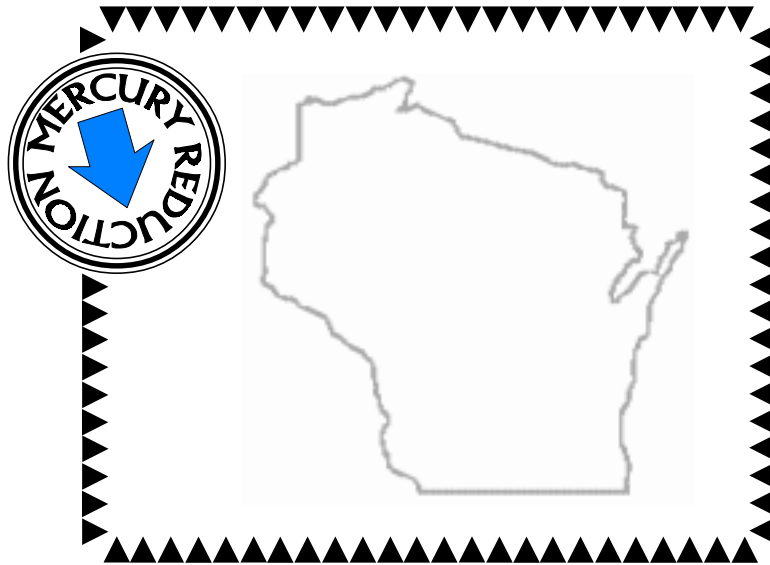



WISCONSIN

MERCURY SOURCEBOOK



**A Guide to Help Your Community
Identify & Reduce Releases of
Elemental Mercury**



This document is a compilation of the best mercury pollution prevention work available to date. We are gratefully indebted to the numerous authors quoted within, whose innovative and groundbreaking research made this SourceBook possible.

The Wisconsin Mercury SourceBook is a working document, and we will continue to update it on a regular basis. Please help us improve this resource by sending your comments, questions, additions, or corrections to:

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You may also call the above number if you would like a copy of the SourceBook.

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May 1997



DRAFT WISCONSIN MERCURY SOURCEBOOK

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The Superior Work Group's Chemical Use Tree: Mercury

Recycling Your Bulbs and Lamps: DNR Fact Sheet

Worldwide Web Sites

Massachusetts Water Resources Authority Infrastructure Maintenance Guidebook
(selected sections)

MASCO Hospital Mercury Workgroup End of Pipe Subcommittee Executive
Summary

Mercury Outreach and Educational Materials Available from MPCA

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HOW TO USE THIS DOCUMENT

The Wisconsin Mercury SourceBook was written to help The Wisconsin Department of Natural Resources implement a new “Mercury Strategy.” The Mercury Strategy is an initiative by the Bureau of Watershed Management, and is an innovative approach to reduce the amount of mercury released to the environment through the use of education, technical assistance, partnership development, and voluntary municipal efforts. It represents a new way of addressing toxics that is based on the development and implementation of comprehensive community mercury reduction plans that focus on the purposeful use of mercury.

This SourceBook is a compilation of the best mercury reduction work to date. It was designed as a working document to help guide communities through the process of writing comprehensive community mercury reduction plans. The SourceBook provides a seven step outline for drafting a reduction plan, and contains source identification materials for nineteen sectors of a community, including case studies, product alternatives, and action ideas for each sector. It is intended for use by anyone involved in drafting a reduction plan for mercury, including sewerage districts, community or trade associations, and government agencies.

SECTION ONE provides general background information on the element mercury, its cycling patterns, and the environmental and health effects of its bioaccumulative tendencies. It provides useful information to anyone involved in promoting a mercury reduction plan or explaining why these reduction efforts are important.

Target: Wisconsin focuses on current pollution prevention efforts underway in the state and is

helpful to those beginning a project. It may help identify an agency that is doing work similar to your intended project, or who may support you in your efforts.

Target: The Great Lakes describes specific activities underway in these important basins. It provides useful project information for communities located in these areas.

Mercury Species and Mercury Transport provide an explanation of mercury’s cycling pattern in the environment. This information helps demonstrate the challenges that arise when trying to measure loadings of mercury to the environment, and is important information to those promoting reduction plans.

