Measuring Atmospheric Mercury: Goals, Methods, and Results

University Plaza Marriott
East Lansing, MI
# Day 1 Agenda - March 26, 2003

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Speaker/Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>7:30 a.m.</td>
<td><strong>REGISTRATION AND CONTINENTAL BREAKFAST</strong></td>
<td></td>
</tr>
<tr>
<td>8:30 a.m.</td>
<td>Welcome by Steven E. Chester, Director, MDEQ</td>
<td></td>
</tr>
<tr>
<td>8:45 a.m.</td>
<td>Moderator - Joy Taylor Morgan, MDEQ</td>
<td></td>
</tr>
<tr>
<td>9:00 a.m.</td>
<td>Serving the Research Needs of Policymakers</td>
<td>Frank Anscombe, USEPA - Great Lakes National Program Office (GLNPO)</td>
</tr>
<tr>
<td>9:20 a.m.</td>
<td>Mercury Monitoring in Michigan and the Great Lakes’ Basin Methods and Source Characterization</td>
<td>Dr. Jerry Keeler, University of Michigan</td>
</tr>
<tr>
<td>9:50 a.m.</td>
<td>Measurement of Mercury Compounds and their Fluxes from Landfills</td>
<td>Dr. Steve Lindberg, Oak Ridge National Laboratory (ORNL)</td>
</tr>
<tr>
<td>10:20 a.m.</td>
<td><strong>COFFEE BREAK</strong></td>
<td></td>
</tr>
<tr>
<td>10:35 a.m.</td>
<td>Mercury Aspects of EPA’s PBT Monitoring Strategy</td>
<td>Melissa Hulting, USEPA - GLNPO</td>
</tr>
<tr>
<td>11:05 a.m.</td>
<td>Fugitive Mercury Emission Source Monitoring</td>
<td>George Southworth, ORNL</td>
</tr>
<tr>
<td>11:35 a.m.</td>
<td>Mercury Monitoring in Steubenville, Ohio: Investigating the Relative Impact of Coal-fired Utility Boilers to Atmospheric Mercury Deposition</td>
<td>Dr. Matt Landis, USEPA National Exposure Research Laboratory</td>
</tr>
<tr>
<td>Noon</td>
<td><strong>LUNCH</strong></td>
<td></td>
</tr>
<tr>
<td>12:30 p.m.</td>
<td>Luncheon Presentation: What is METAALICUS?</td>
<td>Dr. Steve Lindberg, ORNL</td>
</tr>
<tr>
<td>1:00 p.m.</td>
<td>Moderator Remarks</td>
<td>Frank Anscombe, USEPA – GLNPO</td>
</tr>
<tr>
<td>1:15 p.m.</td>
<td>Mercury Trends and Historical Reconstruction</td>
<td>Dr. Tom Atkeson, Florida Department of Environmental Protection</td>
</tr>
<tr>
<td>1:45 p.m.</td>
<td>Monitoring Wet Deposition of Mercury in North America – the Mercury Deposition Network</td>
<td>Marty Risch, U.S. Geological Survey (USGS) Indiana</td>
</tr>
<tr>
<td>2:05 p.m.</td>
<td>Atmospheric Mercury Monitoring in Wisconsin</td>
<td>David Grande, Wisconsin Department of Natural Resources</td>
</tr>
<tr>
<td>2:20 p.m.</td>
<td>Atmospheric Mercury Monitoring in Indiana</td>
<td>Marty Risch, USGS Indiana</td>
</tr>
<tr>
<td>2:35 p.m.</td>
<td>Clean the Rain Campaign: Raising Public Awareness of the Mercury Deposition Issue</td>
<td>Dr. Mike Murray, National Wildlife Federation</td>
</tr>
<tr>
<td>2:50 p.m.</td>
<td>Results of Applying Atmospheric and Environmental Research Inc.’s Suite of Mercury Transport and Fate Models to Wisconsin’s Emission Inventory</td>
<td>Dave Michaud, Wisconsin Energy Corp. (WES) Environmental Department</td>
</tr>
<tr>
<td>3:10 p.m.</td>
<td><strong>COFFEE BREAK</strong></td>
<td></td>
</tr>
<tr>
<td>3:30 p.m.</td>
<td>Identifying Future Needs/Research and Funding Priorities (audience will break into small discussion groups)</td>
<td>All</td>
</tr>
<tr>
<td>3:50 p.m.</td>
<td>Discussion of Subgroup Session Results</td>
<td></td>
</tr>
<tr>
<td>4:20 p.m.</td>
<td>Discussion Summary</td>
<td></td>
</tr>
<tr>
<td>4:45 p.m.</td>
<td>Closing Remarks and Adjourn</td>
<td></td>
</tr>
<tr>
<td>5:00 p.m.</td>
<td><strong>WRAP UP AND RECEPTION</strong></td>
<td></td>
</tr>
</tbody>
</table>
Good Morning and welcome to Michigan! While I have a moment, let me put in a shameless plug for my alma matter – welcome to East Lansing, Michigan – home of the Michigan State Spartans!

I am told that some have traveled great distances to get here. To name a few, we have guests from Canada, Colorado, Tennessee, Massachusetts, and Florida. Your presence here underscores the importance of the topic we are here to discuss and that is mercury and measuring atmospheric mercury.

As you know, mercury is a mobile and ubiquitous compound that readily volatilizes and can deposit locally, but which also moves around the biosphere. This makes mercury a concern that demands collective consideration and collective action. We continue to have much to learn about mercury and we are fortunate to have at this workshop scientists and technicians that can share with us their ideas and research and can serve as a sounding board for discussion on this topic. We very much welcome your input and appreciate your participation today as well as tomorrow. I know that a number of you from other states are doing much in your state to address mercury; while I’m here today I’d like to mention what is happening in Michigan.

Michigan’s two peninsulas are bordered by the Great Lakes. This fresh water is the largest system of fresh water on earth representing roughly 18% of the world supply. Because of the large surface area, it makes them vulnerable to direct atmospheric deposition of pollutants. Michigan also has 11,000 inland lakes within its two peninsulas. These inland lakes have also been shown to be sensitive to atmospheric deposition of mercury.

Since 1988, Michigan’s Department of Community Health has issued a statewide fish consumption advisory for all of Michigan’s inland lakes because of the presence of mercury. It is my understanding that 43 other states have issued fish consumption advisories for their rivers, lakes and streams.

The continued monitoring of mercury in animals such as herring gulls and fish suggest that mercury levels have decreased in the Great Lakes during the past 30 years and that is good news. However, we must remain diligent; sampling by the Centers for Disease Control suggests that 300,000 children are born each year to women whose methyl-mercury exposure is above the level believed to be safe. We’ve made significant progress, but there is still much work to be done in this area.

Now let me touch on several mercury pollution prevention (P2) projects that have been implemented in Michigan. In 1994, Michigan convened a Mercury Pollution Prevention Task
Force with representatives from industry and environmental groups and as a result of this collaborative effort several excellent programs and partnerships were formed in Michigan.

- For instance the MDEQ, with assistance from USEPA and the Michigan Health and Hospital Association has sponsored numerous mercury-thermometer exchanges resulting in the collection of over 40,000 mercury thermometers.

- Working with the Michigan Department of Community Health, MDEQ has conducted nine mercury spill workshops in Michigan to educate emergency responders regarding mercury spill response procedures.

- MDEQ has worked with the Michigan Department of Agriculture to phase out the use of mercury-containing manometers on dairy farms, which is huge because Michigan is a big farming state.

- MDEQ has worked with numerous hospitals to phase out the use of mercury as well as assisting dental offices to eliminate elemental mercury from their offices and to minimize mercury releases. Although in truth, this is the area where we want to do more and make greater progress with dental facilities.

- MDEQ, working with the automobile manufacturers, obtained commitments from the companies to stop adding mercury to automobiles in convenience light switches and this partnership is ongoing and we are continuing to work with the auto industry to further reduce any mercury contamination from this source.

- Finally, MDEQ’s Mercury Reduction Initiative received a national Pollution Prevention award for developing a compact disk (CD) full of practical information that can be used by schools and businesses to eliminate mercury from their buildings. The CD was distributed to 1,100 schools and 500 school superintendents across Michigan to encourage phase-out of mercury prior to the legislative deadline of December 31, 2004. I’m happy to report that nearly 200 schools have completed this phase-out, two years before the deadline!

Collectively, all of these Michigan pollution prevention efforts have resulted in over 10,000 pounds of mercury being collected and removed from circulation.

Let me quickly mention several mercury legislative initiatives in Michigan.

- First, Michigan has adopted a bill that bans the sale of mercury-containing thermometers in Michigan beginning this year and a bill was also adopted that bans mercury use in school by December 31, 2004 and as I mentioned earlier, the outreach efforts by MDEQ have caused 200 schools to complete the phase out before the mandated deadline.

- Lastly, Michigan has also adopted strict mercury emission limits on medical and municipal waste incinerators through our air permitting process and we are now considering legislation to ban the construction of any new medical or municipal waste incinerators.

There are also several research efforts ongoing in Michigan.
In July 2000, the MDEQ purchased a Low-Level Mercury Analyzer which allows water sample testing for mercury to a level 400 times lower than the level achieved previously. Over 7,000 samples are tested each year by this laboratory.

MDEQ has been partnering with the University of Michigan on an Atmospheric Mercury Monitoring Network. You will hear more on this from Professor Jerry Keeler this morning during the program.

Finally, we have been working with the Minnesota Pollution Control Agency and the Wisconsin Department of Natural Resources on identifying fugitive sources of mercury through the use of the Mobile Mercury Monitoring Trailer, which you will also hear about during the program.

In closing, let me emphasize that the reduction of mercury is one of the highest priorities for Michigan and Michigan’s new Governor – Governor Jennifer Granholm. Reduction of mercury is consistent with Governor Granholm’s goals to, “phase out the worst toxic pollutants” (including mercury), in order to “provide healthy communities for Michigan’s families.” In keeping with the Governor’s vision, MDEQ will continue to focus on identifying sources of mercury and aggressively implementing efforts to reduce mercury in our environment.

Let me end as I began and say it’s a great pleasure to welcome you here today. I think your presence and willingness to explore practical and workable solutions to the problems presented by mercury in the environment are greatly needed and greatly appreciated and I thank you for being here today.

8:45 - Moderator Joy Taylor Morgan

Joy Taylor Morgan has worked for the MDEQ-AQD for 13 years where her work has focused on developing programs, regulations and policies that emphasize the reduction and elimination of the atmospheric release of persistent bioaccumulative toxic pollutants that include mercury, dioxins, PCBs, and pesticides. She is currently project manager for two mercury monitoring grants. One is an EPA grant that has provided the funding to purchase mercury monitoring equipment for Michigan, Wisconsin, and Minnesota along with the funding for this workshop. The other is a Michigan Great Lakes Protection Fund grant working in cooperation with the University of Michigan’s Air Quality Laboratory for establishing a mercury monitoring network in the state of Michigan.

9:00 a.m. - Serving the Research Needs of Policymakers: An overview of the toolkit for mercury vapor monitoring, Frank Anscombe, USEPA’s GLNPO

Mr. Anscombe is with EPA’s Great Lakes National Program Office in Chicago. He is an Industrial Ecologist, which means he is someone interested in the environmental consequences of human activities. He has followed several mercury issues since 1994, including the fate of Federal mercury stockpiles. Since 1996, he has worked with the US mercury cell chlor-alkali sector on its voluntary stewardship activities. Frank helped convene an unprecedented 10-day
fugitive emission study inside one factory, which has given him some general opinions about methods for evaluating mercury vapor sources.

It would be remiss not to thank Joy Taylor Morgan and her colleagues for orchestrating this workshop. When Joy began working for Michigan DEQ, she started with a home-court advantage. Attending Michigan State, she had a professor who during the 1970s had written a superb book about mercury.

The ablest mercury air scientist at the USEPA, who happens to be with us, studied at Ann Arbor. Given Michigan's wonderful educational institutions, it seems apt to convene this workshop here.

We meet in the midst of a budgetary bind for many State governments. This has kept some parties from joining us, sad to say including Clancy, the mercury detecting canine from Minnesota. Humans have a couple of hundred sensors with which to detect smells, whereas dogs have 4,000, explaining why Clancy can find mercury. I miss the honor of meeting Clancy, yet less barking may suit the Marriott family.

In my mind, the target customers for this workshop are State environmental agency managers and technical staff.

