

Mercury Deposition Monitoring in the Great Lakes States: Current Activities and Future Directions

**A report of the
Great Lakes State Mercury Deposition Monitoring Discussion Group**

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About this report

This report presents a collective view of the individuals participating in the Great Lakes State Mercury Monitoring Discussion Group. It was compiled by the Great Lakes Commission staff with the substantial input of staff members of the environmental protection agencies of the eight Great Lakes states. Among those contributing to the Discussion Group were: Jon Dettling (GLC); Mark Allen, Orlando Cabrera-Rivera and Jon Heinrich (Wisconsin DNR); Donald Torsello, Nick Lazor, Mike Zuvich, Craig Evans and Krish Ramamurthy (Pennsylvania DEP); Bill Spires and Frederick Jones (Ohio EPA); Gopal Sistla, Jim Ralston, Pat Lavin, Dirk Felton, Kevin Civerolo, SiuHong Mo, Oliver Rattigan and Stanley Byer (New York State DEC); Ed Swain, Rick Strassman and Todd Biewen (Minnesota PCA); Amy Robinson and Joy Taylor Morgan (Michigan DEQ); Tom Horton, Scott Deloney, Jon Bates and Kathy Watson (Indiana DEM); and Jeff Sprague, Marcia Willhite, Melvin Schuchardt, Jim Ross, and Brian Koch (Illinois EPA). None of the views or opinions expressed in the report are intended to represent an official position of the Great Lakes Commission or any of the agencies of its member states listed here. Additional thanks is deserved by the several individuals providing input or review of the report, including: Pierrette Blanchard; Alexis Cain (U.S. EPA, Region 5); David Gay (Illinois State Water Survey); Tom Holsen (Clarkson University); Melissa Hulting (U.S. EPA GLNPO); Jerry Keeler (University of Michigan); Mike Koerber (Lake Michigan Air Directors Consortium); Mike Murray (National Wildlife Federation); and Todd Nettesheim (U.S. EPA GLNPO).

Executive Summary

The purpose of this report is to promote a collaborative and comprehensive approach to addressing the need for increased and enhanced monitoring of mercury deposition with the Great Lakes region of North America. The report provides a review of the purposes and potential uses of monitoring-derived information on mercury deposition and air concentrations, discusses some principles for consideration in establishing new activities, presents an overview of current monitoring activities in the region and provides some recommendations for moving forward. The intended audience of this report is broad and includes policy-makers, environmental protection agencies, researchers, and others interested in addressing this issue.

The need for mercury monitoring in the region is driven by health risks from consumption of mercury-contaminated fish from the Great Lakes themselves and from inland lakes throughout the region, most of which are under mercury-related consumption advisories. Ecological and wildlife health impacts from mercury are also a significant concern. Monitoring information is needed to support assessments of potential control options and to evaluate the effectiveness of current control strategies.

Although there are several valuable mercury monitoring activities within the region, current abilities fall far short of fully providing decision-makers with the best possible information. Gaps in the current monitoring network constrain the decision-making process for protection of human health and the environment. In addition, there are needs for greater coordination of activities to ensure efficiency and comparability, there is a need to better integrate monitoring for mercury in deposition with fish and sediment monitoring, and there are needs to develop and adopt more advanced monitoring technologies and techniques to provide a thorough understanding of mercury deposition within the region.

Introduction

Mercury levels in sport fish caught throughout the Great Lakes region are commonly above widely-accepted thresholds for safe human consumption. As a result, all eight of the Great Lakes states have statewide advisories for all lakes, and most states have similar advisories for their rivers. Combined, these eight states accounted for about 75% of the more than 3000 individual fish advisories in place across the U.S. in 2004 (U.S. EPA, 2005). It is recognized that in many cases, atmospheric deposition is the dominant source of mercury contamination to Great Lakes water bodies. Estimates of the contribution of North American mercury emissions to total North American deposition are in the range of twenty to thirty percent. (Gbor *et al.*, 2007; Seigneur *et al.*, 2004) However, there is recognition of wide variation by location, with highly impacted locations receiving as much as seventy percent or more of mercury deposition from local and continental sources. (Gbor *et al.*, 2007; Keeler *et al.*, 2006; Seigneur *et al.*, 2004)

Although significant emission reductions have been achieved in the past, such as controls placed on waste incinerators in the 1990s, further reductions are being pursued for protection of health and the environment. The largest domestic source sector is coal fired power plants and efforts have been made recently at both the federal and state level to control this sector, including enacted or pending legislation or regulations in most Great Lakes states and the U. S. Clean Air Mercury Rule (CAMR) (U.S. EPA, 2006). In addition, states continue to strive to fulfill the federal mandate to prepare total maximum daily load (TMDL) assessments for water bodies impaired due to atmospheric mercury deposition.

Improved and sustained atmospheric mercury monitoring systems for the Great Lakes region would allow state and federal agencies to: track trends in total mercury deposition; determine the response to increased control measures; assist in identification of sources and/or source regions; support TMDL formulation, and more. This report presents an overview of current mercury deposition monitoring activities in the Great Lakes region, identifies critical uses for such monitoring data and assesses unmet needs.

This report was compiled by a Great Lakes State Mercury Monitoring Discussion Group, comprised of personnel of the eight environmental protection agencies of the Great Lakes States. The Great Lakes Commission staff led the formation and coordination of this discussion group at the recommendation of its Great Lakes Air Deposition Program Management Team. The report is intended to improve coordination and offer background information and guidance for future decisions, but not to be prescriptive of future actions by the Great Lakes state agencies or others working on these issues within the region or more broadly. Emphasis throughout the report on a regional perspective should not diminish from the need to address many of the same issues on national and international scales. The recommendations in the report are addressed broadly to the community of scientists, regulators, resource manager and others who are working to address the issue of reducing mercury deposition to the water bodies of the Great Lakes region and beyond. The recommendations present a collective, but not necessarily unanimous, view of what steps should be taken to adequately understand patterns and sources of mercury deposition and to implement and track reductions in deposition levels.

Section A of this report discusses the needs for and potential uses of mercury monitoring data, with an emphasis on fulfilling the roles and obligations of state agencies. These uses include identifying

deposition levels, status and trends; characterization of sources; supporting the development of Total Maximum Daily Loads and other control programs; evaluating the effectiveness of control actions; supporting model development and use; and supporting research efforts to better understand mercury cycling in the environment. Section BB provides an overview of commonly used and developing methods for measuring mercury in air and its deposition to surfaces. Section C presents an inventory of and information regarding mercury deposition monitoring activities in the Great Lakes region taking place as of 2006. Section D offers an assessment of the adequacy of these current activities in fulfilling the needs identified in Section A and offers a series of recommendations for how the state agencies and their partners in federal government, academia and elsewhere can continue to advance the ability to utilize mercury monitoring technologies in their mission to protect the environment and safeguard human health. These recommendations are also listed in the section below.

Recommendations (from Section D)

Deposition Levels, Status, and Trends

- **Recommendation 1:** To provide a consistent regional measure of wet deposition trends, continue to support the maintenance and operation of existing wet deposition monitoring sites. An assessment should be made of the optimal placement of these and other monitoring locations to provide regional background information, while improving coverage of potentially elevated deposition near source regions, such as urban areas, or sensitive receptors, such as biological hotspots.
- **Recommendation 2:** To enable regional use of the TGM data being collected, maintain the existing sites collecting such data and improve the integration of information from these sites on a regional level. Data from the many TGM monitors throughout the region should be integrated into a centralized data storage location and handled with a common protocol.
- **Recommendation 3:** To meet a need for accurate and cost-effective methods for measuring dry deposition of mercury, compare and evaluate emerging monitoring technologies and select a single option to measure mercury dry deposition in a consistent, comparable manner and at reasonable cost. This option should be refined, standardized, made widely-available, and implemented to detect regional trends in dry deposition.
- **Recommendation 4:** To provide localized estimates of dry deposition and support validation of source-oriented modeling results, establish and maintain several regional sites to monitor speciated ambient mercury. If possible, such sites should participate in a national network and be placed to coincide with monitoring of fish tissue concentrations and sediment cores.
- **Recommendation 5:** To adequately characterize geographic trends in mercury deposition and account for land cover type in estimation of the throughfall/litterfall contribution, the impacts of throughfall and litterfall on mercury loading should be thoroughly incorporated into models of deposition and measurement-based estimates. Research should continue to characterize throughfall/litterfall dynamics and their relation to other mercury deposition metrics.

Source Characterization, Policy Development and Tracking Success

- **Recommendation 6:** To provide broader regional information on mercury source contributions, especially for sensitive receptor locations, a subset of mercury wet deposition stations should be converted to event-sampling protocols and include measurement of trace metals.

- **Recommendation 7:** To provide broad geographic coverage of source-apportioned deposition estimates, source-oriented deterministic modeling of mercury should continue to be improved, tested and then implemented on a continuing operational basis. Monitoring data of various types are needed to validate such models.

Integrating Data Regionally and Across Media

- **Recommendation 8:** To identify the processes and ecosystem characteristics that govern the movement of mercury from the atmosphere, through the ecosystem and within the food chain, additional research should be supported and used to further develop multi-media mercury models on a regional basis, especially for the Great Lakes themselves.
- **Recommendation 9:** To better predict and explain changes in fish mercury concentrations and with regard to atmospheric sources and deposition, improved linkages should be established among mercury monitoring programs for fish, water, sediments and deposition. Opportunities should be identified to establish long-term monitoring of fish, sediment, and mercury deposition that are all representative of a given region.
- **Recommendation 10:** To provide the most accurate assessment of past and current mercury dynamics in the Great Lakes region, promote a broad effort to integrate mercury measurement data for the region from multiple environmental media, following the example of the Northern States Research Cooperative.
- **Recommendation 11:** To provide for comparable assessment of mercury deposition and ecosystem cycling on a national basis, support is needed to establish a robust national mercury monitoring network. Such a network should embrace the principles of the plan outlined in Mason *et al.* 2005, balancing needs for national consistency with allowance for addressing unique regional issues.

Characterizing Urban Sources, Patterns and Influence

- **Recommendation 12:** To identify urban mercury patterns, characterize the influence of urban mercury sources on receptor regions and characterize additional mercury sources, new technologies and statistical techniques should be applied to urban monitoring campaigns and additional studies should be conducted to identify additional sources of mercury emissions and characterize emissions of reactive and organic mercury.

Organization and Collaboration

- **Recommendation 13:** To pursue the goals described here, strong partnerships should be developed between those acting at the state, provincial, federal, tribal, academic and non-governmental levels. In addition, mechanisms are needed within and among agencies that promote interaction of the diverse set of scientists and managers needed to address the mercury problem, including those specializing in atmospheric pollution, chemistry, aquatic pollution, fisheries biology, wetland ecology and many others.

A. Need for Advanced Mercury Deposition Monitoring Systems for the Great Lakes

Mercury monitoring data can be used in numerous ways to achieve the goals of state, local and federal environmental quality and pollution prevention programs. In particular, monitoring data can help agencies answer many questions that are critical to their mission. Described below are some principal informational demands that might be met through a mercury monitoring program. While fully answering any of these questions requires information and analysis beyond that obtained from monitoring systems alone, monitoring data are a critical component of filling these informational needs.

Questions to Answer

What Are the Human and Ecological Health Impacts and Risks?

Preventing and mitigating adverse impacts to humans, wildlife and the ecosystem are among the primary roles of environmental quality, pollution prevention and natural resource protection agencies. Assessing the extent and likelihood of such impacts is therefore an important need. Risks to humans and wildlife from mercury and methylmercury are well-established. That atmospheric mercury is a major source to aquatic ecosystems—and therefore a driver of current and future risk—is also well established. The concentration and trend of mercury in air and precipitation may therefore be seen as qualitative indicators of the level of risk. Quantitative determination of risk requires monitoring and assessment of environmental concentrations further along the exposure pathway, such as in water, sediments, fish and humans.

How Does Atmospheric Mercury Lead to Risk?

Although a general relationship between mercury in the atmosphere and risk from methyl mercury in aquatic ecosystems is well established, there is a considerable amount of uncertainty in many aspects of how mercury is transported, deposited, methylated and bioaccumulated. Improving our understanding of these environmental processes is essential to determining a quantitative relationship between emissions, deposition, fish concentrations and health risk. Monitoring for mercury in the air and precipitation and integration with research activities are important means for addressing these scientific needs. Understanding how environmental factors affect mercury exposure pathways is critical for linking atmospheric concentrations to human or wildlife health outcomes.

What Can be Done: Regulations and Pollution Prevention

In order to prevent or mitigate human and ecological harms and risks, it is necessary to identify possible regulatory and pollution prevention actions that can reasonably be expected to cause significant reduction in environmental concentrations. Determining which regulatory actions will lead to successful and significant environmental outcomes requires detailed knowledge of mercury sources, source-receptor relationships and other environmental processes governing mercury concentrations and exposures. Mercury air and precipitation data are needed for such assessments. Attributing measured mercury levels to particular sources requires specific study designs and the collection of additional information.

Are We Being Successful?

After a regulatory or pollution prevention action is taken, it is important to track its progress and degree of success in achieving the desired environmental result. In addition to generalized trends in environmental mercury, ancillary information is often required to reliably link these environmental changes to the particular sources in question. Monitoring information is a critical ingredient in demonstrating that current and past actions were effective, but also whether further action is needed to meet specified goals.

Information Needs

Answering each of the above questions requires a diverse base of information including measurements of mercury throughout the environment as well as many additional parameters.

Deposition Levels, Status and Trends

Fundamental goals of monitoring for mercury in air and in deposition samples are to determine typical concentrations and characterize patterns of fluctuation in time and space. It is widely accepted that the atmosphere is the prominent pathway for mercury entering the terrestrial and aquatic ecosystems of the Great Lakes region, with the exception of certain areas where localized direct discharges remain a dominant factor. Concentrations in air or in rain can therefore be used as a localized or regionalized indicator of change in the input of mercury to the ecosystem.

Adequately characterizing regional concentrations and trends requires a distributed network of monitoring stations applying consistent methodology. Measurements taken over a long duration (at least many years) will be required to establish whether an increasing or decreasing trend is apparent. Frequent measurements are desired to characterize temporal variability and provide additional statistical power to trend analysis. In addition to a suite of sites needed to resolve regional trends, additional sites may be desired to provide additional status and trend information regarding impacted receptors (such as an impaired water body) or near source regions (such as in urban areas). Obviously, status and trends will only be determinable for those parameters collected; collection of wet deposition only will not provide inference into dry deposition trends and analysis of total mercury concentrations will not necessarily provide inference into reactive or methylated mercury.

Source Characterization

Ancillary information that may be collected as part of a mercury monitoring protocol can provide information necessary to characterize the sources of mercury influencing the measured concentrations. Methods for characterizing sources fall into two primary categories: apportionment to distance, direction or location by wind-trajectory analysis; and apportionment to source types by co-pollutant factor analysis. Wind trajectory analysis can be applied to precipitation or ambient air samples. For each sample, a trajectory is determined from which the air mass originated. This allows statistical calculations of which source regions or directions are most likely to produce high levels of mercury in air or precipitation. A factor analysis approach requires that an appropriate set of co-pollutants (usually a suite of trace metals) be measured in each sample along with mercury. The measurements of these other compounds can then be statistically compared to known source “fingerprints” or assessed to determine principal components, which are assumed to represent distinct source categories. While wind-trajectory techniques will identify potential source locations and/or directions,

factor analysis techniques will identify distinct types of sources (e.g., coal combustion, automobiles, etc.). These two methods are highly complementary and can be used in conjunction to assess sources of mercury deposition.

To provide source characterization, requirements include the collection and analysis of discrete (as opposed to composite) samples to determine co-pollutant (e.g., trace metal) concentrations. To provide adequate statistical power, a large number of samples are needed (e.g., 30-100 or more). Because source-receptor relationships may vary from one location to another, the results obtained at one site may not be fully applicable elsewhere. For examples of the use of these techniques for mercury, see Keeler *et al.*, 2006, Han *et al.*, 2005 and Han *et al.*, 2006.