Testing for Mercury provides a brief description of a variety of testing methods for mercury. It is helpful to those working in a laboratory, or those facing challenges in documenting mercury reductions through sampling methods.

Human and Wildlife Health Effects introduces the dangers of methylmercury consumption for humans and other animals. Much of the driving force behind the need for mercury reduction efforts center around these issues, so it is helpful for anyone promoting mercury pollution prevention.

Anthropogenic Use of Mercury provides an overview of the ways mercury may be introduced to the environment. Brief descriptions of global and national demand for mercury are included, as well as an overview of global, national, and local emission estimates.

SECTION TWO provides detailed steps in helping communities draft a comprehensive community mercury reduction plan. The lead for such an effort could be assumed by a sewerage district or an environmental or community group.

The steps in section two are general and will be repeated as the plans branch out from the general community reduction team to specific sector and facility teams. Please see the charts on “The Three Levels of a Mercury Reduction Program” for more information.

Identify Your Mission is for management and others interested in developing a reduction team. This step provides an important foundation for a comprehensive plan and should not be overlooked. It also provides an overview of why pollution prevention is the preferred method for dealing with mercury.

Select a Reduction Team and Form Partnerships provides guidance in developing a working group for your community. It also provides lists of current partnerships in Wisconsin and potential trade associations that could be especially helpful once a reduction team has identified priority sectors.

Develop a Baseline and Set Goals describes the importance of establishing a mercury history profile and setting objectives for a program. This section is especially helpful for those who evaluate the program and measure its effectiveness.

Identify Sources of Mercury In Your Community provides ideas and guidance in identifying sources of mercury in your community. It includes steps to measure or estimate relative contributions to your wastestream.

Evaluate Tools and Options helps determine criteria to pick reduction activities for targeted sectors. The spotlights highlighted in this chapter, including “Developing a Publicity Campaign,”

“Educational Activities,” and “Recognition and Awards Programs” are of particular interest to community organizations or trade associations that may be involved in outreach activities.

Set Objectives and Implement and Measure and Promote Your Success provides guidance on developing performance measures for the project. These sections are helpful for those who are evaluating the program. The information included on Implementing a Reduction Plan will help those involved in outreach efforts.

SECTION THREE consists of sector-specific information. It is useful for those trying to identify sources of mercury in their community.

Each chapter may be removed from the three ring binder, photocopied, and distributed to local trade associations or industries as you see fit. If you wish to adopt the SourceBook text to suit your own needs, please credit the Wisconsin Department of Natural Resources Mercury SourceBook (Draft), compiled by Kimberly Huber, EPA Grant #NP985072-01-1. Much of the information in the SourceBook is the work of other authors. When this is the case (the reference document title will appear in italics), please attribute the information to **both** the original author and indicate that it was found in the Wisconsin Mercury SourceBook (e.g., your citation would appear: “*Strategies for Mercury Control in Minnesota*, as quoted in *The Wisconsin Department of Natural Resources Mercury SourceBook* (Draft), compiled by Kimberly Huber, EPA Grant #NP985072-01-1”).

Remember, your work helped to make this SourceBook possible. Please help us keep it up-to-date by providing us with your final project reports, etc. We will include this information in future updates of the “Current Mercury Work” table and may include new case studies in future releases.

Information on mercury-containing products is provided for nineteen different sectors. In each chapter, you will find information on *specific* products that are associated with that sector. You will also find *general* information on mercury-containing products that are found in a variety of sectors (e.g., fluorescent lamps). This general information may be repeated from chapter to chapter. We decided to include the general information in each chapter so that you would have a complete, camera-ready resource for each sector.

GENERAL TIPS

If you are confused about a certain term (e.g., what is bioaccumulation?), consult the Glossary or the Index.

Product Information

- ★ To find information about where a *general* type of product may be found in a community (e.g., where could I find mercury-containing thermoelectric devices in my community?), consult the Product-Sector Table in “Identifying Sources” (Step 4 of Section Two).
- ★ To determine where a *particular* product may be found in a community (e.g., where could I find thermoregulators, a type of thermoelectric device?) consult the mercury product listing found in the Appendix.
- ★ For specific information about a particular product (e.g., what is a thermoregulator?) consult the text that accompanies an entry as found in the Index.