Some of you may be interested in general knowledge about the tool-kit of mercury vapor monitoring techniques and how some of these might serve your purposes. Others of you may have specific methodological interests. This workshop aims to support both perspectives: “big picture” versus “how-to”, the generalist like myself versus the technical.

Our presenters will share insights from studies they have conducted. They may offer us intriguing ideas for future research. If so, I will listen to such ideas with interest.

At the same time, my personal viewpoint is that those responsible for minimizing mercury exposures are environmental agencies, States and EPA. In so far as we sponsor research, we would be wise to have it serve our responsibilities, in a discernible way, on a credible time scale. During the next two days, please keep in mind the question of what mercury air measurements will best serve your needs and responsibilities.

We have a diversity of people here, including a sprinkling from industries, environmental groups, and vendors of equipment. I encourage a comfortable atmosphere. I will aim to communicate as best as I can and hope others can correct a few of my inevitable mistakes and be kindly forgiving. I intend to have a very good time these next two days and would wish that for you as well.

Mercury is an infamously elusive substance. It is called quicksilver, owing to its volatile mobility. Mercury is equally an elusive topic for discussion.

Each of us assembles facts into some overall understanding. Our group will inevitably contain many different composite understandings. Also, the priorities for someone else may be profoundly different from your own. We need to be respectful of our diversity of aims and of understanding. The better that we can grasp where others are coming from, then the more that we will learn.
I find it helpful to place mercury vapor measurement methods within a chronological perspective. My understanding is likely far too simplistic, but I will boldly share my ignorance.

One of the first techniques to assess a source of mercury vapor was to measure mercury within nearby vegetation. During the 1970s, studies were published of mercury in vegetation near chlor-alkali factories. These were mostly in Scandinavia. The premise was to measure mercury near a factory and then at distances away from it, to gauge the geographic fallout.

A few years ago, Martha Makholm with Wisconsin DNR published a variation on this theme. She placed mosses at distances from the chlor-alkali factory in Wisconsin. Mosses are only exposed to mercury via the air and not via roots. By placing them at sampling sites for a certain duration, she could see geographic dispersion in relation to the source.

Even though sampling vegetation or soil may have been early approaches to studying air emissions, they can still be relevant today. If one uses a modern vapor analyzer, the wind may not cooperate or a source may be episodic, so that temporary deployment of an analyzer may not encounter mercury vapor. Whereas the exposure of a plant may have a longer term chance to receive mercury and be worth analyzing, if only as a screening tool to find out if there is a nearby source.

Ralph Turner has had a hobby of coring into tree trunks to seek a history of mercury from a nearby emission. He has found that trees push mercury from the biologically active outer ring further into the trunk, so that the chronology in tree rings is somewhat distorted. Yet a tree core can still indicate a trend, even if the years in which this happens are not exact.

Yet there are limitations to sampling vegetation. It is a cumulative measure that cannot capture variability through time. Also, if much of the air emission from a source does not deposit locally, then sampling vegetation can never quantify the emission.

Some of the earliest approaches to measuring mercury vapor directly were to use absorbing material. I once read the emission methods at two U.S. chlor-alkali factories during 1972. For one test, EPA built a sampling train that had all sorts of filters and thereafter some absorbing material. After hours of sampling, the absorbent was sent off to a lab for analysis. At the time of these studies, this was cutting edge work, techniques especially developed, absent anything better being available.

Noble though this effort may have been, it yielded a cumulative value. It could not distinguish temporal variability in emission rate, a major issue with a manufacturing source. Also, an absorbent does not provide quick results, because the analysis is done at a lab, rather than in the field. One does not get timely feedback as to whether the adsorbent is positioned in the best place to find mercury vapor.

Even today, EPA’s emergency response teams take hopcalite absorbent off to a building where there has been a mercury spill. They expose the absorbent to air for 8 hours, to judge whether there is a problem. This is probably fine for their purposes, but this approach is not easily suited if one’s interest is out of doors, in the world at large, seeking a mercury vapor plume. The world is a big place to hunt for a plume even with a modern vapor analyzer, let alone with absorbents.

During the 1980s, people began to collect rainfall and to analyze it for mercury and other substances. Since then, such deposition monitoring has expanded to include dry deposition, and many more people do this sort of work. There may be as many as 50 sites across the U.S.
In addition, advanced equipment has been introduced. Environment Canada has placed Tekran vapor analyzers at 11 sites across Canada. These have been chugging away since 1996 collecting Total Gaseous Mercury. The purpose of this program is said to be to investigate natural processes governing atmospheric levels of mercury, temporal and spatial variability, and it is said “sources” of atmospheric mercury. I would note that all these sites are in rural locations, though three are said to indicate slightly higher deposition indicative of anthropogenic sources.

An early finding has been that there are reduced levels of mercury before sunrise, perhaps indicative of deposition from the atmosphere during the night. Since the vapor pressure of mercury is strongly determined by heat, and predawn hours tend to be the coolest, this daily pattern seems reasonable.

In my mind, I classify such monitoring as contributing to verification of mercury fate models. My opinion is that it would be unfair to ask scientists to speculate about the origins of mercury deposited to their remote sites. If asked, they may do their gracious best to oblige, but the best place to evaluate a source is at that source, not 20 or 100 miles away.

It may prove that in due course, deposition monitoring can distinguish temporal trends, as has been reported from Sweden and Germany. Yet, it should be borne in mind that this monitoring is a point measure. It samples the air at just 11 points across the immensity of Canada.

Another approach to evaluating temporal trends has been to take vertical cores within glaciers or within the bottom sediments of remote lakes. When dated, cores yield a long-term trend of mercury abundance. Ed Swain from Minnesota PCA has taken cores from dozens of lakes around Minnesota. He and Dan Engstrom have found declines since the 1960s in many lakes, though little temporal change in others, perhaps indicative of nearby sources.

It is probably a truism that all measurements have intrinsic strengths and uncertainties. A lake core receives mercury from across a watershed. This provides a much larger catchment area than a measurement at a single point in the atmosphere. On the other hand, a lake core also receives mercury from soil erosion, hence is not purely a measurement of atmospheric deposition. Ice and sediment cores can reveal 100 years of deposition. Deposition monitoring cannot look back in time and will thus take time to yield trends.

There are criticisms of cores. I heard an interesting speaker a few weeks back say that mercury re-volatilizes from ice, undercutting the value of an ice core. He argued that sediment cores are distorted by diagenesis, a tendency for mercury levels to increase toward the surface of sediments. Yet if revolatilization from ice is a consistent process, ice cores can still yield a valid temporal indicator. And many sediment cores show recent declines in mercury, which argues against distortion by diagenesis.

There are a fair number of temporal indicators from this part of the world. They seem to indicate mercury declines during the past three decades. Declines have been greatest on lakes that once received large discharges. The Canadian Fish and Wildlife Service monitors mercury in herring gulls across the Great Lakes. Canada also sponsors temporal monitoring in several Great Lakes fish species. Dr. Mike Myer of Wisconsin DNR has monitored mercury blood levels in common loons from northern Wisconsin during the 1990s.

Birds and fish can reveal temporal trends that may be harder to distinguish at a point in the atmosphere (just as they would be at single point within an ocean). A fish or bird receives
mercury via a food web that is geographically broad. There is also bioaccumulation up that food web. This combination of geographic scope and bioaccumulation can give temporal monitoring within biota power to reveal a trend. A trend may still be present at a single point in the atmosphere, though stochastic variability may mean that monitoring will have to take place for a long time in order for that trend to emerge.

Declines in mercury levels are encouraging. Mercury confers no known biological benefit to living things and is a potent neurotoxin like its heavy metal neighbors on the periodic chart, lead and thallium. So lower levels of mercury are intrinsically healthful. A downward trend may owe to much lower use of mercury within society, since the 1960s, when it was in pesticides and paints. Some people nowadays wonder if environmental levels of mercury can be further lowered. Trends in this part of the world confirm the common sense expectation that lower releases in fact pay off in lower environmental exposures.

A key aspect of this workshop is to make better known that there have been exciting advances in technologies to detect elemental mercury vapor. There are now analyzers that offer near-real time, continuous data. They can be deployed as continuous emissions monitors at stacks; near potential sources; or by companies for worker health purposes.

There seem two general categories of instruments: ones that average over a distance and ones that measure mercury vapor at a point. We are fortunate to have presenters from two companies that offer point instruments, Lumex and Tekran. We were not able to obtain a presentation on the long path optical DOAS, EPA’s instrument for measuring elemental mercury vapor over distance. So I will offer a few pictures to introduce these instruments.

A practical consideration among analyzers is portability. EPA has a van to transport its DOAS. When we get to the source to be evaluated, the DOAS is placed on tripod stands along a fenceline. Michigan, Minnesota, and Wisconsin have a van by which they move their Tekran instrument. The Lumex is 19 pounds with shoulder strap, so conducive to seeking a mercury vapor plume on foot, as are its instantaneous values.

The handheld Jerome instrument is portable, durable, and relatively inexpensive. Is is suited to reading high levels and does not operate continuously.

There are also emerging techniques for measuring non-elemental mercury compounds. The utility of these depends on your needs. As you may appreciate, the basic science of understanding the fate of mercury in the atmosphere is at an early stage. It has only been in recent years that computer age analyzers have been available. They will make possible many future studies to reveal much that is presently unknown about how mercury behaves within the atmosphere. It is important that there be speciating instruments in studies of the fate of mercury vapor.

My own interest is at the other end of the spectrum, at prevention of air emissions. I appreciate that characterizing the species of mercury present in a smokestack may be important to designing an effective control technology. Yet, that task could also be considered the responsibility of emitters. For my interest in nearby assessment of potential emissions, an elemental mercury analyzer seems a highly useful capability.

I would like to reflect briefly about sources of mercury vapor. The Great Lakes State agencies have invested in emissions inventories, to tailor these to their unique economies. Radhica Sastry and colleagues with Ohio EPA published a paper recently on emissions from a steel
facility. There has been similar work by New Jersey DEP. We will hear from George Southworth regarding source assessments in Minnesota. As State agencies obtain mercury vapor analyzers, they can deploy these for source assessment work, so as to expand the knowledge base regarding potential air emissions within their jurisdictions.

There is a fair amount about mercury air emissions to be discovered. I looked at a recent paper by Pacyna estimating global mercury emissions. This attributes 77 percent to combustion of coal and oil by power plants. Production of 4 metals (iron, copper, zinc, lead) places second at 10 percent. Cement production claims third place at 7 percent. Waste disposal rounds out at 6 percent.

I would note that the second most mined metal is aluminum that does not appear in Pacyna’s inventory. Someone at an aluminum firm told me that the level of mercury in bauxite indicates that a refinery emitted more than one ton per year. There are about 20 such refineries around the world, so perhaps 20 tons of mercury vapor.

Annual production of nickel exceeds 500,000 tons, yet it is not in Pacyna’s inventory. Silver and gold of course continue to be much sought. In fact, U.S. gold-mines produce 50 to 100 tons of mercury per year as a collateral byproduct and mines in Nevada are voluntarily pursuing mercury air emission reductions. Yet Pacyna does not provide for industrial mining of gold.

There are also small scale miners who use mercury to obtain gold. There may be several million miners beavering away, across Asia, Africa, and Latin America. They burn off mercury over fires. It is hard to guess their output, since these folks live at the economic fringes. It is possible they could burn off 800 to 1,600 tons of mercury per year.

A specialist on the issue of mercury in oil has written: “A more complete statistical understanding of the amounts of mercury in crude oil and in refined products is needed to be able to provide a defensible estimate of mercury emissions to the atmospheric environment. Accurate measurements of total mercury in crude oil and refined products will require a more rigorous sampling protocol that accounts for the forms of mercury that typically evade measurement.”¹ This paper was reviewed by the American Petroleum Institute, prior to publication. This paper teaches me that mercury levels in oil deposits can vary by origin; mercury levels in Alberta crude oil are 40 times higher during the Devonian era than the Jurassic.

Pacyna’s inventory does not factor natural gas, a fuel of increasing economic importance. Yet there are papers regarding management of mercury at some chemical factories, like fertilizer makers, which use copious volumes of natural gas.

I was interested by a study from the Russian Academy of Sciences. This aimed to see if mercury levels in gas might be predictors of imminent earthquakes. After accumulating a huge amount of data, the Russians noticed that mercury levels in gas deposits vary regularly through time, in a sine wave fashion, presumably owing to forces within the earth.

So I would suggest that determining representative mercury levels in gas and oil deposits would seem no simple matter. Much sampling would be required to robustly understand mercury content in deposits around the world.