Support TMDL and Control Program Development

Among the primary control options available for achieving improvements in impaired water bodies is the Total Maximum Daily Load (TMDL) approach. TMDLs are generally determined on a water-body and pollutant-specific basis. For a given impaired water body, a pollutant loading rate is determined that would be expected to achieve significant reduction in or removal of the impairment. Sources of loading are determined and control options are identified that are necessary to achieve the needed reductions. Application of the TMDL approach to pollutants, such as mercury, that enter water bodies primarily through the atmosphere has proven difficult due to the additional effort needed to characterize sources and the sparseness of control options for sources that may lie outside of the jurisdiction of the agency implementing the TMDL. Nevertheless, TMDLs are an important and applicable method of formulating control strategies and states are required to develop them for impaired or threatened water bodies, as specified in section 303(d) of the Clean Water Act.

Monitoring information can support TMDL development through determining magnitudes of atmospheric inputs to aquatic systems. In addition, more advanced monitoring techniques can assist in identifying and apportioning important atmospheric sources. Integration of monitoring at the regional or continental scales can provide information regarding the relative contributions of local and distant sources. An important consideration in designing a monitoring strategy to support TMDL development is the applicability of source apportionment results from one locale in drawing conclusions about another and the need to integrate information regarding source locations and types (e.g., within state vs. out-of-state coal combustion). In effectively developing TMDLs, accurate estimates of all mercury inputs, including both dry and wet deposition, will be needed.

Support Evaluation of Control Effectiveness and Reduction Efforts

State, federal and local governments implement a variety of regulatory and non-regulatory control programs to limit mercury emissions and achieve reductions in environmental concentrations. Although fish concentrations are the usual desired endpoint, monitoring for changes in air concentrations and deposition levels makes considerable sense, as such changes will be more readily detected and can be more readily attributed to a given control program or reduction strategy. In order to detect reductions in atmospheric levels and associate them with a given reduction strategy, the requirements described above regarding levels/trends and source apportionment will be needed. In particular, apportionment of sources based on type may be required to demonstrate, for example, a reduction in the portion of mercury

attributable to waste incineration. Linkages between atmospheric reductions and improvements in ecosystem concentrations can either be monitored for directly, modeled or assumed based on scientific evidence of mercury cycling dynamics.

Support Model Development and Application

In addition to monitoring, modeling efforts are a complementary approach to answer similar questions. Modeling may offer possibilities to answer critical questions quickly, cost-effectively, and with increased spatial and temporal resolution. The ability to hind-cast and forecast within models allows the ability to provide information for situations in which appropriate monitoring data are unavailable. Similarly, models can be used to produce reliable estimates of certain parameters in geographic areas where measurements are not taken. Modeling and monitoring are highly interdependent and complementary. Modeling efforts require substantial monitoring data to inform model operation and verify model results. To the extent that modeling activities may provide an effective means to answer the questions noted above, supporting monitoring data will be required. Intensive monitoring campaigns obtaining a large amount of data over a short timeframe are often most useful in parameterizing and validating models.

Research

Improving the scientific understanding of mercury transport, deposition, fate and exposure is critical to ensuring that effective actions are taken. Uncertainties surrounding mercury's behavior in the environment are reflected in uncertainties regarding the likely effectiveness of proposed management approaches. Atmospheric and precipitation mercury monitoring data can provide a basis to answer many important questions regarding mercury dynamics. More importantly, when integrated with information collection of other types, they can form part of a larger research strategy to address critical uncertainties.

B. Principles for Advancing Mercury Deposition Monitoring Systems for the Great Lakes

There are many factors that contribute to the determination of monitoring program siting, selection of techniques and technology, information management, and reporting. In most cases, programs evolve from one stage to another as funding and technologies arise that are able to meet identified needs. Constraints on system design are often considerable, especially in a region such as the Great Lakes and for a complex issue such as mercury. Stakeholders in the mercury deposition monitoring process include state, provincial, tribal, local and U.S., and Canadian federal governments, academic institutions, non-governmental organizations, industry groups and the public at large. Within government agencies, stakeholders may exist in numerous departments, including air and water quality control, public health, natural resources, and many others.

While presenting a wide set of potential resources, expertise and support for mercury deposition monitoring activities, this diversity of stakeholders also presents a challenge for coordinating monitoring activities to achieve optimal effectiveness. There are a number of principles for planning monitoring activities that can ensure the usefulness of the information collected on a regional basis and over a long-term. These principles include: focusing on meeting critical needs; including a diversity of technologies; pursuing consistency with other programs and projects; thorough integration of mercury deposition monitoring with mercury monitoring in lakes, sediments and fish; making data comparable and accessible; integration with national efforts; and coordination with modeling efforts in program design. Each of these is described below. A complementary set of principles has been developed to guide activities at a North American scale and should also be taken into consideration.(NADP, 2006b)

Supporting critical needs

Section A describes a number of needs and potential uses for mercury deposition monitoring information. These include tracking deposition levels, status and trends; source characterization; development of Total Maximum Daily Loads and other control programs; evaluating the effectiveness of control actions; and supporting modeling and research activities. Monitoring programs should be developed with an intention of fulfilling one or several of these needs. While a certain program or activity may not be ideally suited to meet all these needs, a range of activities should be pursued that jointly meets the full range of needs identified. While some needs may be sufficiently fulfilled by relatively short-term projects, others, such as tracking of trends, require consistent efforts over a long timeframe.

Balancing diversity and consistency

As noted above, there is a need for a range of mercury deposition monitoring techniques and technologies to achieve the full array of informational needs. This need for diverse information (and therefore a diversity of methods) should be balanced with an emphasis on consistency within the region regarding how information of a certain type is collected and managed. Where possible, consistency will provide better comparability of data across the region and provide more accurate assessments of regional trends and mercury loadings to large receptors such as watersheds and the Great Lakes themselves.

Integration with monitoring in fish and sediments

Monitoring of mercury in air and wet and dry deposition are only a few of components of the environment in which mercury monitoring needs to occur to achieve a better understanding of this issue and to support effective control strategies and track their progress. The risk to human health comes from consumption of mercury-contaminated fish. The threat to wildlife comes through the aquatic food chain, where predatory fish and fish-eating birds and mammals are also exposed through fish consumption. It is necessary therefore to also place a focus on monitoring the mercury content of fish, lakes, sediments and the aquatic food chain. These monitoring efforts should not be distinct from monitoring for mercury deposition. Integration of deposition monitoring efforts with monitoring efforts in other parts of the ecosystem is essential to develop and test our scientific understanding of the relationship between air pollution and fish contamination, as synthesized through mechanistic models. The setting of policy goals for reduced mercury emissions is dependent on development of reliable models that relate mercury in the air to mercury in fish.

In a 2003 workshop and a 2005 article, (Mason *et al.*, 2005) a diverse group of mercury experts outlined the primary components needed to thoroughly track and assess mercury contamination in the ecosystem and the urgent need for integration of monitoring across air, water, sediments and biota by careful planning and co-location of monitoring activities. The approach described is to establish an intensive monitoring site in each of many representative ecological and geographical areas. These intensive sites would be complemented by a cluster of surrounding sites monitoring for fewer parameters but provided heightened geographic resolution on several key metrics. The approach outlined by this group would prove beneficial for the region in promoting an understanding of mercury cycling in its several ecological regions, tracking changes in mercury levels and determining their causes. Critical to the success of this approach is the co-location and integration of mercury deposition monitoring with monitoring in lake waters, sediments and the aquatic food chain.

Accessible and comparable information

Monitoring activities are of value because of the information they produce. In many cases, the usefulness of information will depend on the context of other information that is available of a similar type. For assessments over time and across geography, standardized and comparable methodologies are an important means of assuring that monitored values can be compared within a common framework. In addition, information will have limited usefulness for potential stakeholders, researchers and policy-makers if they are not able to access and evaluate the underlying data. Promoting common methods for data storage and making data broadly available, such as through the internet, are important means of maximizing the value of collected information.

Integration with national US and Canadian initiatives

In addition to identifying and promoting coordination and collaboration at a regional level, it is important where possible to connect regional activities to programs operating at a national or continental level. Generally, initiatives of a larger scale will be more cost effective due to the leveraging of shared resources and economies of scale. In addition, it will be important to be able to compare regional information to a larger context wherever possible. Mercury contamination is well recognized to be a continental and global scale phenomenon and broad coordination with large-scale activities are an important means of understanding how regional phenomena fit into the context of these larger spatial scales. Programs for potential coordination within the U.S. and Canada are numerous and several additional initiatives are beginning to emerge, including NADP's Mercury

Deposition Network (MDN), Environment Canada's CAMNet (see Box 2), the NADP's Atmospheric Initiative (see Box 1), efforts to establish an advanced US national mercury monitoring network (Harris *et al.*, 2007; Mason *et al.*, 2005), efforts to monitor other ecosystem parameters, such as the Long-Term Ecological Research Network, National Estuarine Research Reserve System and many others.

Integration of monitoring with modeling

Whereas models are much less useful in the absence of quality monitoring data for input or for validation of output, monitoring data are also much less useful in the absence of robust modeling techniques to help explain the causes and patterns in the observed phenomena and to provide information about times and locations where monitoring data is absent. Monitoring requirements could be significantly reduced through the development of models capable of accurately relating atmospheric mercury concentrations to fish tissue concentrations. In many cases, the ultimate goal of monitoring programs is to provide reliable information policy-makers can use to set appropriate emission rates. Development and application of mechanistic models is an activity that is substantially intertwined with monitoring programs. If adequately developed, mechanistic models have a much greater ability than monitoring alone to provide actionable information for effective mercury control policies. The most effective program for meeting policy-maker's needs must involve a mixture of monitoring and modeling activities.

The modeling components that will benefit from enhanced monitoring data include air transport and chemical reaction models, models of wet and dry atmospheric deposition, models of transport through the watershed, and models of bioaccumulation in fish. Deliberations over the design of new mercury deposition monitoring activities will lead to the most useful result if they formally include input from modelers at the outset. Although it is beyond the scope of the current report to thoroughly discuss modeling approaches and needs, it warrants emphasizing the importance of documenting these needs and using them to design monitoring programs. In addition, models of mercury transport and ecosystem cycling can be used to identify potential priority locations for monitoring activities.

Box 1: A National Network for Atmospheric and Dry Deposition Trends

In April 2006, a subcommittee of the National Atmospheric Deposition Program (NADP) proposed a new Atmospheric Initiative (AI), which would significantly expand upon the range of mercury measurements collected by the NADP and its many partners under the long-standing and successful Mercury Deposition Network (MDN) (Gay *et al.* 2006)(NADP, 2006a). As initially proposed, the AI would include data from stations collecting speciated ambient mercury data through either the automated method or the manual method, as described in Landis *et al.* 2002. Currently, standard operating procedures for this network are in draft form and several sites have contributed data to a draft data management system. While support of site operation and maintenance will be left to local partners, network coordination, including quality assurance protocols, data management and reporting will be handled centrally through the NADP, providing significant advantages for coordination, comparability and efficiency.

C. Current Programs and Initiatives

There are numerous mercury monitoring activities currently being conducted by the Great Lakes state agencies, as well as a variety of other partners within the region. Figures 1 through 4 depict the current locations and types of mercury monitoring in air and precipitation throughout the region. An attempt has been made to capture here all activities taking place during 2006. In some cases, stations shown here may not have been operating for the entire 2006 calendar year. Additional information on recent but discontinued monitoring activities is presented in Appendix A. Summaries of both recent and current mercury monitoring activities is presented in Appendix B.

Figure 1 and Table 1 show and describe the current stations within the region collecting weekly precipitation samples for analysis of mercury. The stations shown here are part of the MDN, with the only exceptions being the Burnt Island and Point Petre IADN sites in Ontario, which were previously part of the MDN but are now separate from that network. These two sites follow the MDN protocol, with the exception of the use of a different laboratory for sample analysis. All sites shown here analyze samples for only total mercury, with the exception of several sites in Minnesota and Wisconsin, which also have methylmercury analyzed on a 4-week composite basis. Data from the MDN sites are available through the MDN website (<http://nadp.sws.uiuc.edu/mdn/>).

Figure 1: Weekly precipitation monitoring stations within the Great Lakes states and provinces

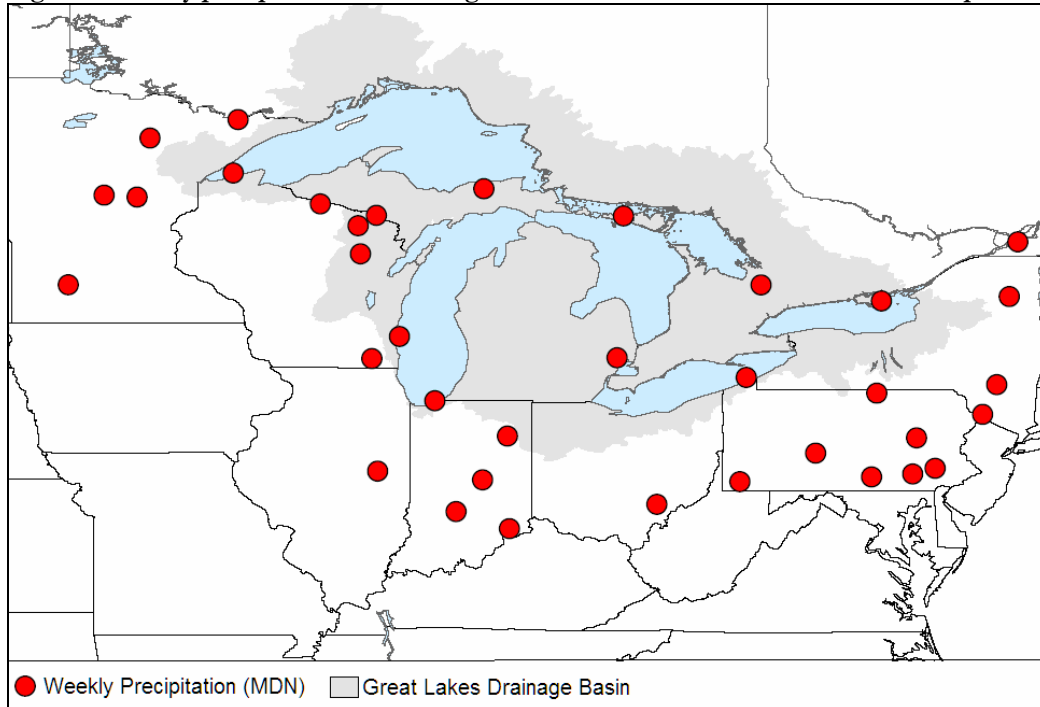


Table 1: Details of current weekly precipitation monitoring stations

Location	Network	Operator	Start Date
Canada			
Egbert, Ontario	MDN (ON7)	Environment Canada	3/7/00
Burnt Island, Ontario	IADN (previously MDN)	Environment Canada	11/27/01
Point Petre, Ontario	IADN (previously MDN)	Environment Canada	10/2/01
St. Anicet, Quebec	MDN(PQ04)	Environment Canada	4/14/98
Illinois			
Bondville	MDN	Illinois State Water Survey	1/6/99
Indiana			
Bloomington	MDN(IN28)	USGS / Indiana DEM	12/15/00
Clifty Falls State Park	MDN(IN21)	USGS / Indiana DEM	1/12/01
Fort Harrison	MDN(IN26)	USGS / Indiana DEM	4/4/03
Indiana Dunes	MDN(IN34)	Nat. Park Service / Indiana DEM / USGS	10/27/00
Roush Lake	MDN(IN20)	USGS / Indiana DEM	10/26/00
Michigan			
Seney Wildlife	MDN(MI48)	US Fish and Wildlife Service	11/11/03
Sterling Heights	MDN(MI31)	Macomb CHD / USGS	9/27/05
Minnesota			
Camp Ripley	MDN(MN23)	Minnesota PCA	7/2/96
Fernberg	MDN(MN18)	U.S. Forest Service / Minnesota PCA	3/5/96
Lamberton	MDN(MN27)	Minnesota PCA	7/2/96
Marcell Forest	MDN(MN16)	U.S. Forest Service / Minnesota PCA	2/27/96
Mille Lacs Band of Ojibwe	MDN(MN22)	Mille Lacs Band of Ojibwe	4/9/02
New York			
Biscuit Brook	MDN(NY68)	Frost Valley YMCA / NYERDA / USGS	3/9/04
Huntington Wildlife	MDN(NY20)	NYERDA / SUNY ESF / Syracuse Univ.	12/10/99
Ohio			
Athens	MDN(OH02)	Ohio University	12/28/04
Pennsylvania			
Alleghany	MDN(PA13)	National Park Service / Pennsylvania DEP	1/7/97
Arendtsville	MDN(PA00)	Pennsylvania DEP	11/14/00
Centralia	MDN	Pennsylvania DCNR	May 2006
Erie	MDN(PA30)	Pennsylvania DCNR / DEP	6/20/00
Hills Creek State Park	MDN(PA90)	Pennsylvania DEP	1/7/97
Holbrook	MDN(PA37)	Advanced Technologies Systems / EPRI	5/27/99
Milford	MDN(PA72)	U.S. Forest Service Pennsylvania DEP	9/14/00
Millersville	MDN(PA47)	Millersville University / Pennsylvania DEP	11/26/02
Valley Forge	MDN(PA60)	National Park Service Pennsylvania DEP	11/23/99
Wisconsin			
Brule River	MDN(WI08)	Wisconsin DNR	3/5/96
Lake Geneva	MDN(WI99)	Wisconsin DNR	1/7/97
Middle Village	MDN(WI32)	Menominee Indian Tribe of Wisconsin	1/22/02
Milwaukee	MDN(WI22)	Wisconsin DNR	10/3/02
Popple River	MDN(WI09)	U.S. Forest Service / Wisconsin DNR	3/5/96
Potawatomi	MDN(WI10)	Forest Country Potawatomi Community	6/7/05
Trout Lake	MDN(WI36)	Wisconsin DNR	3/5/96

As shown in Figure 2 and Table 2, the current distribution of sites measuring mercury in precipitation on an event basis is much more limited. In addition to six sites in Michigan and one in Ohio operated by UMAQL, an MDN site at Devils Lake, Wisconsin also collects precipitation on an event basis. As discussed on page 10, there are important differences in equipment between the UMAQL sites and the MDN sites, leading to a systematic difference in mercury deposition

measurements between these networks. In addition to total mercury, all seven sites run by UMAQL also analyze precipitation samples for a suite of trace metals.