INTRODUCTION

It's slippery stuff

Some of you may remember playing with mercury when you were a child. Its silvery white shimmer was entrancing, and the ability of its glistening mass to split and come back together again was magical. But scientists are now beginning to realize that there is another side to mercury's wily nature. In fact, it is some of mercury's most elemental qualities that make it a difficult substance to handle.

Mercury is a common element that is found naturally in a free state or mixed into ores. It also may be present in rocks or released during volcanic activity. However, most of the mercury that enters the environment in Wisconsin comes from human uses.

Mercury has a number of very unique properties that have led to its widespread use in industry and products. Consider that mercury:

- ◆ is very dense (13.5 grams per cc, versus water with a density of 1 gm/cc)
- ◆ expands and contracts evenly with temperature changes
- ◆ has high electrical conductivity
- ◆ does not readily react with nonoxidizing agents
- ◆ is the only heavy metal that exists as a liquid at room temperature
- ◆ alloys with other metals (e.g., silver, copper, nickel, gold) to form amalgams
- ◆ vaporizes very easily
- ◆ is toxic to living organisms

(The Hunt for Quicksilver and Mercury in Minnesota Slide Show Script)

Mercury has been used in thousands of industrial, agricultural, medical, and household applications. Major uses of mercury include dental amalgams, tilt switches, thermometers, lamps, pigments, batteries, reagents, and barometers. When these products are thrown in the trash or flushed down a drain, the mercury doesn't

go away. Although the mercury may change forms, it doesn't break down because it is an element.

Small amounts of mercury can have serious impacts on natural systems. Mercury evaporates easily and travels in the atmosphere, and is deposited into

soils and lakes. The mercury that enters a lake accumulates in fish tissues and concentrates as larger fish eat smaller fish. A 22-inch Northern Pike weighing two pounds can have a mercury concentration as much as 225,000 times as high as the surrounding water. *(Strategies for Mercury Control in Minnesota)*

These concentrations are significant when one considers the toxic effects of mercury. Most humans are exposed to methylmercury, the most toxic form of mercury, through the consumption of fish.

Methylmercury interferes with the nervous system of the human body and can result in a decreased ability to walk, talk, see, and hear. In extreme examples, methylmercury has resulted in coma or death.

Many animals that eat fish also accumulate methylmercury. Mink, otters, and loons in Wisconsin have been found to have high levels of mercury in their tissue. Mercury can interfere with an animal's ability to reproduce, and lead to weight loss, or early death.

(Mercury in Minnesota Slide Show Script)

Due to its toxicity, persistence, and tendency to bioaccumulate in the environment, mercury has been classified by the International Joint Commission (US and Canada) as a persistent toxic substance subject to the requirements of the Great Lakes Water Quality Agreement. This agreement has been implemented through the IJC's "Virtual Elimination Strategy."

The good news is that the majority of products that use mercury purposefully have acceptable alternatives. For example, electric vacuum gage, expansion, or aneroid monitors are good alternatives to mercury blood pressure monitors. Mechanical switches, magnetic dry reed switches, and optic sensors can replace mercury tilt switches.

Replacing mercury-laden products with less toxic alternatives is referred to as *source reduction*. Source reduction allows us to eliminate the use of mercury in certain waste streams. This is especially beneficial considering the volatile nature of mercury, because mercury can transfer so easily from air to soil to water. It is also the most sensible option given the difficulty of determining quantitative loadings from point sources - it is easier to just eliminate mercury rather than fuss with "allowable levels."

Practicing source reduction in combination with recycling the mercury already in the waste stream can have a significant impact on reducing mercury levels in the environment. Identifying all the sources of mercury in your community can be a big task, but it can also be rewarding. Let's get working!

☞ A peat bog near Duluth, Minnesota has revealed that before 1900, mercury deposition was about one-tenth of what it became by mid-century (1935-1980); since 1980, levels have fallen by a third.

☞ This trend is very much in keeping with recent dated sediment cores from the Great Lakes, which show that mercury levels were extremely low in 1900, surged greatly thereafter, peaking between 1950 and 1970, and have fallen back a bit since.

