were found to significantly co-vary with ambient $O_3$ ($r = 0.50$, $n = 916$, $\alpha = 0.01$). Since $O_3$ is a photochemically produced secondary pollutant that serves as an indicator of increased photochemistry and increased oxidant production, the positive relationship observed between with RGM points to the real-time production of RGM as a result of photochemical oxidants.

An analysis of concurrent $Hg^0$ concentrations provided additional evidence for the photochemical production of RGM. Overall for the 16-week sampling period at Ann Arbor, a significant negative correlation was found between $Hg^0$ and $O_3$ ($r = -0.18$, $n = 526$, $\alpha = 0.01$) (Dvonch et al., 2004). This relationship was particularly pronounced during periods of enhanced $O_3$, such as September 1-5, 1999 ($r = -0.77$, $n = 58$, $\alpha = 0.01$). A significant negative correlation between $Hg^0$ and RGM was also found during this period ($r = -0.35$, $n = 66$, $\alpha = 0.01$), as illustrated in Figure 5 by the sharp decrease in $Hg^0$ together with the increase in afternoon RGM and $O_3$.

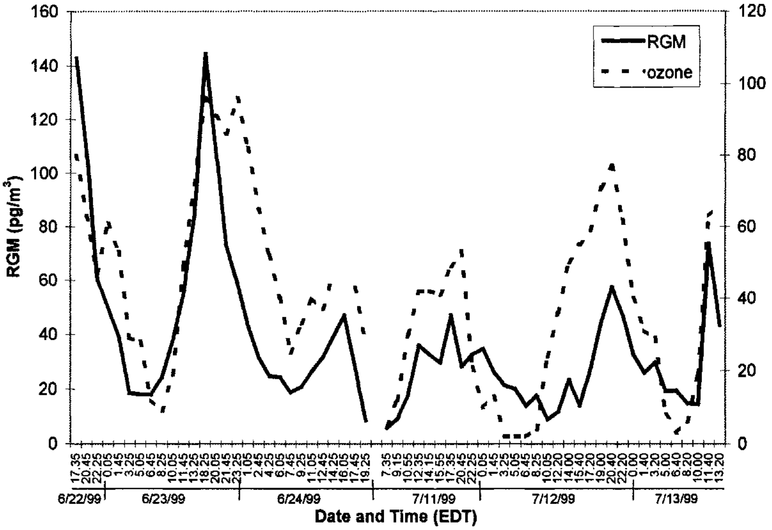

*Figure 4.* Reactive Gaseous Mercury and Ozone Measured at Ann Arbor, MI (June-July, 1999).

The strong diurnal patterns observed provide additional evidence to suggest that RGM is produced via photochemical reactions. As part of their analysis Dvonch et al. (2004) also calculated daily air mass back-trajectories from the site, which suggested that the diurnal RGM maximums observed at Ann Arbor were not due to local source impacts, but instead were a result of RGM production during transport of the air mass. It was also noted that while the increases in RGM represented roughly only 10% of the decreases in $Hg^0$ during periods of elevated $O_3$, a mass balance of the two species should not be expected given the high solubility of RGM relative to $Hg^0$ and the expected deposition during air mass transport.

While a small amount of field-based data have been published to date to assess atmospheric Hg oxidation in northern temperate climates, recent measurements along the west coast of Washington State identified that large and frequent $Hg^0$ losses occurred during summertime periods with increased $O_3$ (Weiss-Penzias et al., 2003), and measurements along the west coast of Ireland suggest $BrO^{\cdot}$ as responsible for $Hg^0$ oxidation (Munthe et al., 2003). The loss of $Hg^0$ and production of RGM on days with increased photochemistry observed in Michigan differ from the above investigations in that these measurements are far removed from influences of the marine environment. Because of this, reactive halogen species which evolved from sea salt would not be expected to be responsible for the observed $Hg^0$ oxidation. Species such as the OH radical are more likely to be important in temperate climates far removed from marine influences, and require further study in future investigations.