A global emission inventory by Pirrone and Keeler provides for wood combustion. One wonders what happens to the mass of mercury contained within trees when they are dissolved into paper and cardboard?

The treatment of municipal waste water often produces sludges which contain mercury. When these are applied to land, how much mercury volatilizes?

With sensitive analytic capability, mercury can be detected everywhere, at trace levels: in water, soil, minerals, fossil fuels, and vegetation. It would seem the rare basic manufacturing industry that could do without such inputs. The greater the volume of inputs, the greater the potential output of mercury. There seem a ubiquity of human activities that receive incidental, trace levels of mercury. Some are well known, others less so.

There have also been few studies of natural emissions of mercury vapor. A team including Steve Lindberg published a paper recently estimating that annual emissions from the soils of just one State, Nevada, are 10 tons per year. For perspective this would be 20 percent of air emissions from all of America’s coal fired power plants.

To sum up, what have I talked about? I have tried to introduce approaches for measuring atmospheric mercury. I mentioned analyzing vegetation; using absorbents to capture mercury for later lab analysis; monitoring deposition at points; and of the exciting advances in real-time vapor analyzers. I distinguished between those that take measures at a point versus optical instruments that measure through distance. I find it useful to distinguish studies that focus on sources versus ones that focus on scientific understanding of the fate of mercury within the environment. Lastly, I have suggested that the knowledge base for both natural and anthropogenic sources of mercury can be improved, in the years ahead.

Thank you for your kind attention.

9:20 a.m. - Mercury Monitoring in Michigan and the Great Lakes’ Basin, Methods and Source Characterization, Dr. Jerry Keeler, University of Michigan

Dr. Keeler is a professor at the University of Michigan and Director of the Air Quality Lab at the University. Before that he was a Visiting Scientist at MIT and a Research Scientist at Harvard School of Public Health. Dr. Keeler holds a Bachelor of Science Degree in Physics and received his Master of Science degree and PhD from the University of Michigan in Atmospheric Sciences. [http://www.sph.umich.edu/ehs/umaql/](http://www.sph.umich.edu/ehs/umaql/)

In 1991, the University of Michigan Air Quality Lab (UMAQL) conducted their first atmospheric mercury measurements for the Lake Michigan Urban Air Toxics Study. At the time gold-coated bead traps made at the UMAQL were used to measure total gaseous mercury. There wasn’t much data in the region, and they took a holistic perspective, they didn’t trust any existing data, they started from scratch making measurements, tweaking and refining the process. They spent the first 5-6 years in the 1990s on measurement and analytical method development. As past of a Cooperative Agreement with the USEPA they developed the EPA Inorganic Compendium for gaseous and particulate mercury (IO5) for both wet and dry techniques. They also spent a significant amount of time developing and testing dry deposition techniques.
From 1994-1996, the UMAQL set up a Great Lakes states’ regional mercury monitoring network, which consisted of 11 sites (funded by the Regional Great Lakes Protection Fund and the USEPA). Every 6th days samples were collected for gaseous and particulate mercury at all of the sites. They found a factor of two increase in particulate mercury in a gradient moving south to north.

They also worked on the mercury component for the Lake Michigan Mass Balance (LMMB) Study and took urban measurements in the Chicago/Gary areas. They found particulate and gas phase mercury levels averaged 2-3 times higher than the levels measured concurrently in surrounding rural areas. Gas phase mercury was at least two times higher in the urban areas and maximum concentrations as much as 10-15 times higher. Particulate mercury was also measured on large particles (>2.5 μm) in the urban areas which would lead to elevated dry deposition near the sources.

In 1996 the UMAQL conducted a 7 month study in Detroit, funded by the Detroit Wastewater Treatment Plant, to determine the contribution of mercury from atmospheric deposition to the plant. They made direct measurements of wet and dry deposition and found a significant amount of deposition in Detroit (similar to levels in Chicago); they found that wet deposition was approximately equal to dry deposition for particulate mercury, and wet deposition was ~20 μg/m²/year. This study also revealed that gas/particulate partition for mercury was very important and indicated the need for a better understanding of the artifacts associated with particulate mercury collection.

For the LMMB study the UMAQL conducted modeling to determine how much atmospheric deposition contributed to mercury loadings to Lake Michigan. They found that 85% of the mercury coming into the lake was from the atmosphere and most of the particulate mercury was in the fine fraction (69 kg/yr). They found wet deposition (614 kg/yr) was most important to the loadings and evasion of elemental mercury (453 kg/yr) was also important. For reactive gaseous mercury (RGM) they estimated that 2-5% of the gas phase was estimated to be RGM. They estimated that the RGM deposition (490 kg/yr) is on the same order as wet deposition, but with a large uncertainty.

This work clearly pointed to the need for RGM measurements. In 1998, an automated RGM technique was developed (Tekran 2537/1130). One of the prototype 1130 instruments was set up a site near Dexter, MI. At this site, the UMAQL found that precipitation strongly affected RGM levels. Measurements of RGM revealed a diurnal pattern and they found that approximately 50% of RGM was removed during rainfall events. Also found that mercury measurements alone are not that useful for understanding the processes that control the levels of mercury in the atmosphere. They suggest that it is important to also look at NOX, CO, PM, O₃, and SO₂ to understand the atmospheric behavior of mercury. They found that under certain meteorological conditions that O₃ was highly correlated with RGM. Some researchers think that O₃ may oxidize elemental mercury to RGM. They are less certain of this hypothesis but they do think that O₃ may simply be an indicator of an oxidative atmosphere and another pollutant may be chemically reacting with mercury. The noted that RGM is not always correlated with O₃ and understanding this will lead to a better understanding of mercury chemistry.

In 2001, UMAQL began a study in Detroit with Michigan State University (MSU) that was to look primarily at PM issues but included mercury measurements. They found the average elemental mercury values were about 3 ng/m³ (twice as high as Dexter or other background sites in the state of Michigan) with peaks of elemental mercury going as high as 100-150 ng/m³. RGM was
not typically correlated with elemental mercury, so sources of elemental and RGM aren’t always related in this urban area.

The UMAQL partnered together with the MDEQ to establish a mercury monitoring network in the state of Michigan, with funding from the Michigan Great Lakes Protection Fund. They are now in their second year of their funding cycle. Their objectives are to provide spatial and temporal trends in the state and to also provide urban speciated data in the state. The data will be used for conducting multi-pathway risk assessments, for TMDL work, to help validate models and to identify source regions.

Six sites were established or continued in Michigan [Eagle Harbor (this site has been in operation since 1995), Pellston (operating since 1992), Grand Rapids (newly established site), Flint (newly established site) and Dexter (operating since 1992) and Detroit.

What are they seeing? The 2537/1130 Tekran shows elemental mercury levels are at about 3 ng/m$^3$ in Detroit with spikes being higher. During summer RGM and PM don’t correlate. However in September 2002, RGM and PM did correlate and it happens frequently in the Fall. They see evidence of local source impacts so in the urban areas there are smaller seasonal differences.

Why do we need this data? One reason is for modeling purposes. The UMAQL has developed a version of the CMAQ Hg Model to try to determine where monitoring sites should be located based on modeling results. The model suggests that we should be able to see strong spatial variability of RGM, and the model suggests that we should see the influence of RGM emissions downwind of large sources; this will guide monitoring studies.

The UMAQL identified a seasonal cycle for mercury in precipitation in the early 1990s with the work of Hoyer et al. Looking at the four current sites (Dexter, Pellston, Eagle Harbor and Grand Rapids), the volume-weighted means are fairly similar (10-14 ng/L), but how does this relate to deposition? They collect event-based data that goes into seasonal averages so they can look at trends at the long-term sites to see how changes in emissions are affecting deposition. They have data from Dexter and from a site in Vermont, which has also been operating since 1992. These sites are providing the longest running sites for mercury event precipitation in the world. There has been no evidence of a down-ward trend (for at least wet deposition); they do see deposition patterns vary as a function of meteorological conditions. Eagle Harbor, in Michigan’s upper peninsula typically has lower deposition than the southern Michigan sites.

Collecting event precipitation samples is critically important for subsequent back trajectory analysis to determine source/receptor information and to identify the location of major sources. The UMAQL is working with EPA=NERL to use these data to further refine hybrid models. Hybrid models can also be run for all other trace elements that are collected. They will use the emissions inventory data with CMAQ and they are working with EPA to refine QTBA to verify receptor modeling.

For their work in Lake Superior they used two-years of data and applied the hybrid model called QTBA to locate sources of the observed mercury. First they looked at particulate mercury and they identified a large gold mine in Canada north of Lake Superior that apparently was emitting significant mercury emissions. They also found that fine particulate and total particulate mass was contributed from sources in the same upwind direction and they believe the gas phase emissions from the gold mine are interacting with particulate matter and contributing mercury loadings to the Basin.
Next steps – include elucidating the factors controlling the atmospheric chemistry and deposition of mercury and playing a leadership role in developing new sampling and analytical methods.

**Question:** How does wet deposition in Detroit compare with Chicago?

**Answer:** It is similar, about 20 µg/m$^2$/yr. Dr. Keeler thinks that in urban areas dry deposition exceeds wet deposition. In rural settings, they are likely similar. So within a 25% error, you could just double wet deposition to approximate total deposition.

9:50 a.m. – Measuring Mercury Emissions from Non-point Sources: Municipal Waste Landfills and a Chlor-alkali Factory, Dr. Steve Lindberg, Oak Ridge National Laboratory (ORNL)

Dr. Lindberg holds a Bachelor of Science Degree in Chemistry from Duke University and holds a Master of Science Degree and PhD in Oceanography from Florida State University. He joined Oak Ridge National Laboratory (ORNL) in 1974 and currently directs a research group on Atmosphere/Earth Interactions. He has worked on environmental mercury issues for almost 30 years and has published over 200 papers and edited 8 books in the fields of atmosphere/surface exchange, trace metal chemistry, and biogeochemical cycling. He holds adjunct Professor status at the University of Michigan and the University of Tennessee. He was elected as Fellow of the American Association for the Advancement of Science in 1992, and was named a Corporate Fellow at Oak Ridge National Laboratory in 2000.

**Landfills as Hg Sources:** Mercury-bearing material enters municipal landfills from a wide array of sources including fluorescent lights, batteries, electrical switches, thermometers, and general waste; however the fate of mercury in landfills has not been widely studied. Using automated flux chambers and downwind atmospheric sampling, we quantified the primary pathways of Hg vapor releases to the atmosphere at six municipal landfill operations in central Florida. These pathways included landfill gas (LFG) releases from active vent systems, passive emissions from landfill surface covers, losses during dumpster and transfer station activities and waste storage, and emissions from daily activities at a working face. We also quantified the potential contribution of specific Hg-bearing wastes including mercury thermometers and fluorescent bulbs, and determined the organic species of Hg in LFG.

Gaseous elemental mercury (Hg$^0$) was released to the atmosphere at readily detectable rates from all sources measured; rates ranged from ~1-10 ng m$^{-2}$ h$^{-1}$ over aged landfill cover, from ~8 - 20 mg/h from LFG flares, and from ~200 - 400 mg/h at the working face. These fluxes exceed our earlier published estimates. Surprisingly, large fluxes were estimated for Hg losses at transfer facilities (~100 mg/h) and from dumpsters in the field (~30 mg/h for 1000 dumpsters), suggesting the need for more measurements on these sources. Attempts to identify specific Hg sources in excavated and sorted waste indicated few readily identifiable sources; due to effective mixing and diffusion of Hg$^0$, the entire waste mass acts as a source.

Broken fluorescent bulbs and thermometers emitted Hg$^0$ at rates of 10s to 100s of µg/h; fluxes decreased exponentially, but remained in the low µg/h range for several days. The speciation of Hg in LFG included Hg$^0$ at µg/m$^3$ levels and methylated compounds (mono- and dimethylmercury) at ng/m$^3$ levels, far above those in background air. We estimate that
atmospheric Hg releases from municipal landfill operations in the state of Florida are on the order of 10-50 kg/y (Lindberg and Price, 1999; Lindberg et. al. submitted)\(^1\).

The nature of landfills designed to reduce waste through generation of methane by anaerobic bacteria suggests the possibility that these systems might also serve as bioreactors for the production of methylated Hg compounds. The toxicity of such species mandates the need to determine if they are emitted in municipal LFG. In the initial study, we measured TGM, Hg\(^0\), and methylated Hg compounds directly in LFG from a Florida landfill. TGM was in the µg/m\(^3\) range, MMM was found in condensate, and this time we positively identified dimethyl mercury (DMM) in the LGF in the ng/m\(^3\) range.