Figure 2: Event-based precipitation monitoring stations within the Great Lakes states and provinces

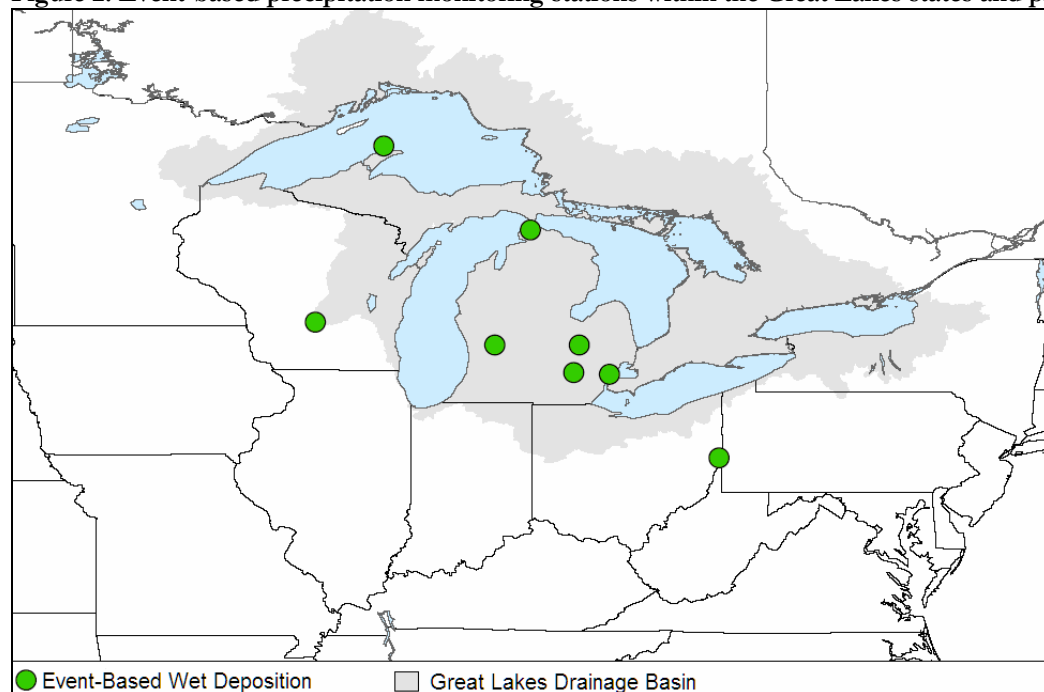


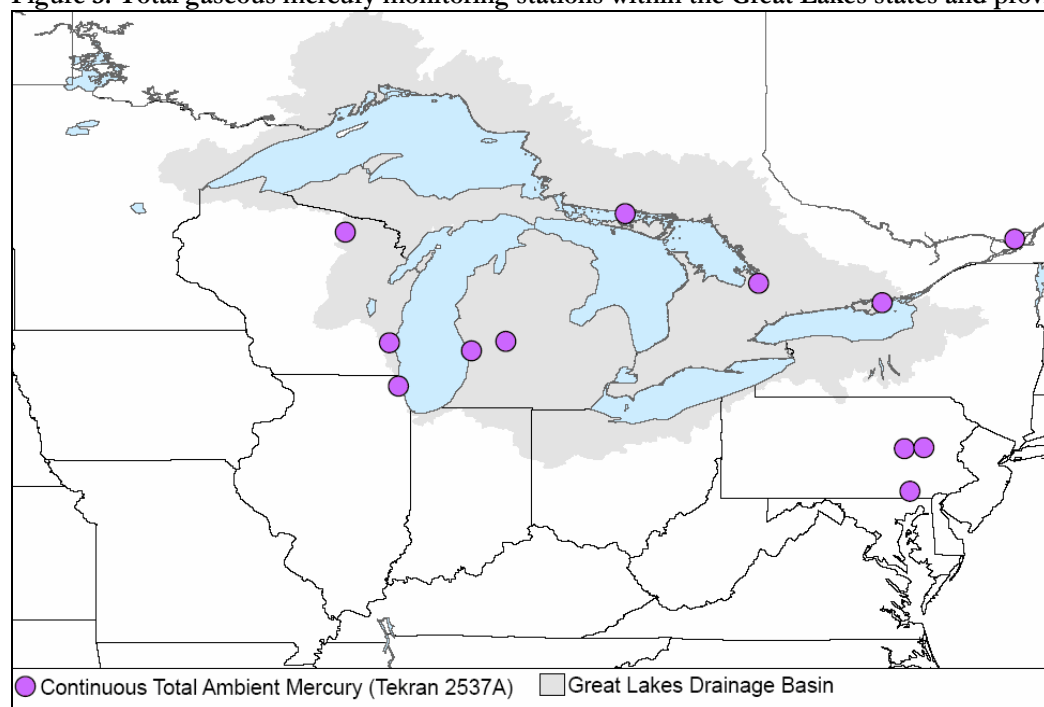
Table 2: Details of current event-based precipitation monitoring stations

Location	Operator	Start Date
Michigan		
Detroit	UMAQL*	2003
Dexter	UMAQL*	1994
Eagle Harbor	UMAQL*	1995
Flint	UMAQL*	2003
Grant Rapids	UMAQL*	2002
Pellston	UMAQL*	1994
Ohio		
Steubenville	U.S. EPA / UMAQL	2003
Wisconsin		
Devil's Lake	Wisconsin DNR (MDN)	1/11/01

* Sites in operation through 2006, expected to cease operation at of January 2007.

Figure 3 and Table 3 show the distribution within the region of TGM monitoring stations. All those stations shown measure TGM in ambient air at high temporal resolution using the Tekran 2537A unit. In addition to four Canadian CAMNet stations located in proximity to the Great Lakes region, there are eight of these units also operating within the Great Lakes states. Not shown in Figure 3, there are eight additional 2537A units operating within the region in combination with the Tekran 1130 and 1135 units to collect speciated mercury data, as described below. The data produced by those machines has the potential to be re-interpreted to provide TGM concentrations if desired, although the comparability of such data to that derived from a unit monitoring TGM directly might be questionable.

Figure 3: Total gaseous mercury monitoring stations within the Great Lakes states and provinces*



* TGM is a component of the mercury species collected by the sites shown in Figure 4.

Table 3: Details of current total gaseous mercury monitoring stations

Location	Operator	Start Date
Canada		
Egbert, Ont.	Environment Canada (CAMNet)	March 2000
Burnt Island, Ont.	Environment Canada (CAMNet)	1998
Point Petre, Ont.	Environment Canada (CAMNet)	1996
St. Anicet, Quebec	Environment Canada (CAMNet)	April 1998
Illinois		
Northbrook	Illinois EPA	
Michigan		
Grant Rapids	Michigan DEQ	June 2006
Holland	Michigan DEQ	June 2006
Pennsylvania		
Centralia (x2)	Pennsylvania DEP	May 2006
Lancaster	PA DEP	6/18/99
Wisconsin		
Milwaukee	Wisconsin DNR	
Potawatomi	Wisconsin DNR	

Note: A trailer housing two Tekran 2537A instruments has been purchased and jointly managed by MPCA, MDEQ and WDNR. Past locations of deployment and additional description are in Appendix A.

The stations currently collecting speciated ambient mercury data are shown in Figure 4, with some additional detail given in Table 4. All sites within the region collecting information of this type in 2006 were using the automated method, although prior initiatives within the region have used the manual method (see Appendix A).

Figure 4: Speciated ambient mercury monitoring stations within the Great Lakes states and provinces

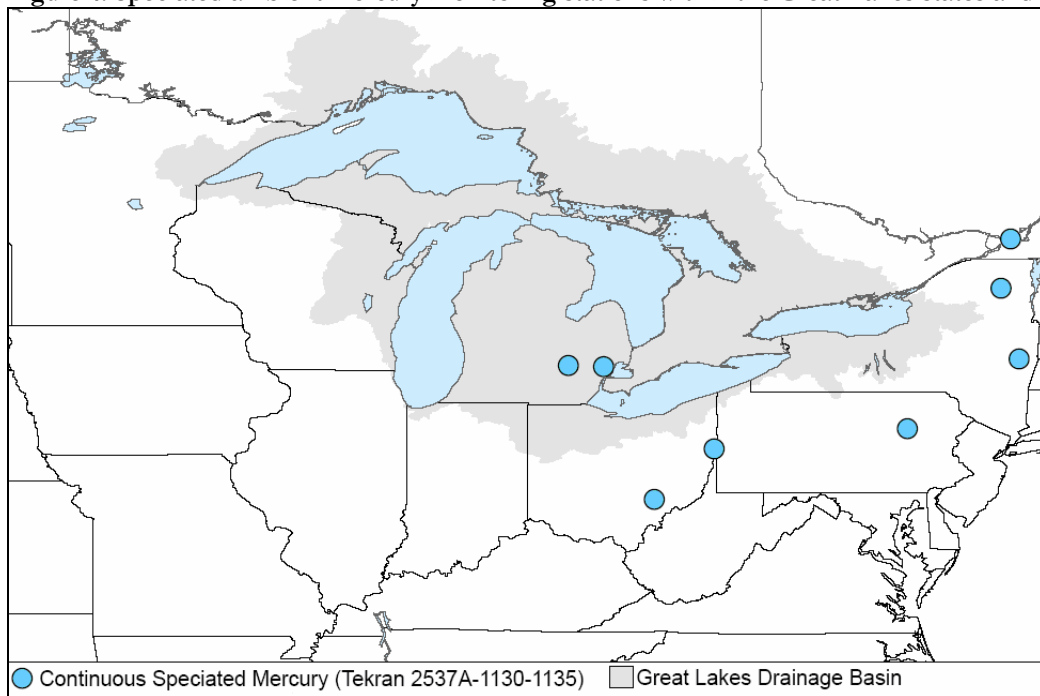


Table 4: Details of current speciated ambient mercury monitoring stations

Location	Operator
Canada	
St. Anicet, Quebec	Environment Canada
Michigan	
Detroit	UMAQL
Dexter	UMAQL
New York	
Huntington Wildlife	Clarkson Univ.
Rensselaer	New York State DEC
Ohio	
Athens	Ohio University
Steubenville	UMAQL – U.S. EPA
Pennsylvania	
Centralia	Pennsylvania DEP

D. Assessment of Current Programs and Recommendations

Below, the potential uses of mercury deposition monitoring information discussed in Section A (Page 7) are revisited, with an assessment of the current ability to fulfill these purposes and recommendations for priority actions needed to advance capabilities in each of these areas. As discussed in the Introduction (page 3), the recommendations are not intended to represent the official position of the organizations contributing to this report, nor to be prescriptive of the future actions of those agencies. They are a starting point for further regional discussion, coordination and action. Other recommendations have been made regarding mercury monitoring and research on a regional level (e.g., Seigneur et al., 2003) and these are intended to be complementary and build upon recommendations made elsewhere.

Deposition Levels, Status and Trends

Wet Deposition

As shown in Figure 1 and Figure 2, there is a substantial number of wet deposition monitoring stations throughout the region. That many of these sites have been operating in a consistent manner for many years provides an important ability to detect spatial and temporal trends in mercury deposition throughout the region. Maintenance of a majority of these sites is critical in providing a similar ability in the future.

While coverage of the MDN is sparse throughout Michigan and Ohio, the event-based precipitation sites in these two states fill those gaps to a considerable extent. However, data comparability between these monitoring methods somewhat hampers assessment of wet deposition at the regional scale (see discussion on page 10). Other areas with lesser wet deposition monitoring density include the western portions of Illinois and Wisconsin and southeastern Minnesota and the area surrounding Lake Ontario. While wet deposition monitoring stations are significantly less densely spaced on the Canadian side of the region, the existence of several MDN stations in Ontario and Quebec do provide important data points on the northern side of the Great Lakes.

There is clearly a substantial amount of variability in the placement and density of wet deposition monitoring stations throughout the region. While a more regular grid-like pattern would provide improved ability to determine regional background deposition levels, it is recognized that clustering of sites in certain areas may be required to characterize gradients near sources, in sensitive areas or for other purposes. In addition, logistical considerations are important in choosing site locations, as significant support is required for site operation and maintenance.

Recommendation 1

To provide a consistent regional measure of wet deposition trends, continue to support the maintenance and operation of existing wet deposition monitoring sites. An assessment should be made of the optimal placement of these and other monitoring locations to provide regional background information, while improving coverage of potentially elevated deposition near source regions, such as urban areas, or sensitive receptors, such as biological hotspots.

Ambient Air Mercury

With the availability of the Tekran 2537A, there is now a considerable amount of data being collected throughout the region representing the concentration of TGM in the ambient air. As shown in Figure 3, there are currently at least 8 of these units operating within the eight Great Lakes states, with an addition 4 operating in southern Ontario and Quebec as part of CAMNet. With a time-scale of several minutes per measurement, these instruments provide an excellent temporal and spatial coverage of ambient elemental mercury concentrations. These instruments, if maintained and operated on a continuing basis, provide an important means of tracking atmospheric mercury trends throughout the region. In contrast to the precipitation information, they may provide some inference of trends in dry deposition and provide a much finer temporal resolution for comparison. In addition, data on ambient concentrations is highly valuable for parameterization and validation of models.

Despite its widespread collection for location-specific purposes, the application of this monitoring data at a regional scale has not occurred. Because of its ease of collection and wide-spread use, consideration should be given to ways in which data from these instruments can be used at the regional level to answer key questions regarding mercury deposition. To facilitate such use, it is necessary to have a central data storage location and protocols for data collection and processing from these instruments. The EPA's AQS database is one available option and at least one station within the region currently submits their continuous ambient mercury data to that repository. Environment Canada's CAMNet provides a strong example of how to form a network from such monitoring stations (see Box 2). CAMNet makes data available online through a data repository (Environment Canada, 2002). Exploring a similar functionality at the regional level might facilitate improved access and analysis of such data from across the region. Innovative internet sites have been developed for other purposes that allow users to explore and analyze environmental data in addition to providing data for download

Recommendation 2

To enable regional use of the TGM data being collected, maintain the existing sites collecting such data and improve the integration of information from these sites on a regional level. Data from the many TGM monitors throughout the region should be integrated into a centralized data storage location and handled with a common protocol. To improve comparability, consideration should be given to adopting a common SOP and calibration routine for sites in the U.S. as is done for CAMNet.