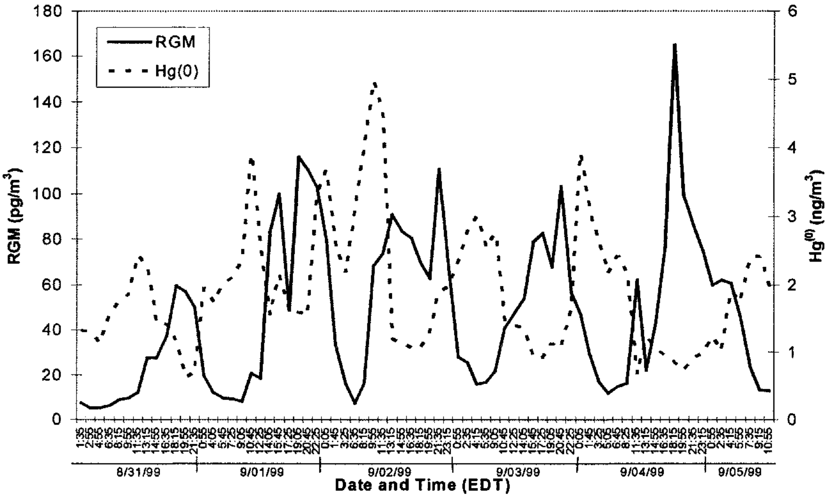

*Figure 5.* Speciated Gaseous Mercury Measured at Ann Arbor, MI (August-September 1999)

## Long-Term Continuous Measurements of Speciated Ambient Hg in Detroit

The intensive speciated Hg data collected in urban areas during 1998-2002 made clear the need for long-term measurements. In September of 2002, the UMAQL in conjunction with the Michigan DEQ established a long-term speciated ambient Hg monitoring site in Detroit, MI. Measurements of $Hg^0$, RGM, and particulate Hg utilizing the Tekran 2537A/1130/1135 Mercury Speciation System were performed. Data are presented here for the first full year of data collection (thru September 2003). Mean levels (± standard deviation) of $Hg^0$, RGM, and particulate Hg were $2.4 \pm 1.4$ ng $m^{-3}$, $16.5 \pm 28.9$ pg $m^{-3}$, and $22 \pm 30$ pg $m^{-3}$, respectively. The UMAQL has also subsequently established long-term speciated ambient Hg monitoring sites at a rural site in Dexter, MI as well as at a regionally impacted site in Stuebenville, OH to quantify the source impacts and levels of speciated ambient Hg across the Great Lakes region.

## Summary and Future Work

Our understanding of the environmental cycle of Hg has drastically improved over the past decade. The importance of urban/industrial areas on the levels and deposition of Hg in the urban areas has been documented. Dry deposition in urban areas likely exceeds wet deposition and the importance of Hg bound to large particles was revealed. Direct emissions of reactive gaseous Hg (RGM) and its role in the total loading of this contaminant were shown to be significant. Deposition of Hg0 and its subsequent accumulation in plant materials results in significant fluxes of Hg to vegetated ecosystems. Elevated RGM was observed during periods of enhanced photochemical activity with high ozone, warm temperatures, and high solar insolation, which indicated that RGM was produced in the atmosphere during atmospheric transport. Changes in the form of both vapor and particulate phase Hg in response to regional changes in atmospheric chemistry suggest that more research is needed to understand the chemical reactions controlling the deposition of this persistent bioaccumulative pollutant.

The Great Lakes region has received considerable attention with respect to the levels and effects of bioaccumulative persistent pollutants (PBTs) such as Hg. Some of the highest concentrations of Hg in precipitation, vapor, and particulate forms have been observed in the region which is consistent with our understanding of the emissions density in the major urban areas in the region. Significant south to north gradients in the levels and deposition of Hg were observed and air mass transport from known source areas could explain the majority of the variability in the Hg deposition recorded.

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