The discovery of methylated species in LFG prompted a larger study of this phenomenon. Since our previous study was confined to a single site, gaseous inorganic and methylated mercury species have now been identified and quantified in landfill gas at six municipal landfills in Florida, Minnesota, and California. Total gaseous mercury consistently occurs at concentrations comparable to coal combustion flue gas at most sites (in the µg/m\(^3\) range), while methylated compounds occur at levels in the ng/m\(^3\) range at many sites. Dimethylmercury is the predominant methylated species, in the range of 10-50 ng/m\(^3\) at most sites, while monomethylmercury was generally lower. Landfills are suggested as a potential anthropogenic source of DMM emissions to air, which may decompose to MMM and could explain the reports of MMM in continental rainfall (Lindberg et. al. 2001; Lindberg et. al. in prep.)\(^1\).

Chlor-alkali Factories as Hg Sources: During winter 2000, a multi-organization research team assessed fugitive (non-stack) Hg air emissions at a Hg-cell chlor-alkali factory in the U. S. using a variety of sophisticated mercury vapor analyzers to assess fugitive air emissions of mercury. The team obtained mercury data over a nine-day period from inside the factory, with the first known concurrent awareness of manufacturing operations. Emissions were measured from the roof vent, the open-sided basement below the production cells, and from surrounding soils and sealed waste ponds. Some emphasis was also placed on assessing the spatial distribution of Hg concentrations within an operating cell room. The team used real-time and near-real-time Hg analyzers including a Tekran 5-minute integrated sampler modified for cell room use, Lumex RA915+ and Jerome 431-X portable Hg analyzers, and a long-path integrating DOAS system for gaseous elemental Hg, coupled with an optical anemometer for measuring vent-averaged air flow rates. The integrated beam (DOAS) and point measurements of Hg\(^0\) compared favorably.

One principal finding is that fugitive air emissions from the cell-room roof vent are episodic and vary with factory operating conditions (maintenance and minor operational perturbations). Therefore, air emissions are likely to vary widely among factories on a worldwide basis, in accordance with operating procedures followed at each. Properly positioned, real-time mercury vapor analyzers are a potentially valuable tool to locate small scale process leaks, and to estimate overall emissions from the cell room building. A preliminary estimate of daily fugitive Hg emissions during this period (~ 400 - 600 g/d) indicated that the bulk of the atmospheric loss was emitted from the roof vent of the main production building. Sealed waste ponds were not important sources, emitting Hg at rates comparable to background soils (Southworth et. al., in press; Kinsey et. al., in press)\(^1\).

\(^1\)References:

Measuring Atmospheric Mercury: Goals, Methods, and Results


10:35 a.m. – A National Routine Monitoring Strategy for Mercury & Other PBTs, Melissa Hulting, GLNPO

Melissa is an Environmental Scientist with EPA’s Great Lakes National Program Office. She is the US Program Manager for the Integrated Atmospheric Deposition Network – also known as IADN – which is a binational US-Canada Persistent, Bioaccumulative Toxic or (PBT) air-monitoring network. She is helping to coordinate PBT monitoring activities both at the national level with her participation in the development of a National PBT Monitoring Strategy and at the North American level through her membership on the Commission for Environmental Cooperation task Force for Environmental Monitoring and Assessment.

Ms. Hulting presented a national routine monitoring strategy with the main objectives to determine long-term trends, determine effects of regulatory action and to build on existing monitoring, and bring all monitoring data together. Hg, dioxin and PCBs are highest priority and they would also like to monitor for DDT and PBDEs. EPA support UNEP and have worked together with other federal agencies, states, locals, etc. on the development of the strategy.

EPA held a couple of workshops, one was with internal EPA staff and the other included external stakeholders.

Why Develop a National PBT Monitoring Strategy? To know what progress is being made on such efforts as “Clear Skies” (if passed) and for coordinating efforts and to develop periodic reports on their web site.

The findings of their workshops included:

- there is no shared vision on monitoring strategy and gaps exist, there is a willingness to cooperate and modeling needs to be a focus
- improved monitoring and data assessment is needed
- the Hg leads include Arnie Kuzmak and Marilynn Engel, they developed a “conceptual model” first and developed and identified needs: They recommended monitoring fish and air
emissions which are the most responsive measure of the effectiveness of programs designed to reduce environmental releases.

- knowledge of the relative contribution of local, regional and global sources are needed
- the variability of bioaccumulation processes from one water body to another reduces the value of cross-sectional monitoring of water-column and sediments (TMDL folks may not agree)
- a priority for Hg monitoring includes expanding speciated air monitoring, improve MDN sites in the west, implement continuous fish tissue surveys and continuing the CDC NHANES (National Health And National Examination Survey)
- EPA plans to put together a group to develop a report, comparable to the Great Waters’ Reports, where it brings everything together
- EPA is trying to get money and want input into the process.
- Next Steps – they are now preparing a working draft, and they want input and participation.

11:05 - Fugitive Emissions of Mercury from Non-Combustion Sources in the Great Lakes Airshed (FuME) George Southworth, ORNL

George has worked as a researcher in environmental chemistry and toxicology at Oak Ridge National Lab since 1974, and is presently a Senior Research and Development Staff member in the Environmental Sciences Division. He received his Master's Degree from the University of Michigan. His research interests have been in the environmental transport and transportation of chemicals on aquatic organisms and communities. His work in mercury research started at the highly contaminated Department of Energy facilities in Oak Ridge where he assisted in efforts to establish cleanup goals and to reduce mercury inputs to surface waters draining those facilities. In 1999, he began working with Dr. Steve Lindberg on studies of mercury cycling between the atmosphere and aquatic and terrestrial systems at sites throughout North America – including Michigan.

The objective of the Fugitive Mercury Emissions from Noncombustion Sources in the Great Lakes Region (FuME) study was to identify and quantify fugitive mercury sources and to collect data on mercury speciation. They worked collaboratively with state air quality scientists and put into practice utilizing the mercury mobile monitoring trailer shared by the states of Michigan, Minnesota and Wisconsin.

First Phase
1. Screening study (using the Lumex)
2. Fenceline monitoring
3. Measure Hg(0), RGM, MMHg and DMHg

For the screening study several sources were monitored including: an electric arc furnace, scrap yards, landfills, dentists, medical waste incinerators, autoclaves, precision instrument manufacturer, fluorescent bulb recyclers, etc.

Fluorescent Bulb recycler – mobile system (Grand Rapids, MI) -
- Bulbs processed in truck, 55 g. drum crushed glass and end caps
- Inside truck – very low emissions from truck
- Crushed glass had significant Hg retained in it, which went into a dumpster
- Found concentrations 100-200 ng/m³ in building (from dumpster levels were much higher, the Jerome pegged)
They also looked at a fixed fluorescent bulb recycling facility in Minnesota that utilized the
dry process – which was very messy! Quite a bit of Hg is retained in the glass.
Open dumpsters > 25,000 ng/m$^3$ (pegged Jerome), in adjacent air > 1 mg/m$^3$
Air inside facility > 25,000 ng/m$^3$ (very dusty)
Where Does Glass Go?

Car Shredder – (MN)
At an EAF, where they shred steel, upwind the concentrations were 0-2 ng/m$^3$ (around the
detection limit) and downwind 13-18 ng/m$^3$ (600 m downwind). This source emitted ~ a few
grams/day – a fairly substantial source (1/10 of a chlor-alkali plant)

Autoclave (Visited one in MI and one in MN)
The Hg was unknown but probably substantial. Air in the facility ranged from 50-800 ng/m$^3$
(MN) and the headspace in the compactor was 8,000 ng/m$^3$ (MN)

Waste Transfer Station (Fla)
Garbage dumped on floor. Levels were 30 ng/m$^3$ when the waste was brought in, levels
increased to 400-900 ng/m$^3$ when trash was dumped. About 1 g/day Hg flux was estimated.

Waste Transfer Station MN)
100 meters downwind, 5-10 ng/m$^3$
RDF shreds waste
Dust control, Hg flux 4-8 g/day
Lot of dust.
Need more data from fugitive emissions from waste receiving facilities.

Fla. Waste
Bailing reduces volume of landfill used/ton
Likely reduces working facility emissions
Hg inside 400 ng/m$^3$

Scrap yards, MN
Typical high concentrations, 15-300 ng/m$^3$
Downwind, 5-10 ng/m$^3$
Upwind (levels around background) 0-2 ng/m$^3$

Scrap yards, MI
Visited facility on a old/cloudy day, found no Hg signal < 5 ng/m$^3$
Not sure why, the facility had excellent housekeeping - they utilized street cleaners, perhaps
they used a different feed?

Qualifying Emissions at Fence line
Outgrowth of Florida landfill studies.
Measured Hg(0) upwind and downwind, including MET data and used a simple box model
or screen 3 to calculate a flux.

Thermometer Manufacturer (MI)
Saw high concentrations in runs. Used a Jerome 431-X to measure at vents
Used a Lumex RA 915+ to measure fluxes in soil (minor fluxes compared to building)
Trailer was set up 100 ft. downwind of building,
Vent flux, 1-2.1 g/Hg/day (measured Hg out of forced air vents each day)  
Fence line flux 2.0-3.2 g Hg/day  
RGM and DMeHg were also measured– all samples below detection limits.

Refinery complex in MN,  
At this facility they really needed a Tekran as the levels were low, saw a downwind signal.  
Detected some RGM numbers, calculated a flux at 15-50 g/day, calculated using the screen 3 model (low confidence with this value)

Chlor-Alkali Plant  
Can generate isopleths by walking around plant.  
Levels decrease as you move away from the facility.  
You can drive around with the Lumex operating in a car.

In summary, screening studies using a Lumex allows one to identify potential sources of Hg(0) at such facilities as scrap yards, solid waste facilities, bulb recycling, autoclaves - these are all good candidates for flux measurements. Fence line monitoring is most effective close to localized sources. The flux estimates were consistent with expected source magnitude.

Question: It seems like most sources were pretty small, 1-2 g/day, do you feel that any would be significant?  
Answer: Likely only EAF would be a significant source (looking at one source at a time, not collectively).

11:35 a.m. - Mercury Monitoring in Steubenville, Ohio: Investigating the Relative Impact of Coal-fired Utility Boilers to Atmospheric Mercury Deposition, Dr. Matt Landis, USEPA  

Dr. Matt Landis currently works at EPA’s Office of Research and Development’s National Exposure Research Laboratory (or NERL) in Research Triangle Park. Matt received his PhD at the University of Michigan under Dr. Jerry Keeler. At EPA he is a Research Environmental Health Scientist. He is the Principal Investigator at the Office of Research and Development’s atmospheric mercury research program and the team leader for the Office of Research and Development’s inorganic mass spectroscopy laboratory. He is running a series (5) of mercury research sites in the US.

Dr. Landis provided an overview of EPA ORD’s research strategy and discussed EPA’s statistical source apportionment model development. Numerous models are currently being worked on including CMB 8.2, UNMIX2, and PMF (positive matrix factorization). Each have their positives and negatives. CMB can model one sample and requires selection of source profiles, UNMIX2 (Multi-linear model) generates source profiles and uncertainties. UNMIX2 was used to analyze 3 years of data collected in Philadelphia which source apportioned PM2.5 data (also used PMF model). The plan is do conduct a similar source apportionment effort in Steubenville, OH.

EPA will monitor and develop hybrid receptor models (working in cooperation with U of M). They will conduct meteorological transport analysis and use the QTBA (quantitative transport
bias analysis) model developed by Dr. Keeler at U of M. This will aid in the identification of sources.

Examples of meteorological cluster model and QTBA results to identify source specific area were given. The QTBA example was from 10 monitoring sites for Hg(0) and DMMeHg in the Great Lakes Basin.

At the Stubenville OH site (located on the border of W. Virginia and close to PA) tracers for sources will be monitored, conducting aerosol characterization (daily), event precipitation and trace elements. They built a platform to hold the monitoring equipment, 3-Dicots, MIC B collector for precipitation (the method was published 6 years ago). They also will monitor for mercury using Tekrans (2537A, 1130 and 1135) and will have MET data collected. A trailer has been deployed that houses the Tekrans.

Dr. Landis stressed that while the instruments are extremely useful, they are only useful if strict standard operating procedures are followed, the method for measuring divalent inorganic reactive gaseous mercury was published by Landis et al in ES&T 2002 36:3000-3009).

Some Stubenville data was collected for a few days in December 2002. Data shows RGM increasing while SO$_2$ increases.