Dry Deposition

Information regarding dry deposition is considerably less abundant throughout the region than for wet deposition. The few dry deposition monitoring programs that exist have used the technique of estimating dry deposition based on measurements in ambient air. Despite these efforts, regional coverage of dry deposition measurements is far from adequate. Improving dry deposition estimates within the region should be a priority if the goal is to identify total atmospheric deposition to the region's waters and watersheds.

While there are numerous methodological options for improving the regional dry deposition information base, many options have some significant expenses or logistical constraints that decrease the extent to which they could be broadly applied in a regional network. Several direct measurement methods may present a cost-effective option to obtain dry deposition estimates.

However, the required equipment and methods are not standardized and are not commercially available. In addition, the information collected by these methods lacks the chemical speciation and high temporal resolution that is offered by other methods. A better understanding of the advantages and disadvantages of various options is needed prior to justifying widespread investment in a given technology. Direct measurement techniques for mercury dry deposition need to be further developed and compared. A particular emphasis should be placed on cost-effectiveness of various technologies and the potential to drive costs down through economies of scale.

Recommendation 3

To meet a need for accurate and cost-effective methods for measuring dry deposition of mercury, compare and evaluate emerging monitoring technologies and select a single option to measure mercury dry deposition in a consistent, comparable manner and at reasonable cost. This option should be refined, standardized, made widely-available, and implemented to detect regional trends in dry deposition.

The NADP has proposed the creation of a network that would complement the existing MDN by including speciated ambient mercury measurements collected by either the manual or automated methods (Gay *et al.*, 2006). This network would provide methodological standardization and data management, processing and reporting on a national basis for stations routinely collecting data by either of these methods (see Box 1). While expansion of speciated data collection within the region via the automated systems is highly favorable, it is unlikely to be feasible to significantly increase and sustain the number of automated speciated mercury samplers within the region due to fiscal constraints and the labor-intensive nature of these methods. The manual-collection/modeling method may offer a more cost-effective and labor-efficient means of determining dry deposition trends as a regional background. However, even at a high level of site density, a dry deposition monitoring network may have limitations due to the relatively high spatial variability of dry deposition compared to wet deposition. Reactive gaseous mercury, the primary driver of dry deposition can vary acutely in areas with significant sources and even a monitoring network with several sites per state may be inadequate to fully characterize these gradients.

Dry deposition would be most thoroughly and cost-effectively characterized by a robust regional modeling system (see recommendation 7 below). Monitoring data, such as the speciated ambient measurements that would take place under the MTN would be a critical component of validating and parameterizing such a system. To support this modeling effort and to provide a regional background measure of dry deposition, establishment of a handful of additional speciated ambient measurement sites and coordination of the information collected by such sites are essential. The MTN provides a reasonable option for coordinating such sites on a national basis. As shown in Figure 4, there is currently a substantial basis of needed equipment within the region and a growing base of expertise in operating it. However, meeting the challenge of maintaining and operating these stations on a consistent basis in the future will require additional support and regional coordination. In addition, there are clearly large portions of the region not currently represented by monitoring of this type, particularly the western portion of the Great Lakes basin.

Recommendation 4

To provide localized estimates of dry deposition and support validation of source-oriented modeling results, establish and maintain several regional sites to monitor speciated ambient mercury. If possible, such sites should participate in a national

network and be placed to coincide with monitoring of fish tissue concentrations and sediment cores.

Litterfall and Throughfall

While it is recognized that litterfall and throughfall are extremely important components in determining the total deposition to forested landscapes, a regional monitoring program that would examine the influence of these processes may not be the most desirable approach. Information on throughfall and litterfall is most relevant when placed within the context of the overall deposition at a given location and is therefore most appropriately conducted at research sites where other mercury measurements are taking place. The evidence that exists suggests that the litterfall and throughfall depositional loads are a relatively consistent factor of the direct deposition loads. Combining accurate regional estimates of wet and dry deposition with geographic data on land cover may therefore present an acceptable means of accounting for the litterfall/throughfall contribution to total loadings (see, for example, (Miller *et al.*, 2005). Further research is needed to better identify the relation of throughfall/litterfall to ambient mercury levels or wet/dry depositional loadings and to characterize the causes of variability.

Recommendation 5

To adequately characterize geographic trends in mercury deposition and account for land cover type in estimation of the throughfall/litterfall contribution, the impacts of throughfall and litterfall on mercury loading should be thoroughly incorporated into models of deposition and measurement-based estimates. Research should continue to characterize throughfall/litterfall dynamics and their relation to other mercury deposition metrics.

Source Characterization, Policy Development and Tracking Success

Characterization of sources of mercury can be done in several ways. Recently, statistical source apportionment has been applied to wet deposition samples taken at Steubenville, Ohio, showing a relatively high (~70%) contribution of coal combustion to wet deposition at that site (Keeler *et al.*, 2006). Conclusions of this type require analysis of trace metals in the precipitation samples and the underlying statistics are most robust when each sample represents a discrete event. Within the region, such analysis would therefore currently be feasible for only a few locations. Event-precipitation samples also allow analysis of wind back-trajectories either for outlying values or for the dataset as a whole. While results of such studies might be assumed to be representative on a regional scale, they can be highly influenced by local mercury sources, as is the case in Steubenville, which may limit their broader applicability. Source apportionment results of this type are restricted to wet deposition and methods remain to be developed for apportioning sources of dry deposition from a receptor modeling approach. Continuing such monitoring where it exists and establishing several additional sites of this type within the region would greatly support effective policy development.

Recommendation 6

To provide broader regional information on mercury source contributions, especially for sensitive receptor locations, a subset of mercury wet deposition stations should be converted to event-sampling protocols and include measurement of trace metals.

Source characterization can also be done using deterministic, source-oriented models (e.g., CMAQ, CAMx). The U.S. EPA has applied such approaches in their analysis leading to the Clean Air Mercury Rule and attempted to quantify the contribution of coal utilities to deposition within 36x36 km grid cells by using CMAQ to calculate deposition with utilities included and excluded from the emissions profile (Beusse *et al.*, 2006). Similar efforts are underway on a regional scale through various research projects that incorporate improvements on the CMAQ model (Great Lakes Commission, 2006). Characterization of sources through such models, although generally introducing greater uncertainty than receptor-oriented modeling, offer greater spatial and temporal coverage and are complementary to receptor-oriented modeling in that the results can be inter-compared to provide validation. In addition, they present a considerable advantage for determining sources of deposition to large receptors, such as the Great Lakes, where one or even several monitoring stations may not provide adequate representative coverage.

Recommendation 7

To provide broad geographic coverage of source-apportioned deposition estimates, source-oriented deterministic modeling of mercury should continue to be improved, tested and then implemented on a continuing operational basis. Monitoring data of various types are needed to validate such models. Atmospheric models should be strongly linked to models of mercury cycling in wetlands, lakes and the food chain.

Integrating Data Regionally and Across Media

As the ultimate goal of monitoring mercury deposition is prevention of its accumulation in aquatic food chains, it is essential to understand the processing of mercury within the ecosystem to interpret mercury deposition data in a meaningful way. While simplifying assumptions can often be made, such as that mercury deposition and food chain accumulation of methylmercury are proportional on a 1:1 basis (see, for example, Cocca 2001), better information is needed to determine both the precise nature of this relationship and the temporal scale over which deposition reductions would result in food chain reductions. Preliminary data from the METAALICUS study suggest the relationship is strong and deposition reductions may translate rapidly to the food chain, at least in some environments (Orihel *et al.*, 2006).

There have been several recent efforts to characterize the factors that determine the sensitivity of a given lake to mercury accumulation within its food chain, as this variation has been shown to be much greater than could be explained by atmospheric deposition (Kamman *et al.*, 2005; Roué-LeGall *et al.*, 2005; Wiener *et al.*, 2006). Within the Northeastern United States and Southeastern Canada a set of “biological mercury hotspots,” or areas at elevated risk of mercury-related impacts have been identified based on models incorporating existing monitoring data and other regional environmental conditions and parameters. (Evers *et al.*, 2007) While such techniques show promise for characterizing inland lakes, the Great Lakes themselves offer a unique challenge due to their size and complexity. Fully characterizing mercury fate within the lakes, and its linkage to atmospheric deposition, will require robust multi-media modeling.

Recommendation 8

To identify the processes and ecosystem characteristics that govern the movement of mercury from the atmosphere, through the ecosystem and within the food chain, additional research should be supported and used to further develop multi-media mercury models on a regional basis, especially for the Great Lakes themselves.

Tracking of trends or patterns in atmospheric mercury or in mercury deposition will be most effective if strong links can be made to outcomes in fish tissues and trends in the long-term sedimentary record. Similarly, efforts to monitor mercury in rivers, lakes, and fish will benefit from complimentary complementary efforts to monitor mercury deposition within the same water basin. Many institutions and governmental agencies within the region monitor for mercury concentrations in fish tissues, although integration of such efforts with mercury deposition monitoring has often been insufficient. It should be possible to identify, in a relatively small area, long-term monitoring sites for fish, sediment, and deposition that are all representative of the region's ecology, geology, and mercury deposition. Ideally, the deposition monitor would be located within the watershed, but that goal should not be a requirement for long-term monitoring if there is not a local mercury emission source or a local gradient in precipitation, which can occur due to orographic effects. At certain sites that can be considered representative of a given ecological region, it would be highly beneficial to have co-located mercury monitoring programs for atmospheric deposition, water, fish and sediments, among other parameters as suggested in Mason et al., 2005. The need to monitor intensively across several environmental compartments at representative sites should not diminish detract from the need to also monitor broadly across a broad geography to determine trends and patterns. For broader monitoring programs, means should be sought to build better linkages among atmospheric deposition monitoring and mercury monitoring elsewhere in other compartments of the environment to provide a complete picture of mercury's distribution and movement within the Great Lakes region.

Recommendation 9

To better predict and explain changes in fish mercury concentrations and with regard to atmospheric sources and deposition, improved linkages should be established among mercury monitoring programs for fish, water, sediments and deposition. Opportunities should be identified to establish long-term monitoring of fish, sediment, and mercury deposition that are all representative of a given region.

The collection of information on mercury levels in the environment of the Great Lakes region has been done under a wide variety of initiatives over a span of many years. To enable thorough assessment of the entry, processing and fate of mercury within the ecosystem, it is necessary to have integrated datasets spanning a broad scale of time, space and environmental media. Unfortunately, much previously collected data within the region is not centrally available at the present time for such assessments. Often, funding allocated to monitoring programs is barely sufficient to support data collection and quality assurance and provides little or no support for data analysis and interpretation.

Bringing together a diversity of datasets of previously collected information would provide considerable added value to prior monitoring and research investments and would provide an unprecedented ability to draw important conclusions regarding mercury dynamics in the Great Lakes region. From 2001-2004, the Northern States Research Cooperative coordinated such a data compilation effort involving the northeastern portion of the United States and the southeastern portion of Canada (Evers and Clair, 2005; NSRC, 2001). The data compilation effort enabled a wide range of important conclusions regarding mercury's entry and fate within that region. Adopting a similar approach for the Great Lakes would enable a powerful assessment of past and current data, as well as provide a platform for integrated environmental mercury assessment into the future.

Recommendation 10

To provide the most accurate assessment of past and current mercury dynamics in the Great Lakes region, promote a broad effort to integrate mercury measurement data for the region from multiple environmental media, following the example of the Northern States Research Cooperative. A considerable amount of value could be gained by modest additional investments in analyzing data that has already been collected.

It is important to place mercury information for the Great Lakes within a context of other portions of North America. With a handful of notable exceptions (such as the MDN), past mercury efforts within the Great Lakes region and elsewhere in the U.S. have been either uncoordinated across space, or coordinated on a limited regional scale. Better national (and international) coordination is essential for providing the ability for regional inter-comparisons and national assessments. In addition, national networks provide efficiency compared to smaller efforts. Finally, a robust national-level system is more likely to be maintained over a long-term and is more likely to achieve parallel support within Canada, an essential consideration in the binational Great Lakes region. Achieving this will clearly require commitment and partnership at the national, state and local levels. Building upon a 2003 workshop intended to define a vision for improved mercury monitoring on a national scale, a group of experts have published a conceptual outline for a national network (Harris *et al.*, 2007; Mason *et al.*, 2005). The outline presented there is highly consistent with the findings of the present assessment.

Recommendation 11

To provide for comparable assessment of mercury deposition and ecosystem cycling on a national basis, support is needed to establish a robust national mercury monitoring network. Such a network should embrace the principles of the plan outlined in Mason *et al.* 2005, balancing needs for national consistency with allowance for addressing unique regional issues.

Characterizing Urban Sources, Patterns and Influence

Urban areas clearly contain higher densities of mercury sources than rural areas and therefore have much higher ambient mercury concentrations and greater deposition. There is also much wider variation in total mercury air concentrations and the relative proportions of mercury species in urban areas compared with rural sites (Gabriel *et al.*, 2005; Lynam and Keeler, 2005). In addition to considerations of direct mercury emissions, there is evidence that urban photochemistry can alter the mercury species composition in the urban atmosphere (Liu and Keeler, 2005; Lynam and Keeler, 2006). As a result, urban areas can present complex patterns of mercury deposition which can be challenging to adequately characterize by short-term, stationary monitoring campaigns. It is therefore challenging to quantify the extent of the urban influence and the pattern of deposition on the expanding fringe between urban and rural areas within the region. It is also more challenging to identify and characterize additional sources which may exist within a complex urban airshed.

Such efforts would be aided by the increased availability of mobile mercury monitoring options, of which there has been some recent progress in developing and adopting. Within the Great Lakes region, a mobile trailer with dual Tekran 2537A TGM monitors has been used by state governments for a variety of purposes (Taylor-Morgan *et al.*, 2003). Efforts have been made elsewhere to measure mercury from airplanes using gold traps (Artaxo *et al.*, 2000), although necessary sampling durations

may limit the usefulness of such techniques to provide good characterization of spatial patterns or specific plumes. Described in Appendix BB, passive samplers for mercury would present a low-cost option for obtaining time-integrated averages at a large number of sites.

In addition to developing such technologies, improved guidance should be developed to assist state and local managers in designing urban mercury monitoring campaigns and statistical tools and models should continue to be improved and applied to characterize urban mercury patterns. Beyond characterizing mercury patterns and transformation processes in the urban atmosphere, work is needed to better identify unknown sources of mercury to the environment and to better characterize the species of mercury emitted from known sources. Such information will be valuable in assessing the relative importance of certain sources within the context of total mercury releases and deposition.

Recommendation 12

To identify urban mercury patterns, characterize the influence of urban mercury sources on receptor regions and characterize additional mercury sources, new technologies and statistical techniques should be applied to urban monitoring campaigns and additional studies should be conducted to identify additional sources of mercury emissions and characterize emissions of reactive and organic mercury.

Organization and Collaboration

Implementing the above recommendations will clearly require substantial coordination on the regional level, as well as integration with and support from national mercury efforts. In pursuing these goals, partnerships should be strengthened among state and provincial agencies, U.S. and Canadian federal agencies, municipal and tribal governments, academia, and other for-profit and non-profit entities. Rationale for strong regional, national and binational coordination includes: increased cost-effectiveness; sharing of data and information; and improved comparability among sites due to common methods and protocols, among others.

In addition to communication among various levels of government and with the broad stakeholder community, the mercury issue presents a unique challenge in that it requires expertise in a variety of fields that are otherwise often kept distinct. Gaining a full understanding of mercury contamination and determining effective methods for mitigating its impacts requires expertise in atmospheric sciences, organic and inorganic chemistry, aquatic sciences, fisheries biology, among many other disciplines. It is often the case that this expertise is housed in different departments within agencies, universities and professional meetings, for the good reason that many environmental issues do not engage the full extent of these many disciplines. To effectively address the mercury issue, there will be a need to create mechanisms within and among agencies, universities and the full community working on this issue that promote collaboration across the typical institutional boundaries of atmospheric and aquatic research and management.

Recommendation 13

To pursue the goals described here, strong partnerships should be developed between those acting at the state, provincial, federal, tribal, academic and non-governmental levels. In addition, mechanisms are needed within and among agencies that promote interaction of the diverse set of scientists and managers needed to address the mercury problem, including those specializing in atmospheric pollution, chemistry, aquatic

pollution, fisheries biology, wetland ecology and many others.