-(Great Lakes Virtual Elimination Project, Frank Anscombe)

CONSIDER MERCURY'S WILY NATURE

- ◆ It is ubiquitous in the environment - present in soils, rocks, and water
- ◆ There are more than 2,000 applications of mercury in industry or consumer products
- ◆ It easily and rapidly changes forms in the environment to form several organic and inorganic states
- ◆ It transfers from the atmosphere to soil to water and back again

BIBLIOGRAPHY

This document was designed to be a collaboration of the best mercury information available to date. We are gratefully indebted to the work of authors below, without whose innovative and ground-breaking research this report would not be possible. Please note that many of these sources were quoted directly:

Great Lakes Virtual Elimination Project, Frank Anscombe, as published in National Forum on Mercury in Fish: Proceedings, USEPA Office of Water, June 1995. EPA 823-R-95-002

Mercury in Minnesota Slide Show Script, Western Lake Superior Sanitary District, November 1995

Mercury Pollution Prevention In Michigan: Summary of Current Efforts and Recommendations for Future Activities, The Michigan Mercury Pollution Prevention Task Force, April 1996

The Hunt for Quicksilver, presented at AERB's Wastewater Discharge Compliance Conference, November 17, 1992 by Frank Altmayer, Scientific Control Labs, Inc.

Strategies for Mercury Control in Minnesota, MPCA Mercury Task Force, July 1994

MERCURY IS A TOXIC SUBSTANCE OF SPECIAL CONCERN

Numerous detailed assessment procedures developed in Canada, the United States and elsewhere worldwide have identified chemicals that pose a threat and rank them according to the nature and extent of that threat. The Virtual Elimination Task Force, established under the U.S./Canadian International Joint Commission, established a classification and scoring scheme based on these assessments that focuses on production volume, bioaccumulation, and persistence. Based on these criteria, mercury has been chosen as a chemical targeted for “virtual elimination.”

Similarly, the Binational Program to Restore and Protect Lake Superior has identified mercury, along with chlordane, DDT, dieldrin, hexachlorobenzene, octachlorostyrene, PCBs, 2,3,7,8-TCDD, and toxaphene as chemicals of concern. (*A Strategy for Virtual Elimination of Persistent Toxic Substances, vol 1*)

The Virtual Elimination Task Force examined these lists and produced a set of criteria to screen, score, identify, and rank chemicals:

- ◆ **Amounts produced/used/released**
Production or releases of over 1,000,000 pounds
- ◆ **Presence/behavior in ecosystem including persistence, bioaccumulation, extent of distribution**
Persistence is described in terms of half-life; bioaccumulation is the tendency for a substance to be taken up by and accumulate in the tissues of biota and humans, measured by the bioaccumulation factor (BAF)
- ◆ **Chemical properties**
Chemical properties that may contribute to increased bioaccumulation
- ◆ **Toxicological properties**
Including short term effects (acute toxicity) and long term effects (chronic toxicity); reproductive, developmental, neurobehavioral, mutagenic, teratogenic and carcinogenic effects
- ◆ **Exposure potential**
Includes bioaccumulation potential, persistence, and amount of chemical that is produced and/or released to the environment
- ◆ **Threats to ecosystem integrity or evidence of cause-effect linkage between persistence toxic substances and biological injury**
Linkage of injury of selected species in the Great Lakes, posing a threat to the integrity of the ecosystem or a link between persistent toxic substances and human health problems

The Minnesota Pollution Control Agency has developed an indexing system to compare the potential environmental impacts of toxic substances emitted into the air. Out of a study of 183 substances, the MPCA determined that only dioxin poses a greater environmental hazard for equivalent amounts released into the air. Mercury scored high because 1) it does not degrade and has a tendency to bioaccumulate in food chains, and 2) mercury is a potent neurotoxin.

-Strategies for Mercury Control in Minnesota

The Minnesota Pollution Control Agency analyses of mercury damage costs provide rough estimates of the environmental harm caused by mercury emissions. Their 1995 estimates ranged from \$4,400 to \$9,800 per pound of mercury.