Data from Florida in 2001 was presented that showed RGM and SO$_2$ correlated, due to a coal fired power plant.

Data was collected with North Carolina DEQ surrounding a medical waste incinerator that showed a 2 hour average concentration of RGM $> 2.5$ ng/m$^3$ downwind. So it is very important to analyze RGM as well. Hg(0) was around 4 ng/m$^3$.

EPA will also do intensive monitoring in Ohio. EPA has deployed a 24 ft. mobile trailer outfitted with complete gas and aerosol characterization capabilities. They can also measure filters.

Another project they are working on is their “high volume slurry sampler”. This high volume slurry sampler, created by John Ondov builds particles to a uniform size, then separates them, collects H$_2$O and aerosols and can do 30 minutes of aerosol samples, can do very rapid sample collection. Also they can analyze 48 samples/day – can reduce monthly samples to weeks.

So this study in Ohio that will be using statistical models and high resolution data will be a very valuable tool and will continue several years in Ohio.

**Question:** One person commented that modelers really need data from slurry sampler which would produce high resolution data. How long will it take to get the results?

**Answer:** About two years.

Dr. Landis stated that the Coral Springs, FL site is also running and he would like to tie in these two sites to a PBT network. Although EPA policy is that ORD is not to run “routine” sites. Although if you want to confirm effects of certain sources like coal fired utilities and regulatory impacts you need long-term higher resolution sites.
Luncheon Presentation - What is METAALICUS, Dr. Steve Lindberg, ORNL

What is METAALICUS? It stands for “Mercury Experiment to Assess Atmospheric Loadings In Canada and the United States” (http://www.biology.ualberta.ca/metaalicus/metaalicus.htm).

METAALICUS is a whole-ecosystem experiment in which mercury loading to a headwater lake and its watershed is being altered experimentally. These events represent the first whole-ecosystem additions of stable Hg isotopes anywhere.

The mercury is being added as stable, non-radioactive isotopes of inorganic mercury (Hg(II)). The power of using isotopes lies in the ability to follow the newly deposited mercury separately from background mercury. Furthermore, different mercury stable isotopes are being added to the upland, wetland and lake surface (\(^{200}\)Hg, \(^{198}\)Hg and \(^{202}\)Hg respectively) to determine the relative contributions of these sources to fish mercury levels.

A combination of field, laboratory and modeling studies is being used during METAALICUS. Field programs include pilot studies and baseline work that began in 1999, and the full scale experiment from 2001 through 2003. Long term follow-up studies are expected beyond 2003.

Mercury concentrations are being tracked in all compartments in the lake, watershed, and atmosphere. Detailed process studies are also being carried out to follow the movement and transformations of mercury through the watershed and lake, as well as air/surface exchange of mercury. Production of methylmercury (MeHg) is being studied in the lake sediments, upland and wetland, as is the bioaccumulation of MeHg into benthic organisms, plankton and fish. Methylmercury is being followed specifically because it is the dominant form in fish and the most toxic form of mercury in the environment. This process-based approach will allow us not only to document what happens, but also to understand why. This is essential if we are to use the results of the study to make predictions for other locations. The approach will also provide critical information for an existing model that predicts fish mercury concentrations in lakes and the effects of remedial actions such as reductions in mercury loading.

Study Area and Site: The Experimental Lakes Area (ELA) is situated in western Ontario, Canada. ELA lakes have been used over the past 30 years to provide leading limnological studies in freshwater lakes, including landmark whole-lake studies of the effects of nutrients, acidification and reservoir construction. Lake 658 was selected for the study. It is a small, oligotrophic, headwater lake on the Canadian Shield and is one of the lakes reserved for research at ELA.

How Much Hg is being Added? Not much: ELA is a low deposition area for mercury, with approximately 7 ug m\(^{-2}\) yr\(^{-1}\) of wet mercury deposition. The low mercury deposition rate at ELA means that adding the equivalent of about half a teaspoon of mercury over a 3 year period is enough to increase wet Hg deposition to the 52 ha Lake 658 ecosystem (lake and watershed) by 4-5 fold. This will result in a mercury deposition rate to the experimental system that is comparable to rates currently observed in some parts of the US Northeast and Florida.

Activities To Date: After two years of pilot and baseline studies, METAALICUS went “full scale” in June 2001. Isotopes are being applied to the upland, wetland, and directly to the lake surface. The upland, wetland and lake are receiving isotopes at a rate of 25 ug m\(^{-2}\) yr\(^{-1}\) for up to 3 years. The upland and wetland areas are being sprayed once per year in May/June by an airplane flying low over the canopy. Isotopes are being applied directly to the lake by mixing
from a boat at a depth of 0.7m, over a series of up to 10 applications during the ice-free season. The pilot studies are also yielding fundamental new information about mercury behavior. For example, when mercury was applied to pilot upland plots, the quantity of mercury exported in runoff depended significantly on whether the test conditions induced flow during the test event itself. During simulations of light rain or dry deposition, little of the mercury applied was exported in runoff for the remainder of the year. Significantly more of the applied Hg was exported in runoff if surface flow occurred during the event. Volatilization rates, by contrast, were higher during the simulation of dry/light rain conditions, exceeding the mercury export in runoff under such conditions. The pilot studies included:

- Isotopic Hg(II) additions to small upland and wetland plots (1100m$^2$ and 300 m$^2$ respectively), and a pine tree stand.
- Isotopic Hg(II) additions to a set of four lake mesocosm enclosures, each 10m diameter. Two enclosures received 30 ug m$^{-2}$ in one dose, while the other two had the same dose spread over 5 applications.

Future Activities and Schedule: The full-scale addition experiment at Lake 658 started in June 2001 and will run for three years. Furthermore, a series of 10-12 enclosures will be dosed with different levels of stable Hg(II) in 2002 to further examine the relationship between Hg(II) load and fish Hg levels. 2004 will be dedicated to final reporting and publishing for the study. Less intensive sampling in the longer term will also likely be implemented.

The Study Team: The project team includes more than 50 people, including leading mercury researchers and advisors from the United States, Canada and Sweden. The team has extensive experience with whole ecosystem mercury experiments and a history of successful collaboration.

Communications: To ensure timely dissemination of research results we will employ:

- annual workshops and presentations for government, industry and team members,
- publications in newsletters and primary research journals throughout the study, and
- general information distribution via the world-wide-web (address below).

METAALICUS Funding: METAALICUS presently has funding from the Canadian Department of Fisheries and Oceans, US EPA, USGS, US Department of Energy, the Electric Power Research Institute, Wisconsin DNR, the National Sciences Engineering and Research Council of Canada, Environment Canada, and the Canadian Forest Service.

1:00 p.m. - Moderator Remarks, Frank Anscombe, USEPA - GLNPO

The Oak Ridge study regarding air emission of methylmercury from landfills is welcome, yet also unique. This very uniqueness runs the risk of leading some to suppose that landfills are the crucial source of methylmercury air emissions. In fact, all mercury in the environment is concurrently subject to methylating and demethylating bacteria. Wherever there are air emissions, these will contain some methylmercury content. It has been estimated that air emissions of mercury from soils in Nevada may be 10 tons per year. This emission would very likely include a methylmercury component. One does not need a landfill for air emissions with a methylmercury component.
It is sometimes stated that elemental mercury spreads long distances and thus some people may assume that it is environmentally benign. This is not so on a Biospheric scale. There are known processes that change elemental mercury vapor into water soluble forms that deposit to earth. Thus, those who overlook the harm of elemental mercury vapor are doing so on parochial geographic grounds that the mercury falls on some other state or nation. If every state and nation takes this viewpoint of disregarding impacts to others, then there is a "Problem of Collective Action" in that the pursuit of self-interest leads to a diminished aggregate result. Reducing mercury levels in the U.S. requires other nations to contribute emission reductions and we in turn are part of reducing their levels. Reducing mercury levels is a shared challenge that involves shared contributions.

1:15 p.m. - Florida Mercury Trends, Dr. Tom Atkeson, Florida Department of Environmental Protection

After nine years with the Florida Department of Health as Chief of the Environmental Epidemiology Program, where he was involved in a wide variety of environmental contaminants issues, Dr. Atkeson joined the Department of Environmental Protection in 1992. His responsibilities are to coordinate Florida's response to the finding of high levels of mercury in fish and wildlife. His primary efforts are devoted to planning a long-term research program aimed at defining the causes of mercury contamination in Florida and coordinating the activities of a variety of local, state, federal and private agencies in pursuit of those research objectives. He currently is the “Mercury Coordinator” for the Florida Department of Environmental Protection in the Division of Resource Assessment and Management. Dr. Atkeson's background is in zoology and wildlife biology, with education at Auburn University and the University of Georgia.

In Florida they have made some improvements in the state, but there is still a global Hg(0) impact. There is a concern for wildlife, including wood storks and Florida panthers from MeHg exposure. Fish advisories are widespread, and Florida is one out of 44 states with an advisory.

The Everglades is a very sensitive area and prone to contamination, it is very flat with some “tree islands.”

The Florida Atmospheric Mercury Study (FAMS) ran for three years at nine sites, the study was conducted using towers to house monitors. They found that 98% of the mercury entering the Everglades is a result of atmospheric deposition (125-150 kg/yr), which was an astonishing result!

Where does the Hg come from? He doesn’t think anyone totally understands, but you need to know the speciation of mercury: Hg(p), Hg(0) and Hg(II), all operate over different spatial scales Hg(p) and Hg(II) have a more local impact. Sources can be local, regional, and global. Today Florida can see some local successes. The transport across the US is toward the Northeast, however Florida is in a different meteorological regime. Deposition is dominated in summer months.

In South Florida, ~ 5 million people live along the coast, with the highest per capita in the US reliance on incinerators (5 municipal waste combustors and several large medical waste incinerators). Wind rose shows the Hg goes northwest. At least 50% of Hg deposition to the Everglades in the mid-1990’s came from local sources. There are high levels of Hg in Everglades fish. Sulfate reducing bacteria require carbon and sulfate, sulfate sources to the
Everglades contributes to increases in methylation. When sulfates decrease, methylation is reduced. Emissions of sulfate and Hg contribute to the MeHg problem. When sulfate is exposed to sun, wet and drying cycles also lead to increased methylation - 30 ng/l of MeHg in Everglades has been seen.

They are trying to figure out how to develop TMDLs for atmospheric mercury. The Everglades Hg cycling model is being used.

Modeling study: Shows a 1:1 relationship to atmospheric load to Hg concentration in fish. The response time (faster than others) expect 28% reduction in fish in a decade and approach equilibrium in 30 years.

Hg trends: Ice cores in Wyoming shows levels back to 1700. The USGS did a world materials flow in 2000 and in the last 30 years there have been a declined which peaked in ~1970s.

They conducted a historical reconstruction back to 1930s in Florida. 1994 was the first FAMS study (reductions had already occurred). Core studies in the Everglades in 1995 shows the history of operating municipal waste combustors. Controls and P2 have helped in the Hg reduction from these sources. How fast have the Everglades responded? Large mouth bass in the late 1980’s were about 1.5 ppm, a 60% decline has occurred by 2001. Wading birds also shows a 60% decline. EPA’s REMAP project 1995-1996 compared to 1999 show a significant change. Health advisories for fish have been downgraded by Florida State Health Dept. in the Everglades. Air emissions from Florida sources have decreased. It took 15 years in to see a 60% decline. This is due to local Hg(II) deposition decline.

Bottom Line: Need to keep in mind how sulfate interacts with Hg. We can’t ignore the Hg(0) problem. To the extent that emissions are from RGM, you will see a benefit in the environment within a couple of decades. The global cycle is impacting certain areas more than others.

Comment – Similar results to Florida are also been seen in Wisconsin’s Lower Trout Lake. As sulfate decreases, also mercury deposition decreases and also a decline in perch is evident.
- pH is marker for sulfate, so its linked to acid rain.
- Sulfur reducing bacteria require sulfate and carbon for metabolism by bacteria.

1:45 p.m. - Monitoring Wet Deposition of Mercury in North America – the Mercury Deposition Network, Marty Risch, USGS, Indiana

*Martin ("Marty") Risch has been a hydrologist with the U.S. Geological Survey (USGS) in Indianapolis, Indiana since 1990. Since 2000, he has been project chief of multi-year, statewide monitoring for atmospheric deposition of mercury and trace metals. He completed a study of low-level mercury in the Grand Calumet River watershed in northwestern Indiana in 2002. Marty has managed numerous hydrogeologic and water-quality investigations throughout Indiana and authored USGS reports about the results. He was chief of the ground-water program at the Indiana Department of Environmental Management for 6 years prior to joining the USGS. He holds a degree in environmental science from Purdue University and a graduate degree from Indiana University.*

The Indiana mercury monitoring program is part of the NADP-MDN (National Atmospheric Deposition Program – Mercury Deposition Network). NADP is made up of over 100 agencies. It was started in 1978 as part of the NTN (National Trends Network) to understand acid rain and
pH and major ions were measured at over 200 sites. In 1995 the MDN was started, now there are 80 sites and MeHg is also monitored at about 20 sites. Weekly samples are analyzed for total mercury.