References

- Ames, M., Gullu, G., and Olmez, I. (1998). "Atmospheric Mercury in the Vapor Phase and in Fine and Coarses Particulate Matter at Perch River, New York." *Atmospheric Environment*, 32(5), 865-872.
- Artaxo, P., Calixto de Campos, R., Fernandes, E. T., V. Martins, J., Xiao, Z., Lindqvist, O., Fernandez-Jimenez, M. T., and Maenhaut, W. (2000). "Large scale mercury and trace element measurements in the Amazon basin." *Atmospheric Environment*, 34(24), 4085-4096.
- Beusse, R., Blair, C., Canes, H., Charen, S., Fabirkiewicz, S., Hatfield, J., Hauck, E., and Orden, J. V. (2006). "Monitoring Needed to Assess Impact of EPA's Clean Air Mercury Rule on Potential Hotspots." 2006-P-00025, U.S. Environmental Protection Agency, Washington, DC.
- Blanchard, P., Froude, F. A., Martin, J. B., Dryfhout-Clark, H., and Woods, J. T. (2002). "Four years of continuous total gaseous mercury (TGM) measurements at sites in Ontario, Canada." *Atmospheric Environment*, 36(23), 3735-3743.
- Buchsbaum, A., Ho, W., Lipman, Z., and Murray, M. (2003). "Rain Check Upper Peninsula: Mercury Levels in the Precipitation of Marquette County, Michigan." National Wildlife Federation, Ann Arbor, Michigan.
- Caldwell, C. A., Swartzendruber, P., and Prestbo, E. (2006). "Concentration and Dry Deposition of Mercury Species in Arid South Central New Mexico (2001-2002)." *Environmental Science and Technology*, 40(24), 7535-7540.
- Cobos, D. R., Baker, J. M., and Nater, E. A. (2002). "Conditional sampling for measuring mercury vapor fluxes." *Atmospheric Environment*, 36(27), 4309-4321.
- Cocca, P. (2001). "Mercury Maps: A Quantitative Spatial Link Between Air Deposition and Fish Tissue Peer Reviewed Final Report." EPA-823-R-01-009, United States Environmental Protection Agency.
- Engstrom, D., and Swain, E. (1997). "Recent declines in atmospheric mercury deposition in the upper Midwest." *Environmental Science & Technology*, 31(2), 960-967.
- Environment Canada. (2002). "NAtChem/Toxics Database."
- Ericksen, J. A., Gustin, M. S., Schorran, D. E., Johnson, D. W., Lindberg, S. E., and Coleman, J. S. (2003). "Accumulation of atmospheric mercury in forest foliage." *Atmospheric Environment*, 37(12), 1613-1622.
- Evers, D. C., and Clair, T. A. (2005). "Mercury in Northeastern North America: A synthesis of Existing Databases." *Ecotoxicology*, 14(1), 7-14.
- Evers, D. C., Han, Y.-J., Driscoll, C. T., Kamman, N. C., Goodale, M. W., Lambert, K. F., Holsen, T. M., Chen, C. Y., Clair, T. A., and Butler, T. (2007). "Biological Mercury Hotspots in the Northeastern United States and Southeastern Canada." *Bioscience*, 57(1), 29-43.
- Fernandez, J. A., Aboal, J. R., and Carballeira, A. (2000). "Use of native and transplanted mosses as complementary techniques for biomonitoring mercury around an industrial facility." *Science of the Total Environment*, 256(2-3), 151-161.
- Fitzgerald, W., Engstrom, D., Mason, R., and Nater, E. (1998). "The case for atmospheric mercury contamination in remote areas." *Environmental Science and Technology*, 32, 1-7.
- Gabriel, M. C., Williamson, D. G., Brooks, S., and Lindberg, S. (2005). "Atmospheric speciation of mercury in two contrasting Southeastern US airsheds." *Atmospheric Environment*, 39(27), 4947-4958.
- Gay, D., Risch, M., Prestbo, E., and Schmeltz, D. (2006). "DRAFT - The Mercury Trends Network (MTN): A New Initiative for the National Atmospheric Deposition Program."
- Gbor, P. K., Wen, D., Meng, F., Yang, F., and Sloan, J. J. (2007). "Modeling of mercury emission, transport and deposition in North America." *Atmospheric Environment*, 41(6), 1135-1149.
- Great Lakes Commission. (2006). "Great Lakes Air Deposition (GLAD) Program: Project Descriptions."
- Hall, B. D., Manolopoulos, H., Hurley, J. P., Schauer, J. J., Louis, V. L. S., Kenski, D., Graydon, J., Babiartz, C. L., Cleckner, L. B., and Keeler, G. J. (2005). "Methyl and total mercury in precipitation in the Great Lakes region." *Atmospheric Environment*, 39(39), 7557-7569.

- Han, Y.-J., Holsen, T. M., Hopke, P. K., and Yi, S.-M. (2005). "Comparison between Back-Trajectory Based Modeling and Lagrangian Backward Dispersion Modeling for Locating Sources of Reactive Gaseous Mercury." *Environmental Science and Technology*, 39(6), 1715-1723.
- Han, Y.-J., Holsen, T. M., Lai, S.-O., Hopke, P. K., Yi, S.-M., Liu, W., Pagano, J., Falanga, L., Milligan, M., and Andolina, C. (2004). "Atmospheric gaseous mercury concentrations in New York State: relationships with meteorological data and other pollutants." *Atmospheric Environment*, 38(37), 6431-6446.
- Harris, R., Krabbenhoft, D. P., Mason, R., Murray, M. W., Reash, R., and Saltman, T. (2007). "Ecosystem Responses to Mercury Contamination." CRC Press.
- Holsen, T. (2006). "Personal Communication."
- Hopke, P. K., Liu, W., Han, Y.-j., Yi, S.-M., Holsen, T. M., Cybart, S., and Milligan, M. (2003). "Measured summertime concentrations of particulate components, Hg₀, and speciated polycyclic aromatic hydrocarbons at rural sites in New York State." *Environmental Pollution*, 123(3), 413-425.
- Kamman, N. C., Chalmers, A., Clair, T. A., Major, A., Moore, R. B., Norton, S. A., and Shanley, J. B. (2005). "Factors Influencing Mercury in Freshwater Surface Sediments of Northeastern North America." *Ecotoxicology*, 14(1), 101-111.
- Kapadia, N., Lipman, Z., and Murray, M. (2004). "Rain Check Cleveland: Environmental and Conservation Groups Monitor Mercury Levels in Ohio's Precipitation." National Wildlife Federation, Ann Arbor, Michigan.
- Keeler, G. J. (2006). "Personal Communication." Ann Arbor, Michigan.
- Keeler, G. J., Landis, M. S., Norris, G. A., Christianson, E. M., and Dvonch, J. T. (2006). "Sources of Mercury Wet Deposition in Eastern Ohio, USA." *Environmental Science and Technology*, 40(19), 5874-5881.
- Kolka, R. K., Grigal, D. F., Nater, E. A., and Verry, E. S. (2001). "Hydrologic cycling of mercury and organic carbon in a forested upland-bog watershed." *Soil Science Society of America Journal*, 65(3), 897-905.
- Kolka, R. K., Nater, E. A., Grigal, D. F., and Verry, E. S. (1999). "Atmospheric inputs of mercury and organic carbon into a forested upland bog watershed." *Water Air and Soil Pollution*, 113(1-4), 273-294.
- Lai, S. O., Holsen, T. M., and Sharac, T. J. "Direct Dry Deposition Measurements of Hg with Water and Knife-edge Surface Samplers." *2005 Conference of the International Association for Great Lakes Research*, Ann Arbor, MI.
- Landis, M. S., and Keeler, G. J. (1997). "Critical evaluation of a modified automatic wet-only precipitation collector for mercury and trace element determinations." *Environmental Science and Technology*, 31(9), 2610-2615.
- Landis, M. S., Stevens, R. K., Schaedlich, F., and Prestbo, E. M. (2002). "Development and Characterization of an Annular Denuder Methodology for the Measurement of Divalent Inorganic Reactive Gaseous Mercury in Ambient Air." *Environmental Science and Technology*, 36(13), 3000-3009.
- Lindberg, S., Kim, K., Meyers, T., and Owens, J. (1995). "Micrometeorological Gradient Approach for Quantifying Air-Surface Exchange of Mercury Vapor - Tests Over Contaminated Soils." *Environmental Science and Technology*, 29(1), 126-135.
- Liu, B., and Keeler, G. J. "Filed Observations of the Interactions of Gas Phase Mercury and Ozone at an Urban Site." *2005 Conference of the International Association for Great Lakes Research*, Ann Arbor, MI.
- Lough, G. C., Hall, B. D., Olson, M. L., Schauer, J. J., Bruening, S. L., and Von Schneidmesser, E. A. "Understanding the Origins and Speciation of Atmospheric Mercury in a Major Urban Area on the Shores of the Great Lakes." *2005 Conference of the International Association for Great Lakes Research*, Ann Arbor, MI.
- Lyman, S. N., Gustin, M. S., Prestbo, E. M., and Marsik, F. J. (2007). "Estimation of Dry Deposition of Atmospheric Mercury in Nevada by Direct and Indirect Methods." *Environ. Sci. Technol.*, 41(6), 1970-1976.
- Lynam, M. M., and Keeler, G. J. (2002). "Comparison of methods for particulate phase mercury analysis: sampling and analysis." *Analytical and Bioanalytical Chemistry*, 374(6), 1009-1014.
- Lynam, M. M., and Keeler, G. J. (2005). "Automated Speciated Mercury Measurements in Michigan." *Environmental Science and Technology*, 39(23), 9253-9262.

- Lynam, M. M., and Keeler, G. J. (2006). "Source–receptor relationships for atmospheric mercury in urban Detroit, Michigan." *Atmospheric Environment*, 40(17), 3144-3155.
- Lynch, J. A., Carrick, H. C., and Horner, K. S. (2005). "Mercury Deposition in Pennsylvania: 2005 Status Report." Pennsylvania State University Environmental Resources Research Institute, University Park, Pennsylvania.
- Makholm, M., and Bennett, J. (1998). "Mercury accumulation in transplanted Hypogymnia physodes lichens downwind of Wisconsin chlor-alkali plant." *Water Air and Soil Pollution*, 102(3-4), 427-436.
- Marsik, F. J., Keeler, G. J., and Landis, M. S. (2007). "The dry-deposition of speciated mercury to the Florida Everglades: Measurements and modeling." *Atmospheric Environment*, 41(1), 136-149.
- Marvin, C., Painter, S., and Rossmann, R. (2004). "Spatial and temporal patterns in mercury contamination in sediments of the Laurentian Great Lakes." *Environmental Research*, 95(3), 351-362.
- Mason, R. P., Abbot, M. L., Bodaly, R. A., O. Russell Bullock, J., Driscoll, C. T., Evers, D., Lindberg, S. E., Murray, M., and Swain, E. B. (2005). "Monitoring the Response to Changing Mercury Deposition." *Environmental Science and Technology*, 39(1), 14a-24a.
- Miller, E. K., Vanarsdale, A., Keeler, G. J., Chalmers, A., Poissant, L., Kamman, N. C., and Brulotte, R. (2005). "Estimation and Mapping of Wet and Dry Mercury Deposition Across Northeastern North America." *Ecotoxicology*, 14(1), 53-70.
- Moreno, T., Higuera, P., Jones, T., McDonald, I., and Gibbons, W. (2005). "Size fractionation in mercury-bearing airborne particles (HgPM10) at Almaden, Spain: Implications for inhalation hazards around old mines." *Atmospheric Environment*, 39(34), 6409-6419.
- Munthe, J., Wangberg, I., Pirrone, N., Iverfeldt, A., Ferrara, R., Ebinghaus, R., Feng, X., Gardfeldt, K., Keeler, G., Lanzillotta, E., Lindberg, S. E., Lu, J., Mamane, Y., Prestbo, E., Schmolke, S., Schroeder, W. H., Sommar, J., Sprovieri, F., Stevens, R. K., Stratton, W., Tuncel, G., and Urba, A. (2001). "Intercomparison of methods for sampling and analysis of atmospheric mercury species." *Atmospheric Environment*, 35(17), 3007-3017.
- Murray, M. (2006). "Personal Communication." Ann Arbor, Michigan.
- NADP. (2005). "Monitoring Mercury Deposition: A Key Tool to Understanding the Link between Emissions and Effects." *NADP 2005-01*, National Atmospheric Deposition Program, Illinois State Water Survey, Champaign, Illinois.
- NADP. (2006a). "Atmospheric Mercury Initiative Website (<http://nadp.sws.uiuc.edu/mtn/>)." US Department of Agriculture.
- NADP. (2006b). "Guiding Scientific Principles for Atmospheric-Mercury Monitoring in North America; <http://nadp.sws.uiuc.edu/mtn/GuidingScientificPrinciplesNov06.pdf>."
- NSRC. (2001). "Mercury Research Group. <http://www.briloon.org/bri/workinggroups/nsrc.htm>" Northern States Research Cooperative.
- Orihel, D. M., Paterson, M. J., Gilmour, C. C., Bodaly, R. A., Blanchfield, P. J., Hintelmann, H., Harris, R. C., and Rudd, J. W. M. (2006). "Effect of Loading Rate on the Fate of Mercury in Littoral Mesocosms." *Environmental Science and Technology*, 40(19), 5992-6000.
- Pepi, M., Reniero, D., Baldi, F., and Barbieri, P. (2006). "A Comparison of MER::LUX Whole Cell Biosensors And Moss, A Bioindicator, For Estimating Mercury Pollution." *Water, Air, and Soil Pollution*, 173(1 - 4), 163-175.
- Perry, E., Norton, S. A., Kamman, N. C., Lorey, P. M., and Driscoll, C. T. (2005). "Deconstruction of Historic Mercury Accumulation in Lake Sediments, Northeastern United States." *Ecotoxicology*, 14(1), 85-99.
- Rea, A. W., Keeler, G. J., and Scherbatskoy, T. (1996). "The deposition of mercury in throughfall and litterfall in the Lake Champlain watershed: A short-term study." *Atmospheric Environment*, 30(19), 3257-3263.
- Rea, A. W., Lindberg, S. E., and Keeler, G. J. (2001). "Dry deposition and foliar leaching of mercury and selected trace elements in deciduous forest throughfall." *Atmospheric Environment*, 35(20), 3453-3462.
- Roué-LeGall, A., Lucotte, M., Carreau, J., Canuel, R., and Garcia, E. (2005). "Development of an Ecosystem Sensitivity Model Regarding Mercury Levels in Fish Using a Preference Modeling Methodology: Application to the Canadian Boreal System." *Environmental Science and Technology*, 39(24), 9412-9423.