Hg in precipitation is important due to human health impacts from deposition and accumulation in fish, there is also a risk to wildlife. Numerous fish advisories are currently in place in the US - ~ 50-75% of the mercury input to lakes and streams is from wet deposition (now we are finding that dry deposition can be very important as well).

MDN sites may be impacted from local, regional or global sources. Most MDN sites are in the northeast. There are 4 sites in Indiana and MN and WI has several sites.

The key features of the network are that its long-term monitoring (> 5 years), sites are regionally represented, identical sampling and methods are used by the same laboratory (Frontier Geoscience) and the data is quickly available on the web; the data is released quarterly. The volume weighted mean is calculated and an annual mean is reported. Concentrations range from 6-26 ng/l and 9-13 ng/l in the Great Lakes. Deposition ranges from 3-26 µg/m²/yr, with Florida having recorded the highest deposition. Seasonality of deposition is observed, the summer being the highest due to higher rainfall, temperature and higher oxidant levels and a southern air flow. The MDN database shows long-term trends and seasonal trends and it may help to “ground truth” models. The future of MDN is expected to expand sites in the west, add trace metals and look into adding dry deposition.

2:05 p.m. - Mercury Monitoring Efforts in Wisconsin, David Grande, Wisconsin Department of Natural Resources.

Mr. Grande is the toxics chemist for the air monitoring program at the Wisconsin Department of Natural Resources. With a BS degree and over 10 years of air pollution monitoring experience, Mr. Grande has designed and participated in a number of innovative programs involving both source and ambient testing for a variety of hazardous air pollutants.

In Wisconsin, they conduct mercury deposition monitoring, ambient Lumex surveys, Lumex emissions tests and they conduct ambient Tekran measurements with equipment shared with MN and MI. They have 6 sites that are part of the MDN. For the Lumex monitoring tours they have visited a Hg recycling facility, fluorescent light recycler and a neon sign manufacturer. They conduct “stealth” monitoring along the fenceline where the sources don’t know you are there. This has allowed them pinpoint some sources. Intermittent sources like car crushers are more difficult to pinpoint. He visited an EAF where they found 12,000 ng/m³ in the baghouse, which would equate to 40-50 lbs/year.

In 2003, they plan to visit a crematorium, metal shredder and a vehicle crusher. They have used the Tekran 2537As at Vulcan, a chlor-alkali plant, which is estimated to emit ~1,100 lbs/yr of mercury which makes up 20% of their inventory. Generally these are all fugitive emissions.

They also conduct lichen studies in Wisconsin. They found the maximum concentration (5 minute average) of > 3,000 ng/m³. They also saw a zero value and they are not sure why. They want to monitor for RGM in 2003.

They visited “Mercury Waste Solutions”, a mercury recycler, located in southeast Wisconsin. They process 60,000-70,000 lbs Hg/yr and they are storing 85,000 lbs from Maine, from the
closure of a chlor-alkali facility. They don’t report any emissions; theoretically they are below the reporting limit. The maximum concentration they have seen (5 minute average) was > 2,500 ng/m$^3$ (similar to the Vulcan chlor-alkali plant data.)

Future plans include continue ambient measurements, Lumex site inspections, emission tests for mobile sources, crematoria, and EAFs and they want to conduct RGM measurements at Vulcan.

2:20 p.m. – Monitoring Program for Atmospheric Deposition of Mercury in Indiana, Marty Risch, USGS, Indiana

The USGS is partnering with the Indiana Department of Environmental Management (IDEM) on mercury monitoring. Monitoring mercury is important because of public health concerns. EPA has set a standard to meet in fish at 0.3 mg/kg (ppm). IN has been monitoring fish since 1983 and several fish advisories exist in IN.

IN’s state water quality standard is 12 ng/l and 1.3 ng/l is the limit for protection of wildlife for the Great Lakes tributaries. Three years ago IN had no deposition data for mercury, IN wanted to know if local sources influenced deposition and if there is a seasonal or annual trend and they wanted to be able to compare data in other states. They have a site by Clifty Creek Power Plant (2 miles away from the plant), statistical analysis could not show a significant difference in mercury levels. (EGRID EPA’s database shows the regional coal plants)

They now have two years of results, 368 weekly deposition samples were analyzed and 45% of the weekly samples for total mercury exceeded the IN water quality standard of 12 ng/l. They normalize the deposition by dividing the annual deposition by precipitation. They do see a seasonal difference with deposition higher in the summer. MeHg concentrations are < 4/10 of a percent of total mercury and does not show any seasonality. They also measure trace metals. They plan to add an MDN site at Indianapolis, IN and they also want to add dry deposition. For more information see their Web Site: http://in.water.usgs.gov/newreports/mercury

Comment: To really know if a water quality standard is exceeded, you really need to know the “evasion” rates as a point of comparison.
Measuring Atmospheric Mercury: Goals, Methods, and Results

2:35 p.m. - Clean the Rain Campaign: Raising Public Awareness of the Mercury Deposition Issue, Dr. Mike Murray, National Wildlife Federation

Mike joined the Great Lakes office of the National Wildlife Federation (NWF) as Staff Scientist in 1997. Mike’s recent work has been in the area of scientific and policy aspects of the atmospheric deposition of toxic chemicals in the Great Lakes region. Ongoing work includes coordinating and conducting research as part of NWF’s Clean the Rain educational and advocacy campaign, policy and scientific research in diverse areas, including mercury fate and transport, Total Maximum Daily Load plans, water quality standards development, and fish advisory protocols and communication, and commenting on regulations and action plans pertaining to toxic chemicals in the U.S. Mike received M.S. and Ph.D. degrees in Water Chemistry from the University of Wisconsin-Madison, is an adjunct lecturer at the University of Michigan’s School of Public Health, and has served on several technical review and conference planning committees.

Because of the widespread nature of mercury contamination (with 43 states having some type of mercury advisory in place), the NWF has been working on a public awareness campaign on mercury deposition issues. Their approach for reducing mercury levels includes pushing for strong regulations including MACT standards for air releases, reducing direct water discharges (in particular to meet Great Lakes Initiative criteria), advocating for cleanup of contaminated sediments, and implementing pollution prevention activities. Their primary goal is to raise awareness to the general public that air deposition is a significant source of mercury and to increase pressure on governments to adopt stricter environmental standards and regulations (their monitoring is not for research purposes). They are calling for adoption of statewide mercury phase-out goals so that by 2020, a goal of virtual elimination is achieved.

While there is no MDN monitor in Michigan, there has been a lot of data collected by Dr. Jerry Keeler’s Air Quality Laboratory at the University of Michigan. NWF has focused their efforts thus far in Michigan since their regional field office is located in Michigan and they saw an opportunity to influence policy. (Sampling is now being expanded to other states, including Minnesota, Illinois, and Ohio.) They have focused their efforts in urban areas and work with local partners and sample for short periods. They collect wet deposition only, using a MIC-B sampler, with a goal of sampling individual events where possible. The analysis is CVAA (EPA Method 245.1) with a detection limit of 1-2 ng/l.

NWF’s first report on mercury in precipitation covered the Great Lakes region and was released in 1999. They reported precipitation data obtained from several agencies and researchers, including data for Detroit collected as part of a study by the Detroit Water and Sewerage Department (DWSD), and analyzed at Dr. Jerry Keeler’s laboratory. The levels were as high as 117 ng/l. Since there is no rain standard for mercury, they compared the values to the surface water quality standard of 1.3 ng/l for protection of wildlife and 1.8 ng/l for the protection of human health. (Through a memorandum, EPA has given states the option of using a higher human health criterion of 3.1 ng/l.) NWF collected samples in Michigan in 2002. Analyses of the precipitation samples for mercury were performed by the Physics Department at the University of Minnesota-Duluth. The samples collected in Michigan ranged from 1.5-206 ng/l. The highest sample was obtained in Southfield, MI; however, this was for a small event. Because of the limited data, it is difficult to compare with longer term data sets in similar locations. The very limited data (four samples) for North Muskegon in July 2002 were less than half the average summer mercury concentrations obtained by Matt Landis for samples collected at South Haven in 1995. Mercury data for samples collected at four sites in southeast Michigan.
in spring, summer, and fall 2002 were in the range of the samples from the mid-1990s that were collected or the DWSD project and analyzed by Dr. Keeler’s laboratory.

(NOTE: As noted before, the sampling is not part of a research project, nor is it geared to monitoring trends. We are examining the MDN for trends, as well as other research efforts in the region and beyond.) The NWF has proposed a Michigan Mercury Phaseout plan with the goal of 90% reduction in mercury air emissions by 2010 and virtual elimination by 2020. They also want a reduction of mercury in water discharges and a 90% clean up of mercury contaminated sites. The NWF has proposed that Michigan achieve these targets through development of a mercury phase out rule. They plan to release a cost estimate for reducing mercury releases in Michigan in fall 2003. For more information go to: http://www.nwf.org/cleantherain.

2:50 p.m. – Simulation of Mercury Deposition in Wisconsin, Dave Michaud, WEC, Environmental Department

Mr. David T. Michaud is a Principal Environmental Scientist and a member of the Corporate Environmental Strategy Team for Wisconsin Energy Corporation, which is headquartered in Milwaukee, Wisconsin. The team is largely responsible for monitoring environmental issues, participating in the development of environmental regulations and legislation, and assisting operating departments with special compliance and permitting tasks. Mr. Michaud’s current tasks include fish protection strategies for hydroelectric plants, as well as hazardous air pollutant assessment and control, and fine particulate matter characterization. Mr. Michaud received his B.S. and M.S. degrees in Biology from Marquette University. His graduate research was focused on the physiological effects of mercury on fish physiology. He currently serves as chair of the Electric Power Research Institute’s (EPRI’s) Air Quality, Health and Risk Assessment Business area’s Advisory Committee and is co-chair of UARG’s Hazardous Air Pollutant Committee. He also serves as a member of the University of Wisconsin Sea Grant Advisory Council.

The work being presented was funded by the Wisconsin utilities and managed by EPRI. They simulated mercury deposition in Wisconsin by using the Trace Element Analysis Model (TEAM) that uses a 20 km grid. 1998 meteorology data was used and the AER/EPRI and WDNR emissions inventories were used. Three different scenarios were used, they 1) zeroed out all WI emissions, 2) zeroed out all WI emissions as well as the power plant emissions from several surrounding states emissions, and 3) zeroed out WI power plant emissions.

The inventories for WI varied somewhat with the original AER/EPRI inventory, which was estimated at 1,132 lbs/yr vs. 2,045 lbs/yr for the WDNR inventory. Since the AER inventory inadvertently omitted chlor-alkali and mobile sources, AER used the WI inventory for the modeling runs. The 1999 ICR database provided the power plant data. They used Hg\(^0\) as well as Hg(II) data; medical waste incinerators were determined to emit the highest amount of Hg(II) in WI.

Virtually all the coal burned in WI is western subbituminous (powder river basin ) coal that tends to yield more elemental mercury than oxidized when it is burned in utility boilers. Bituminous and Eastern coals tend to emit higher amounts of Hg(II). MDN data (1998) was used for model validation which showed fairly close results (modeled versus actual) with the normalized difference ranging from 4-36% for grid cells containing the four WI MDN stations that existed in 1998. W136 MDN site is at Trout Lake and W199 MDN site is at Lake Geneva which is closer
Measuring Atmospheric Mercury: Goals, Methods, and Results

to other sources. The forecasted estimate for dry deposition was < 5 \( \mu \text{g/m}^2/\text{yr} \) (although urban areas can be quite high). The model suggested wet deposition in WI was in the range of 10-15 \( \mu \text{g/m}^2/\text{yr} \).

For the scenario model runs (for scenario #2) with no WI emissions and no emissions from surrounding states, it showed substantial reductions in total deposition (up to 17%). The model may overweight deposition as the default speciation values {e.g., the default values for Hg(II)} for most of the non-point sources may be too high.

For scenario #3, when WI power plants were zeroed, there was a –1% to 4% impact on deposition simulated. There are a lot of these plants located on the Lake Michigan shoreline (e.g., downwind of the WI MDN sites) and likely emit more elemental mercury.

In summary, emissions of mercury from WI contribute < 25% of mercury total deposition in WI and <10% at MDN sites. Emissions of mercury from power plants in surrounding states also contribute <25% of total deposition in WI and <7% at MDN sites. Emissions of mercury from WI power plants contribute <1% at 3 of the MDN site and <4% at the 4th. Likely these are the upper limits based on uncertainties in power plant plume mercury chemistry.

3:30 - 4:20 - Summary of Subgroup Discussion for March 26, 2003

Participants were split into five groups and were given five questions to consider and answer as a group. The five questions follow with a description of each group’s response. This summary will be part of the final report to EPA. The workshop was funded, in part, from a grant from EPA’s Great Lakes Atmospheric Deposition funds.

Questions for Subgroup Discussion

1) What should be high priority areas for atmospheric mercury monitoring research?

Group #1 – Monitoring in urban areas, including sampling and speciation (possibly sacrificing some MDN sites to do this) are high priority. Targeting certain monitoring locations and add trace metals are also high priority.

Group #2 – More speciation measurements are needed. We need to better link emissions with bioaccumulation. Speciation at different altitudes is also important for modeling. We also need long-term monitoring to assess whether global background is increasing or decreasing. We also need better emission inventories.

Group #3 – Narrowing the uncertainties of global emissions is a high priority. A more comprehensive suite of pollutants should be monitored to improve the chemistry for “groundtruthing” of models.
Group #4 – “Super sites” are a priority; consider collecting more data at fewer sites. Validating protocols so that there is a “monitoring standard”. Improve speciation knowledge and improving our understanding of dry deposition.

Group #5 – Dry deposition data are high priority. Dry deposition is important to terrestrial and aquatic ecosystems. The relative importance of dry deposition of elemental mercury versus reactive gaseous mercury depends on the role of inputs of terrestrial plant litter to aquatic systems. Education is important on identifying regional and local sources and the risks associated with them. Determining what other atmospheric processes correlate with mercury chemistry in the atmosphere. Improving the link between atmospheric deposition of mercury and mercury bioaccumulation in aquatic life, especially watershed stream interaction. Determining what vector gets mercury into biosystem, elemental or reactive mercury?
2) **What are the trends in atmospheric mercury levels and mercury deposition over the last 10 years? If no declines are apparent how can this be explained, given reported decreases in mercury emissions in North America?**

Group #1 – We need more data due to monitoring locations. Emissions are not being accounted for – it is also important to look at fish tissue data. Additionally sulfur and ozone could impact deposition over 10 years.

Group #2 – Ten years is not enough to see a trend, we need to monitor for as long as possible (It took 23 years to see a trend for SO2.). The best approach for this would be to have “super sites” that include both wet and dry deposition or more sites with fewer measurements. The NADP sites are good and consistent.

Group #3 - Scales and magnitudes of trends are likely to be a function of the relative magnitude of local and global sources on ecosystem loadings at a particular site. We should have a global scale of trends to know the impact of individual sites. If an area is more pristine you may not see a change. Typically wet deposition is used when trying to determine trends and this application may not be the best (dry deposition may also need to be added to include total deposition).

Group #4 - Trends may not be conclusive as there are many complexities in the data, the time period of data collection may not be long enough. There may also be a lot of uncertainty with emission inventory estimates, product phase out estimates.

Group #5 - World-wide trends are not evident. It depends on what scale you are looking at regional, national or global. Other measurements other than wet deposition may be better trend indicators, such as dry deposition. We have not been monitoring long enough, NADP has been in operation since the 1970s.

3) **What level of confidence do we have that the major sources or source categories within the United States have been identified? How can we improve the mercury emissions inventory?**

Group #1 – This group had confidence in the major sources, but stated that we need better data for Iron and Steel Foundries, Motor Vehicles and we need more stack testing and CEM applications.

Group #2 – We need better emission inventories for both natural and anthropogenic emissions from “cradle to grave”. Better emissions data for oil as
Measuring Atmospheric Mercury: Goals, Methods, and Results

well as mercury content in oil from various regions (this can impact the refining process). Mercury emission estimates from diesel combustion are needed.

Group #3 - This group had modest confidence that the major sources within the US have been identified. We need better emission estimates for crude products. Source characterization needs to be improved, we should re-visit sources that now have controls and see what the emissions are at these controlled facilities.

Group #4 - We have enough data now on power plants, but we have other questions including methylmercury emissions from landfills and motor vehicle emissions. We need more information on zinc smelters, aluminum smelters, steel mills, the oil and gas sector (e.g. oil and gas refineries) and fuels including motor vehicle fuels. We need an improvement on emission factors, specifically on refineries and mobile sources....

Group #5 – Everyone should read how emission estimates are made; there is room for much improvement. Some major sources that still need to be better quantified include mining.

4) What type of information on mercury would be most helpful for your job?

Group #1 – Better emission factors, better characterization of sources, mass balance work and a general clearinghouse/database is needed. Additionally, having regular meetings like this one would be very helpful.

Group #2 – Trend data and better emission factors would help.

Group #3 - Speciation data on more sources would help. Determining better what is reactive gaseous mercury, is it Hg(I) or Hg(II)? Improving information transfer that would facilitate using the best data for models would be helpful. Better communication between research communities and program people and improved communication between the air, water, fish and sediment folks (state of Florida is a good example).

Group #4 – Making sure the best science and data make their way into emission inventories (better emission factors). Determining which products cause the biggest releases, how to get the “best bang for the buck”, conducting life cycle analysis may be helpful. Determining methylmercury loadings from the atmosphere. Models that link emissions to atmospheric deposition and providing training on the models to state agencies.

Group #5 - Education of managers on the “why” and “how” of mercury. Why is mercury a problem and how should we deal with it. Better information on how much is local contamination caused by local or regional sources. Better information on why we should reduce emissions in our state, if we can’t measure the effects of mercury exposure or the results of reduction. Include mercury in all industrial emission measurement programs.
5) What are the most significant barriers in conducting mercury research in your respective state, province, city, department, etc. (besides money)?

Group #1 – Lack of communication between researchers and state folks is a barrier. There may be a loss of interest in mercury. Barriers may occur because mercury research can often be long and complex work and another barrier would be lack of public support.

Group #2 – Ran out of time..

Group #3 - The perception that if regulations are going to occur, why conduct research (example, acid rain). Lack of qualified researchers that are using such equipment as the Tekran and Lumex instrument may be a barrier because there may then be a question of the quality of the data. Increasing the simplicity of the instruments makes everyone think they can do research, when the individual may not be qualified to study a particular science question. There is a need for better understanding with how the equipment works. We need to improve education and need to stay connected with researchers from all areas.

Group #4 – Regulating agencies tend to have a media specific focus. There is a lack of communication. Fear of regulation by emitting sources. Method development for mercury monitoring and lack of training on equipment.

Group #5 – Lack of education. Need a better understanding of critical pathways of human and wildlife exposure. Focusing on inventories and concentration rather than fluxes and pathways among decision makers (funding agencies, regulators). Need longer term studies with continuity. Do the individual states have any control if all the mercury use and emissions stopped, would deposition change? Would human health issues change if states change rules individually? This can be a real stopper for state agency decision makers.
### Day 2 Agenda - March 27, 2003

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
</tr>
</thead>
<tbody>
<tr>
<td>7:00 a.m.</td>
<td><strong>REGISTRATION AND CONTINENTAL BREAKFAST</strong></td>
</tr>
<tr>
<td>8:00 a.m.</td>
<td>Welcome by Joy Taylor Morgan, MDEQ</td>
</tr>
<tr>
<td>8:15 a.m.</td>
<td>Field Flux Applications Using Automated Mercury Analyzers</td>
</tr>
<tr>
<td></td>
<td>Dr. Steve Lindberg and George Southworth, ORNL and Frank Schaedlich, Tekran, Inc.</td>
</tr>
<tr>
<td>8:45 a.m.</td>
<td>Demonstration of Lumex and Attachments</td>
</tr>
<tr>
<td></td>
<td>Joseph Siperstein, Lumex Company</td>
</tr>
<tr>
<td>9:15 a.m.</td>
<td>Use of Lumex for Participants</td>
</tr>
<tr>
<td></td>
<td>All</td>
</tr>
<tr>
<td>10:15 a.m.</td>
<td><strong>BREAK</strong></td>
</tr>
<tr>
<td>10:30 a.m.</td>
<td>Automated Speciated Mercury Monitoring using Tekran Model 1130 and 1135</td>
</tr>
<tr>
<td></td>
<td>Frank Schaedlich, Tekran, Inc.</td>
</tr>
<tr>
<td>11:00 a.m.</td>
<td>Mobile Mercury Monitoring Trailer Demo</td>
</tr>
<tr>
<td></td>
<td>David Grande, Wisconsin Department of Natural Resources</td>
</tr>
<tr>
<td>11:30 a.m.</td>
<td><strong>ADJOURN</strong></td>
</tr>
</tbody>
</table>

**NOTE:** Day 2 agenda was rearranged from the above original agenda. Following are the speakers in order of the new agenda timeline.

**8:15 a.m. - Demonstration of Lumex and Attachments - Ohio Lumex Co. RA915+ Mercury, Joseph Siperstein, Lumex Company**

Joseph graduated from Chernovtsy State University (and if you’re not familiar where this is located – don’t feel bad as its located in West Ukraine) – where he received a Master of Science Degree in Physical Chemistry and Chemical Engineering. He has 25 years of experience in analytical instrumentation, process design and process control equipment. He is currently president of Ohio Lumex Company located in Twinsburg, Ohio.

The goal for Lumex use was to make it a simple and sensitive instrument as well as have the ability to sample mercury in all media including air, water and soil and provide quick results. The basic model is the RA915+ which has a detection limit of 2 ng/m3 and has no gold traps and can provide results in seconds. The basic model has a pyrolysis attachment (R291C) that can provide results in soil, or urine, blood or fish tissue and will provide results in one minute with a detection limit as low as 10 ppb. R291 samples for mercury in water by CVAA, and reduces mercury by using stansus chloride and can achieve low detection limit down to 0.5 ng/l (EPA method 1631 allows this method using CVAA).

The new attachment for the RA915+ (R291C) can sample for urine, blood, fish, etc. and can use manual sampling with a detection limit of 0.5 ppb, the direct analysis take < 1 minute. It can also be used for gases (like CEMs) at power plants.

Inside the RA915+ machine is an AA spectrometer with Zeeman correction. It contains a mercury lamp in a magnetic field and has a light source with a multipath cell. It measures the
differential signal for mercury and converts mercury atoms inside the chamber. Any interferences like PM, SO2, hydrogen sulfide are not a problem. Ozone may cause an interference, but you can adjust the optical path so there is no interference.

You can use the Lumex in your car while you drive around a source. They drove 35 mph and found a smelter and waste dump in Slovenia and then the concentrations can be mapped.

They tested mercury in natural gas and found mercury up to 42% (in former Soviet Union), in gas wells mercury ranges from 0.2-2 $\mu$g/m$^3$. Natural gas processing plant in U.S. usually removes the mercury.

Joseph then demonstrated the equipment for air and soil sampling.

**Question:** What about testing sand or gravel?
**Answer:** Don’t do it! The sample must be chemically digested and homogenized to test it.

**Question:** What about testing flammable gases?
**Answer:** Don’t do it – it could explode!

For advanced users in “air mode” you can connect the RA915+ to a lap top and the data will be logged automatically, it will baseline itself and log the data for as long as you want. It will give you an average concentration and an excel file of data.

Maintenance issues: use filters (<1 $\mu$m). They will clean optics for about $400.00. Make sure you don’t place instruments on contaminated floor and since its not motion sensitive you can use it in vehicles.

**8:45 a.m. - Hands On Training Session (for Lumex and Tekran equipment)**
9:15 a.m. - Automated Speciated Mercury Monitoring using Tekran Model 1130 and 1135, Frank Schaedlich, Tekran Inc.

Frank graduated from the University of Toronto – specializing in computer science, physics and chemistry. Upon graduation he established a software company dedicated to computer applications for environmental applications. Frank is the founder of Tekran, Inc. which is a company that specializes in the development and manufacture of mercury monitoring instrumentation. He holds several US and International patents dealing with technology and processes for mercury measurement.