- Saber, C. D. (2005). "Dry Deposition and Overall Deposition Velocity of Polycyclic Aromatic Hydrocarbons Using Velcro as a Surrogate Surface," Gannon University, Erie, Pennsylvania.
- Sakata, M., and Marumoto, K. (2004). "Dry deposition fluxes and deposition velocities of trace metals in the Tokyo metropolitan area measured with a water surface sampler." *Environmental Science and Technology*, 38(2190-2197).
- Seigneur, C., Karamchandani, P., Vijayaraghavan, K., Lohman, K., and Yelluru, G. (2003). "Scoping Study for Mercury Deposition in the Upper Midwest: Report Prepared for the Midwest Regional Planning Organization." *CP149-03-01a*, Atmospheric & Environmental Research, Inc., San Ramon, CA.
- Seigneur, C., Vijayaraghavan, K., Lohman, K., Karamchandani, P., and Scott, C. (2004). "Global Source Attribution for Mercury Deposition in the United States." *Environmental Science and Technology*, 38, 555-569.
- Sheehan, K., Fernandez, I., Kahl, J., and Amirbahman, A. (2006). "Litterfall Mercury in Two Forested Watersheds at Acadia National Park, Maine, USA." *Water, Air, and Soil Pollution*, 170(1 - 4), 249-265.
- Skov, H., Brooks, S. B., Goodsite, M. E., Lindberg, S. E., Meyers, T. P., Landis, M. S., Larsen, M. R. B., Jensen, B., McConville, G., and Christensen, J. (2006). "Fluxes of reactive gaseous mercury measured with a newly developed method using relaxed eddy accumulation." *Atmospheric Environment*, 40(28), 5452-5463.
- St. Denis, M., Song, X., Lu, J. Y., and Feng, X. (2006). "Atmospheric gaseous elemental mercury in downtown Toronto." *Atmospheric Environment*, 40(21), 4016-4024.
- Swain, E., Engstrom, D., Brigham, M., Henning, T., and Brezonik, P. (1992). "Increasing rates of atmospheric mercury deposition in midcontinental North America." *Science*, 257, 784-787.
- Tasdemir, Y., and Holsen, T. M. (2005). "Measurement of particle phase dry deposition fluxes of polychlorinated biphenyls (PCBs) with a water surface sampler." *Atmospheric Environment*, 39(10), 1845-1854.
- Tasdemir, Y., Odabasi, M., and Holsen, T. M. (2005). "Measurement of the vapor phase deposition of polychlorinated biphenyls (PCBs) using a water surface sampler." *Atmospheric Environment*, 39(5), 885-897.
- Tasdemir, Y., Odabasi, M., and Holsen, T. M. (2007). "PCB mass transfer coefficients determined by application of a water surface sampler." *Chemosphere*, 66(8), 1554-1560.
- Tasdemir, Y., Odabasi, M., Vardar, N., Sofuoglu, A., Murphy, T. J., and Holsen, T. M. (2004). "Dry deposition fluxes and velocities of polychlorinated biphenyls (PCBs) associated with particles." *Atmospheric Environment*, 38(16), 2447-2456.
- Taylor-Morgan, J., Swain, E. B., and Allan, M. (2003). "Identification of Atmospheric Mercury Sources in the Great Lakes States through an Ambient Monitoring Program." Submitted to U.S. EPA by MDEQ, MPCA and WDNR, Chicago, IL.
- Tekran. (2006). "Model 1135 Particulate Mercury Unit - Description." *Rev 02/2006*, Tekran Instruments Corporation, Toronto, Ontario.
- Thomas, J., Holsen, T. M., and Dhaniyala, S. (2006). "Computational fluid dynamic modeling of two passive samplers." *Environmental Pollution*, 144(2), 384-392.
- U.S. EPA. (2005). "2004 National Listing of Fish Advisories ", <http://www.epa.gov/waterscience/fish/advisories/fs2004.html>.
- U.S. EPA. (2006). "Clean Air Mercury Rule (Final)." Washington D.C., <http://www.epa.gov/oar/mercuryrule/>.
- Welker, M. (1997). "Quality Assurance Plan: Mercury Deposition Network."
- Wiener, J. G., Knights, B. C., Sandheinrich, M. B., Jeremiason, J. D., Brigham, M. E., Engstrom, D. R., Woodruff, L. G., Cannon, W. F., and Balogh, S. J. (2006). "Mercury in Soils, Lakes, and Fish in Voyageurs National Park (Minnesota): Importance of Atmospheric Deposition and Ecosystem Factors." *Environmental Science and Technology*, 40(20), 6261-6268.
- Yi, S. M., Shahin, U., Sivadechathep, J., Sofuoglu, S. C., and Holsen, T. M. (2001). "Overall elemental dry deposition velocities measured around Lake Michigan." *Atmospheric Environment*, 35(6), 1133-1140.

Appendix A: Recent Great Lakes Mercury Deposition Monitoring

In addition to the many current mercury deposition monitoring activities described in section C, there have been many additional efforts in recent years to collect information of this type that are no longer operating. In a few cases, projected long-term activities were discontinued, but most often these represent short-term monitoring or research projects that collected information with one or several of the technologies described in section B. The types and locations of these activities are shown in Figure 5 and additional details are in Table 5. provides some additional details regarding some of these activities.

Figure 5: Recent but not active mercury monitoring in the Great Lakes region

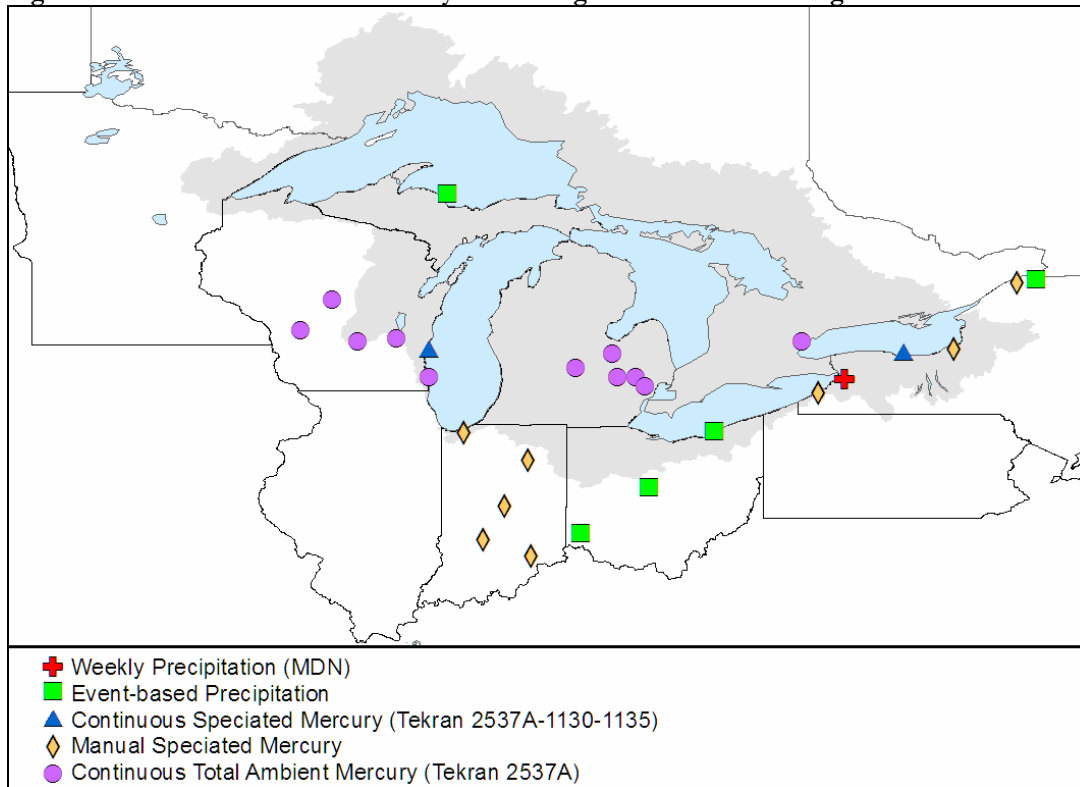


Table 5: Details of recent monitoring activities

Location	Network	Operator	Collection	Analysis	Start Date	End Date
Canada						
Dorset, Ontario	MDN(ON03)	Environment Canada	Weekly composite precip.	Total Hg	1/27/97	12/29/98
Toronto, Ontario		Ryerson University	Continuous (Gardis-1A and Tekran 2537A)	Elemental Mercury	June 2001	Feb. 2002
Indiana						
Bloomington	MDN (IN28)	USGS/Indiana DEM	Weekly composite precip.	MeHg 10 Trace Metals	Jan. 2001 Jan. 2002	Dec. 2003 Dec. 2002
Indiana Dunes	MDN (IN34)	NPS/USGS/Indiana DEM	Weekly composite precip.	MeHg	Jan. 2001	Dec. 2003
Clifty Falls State Park	MDN (IN21)	USGS / Indiana DEM	Manual ambient sampling Weekly composite precip.	Dry Deposition (THg) MeHg 10 Trace Metals	Feb. 2004 Jan. 2001 Jan. 2002	Aug. 2004 Dec. 2003 Dec. 2002
Fort Harrison	MDN (IN26)	USGS / Indiana DEM	Manual ambient sampling	Dry Deposition (THg)	Feb. 2004	Aug. 2004
Roush Lake	MDN (IN20)	USGS / Indiana DEM	Manual ambient sampling Weekly composite precip.	Dry Deposition (THg) MeHg 10 Trace Metals	Feb. 2004 Jan. 2001 Jan. 2002	Aug. 2004 Dec. 2003 Dec. 2002
Michigan						
Isle Royale		UW Madison	Weekly composite precip.	Total Hg and MeHg	1997	1999
Marquette County		NWF	Event precipitation	Total Hg	April 2003	April 2003
Taquemmenon Falls		UMAQL	Event precipitation	Total Hg and MeHg	1997	1998
Southfield		Michigan DEQ	Continuous (Tekran 2537A)	Elemental mercury	12/01 06/01	02/02 07/02
Detroit (Yellow Freight)		Michigan DEQ	Continuous (Tekran 2537A)	Elemental mercury	12/01 06/01	02/02 07/02
			Continuous (Tekran 2537A) (x2)	Elemental Hg	10/04	12/05
Lansing		Michigan DEQ	Continuous (Tekran 2537A) (x2)	Elemental Hg	05/03	07/03
South Lyon		Michigan DEQ	Continuous (Tekran 2537A)	Elemental Hg	03/04	05/04
Flint		Michigan DEQ	Continuous (Tekran 2537A)	Elemental Hg	04/05	06/05
River Rouge		Michigan DEQ	Continuous (Tekran 2537A)	Elemental Hg	04/05	06/05
New York						
Sturgeon Point	MDN(NY97)		Weekly composite precip.	Total Hg		
Rochester		New York State DEC.	Continuous (Tekran 2537A-1130-1135)	TGM, RGM and Hg _p		
Potsdam		Clarkson Univ.	Manual collection (every 3 days)	TGM and RGM	May 2000	March 2004
			Event precipitation	Total Hg	Fall 2003	April 2005

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Location	Network	Operator	Collection	Analysis	Start Date	End Date
Stockton		Clarkson Univ.	Manual collection (every 3 days)	TGM and RGM	May 2000	March 2004
Sterling		Clarkson Univ.	Manual collection (every 6 days)	TGM and RGM	April 2002	March 2004
Ohio						
Cleveland		National Wildlife Federation	Event precipitation	Total Hg	10/03	12/03
Columbus		National Wildlife Federation	Event precipitation	Total Hg		
Cincinnati		National Wildlife Federation	Event precipitation	Total Hg		
Wisconsin						
Milwaukee		UW Madison	Continuous (Tekran 2537A-1130-1135)	TGM, RGM and Hg _v		
Mayville		Wisconsin DNR	Continuous (Tekran 2537A)	Elemental Hg	8/03/04	10/08/04
Chiwaukee Prairie		Wisconsin DNR	Continuous (Tekran 2537A)	Elemental Hg	05/22/03	06/26/03
					02/01/05	03/02/05
Milwaukee SSCHC		Wisconsin DNR	Continuous (Tekran 2537A)	Elemental Hg	06/26/03	08/08/03
					01/03/05	03/01/05
Devil's Lake		Wisconsin DNR	Continuous (Tekran 2537A)	Elemental Hg	2/15/03	3/13/03
Wildcat Mtn.		Wisconsin DNR	Continuous (Tekran 2537A)	Elemental Hg	08/22/03	10/13/03
Port Edwards		Wisconsin DNR	Continuous (Tekran 2537A)	Elemental Hg	8/16/02	9/27/02

Appendix B. Overview of Monitoring Technologies

Wet Deposition

The most common method for monitoring of mercury deposition is to measure the amount of mercury in precipitation samples. Although this is often the only monitoring type done at many locations, it is important to recognize that the results determine only the amount of wet deposition. Depending on the location, the contribution of wet deposition to overall deposition can vary from roughly one-fourth to three-fourths, or even more widely (there remain many uncertainties concerning the magnitude of dry deposition of mercury due to the challenges in directly measuring dry deposition).

Wet deposition methodologies may vary in their details, but all share the basic approach of collecting a precipitation sample which is sent to a laboratory for analysis. Methodological differences may exist, such as the type of reservoir used for the collection, storage procedures and analytical methods. Fortunately, the existence of the Mercury Deposition Network (MDN) has provided significant standardization of methodology for those sites participating in that network. Among methodology choices that must be made, that which will have the largest influence on the applicability of the data for various purposes is the schedule for sample collection. The two most popular options are weekly composite sampling (the MDN default) and event-based sampling (used at a few MDN stations and by other efforts, see Table 2).

Weekly Composite Collection / Analysis

The majority of sites collecting weekly composite precipitation samples for mercury analysis are a part of the MDN and therefore follow that network's protocols (NADP, 2005). MDN protocol includes the use of a standardized sample collection system, which is a customized version of the Aerochem Metrics collector. The sample and sampling chain is replaced once per week and the collected sample is sent for analysis. For the MDN, sample analysis is centralized to reduce analytical differences. (Welker, 1997) The standard MDN analysis includes only total mercury, although some stations may add additional analytes such as methylmercury.

Advantages of the weekly composite sampling routine are the cost effectiveness (see Box 3) and comparability with other stations across the nation. Much of this advantage is present due to the national MDN. For seasonal trend analysis, the regular collection schedule provided by this method also presents an advantage. A disadvantage of the weekly collection method is the difficulty in associating samples with discrete precipitation events and therefore in using source apportionment techniques.

Event-based Collection / Analysis

Event-based collection addresses an important shortcoming of weekly composite analysis by allowing each precipitation event to be associated with a distinct sample. This allows further analysis to associate concentrations in precipitation with the weather systems that produced them, including which potential source regions a given air mass may have passed over prior to reaching a monitoring station. Most current event-based collection in the Great Lakes region (see Table 2) utilizes an automated sampling chain in which a sampling reservoir is uncovered when a rain sensor is activated. When precipitation ceases, the sampler is covered and the sampling chain is automatically replaced so that the next event is captured with clean equipment and in a separate container (Landis

and Keeler, 1997). Such samplers are usually designed to store several samples before needing to be serviced by a field technician. Although the data produced by such a system is generally preferred to weekly-composite sampling because of its utility in source identification, there are increased start-up costs to acquire an automated sampling system as well as potentially greater operational costs. Although there has not yet been a national network to provide the standardization and cost-effectiveness of the MDN, the National Atmospheric Deposition Network (NADP) has proposed to establish such a network (Gay *et al.*, 2006)(see Box 1).

Wet Deposition Method Comparison

For the majority of samples taken within the Great Lakes region over the past decade, wet deposition samples taken on a weekly composite routine cannot be directly compared to those taken on an event basis. This is less a result of the collection frequency and much more an artifact of differences in equipment. The sampler housing, sampling train components, and most notably the rain sensors differ between the standard equipment used at the weekly-sampling MDN stations and those used at the event-sampling stations in Michigan and Ohio operated by the University of Michigan Air Quality Laboratory (UMAQL).

Comparison studies between the types of samplers have shown a difference of 9-22%, with the UMAQL (modified MIC-B) samplers collecting samples enriched in mercury relative to the MDN (Aerochem) samplers (Miller *et al.*, 2005). The explanation of this systematic bias includes the geometry of the collection funnel (which can affect collection efficiency, particularly for heavy rainfall and snow), the sealing of sampling containers and the sensitivity of the rain sensors (Keeler, 2006). The responsiveness of rain sensors may play the largest role, as snow may be ineffectively sampled by sensors with low sensitivity and light rains and early stages of rain event may be missed. The beginning of a rain event will usually contain the highest mercury concentrations, as mercury in the atmosphere is scavenged very effectively by rain. These differences between equipment type and their impact on results are important to note when any assessment is being done involving data from multiple sampler types. Fortunately, most or all monitoring activities in the region conform to one of these two standard equipment setups.

It bears pointing out that trace metal analysis by the UMAQL stations has important implications for the ability to conduct source apportionment analysis on the resulting data. This difference is independent of the equipment-related differences between the two networks and trace metal analysis can be conducted using an MDN collection system. Source apportionment based on trace metal “fingerprints” is most effective when samples are collected on an event basis, as patterns of sources will be easier to resolve if precipitation from separate events are not mixed.