Monitoring for total gaseous mercury or TGM was invented in 1979 and originally used gold coated silica filled cartridges with CVAFS. In the mid – 1990s they automated this method with a detection limit of < 0.1 ng/m³ and auto calibration (model 2537A). The instrument however is not portable, as it weighs about 50 lbs. It is capable of unattended operation. Zero air flows through the instrument and it has a permeation source and two dual cartridge assemblies (for comparison), a mass flow controller with argon as a carrier gas and it uses a standard atomic fluorescence detector.

In the development of this instrument, the goal was to have it rack mountable, easy to use, to have two analog chart outputs (for back-up) and outputs in ng/m³. The lamps for the 2537A last about one year with an unlimited shelf life. The instrument also has no zero drift. The data readings are based on sample volumes corrected to 0º C, 760 mm (which is very important for comparing data). The instrument is capable of providing "true background" levels and can detect down to pictogram levels and with accessories one can also measure process gases and speciated forms of mercury. When used at a chlor-alkali facility they could detect a signal 18 miles away, good wind rose were possible, the highest level was 6 ng/m³. Use at the Arctic showed elemental mercury being oxidized and they could show the analyzer was working properly with the permeation source. Reactive Gaseous Mercury or RGM automated method was also developed as well as a method for particulate mercury.

A summary of the terminology by different scientists would be helpful:

- Elemental Mercury = Hg(0) = Gaseous Elemental Mercury (GEM)
- Reactive Gaseous Mercury (RGM) = Hg(II) = Hg²⁺
- Particulate Mercury = Hg⁰ = Total Particulate Mercury (TPM)
- Hg(0) - 90% of atmospheric loadings and has a long residence time
- Hg(II) – water soluble forms, short residence time and is usually a few percent of TGM

RGM is more difficult to monitor because the method must be 1 to 2 orders of magnitude more sensitive, the levels are in the pictogram range, typically 100 times lower than Hg(0) concentrations and you need to exclude particulate mercury and RGM is very sticky. The instrument that measures RGM is Model 1130 which has been patented by Tekran. It uses a quartz KCl coated denuder which is thermally desorbed and regenerated. It absorbs RGM while passing Hg(0) with laminar flow. Model 2537A reads Hg(0) during the desorption phase and zero air is used as a carrier and RGM is released as Hg(0) and analyzed. The denuder is slightly warm and the denuder captures all the RGM while passing Hg(0). The total sample flow is 10 liters/minute. Then the analyzer measure Hg(0). The denuder can be located out of doors, contains denuder element within high performance oven. It has a pump module that generates the extra flow for RGM and generates zero air for desorption and for the 2537A model. The denuder needs to be changes every 1-2 weeks which is easy to do and operates in
any environment. It offers high time resolution and has been extensively validated by several scientists.

Particulate Mercury – model 1135. Hg\textsuperscript{p} is even more difficult to monitor, its generally thought to be in the fine fraction, 3 µm and is usually a few percentage of total mercury. It has a short range of deposition. The method must also be 1-2 orders of magnitude more sensitive than for Hg(0) and the method must reject Hg(0) component and RGM (however some filters retain RGM). For the 1135 model the sample passes thru the impactor to eliminate coarse particles (> 2.5 µm). Coated denuders capture RGM and eliminates the RGM artifacts, uses a quartz regenerable filter and quartz wool captures the bulk of the PM. Carbon based PM on filter is oxidized to CO\textsubscript{2} during desorption cycle (all within a ceramic tube). Model 1135 stacks on top of the 1130 model. The detection limit is < 2 pg/m\textsuperscript{3} and allows simultaneous determination of Hg(0), RGM and Hg\textsuperscript{p}. Sometimes PM peaks go up while Hg(0) drop. For operation it needs an outdoor location within 25 feet of the 2537A model, often they are placed on a roof top, the fetch is very important and vertical height should be 3-10 m above grade. The equipment has significant power requirements with 1200 VA for the 1130 and 1300 VA for the 1135. You should visit the site at least once/week to change the denuder, filters, check leaks, etc. You’ll need to have extra denuders on hand and they need to be rinsed with deionized water. For more information go to: [www.tekran.com](http://www.tekran.com).

10:30 a.m. - Field Flux Applications Using Automated Mercury Analyzers, Dr. Steve Lindberg and George Southworth, Oak Ridge National Laboratory - Oak Ridge Tennessee

Dr. Lindberg received his PhD from Florida State University and has worked on environmental mercury issues for almost 30 years. He has published over 200 papers and edited 8 books in the fields of atmosphere/surface exchange, trace metal chemistry and biogeochemical cycling.

George Southworth – received his Master of Science degree from the University of Michigan and has worked with Dr. Lindberg in the “mercury group” since 1999 studying mercury cycling between the atmosphere and aquatic and terrestrial systems at sites throughout N. America – including Michigan.

Dr. Steve Lindberg

Steve recently honored Dr. Bill Schroeder who has had an amazing career in atmospheric mercury research and retired on February 28, 2003.

Measuring fluxes are all about quantifying concentration differences, you can use flux chambers or use a tower and measure the gradient. The Tekran Automated Dual Sampler (TADS) allows sampling at two gradients. In 1996, which Steve calls the “enlightened era” when they quit using manual gold traps, they used Tekrans for the flux studies. They had to first do a “bias test” to show that no bias is occurring from the Teflon tubing. They checked the sampling lines and calculated the differences (which should be close to zero). The gradient method is not as sensitive as using flux chambers. The first data collected was from cat tails that showed a diel cycle, they separated the data and plotted it to determine if the surface was a source or a sink (Lindberg et. al. 2002)\textsuperscript{2}. 
Flux chambers were first used in 1975 at a chlor-alkali plant (which was in the µg level) they also looked at the Almaden mine site, now however they can measure fluxes over any surface at very low levels (he published 2 papers on this in 2002 in Atmospheric Environment). They have used commercial food covers for flux chambers made of polycarbonate which is an excellent material but it does cut off 10-15% of UV rays. They have now learned that mercury transpiration is a major pathway of mercury movement in aquatic macrophytes in the Everglades. This data would not be readily attainable without the use of Tekran instruments.

They are now able to model the natural mercury emissions from enriched and background soils. There are however some problems with the Tekrans.

- Because of the 2 gold traps in the Tekran, a “sawtooth” effect occurs – he suggests sometimes you might be able to trust the higher number and suggests always using soda lime traps at inlet of Tekran).
- Portability – they are not, and he urged the need to develop a more portable, near-real-time field Hg analyzer which operates at background levels.
- There are potential problems if you first program the Tekran for the 1130 and then use it for flux measurements without reprogramming it because the TADS sends a flag to Tekran – which uses a multiplier by a factor of 6, but applies that to the data from only one sampling line.

Other applications of the Tekran include work in the Arctic showing Hg(0) depletions. They first started this work in 1999 where they first set up speciation studies and they hypothesized that Hg(0) was being oxidized to Hg(II). They got very low Hg(II) concentrations, almost non-detect. Then they went there for Polar Sunrise (1/21) when its -50ºC and showed Hg(0) depletion occurs through the formation of RGM, RGM was as high as 1,000 pg/m³. This data was published by his team in a 2002 ES&T article (Lindberg et. al. 2002).

Other applications of the 2537A include real time data for DGM in the water column, where Hg(II) is reduced to Hg(0). They purge samples into the Tekran to get DGM data within one hour (20-30 pg/liter is typical DGM numbers) (Lindberg et. al. 2000).

References:


George Southworth - Applications of the Lumex.

The Lumex RA915+ was used at a chlor-alkali plant and saw high concentrations. The Lumex is a portable, real-time airborne elemental mercury analyzer that uses a Zeeman correction with and atomic absorption spectrometer. The data compared well with the Tekran.

At different areas at Oak Ridge the Lumex was used where they were conducting air stripping using ozone and working on a treatment system of contaminated spring water (3-6 µg/l of mercury). Using ozone + UV rays + SnCl₂ than air they could get 80% out, but they are still trying for the last 20% of mercury. The UV light helps to get rid of the ozone and they used the Lumex to measure Hg(0) in the ozone stream. The ozone absorbs UV light and they also used the Lumex to determine Henry’s Law Coefficient by continuous sparge.

The Lumex was also used to measure the effects of wind on a flux chamber, on windy days they were losing some mercury (for METAALICUS study). The flow rate can be adjusted with a flow meter and generate a K curve.

A Lumex was also used to measure Hg(0) in landfill gas, but they didn’t use the pump due to explosive concerns.

For direct soil/air flux with a flux chamber, a good mercury signal was received at a thermometer manufacturing plant in Michigan.

The Lumex was also used to estimate the plume dispersion height at the working face of a landfill (some sort of tripod is needed for this work).

Steve Lindberg - Dry Deposition

What is dry deposition? There are ways that they can validate dry deposition with models. However, dry deposition is likely not worth the effort at remote sites, but it is very important at urban sites. Hg(0) can be absorbed directly thru the foliage thru their stomata at relatively low velocity, but it can be a very significant flux because it makes up the majority of the atmospheric mercury. Most people ignore dry deposition, but it is very significant and should not be ignored. (see ES&T 2001, 35 (flux paper).

At the Experimental Lakes Area (ELA) in Canada they saw about 7 µg/m²/yr in wet deposition, for litterfall about 12 µg/m²/yr, throughfall about 8 µg/m²/yr (throughfall is the flux of mercury in rainfall below the canopy) and net throughfall about 1 µg/m²/yr (which is the difference between throughfall and wet deposition). Net throughfall likely represents the dry deposition of RGM. If litterfall is from the atmosphere, then it's a very large flux, in fact much larger than wet deposition. They can model the dry deposition of RGM using nitric acid vapors as a surrogate.
and come up with an estimate of approximately 0.2-0.6 µg/m²/yr. So it is close to net throughfall.

Dry deposition of mercury is approximately 4-13 µg/m²/yr, which compares to litterfall. So at remote sites, mercury deposition is dominated by the global pool of elemental mercury – so don’t ignore the global pool!

Based on lab studies, he is convinced that the mercury in litterfall (in leaves) comes from the atmosphere and they can validate dry deposition at remote forested sites with models. Dry deposition can not be greater than litterfall and net throughfall. Litterfall and throughfall is always larger than wet deposition, sometimes 2-3 times larger than wet deposition. So we really need to understand dry deposition.

Re-emission was estimated at approximately 1 µg/m²/yr at the ELA site, so it is clearly a “sink” for mercury.

11:00 a.m. - Mobile Mercury Monitoring Trailer Demonstration, David Grande, Wisconsin Department of Natural Resources

WORKSHOP EVALUATION SUMMARY

A total of 59 people attended day one and 64 people attended day two with an overall rating for both days of 4.6 on a scale of one to five, with five being excellent. From day one, eight out of ten respondents plan to take action as a result of this workshop and from day two, six out of ten respondents plan to take action as a result of this workshop.
## ATTACHMENTS

**POWERPOINT PRESENTATIONS**

For copies of presentations, please contact Joy Taylor Morgan [taylorJ1@michigan.gov](mailto:taylorJ1@michigan.gov) or Maggie Sadoff [sadoffm@michigan.gov](mailto:sadoffm@michigan.gov)

| Attachment 1 | Mercury Monitoring in Michigan and the Great Lakes’ Basin: Methods and Source Characterization, Dr. Jerry Keeler, U of M |
| Attachment 2 | A National Routine Monitoring Strategy for Mercury & Other PBTs, Melissa Hulting, GLNPO |
| Attachment 3 | Fugitive Emissions of Mercury from Non-Combustion Sources in the Great Lakes Airshed (FuME), George Southworth, ORNL |
| Attachment 4 | Mercury Monitoring in Steubenville, Ohio: Investigating the Relative Impact of Coal-fired Utility Boilers to Atmospheric Mercury Deposition, Dr. Matt Landis, USEPA, NERL |
| Attachment 5 | Brochure on: What is METAALICUS? |
| Attachment 6 | Florida Mercury Trends, Dr. Tom Atkeson, Florida DEP |
| Attachment 7 | Monitoring Wet Deposition of Mercury in North America - the Mercury Deposition Network, Marty Risch, USGS - Indiana |
| Attachment 8 | Mercury Monitoring Efforts in Wisconsin, David Grande, WDNR |
| Attachment 9 | Monitoring Program for Atmospheric Deposition of Mercury in Indiana, Marty Risch, IUSGS |
| Attachment 10 | Clean the Rain Campaign: Raising Public Awareness of the Mercury Deposition Issue, Dr. Mike Murray, NWF |
| Attachment 11 | Simulation of Mercury Deposition in Wisconsin, David Michaud, WEC |