Dry Deposition

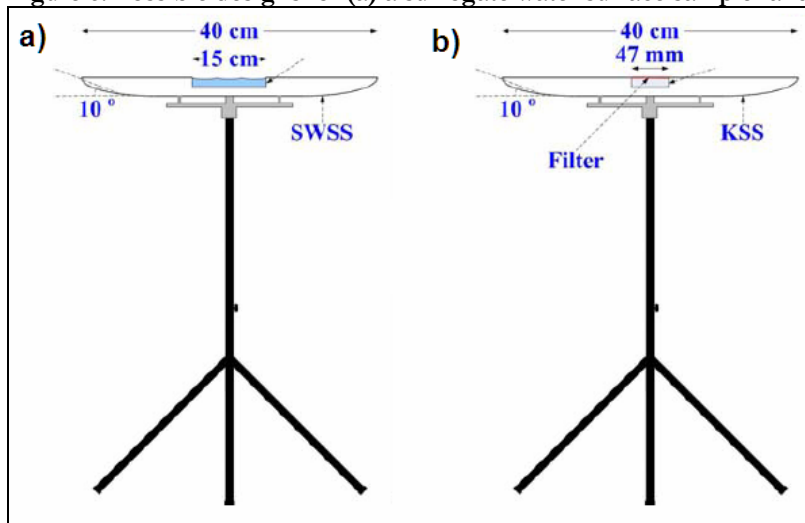
Dry deposition of mercury has proven much more difficult to sample directly than wet deposition. Although several methods have been developed, few if any have been used with any spatial or temporal consistency as part of a monitoring program. Several of the methods that have been developed experimentally are detailed below. To determine dry deposition on a routine basis, estimating dry deposition based on ambient air sampling and assumed or modeled deposition velocities has proven to be a more common option than direct measurement. Nevertheless, several methods for direct measurement of dry deposition have been developed and field tested in recent years, both within the Great Lakes region and elsewhere. The methods mentioned below have successfully been used in obtaining a detectable sample on a time period as short as 1-2 days and

over a period of as long as 2 weeks. A weekly-integrated routine, similar to the MDN schedule, is therefore a logical possibility for these methods.

Water Surface Sampler

One approach to measurement of dry deposition has been through the use of a water surface sampler. In this technique, an exposed pool of water is connected to a pump that circulates the water over the collection surface and within the sampling device (Sakata and Marumoto, 2004). Within the pump loop, filters and adsorbents have been used to capture dissolved analytes and/or suspended particles. The approach has been used successfully to sample for both mercury and organic (e.g., PCB) deposition (Marsik *et al.*, 2007; Tasdemir and Holsen, 2005; Tasdemir *et al.*, 2005; Tasdemir *et al.*, 2007). Methods have also been developed and tested where a non-circulating water surface, similar to a Petri dish, is used (Lai *et al.*, 2005). Obviously, such a sampler will most closely approximate the rate of deposition and evasion of mercury from a relatively still water body and may be less applicable to surfaces with different properties. Altering the water chemistry can affect the collection efficiency for different mercury species. For example, acidified water will collect all mercury species, similar to the gold filter option described in the next section, but has a somewhat higher resistance than gold (Holsen, 2006). A schematic of a possible design for a Petri-dish style water surface sampler is shown in Figure 6.

Figure 6: Possible designs for (a) a surrogate water surface sampler and (b) a knife edge surface sampler



Knife Edge Surface Samplers

Similar in some ways to a water surface sampler, knife-edge samplers use a solid medium rather than water to collect deposition samples. For mercury sampling, exposed filters have been used in place of the water pool, with different filter types being used to collect different mercury species (Lai *et al.*, 2005). In theory, quartz fiber filters will collect only the particulate phase, whereas KCl-coated filters will collect both the particulate and reactive mercury and gold-coated filters collect particulate, elemental and reactive mercury. Potentially, a set of multiple filters (quartz, KCl-coated and gold coated) could be simultaneously deployed to characterize both the particulate and gaseous components of dry deposition. No air is actively pulled through these filters; they are used only as an exposed surface to collect deposition. Clarkson University has developed a modification to the MIC-B precipitation sampler in which an additional compartment, housing a knife-edge surface sampler, is uncovered and the sampler is raised above the sampler housing during dry weather and covered

during wet weather (Holsen, 2006). Combined with the wet deposition collection methods mentioned above, a single collector (e.g., Aerochem, MIC-B) might be customized to obtain both wet and dry deposition samples. A schematic for a sampler of this type is shown in Figure 6.

In addition to the exposed filters mentioned above, other materials have been experimented with as surrogate surfaces. Ion exchange membranes have been used successfully in such applications (Caldwell *et al.*, 2006; Lyman *et al.*, 2007). Another knife-surface sampling technique that has been employed involves greased surface deposition plates. In this method, one or several horizontally-oriented strips are covered with a grease which collects particles and gases depositing from the air (Tasdemir *et al.*, 2007; Tasdemir *et al.*, 2004; Yi *et al.*, 2001). It has been used for both organic compounds and elements, but not for mercury. In an attempt to represent a surface with a more turbulent near-surface wind flow, metallic Velcro has been used attached to a wind vane with a sharp leading edge to collect dry deposition samples of PAH (Saber, 2005). However, this method has not yet been adapted to mercury.

Calculation from Ambient Measurements

Although not a direct measurement of dry deposition, calculation of dry deposition from measurements of mercury in ambient air is perhaps the most common method of determining a dry deposition value. Ambient air mercury concentrations are used to determine dry deposition through a series of equations relating ambient concentration to deposition. Several assumptions must be made for this approach, including a particulate size distribution for particulate mercury, and settling velocities for particles and gaseous and reactive mercury. As particulate, gaseous and reactive mercury will each deposit at much different rates, it is essential to have measurements of all three species to reliably determine total deposition. In addition, it is important to account for the efflux of mercury from the surface, especially for elemental mercury, in order to determine net deposition.

A potential concern with this method of calculation is the exclusion of mercury on large particles. The primary speciated ambient mercury techniques described below exclude particles larger than 2.5 microns in diameter (Landis *et al.*, 2002; Tekran, 2006). There is evidence that a significant portion of mercury is on particles larger than this cut-off. For example, measurements taken at Perch River, New York, show that while the sub-2.5 micron fraction exceeds the 2.5-10 micron fraction, both are significant and the 2.5-10 micron fraction contributes more than a quarter of the total particulate mercury (Ames *et al.*, 1998). In addition, evidence suggests that the >10 micron fraction may be a substantial contributor as well (Moreno *et al.*, 2005). This >2.5 micron fraction is of particular significance due to its relatively high deposition rate. While this issue may lead to a significant underestimate of particulate-associated mercury deposition, the effect on total deposition will be less significant, as particulate deposition is believed to contribute at most a few percent to total mercury deposition (Miller *et al.*, 2005) under most circumstances.

Comparison of Direct and Indirect Dry Deposition Methods

As noted above, while both direct and indirect methods for measuring dry deposition are available, most current dry deposition monitoring programs are using or intending to use the indirect method (calculation from ambient air measurements). Each approach has advantages and disadvantages.

Both method types require some consideration of the representativeness of the measurements or calculations for what they are intended to represent. For indirect methods, it is clear that equation-derived deposition estimates will only approximate actual deposition. For direct measurements, there

is uncertainty regarding how well the surface collecting the deposition, such as an exposed filter, will represent the natural surfaces which it is intended to represent. Air-flow and chemical composition differences may lead to some differences in mercury deposited to natural and surrogate surfaces. However, such methods have the advantage of being directly comparable across time and space. In contrast, direct measurement on natural surfaces would be less comparable due to variations in surface characteristics.

The indirect method allows for greater flexibility in the temporal scale over which deposition is estimated. While the direct methods will produce samples that represent a timescale of about 1-14 days, the indirect methods are capable of producing estimates with the temporal resolution of the ambient sampling routine. For the speciated Tekran system (described briefly on page **Error! Bookmark not defined.** and thoroughly in (Landis *et al.*, 2002)), this is a timescale as fine as 1-2 hours and can be integrated to produce deposition estimates at any larger timescale desired. The indirect method using manually obtained measurements presents some flexibility regarding the mobility of the instruments and the ability to easily take measurements at multiple locations. A comparison of rough cost estimates for the sampling options is given in Box 3. While the direct measurement results are inherently a measure of deposition, the measurements of ambient concentrations must be processed to produce deposition estimates, which may present an added cost.

Finally, it is important to consider the utility of the information collected in supporting other potential uses. While directly-measured deposition data will solely reflect a measurement of deposition, ambient air measurement might be used for a multitude of purposes, such as source-tracking, modeling, and other research purposes.

Micrometeorological Techniques

Micrometeorological techniques have been applied to characterize mercury evasion from soils since the mid-1990s (Lindberg *et al.*, 1995). Recently, there has been additional progress in developing micrometeorological techniques for quantifying deposition and evasion of mercury, including development of relaxed eddy accumulation (REA) approaches. Briefly, REA is a conditional sampling technique in which multiple sampling systems are equipped simultaneously and flow is switched among them depending upon the flux of ambient air. One sampling train is used when airflow is in the upward direction and another is used when flow is downward. By analyzing the differences in concentrations among upward and downward drafts, the overall vertical flux of mercury can be computed. Such methods were developed at the University of Minnesota for measurement of gaseous mercury (Cobos *et al.*, 2002) and have recently been adapted for measurement of reactive mercury flux (Skov *et al.*, 2006). Such methods are fairly intensive in effort and are therefore more applicable in a research context than for monitoring programs at the current time. They may present an important means of validating modeling assumptions (such as deposition velocities) used to estimate deposition from ambient concentrations.

Ambient Air

Measurement of mercury in ambient air is another common activity and several methodology choices are available. Among the major features distinguishing various methodologies are the temporal resolution of sampling, the detection limit, accuracy, and the species of mercury that are measured. While several options are available to measure total mercury, the most advanced

technologies can distinguish among gaseous, particulate and reactive mercury, providing additional information to identify sources, trends and estimate deposition patterns.

Total Gaseous Mercury

For measurement of total gaseous mercury (TGM) in ambient air, there are several complete and self-contained systems available, offering high temporal resolution and ease of use. Passive sampling is a cost-effective option when nothing more than long-term integrated measurements are desired, although passive sampling approached with highly accurate quantitation of the volume sampled are still in development.

Tekran Instruments Corporation (www.tekran.com) produces sensors most commonly used for monitoring of mercury on a routine basis in ambient background air. The Tekran 2537A unit offers high sampling frequency (1 sample per 2-3 minutes) and a detection limit of $<0.1 \text{ ng/m}^3$. Although the unit itself is not highly portable, installation in a mobile van or trailer is not unusual (see Appendix A for a description of a trailer shared by MPCA, MDEQ and WDNR). The unit can be operated on its own to produce measurements of TGM or in combination with Tekran units 1130 and 1135 to provide speciation.

Box 2: The Formation of a Network to Collect TGM Measurements Across Canada

Whereas measurements of TGM within the Great Lakes states are now a common activity, there is no established means of networking among these sites to provide standardization of protocols, comparability of data or a common data access point. In contrast, TGM stations in the Canadian half of the Great Lakes region are part of a robust national networking program, CAMNet. The example set by and lessons learned by Environment Canada in the formation of CAMNet may be useful to those in the U.S. portion of the Great Lakes—or at a national level—if they choose to network in a similar fashion. Formation of CAMNet was a lengthy process, driven from the bottom-up by those running separate monitoring efforts. While the network formation was driven by the site operators, recognition and support at a high level within their organizations was essential.

Several steps were critical in the process of forming this network. First, it was necessary to establish a common standard operating procedure (SOP) for all participating sites. A thorough SOP was developed for the Tekran 2537A in initiating CAMNet. Having a common calibration protocol was also important to identify systematic inter-site differences. CAMNet uses the same calibration personnel and equipment at all sites. There must also be common quality assurance / quality control (QA/QC) software to handle processing of data. Again, CAMNet has developed its own software adaptations for this purpose. CAMNet site operators have agreed on a two-year holdback period on the data before entering it into an online database for public access. All data are integrated on an hourly basis, although it is collected at a wide range of frequencies at different sites.

Passive Samplers

While the automated systems mentioned above provide very high time resolution, passive sampling options are also available which offer time-integrated sampling to provide estimates of ambient concentrations or patterns over weekly to yearly intervals. A basic and inexpensive option for assessing spatial trends in atmospheric mercury is the use of transplanted lichens (Makhholm and Bennett, 1998) or moss (Fernandez *et al.*, 2000; Pepi *et al.*, 2006). These “bio-sensors” offer qualitative rather than quantitative assessment of mercury deposition and are best used in applications where a comparative rather than an absolute measure is desired, such as the gradient in mercury levels at various distances from a large source. For more precise measurements, gold traps

have been used in some applications as a passive sampler by exposing them to the atmosphere and then analyzing them for mercury content. As with other passive samplers, such as PUF disks or XAD-2 resin used for organic compounds, difficulty in quantifying the amount of air “sampled” leads to large uncertainties in the determined concentration. Researchers at Clarkson University are currently developing a passive sampler housing and computer model that would allow more accurately quantified passive sampling of mercury using gold foil disks (Great Lakes Commission, 2006; Thomas *et al.*, 2006).

Speciated Mercury (Gaseous, Reactive and Particulate)

While the ambient mercury monitors mentioned above will measure total mercury, there are many applications in which it is desirable to also determine the relative proportions of mercury species, including gaseous elemental (GEM), reactive gaseous (RGM), and particulate (Hg_p). In particular, such measurements are important in accurately quantifying dry deposition, as the deposition rates of the three forms vary widely. Speciated measurements are also needed to better understand the cycling of the three species in the environment and in the air, which is yet to be well understood. For example, there are significant questions regarding how rapidly reactive mercury in an emission plume is converted to elemental and how elemental mercury is converted to RGM with high ozone levels. The two principal methods for collecting speciated mercury described below are nearly equivalent in terms of the analytical technique. Differences exist in the temporal resolution of the information that is collected, the portability and flexibility in collection time/locations, and the up-front and long-term costs. Importantly, both methods use a denuder upstream of the particulate filter, which eliminates an artifact in the particulate sampler caused by RGM (Lynam and Keeler, 2002). Other programs monitoring for mercury in particulate mercury samples might therefore not be directly comparable to results from these fully-speciated methods. In addition to these two approaches, other methods have been developed, validated and inter-compared (Munthe *et al.*, 2001).

Manual Method

The manual method consists of a flow-controlled pump connected to a sampling train. Air is pulled through a KCl-coated annular denuder and then through a quartz or Teflon filter and through traps of gold-coated quartz (Landis *et al.*, 2002). The denuder, filter and traps are then taken for laboratory analysis. The advantages of the manual method are the low up-front equipment investment, its portability, and relative ease of equipment maintenance.

Automated Method

In concept, the automated method is nearly identical to that for the manual method (Landis *et al.*, 2002). The difference being that automation of the sampling and analysis processes allow for high-temporal resolution monitoring of mercury species by a system that can be unattended for significant periods of time. Measurements of elemental mercury are produced as rapidly as every 2-3 minutes (typically done at 5 minute intervals) and estimates of particulate and reactive mercury are produced with a frequency as low as one sample every two hours (three hours is a common routine). This system therefore has a distinct advantage for collecting data to determine the complex patterns in mercury speciation that have been shown to develop on a timescale of hours, if not more rapidly (Lynam and Keeler, 2005) and on a cost-per-sample basis. Disadvantages are the up-front investment (see Box 3) and the need for expertise in maintenance in operation.

Sediment Core Analysis

If undisturbed, lake sediments provide an excellent long-term record of mercury deposition. (Fitzgerald *et al.*, 1998) All other things being equal, it can generally be assumed that changes in atmospheric deposition will be proportional to mercury flux as measured in a sediment core. Cores of undisturbed sediments can be analyzed to reveal a course of deposition trends over the period of one to many centuries, with a temporal resolution of several years to a decade.

In brief, methods include the collection of a vertically intact core of sediment, which is then sectioned to yield multiple samples corresponding to various depths. Approximate dates of each segment can be determined for the last 100 years by lead-210 analysis and for older sediments through other dating techniques.

The availability of recent deposition estimates from sediments are significantly constrained by the need for sediments to be largely undisturbed, and be from water bodies with good depositional zones and generally lacking any direct discharges of mercury. While the Great Lakes themselves have been extensively analyzed for mercury in surface sediments (Marvin *et al.*, 2004), these measurements are not useful for accurately quantifying atmospheric inputs due to the significant direct mercury inputs to the lakes and their tributaries.

The best record of mercury in sediments from relatively undisturbed, non-industrialized lakes within the Great Lakes region is from Minnesota, where several studies have been conducted to determine differences in mercury deposition throughout the state. (Engstrom and Swain, 1997; Swain *et al.*, 1992) In addition to providing excellent records of the relative increase in current deposition compared to pre-industrial times, analysis of sediments from many locations provides a time-integrated measurement of spatial differences in deposition. For example, strong spatial gradients in the Minnesota sediments suggest an influence of local and regional sources, as opposed to global sources. The sediment record from Minnesota also provides considerable value in establishing a pre-industrial baseline of mercury deposition prior to the past two centuries when human activities began to strongly dominate the overall pattern of mercury emissions. Because spatial variation in mercury deposition was likely much less in the pre-industrial era, this background record in Minnesota may well be applicable on a regional basis. A good basis of sediment mercury measures in the Northeastern U.S. is also available and may provide similar information with greater proximity to the Eastern portion of the Great Lakes region (Kamman *et al.*, 2005; Perry *et al.*, 2005).

Throughfall and Litterfall

Forests present complex surfaces that efficiently remove mercury from the atmosphere due to their large surface areas and the surface properties of leaves. Mercury can therefore accumulate on or within the leaves and be delivered to the forest floor when washed off by rain (“throughfall”), or when leaves drop to the forest floor (“litterfall”). Because of these mechanisms, mercury deposition within forests can be of greater magnitude and complexity compared to non-forested ecosystems. Methods have therefore been developed to measure throughfall and litterfall. It can be assumed that throughfall minus wet deposition is approximately the amount of dry deposition to the forest canopy.

Where studied, it has generally been found that litterfall mercury flux equals or exceeds under-canopy throughfall flux, of which 1/3 to 1/2 can typically be attributed to wash-off from the canopy (Kolka *et al.*, 2001; Rea *et al.*, 1996; Sheehan *et al.*, 2006). The total under-canopy mercury load

delivered to the forest floor is therefore 2- to 4-fold the magnitude of the load in an equivalent, non-forested location. It has been shown by examining elemental ratios in air, precipitation and throughfall (Rea *et al.*, 2001), and by growing vegetation in controlled mesocosms (Ericksen *et al.*, 2003), that most or all of the mercury in throughfall and litterfall is atmospherically derived rather than mobilized from soils and delivered by the tree's circulation.

As throughfall is precipitation that falls on the tree canopy, washes over the tree or leaf surface and then drops to the forest floor, the methods discussed above for wet deposition collection are equally applicable to throughfall measurements. Sampling both under a canopy and in a nearby non-forested location can provide an estimate of the relative contribution of the wash-off process to the total mercury measured in throughfall. For example, a study in the Lake Champlain watershed resulted in a total throughfall measurement of 12 ng/L, whereas nearby precipitation measurements showed 6.5 ng/L, (Rea *et al.*, 1996) implying an approximate 5.5 ng/L attributable to the wash-off of dry-deposited mercury within the canopy. Similar results were found in a Minnesota study, where total throughfall of 13.0 $\mu\text{g m}^{-2}$ was twice as large as deposition in the open (6.5 $\mu\text{g m}^{-2}$; Kolka *et al.*, 1999).

Methods have also been developed to sample "stemflow," the water running down the body of a tree. Such samples can be obtained by a system in which Teflon tubing is spiraled around the trunk of a tree and directs the stemflow water into a bottle. Mercury measured (on an areal basis) in stemflow in northern Minnesota ranged from 1 percent of the value measured in throughfall in a black spruce bog to about 10 percent in an aspen upland (Kolka *et al.*, 1999).

Litterfall sample collection is quite straight-forward, involving the collection of fallen leaves. To discern when a given leaf fell, improve the confidence regarding from which tree, and control for possibilities of contamination after falling, a collector box is usually used.

Box 3: Cost Comparison of Mercury Monitoring Technologies

Among the important considerations in weighing different technology options are the up-front and long-term costs of acquiring data of a certain type. For a given technology, actual costs will vary somewhat give the specifications and scale of each application. The following table gives a rough estimate of approximate costs of several of the technologies mentioned above.

Technology	Equipment and Set-up	Annual Operation	5-year Average
MDN Weekly THg in Precip.	\$11,000*	\$12,100	\$15,000
MDN THg and MeHg in Precip. (weekly)	\$11,000*	\$12,100 + \$6200	\$21,200
MDN THg and MeHg in Precip. (4 week)	\$11,000*	\$12,100 + \$2000	\$16,900
MDN Daily THg in Precip.	\$11,000*	\$28,200	\$35,600
MDN Daily THg and MeHg in Precip.	\$11,000*	\$28,200 + \$18,700	\$54,300
Automated TGM – Tekran 2537A	\$40,000	\$10,000	\$18,000
Automated RGM-Hg _p -GEM – Tekran 2537A-1130-1135	\$115,000	\$50,000**	\$73,000
Manual RGM-Hg _p -GEM	\$29,000	\$39,000†	\$44,800
Direct Dry Deposition - KSS with Filters	\$10,000‡	\$10,000‡	\$12,500‡

* \$5600 if collocated with existing National Trends Network (NTN) site

** Assumes \$15,000 for maintenance/parts and \$35,000 for site operator

† Assumes \$29,000 for sample analysis and \$10,000 for site operator; 25% QA samples

‡ Costs for the direct dry deposition are very approximate. This technology is not presently commercially available. Analytical costs will depend on the number of sampling periods per year and the number and types of filters used for each sample.

Appendix C: Summaries of Mercury Deposition Monitoring Initiatives in the Great Lakes Region

Mercury Deposition Network (MDN)

Within the eight Great Lakes states, there are 33 currently operating MDN sites. In addition, a handful of MDN sites on the Canadian side of the Great Lakes offer compatible data for that side of the drainage basin. In all, these sites offer a comprehensive regional system for collecting and assessing regional data on mercury wet deposition amounts and general spatial and temporal trends. In addition, many of the MDN sites play host to additional monitoring efforts. Designed largely as a system to measure background concentrations, few MDN sites are located in urbanized areas where deposition is the highest. As a result, the urban-rural gradient is poorly characterized within the MDN network. Sites have been gradually phased in over the course of more than a decade, so that the length of the historical monitoring record varies from site to site, with one discontinued site in the region offering past, but not current data.

UMAQL Network and other Michigan mercury monitoring

The University of Michigan Air Quality Laboratory (UMAQL) operates a series of six monitoring sites throughout Michigan. A mixture of three urban and three rural sites offer an important means of characterizing the urban-rural gradient in mercury deposition. All six sites collect event-based precipitation samples which are analyzed for total mercury, as well as a series of trace metals which allow for statistical source apportionment analysis. In addition, sites in Detroit and Dexter (a rural site about 50 miles west of Detroit) conduct automated monitoring for speciated mercury in ambient air (Tekran 2537A-1130-1135), as well as sampling for trace metals and criteria pollutants. All sites have been in operation since at least 2001. The Eagle Harbor and Flint monitoring sites ceased operation in 2006.

The MDEQ also operates continuous elemental mercury (Tekran 2537A) monitors in Grand Rapids and Holland, Michigan. Total and methyl mercury were also monitored in event-based precipitation samples at Tahquamenon Falls, Michigan from 1997-1998, at Eagle Harbor, Michigan from 1997-1999 and in weekly composite samples from Isle Royale, Michigan from 1997-1999 (Hall *et al.*, 2005). Recently, an MDN station has been established at Sterling Heights, Michigan, although it is scheduled to close in spring of 2007. In 2003, National Wildlife Federation collected several event-based precipitation samples in Marquette county for mercury analysis (Buchsbaum *et al.*, 2003).

Multi-state Mobile Monitoring Laboratory

Three of the Great Lakes states, Michigan, Minnesota and Wisconsin, share a Mobile Mercury Monitoring Laboratory (M3L), consisting of a mobile trailer which houses two Tekran 2537A continuous TGM analyzers, meteorological monitoring equipment, data loggers and computing facilities. Beginning in 2000, the M3L has been shared among the three states on a rotating schedule of 3-6 month periods. There have been a wide variety of uses of the M3L, including quantification of mercury sources, monitoring of mercury spill sites, investigating gradients in complex source regions, and co-location with deposition samplers. Many past locations are depicted in Figure 5.

Steubenville and other Ohio mercury monitoring

Methods similar to those used for the Michigan network have been used in Steubenville, Ohio under a joint project of the U.S. EPA and UMAQL. This site is located in a region with several large mercury sources, particularly coal power plants. It is also one of the sites of the Harvard University “Six Cities” study examining relationships between air quality and community health. The methods used are event-based precipitation monitoring for mercury and trace metals and speciated ambient mercury monitoring (Tekran 2537A-1130-1135). Ambient elemental mercury (Tekran 2537A) is also being monitored by Ohio University in Athens, which also hosts an MDN station. Several particulate monitoring sites, in Marion and East Liverpool, analyze for mercury as one of many trace elements. Finally, National Wildlife Federation conducted event-based precipitation monitoring in Cleveland for several months in 2004 (see below) (Kapadia *et al.*, 2004).

New York DEC and Clarkson University mercury monitoring

In addition to two MDN sites sponsored by the New York Energy Research and Development Authority, the New York State Department of Environmental Conservation is currently operating a speciated ambient mercury monitoring system (Tekran 2537A-1130-1135) in Rensselaer, New York. The same instrument was operated in Rochester, New York from August 2004 through September 2005. Because of maintenance difficulties, the future location and use of the instrument is currently uncertain.

Researchers at Clarkson University and collaborators at other institutions have conducted a variety of mercury monitoring activities at multiple locations around New York State. In summer (May-Aug.) 2000 and 2001, daily vapor-phase elemental mercury samples (23h sampling using gold-coated traps) were collected at Stockton and Potsdam, New York (Hopke *et al.*, 2003). In April 2002, a site was established at Sterling, New York and has been taking every-sixth-day samples for elemental (as above) and reactive (collected using an annular denuder, similar to the “manual method” above), although the elemental measurements are now being done using a Tekran 2537A. In June 2002, the Stockton and Potsdam sites began sampling for reactive mercury every third day (Han *et al.*, 2004). In 2003, similar (daily?) samples were taken for one week in each spring, summer and fall over Lake Ontario using the U.S. EPA’s RV Lake Guardian. Clarkson University is also operating a speciated mercury monitoring system at the Huntington Wildlife Area MDN station.

Mercury Monitoring Activities in Indiana

As of 2006, the Indiana Department of Environmental Management (IDEM) in partnership with the United States Geological Survey (USGS) operates five MDN sites in the state of Indiana. The locations and monitoring start dates are as follows: Roush Lake (10/26/00), Clifty Falls State Park (1/12/01), Bloomington Airport (12/15/00), Fort Harrison (4/4/03), and Indiana Dunes National Lakeshore Park (10/27/00). All five sites currently collect only weekly composite precipitation samples, which undergo analysis for total mercury. (See Appendix A for a list of past monitoring activities that have taken place at these monitoring sites but have since been discontinued.)

The five monitoring sites are located in both rural and urban areas, some near major local and regional anthropogenic sources of atmospheric mercury, and one in very close proximity to Lake Michigan and the Chicago, Illinois Metropolitan area.

In addition, IDEM has numerous programs to monitor for mercury in rivers, fish, wastewater effluent, and other media.

Pennsylvania DEP mercury monitoring

There are currently 9 operating MDN stations in Pennsylvania, with the latest addition in Centralia in May 2006. The Pennsylvania Department of Environmental Protection (PDEP) supports the operation of eight of these sites (Lynch *et al.*, 2005). The Centralia site is also conducting monitoring of speciated mercury in ambient air (Tekran 2537A-1130-1135), as well as continuous monitoring of elemental mercury (Tekran 2537A) at two nearby satellite locations. The PDEP also maintains a continuous elemental mercury monitor (Tekran 2537A) in Lancaster. The Pennsylvania MDN sites offer a broad coverage of the state's geography for monitoring elemental mercury. While the ambient mercury monitoring is confined to the eastern portion of the state, it offers an important southeastern monitoring point for the Great Lakes region.

Wisconsin DNR mercury monitoring

Of eight MDN sites in Wisconsin, six are supported by the Wisconsin DNR. All sites follow the standard MDN protocol, except for the site at Devil's Lake, which collects precipitation on an event-basis. Samples from the six WDNR sites are combined monthly for methyl mercury analysis. In addition, the WDNR has partnered with academic and tribal partners to establish TGM monitoring stations in Milwaukee and Lake County, Wisconsin, which have been operating since January and August, 2005, respectively. Prior to establishing these sites, the ambient monitoring equipment was used for 1-2 month periods at six different sites within the state since August 2002. Prior to 2005, a year of speciated ambient mercury monitoring was conducted in Milwaukee by researchers from the University of Wisconsin (Lough *et al.*, 2005).

Illinois EPA mercury monitoring

In addition to an Illinois State Water Survey operated MDN station in Bondville, Illinois EPA operates a continuous elemental mercury analyzer (Tekran 2537A) at a Northbrook, Illinois site in suburban Chicago.

National Wildlife Federation mercury monitoring

The National Wildlife Federation worked with a variety of local partners over the past several years to conduct event-based precipitation collection and analysis for mercury at a variety of locations within the basin. Sampling was done with a MIC precipitation collector controlled by a rain sensor. Samples were sent to the University of Minnesota at Duluth for analysis. The number of samples collected at each site ranged from a few to as many as ten. Locations sampled included Columbus, Cincinnati and Cleveland, Ohio (Kapadia *et al.*, 2004; Murray, 2006), Marquette, Michigan (Buchsbaum *et al.*, 2003), and several locations in Wisconsin, Illinois and Minnesota. In many cases, the sampling was done in locations where other mercury precipitation sampling has not occurred, providing additional spatial resolution to the regional data holdings. At the current time, NWF has no distinct plans to conduct additional monitoring of this type.

Canadian Mercury Network (CAMNet)

Environment Canada operates the Canadian Atmospheric Mercury Measurement Network (CAMNet). Of eleven sites nationwide, four are in close proximity to the Great Lakes – St. Lawrence River basin: Point Petre, Egbert and Burnt Island, Ontario, and St. Anicet, Quebec. All

four sites conduct continuous monitoring for elemental mercury in ambient air (Tekran 2537). Elemental mercury monitoring at Egbert and Point Petre began in January 1997 and at Burnt Island in April 1998 (Blanchard *et al.*, 2002). Two sites, Egbert and St. Anicet also collect weekly composite precipitation samples and are a part of the MDN. The other two stations, Point Petre and Burnt Island are IADN Master Stations (see below) and therefore also measure for many other substances, including many trace metals, in atmospheric and precipitation samples.

Independent of the CAMNet, Researchers from Ryerson University operated continuous TGM monitors (a Gardis-1A and then a Tekran 2537A) for a period of about 8 months in Toronto, Ontario.(St. Denis *et al.*, 2006)

Speciation Trends Network (STN)

Many states operate particulate monitoring stations as part of the U.S. EPA's Speciation Trends Network (STN). Stations participating in this network sample for fine particulates in air either every third or every sixth day, depending on the site. Particulate filter samples are analyzed for a suite of trace metals, including mercury. The STN therefore may provide a generalized regional dataset for particulate mercury. Many states operate several of these stations, with some having ten or more.

Integrated Atmospheric Deposition Network (IADN)

The Integrated Atmospheric Deposition Network (IADN) is a partnership between the U.S. EPA and Environment Canada to monitor for a range of persistent toxic substance in the air and precipitation of the Great Lakes region. Although mercury monitoring is not done at any sites (with the exclusion of two co-located CAMNet sites and a co-located MDN site at Brule River, Wisconsin), the established infrastructure and international framework provide important advantages that might be leveraged in establishing a more concerted and consistent mercury monitoring regime on a regional scale.

Other Mercury Monitoring

Several states or other entities have conducted additional air mercury monitoring in recent years. Several states have Lumex mercury vapor analyzers and have used these to monitor near facilities and/or impacted areas. Examples include monitoring at a mercury recycling facility, a chlor-alkali chemical plant, a fluorescent light bulb recycling plant and a metal shredding and recycling facility in Wisconsin and monitoring of an Area of Concern (Deer Lake), a lamp shredder, a steel shredder, a dental product manufacturer, among others, in Michigan. Wisconsin, Minnesota and Michigan share a mobile mercury monitoring trailer equipped with two Tekran 2537A instruments. This trailer has been used in numerous projects to measure mercury near known or suspected sources as well as at impacted areas. Other methods have been used either on experimental bases or as part of discrete investigations. For example, Wisconsin DNR has done some ambient passive mercury monitoring with gold traps as well as some monitoring aboard aircraft with gold sand tubes. In addition, most states have significant mercury monitoring activities in other media that may be worth considering in determining placement of air monitors.