- Minnesota Pollution Control Agency Grant Request, Market-Based Incentive Grant Program, memo to Rick Tonelli, USEPA Region 5 from Peder Larson, MPCA, September 20, 1996

Mercury is identified as a targeted toxic substance in:

- ◆ The Priority Substances List of the Canadian Protection Act
- ◆ The List of Chemicals for ban or phase-out from the Canadian Ministry of Environment and Energy
- ◆ The list of 11 critical pollutants identified by the International Joint Commission for “Virtual Elimination”

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This document was designed to be a collaboration of the best mercury information available to date. We are gratefully indebted to the work of authors below, without whose innovative and ground-breaking research this report would not be possible. Please note that many of these sources were quoted directly:

Mercury in Wildlife, Charles F. Facemire, as published in *National Forum on Mercury in Fish: Proceedings*, USEPA Office of Water, June 1995. EPA 823-R-95-002

Strategies for Mercury Control in Minnesota, MPCA Mercury Task Force, July 1994

A Strategy for Virtual Elimination of Persistent Toxic Substances, Volume 1 and 2, International Joint Commission, August 1993

TARGET: WISCONSIN

POLLUTION PREVENTION ACTIVITIES

THE DEPARTMENT OF NATURAL RESOURCES

Ad Hoc Workgroup:

Leaders from a variety of bureaus in the DNR drafted a status report on mercury in Wisconsin's environment. This was intended to provide the Wisconsin Natural Resources Board and the public with information on mercury sources and levels in Wisconsin's environment and the potential effects of mercury bioaccumulation in aquatic ecosystem food chains. Some of the information included in this SourceBook originated from the Ad Hoc Committee report.

Energy Efficiency Workgroup:

A multi-state effort to work with utilities to develop a strategy to reduce mercury emissions from coal fired power plants.

Lake Superior Binational Program:

WDNR is working in partnership with a number of agencies to restore and protect this lake. Its Zero Discharge Demonstration

Project is working to eliminate discharges of nine toxic bioaccumulating substances (mercury is one of these pollutants). WDNR is also working to develop a Lakewide Management Plan (LaMP) for Lake Superior that will foster a basin wide ecosystem approach to resource management.

Special Research Projects:

The Wisconsin Department of Natural Resources has been monitoring mercury in the environment since the 1970s. Early studies focused primarily on mercury in wildlife and fish, and on point-source releases of mercury into Wisconsin waterways.

The Department is integrating mercury research from its various divisions and bureaus. Mercury levels have been quantified within ecological "pools" (humans, game fish, fur bearers, piscivorous birds, water, lake sediments, precipitation, etc.); however, relatively few rate of transfer measurements between pools exist.

Air Management:

Have air management write up a summary.

Wastewater:

The SourceBook you are not reading was designed to help implement The Bureau of Watershed Management's new Mercury Strategy. This new effort directs resources toward sources identification and pollution prevention efforts, and moves away from wastewater treatment plant effluent limits. The ultimate goal is to develop partnerships with communities to help them reduce their mercury discharges at the source through pollution prevention.

Solid Waste:

Brief description of Universal Waste rule/team.

Bureau of Cooperative Environmental Assistance:

The Bureau of Cooperative Environmental Assistance (CEA) works closely with The Solid and Hazardous Waste Education Center (SHWEC -- see below) in establishing educational priorities and carrying out training programs.

CEA is also spearheading a project for an integrated database that allows for direct comparison of Toxics Release Inventory, air,

water, and hazardous waste data. The data for mercury is represented in the “Sources of Mercury” chapter.

The Hazardous Waste Minimization Program operates a clearinghouse that distributes publications on waste reduction and pollution prevention. Some of the mercury-related publications mentioned in the following chapters are available free of charge through this service. An order form for these publications is included in the “Resources” chapter.

counties. Extension staff make contacts with local businesses and provide educational outreach and follow-up.

With funds from the Lake Michigan Federation and Citizens for a Better Environment, SHWEC developed the Greater Milwaukee and Southeast Wisconsin Pollution Prevention Information Exchange. The Exchange provides a forum for companies to exchange information about pollution prevention technologies.

Additionally, SHWEC administers the Great Lakes Technical Resource Library (GLTRL). GLTRL is a database of pollution prevention information that includes over 6,000 papers, pamphlets, books, audios, and videos, as well as information on more than 1,500 vendors and manufacturers of pollution prevention equipment and services.

SOLID AND HAZARDOUS WASTE EDUCATION CENTER

*The Solid and Hazardous Waste Education Center (SHWEC) at the University of Wisconsin-Extension provides waste reduction and pollution prevention assistance to Wisconsin businesses. Pollution prevention specialists assist companies with on-site pollution prevention assessments and provide telephone consultations, written reports, training seminars, workshops, and satellite teleconferences. The specialists work through the County Extension Offices which exist in all seventy-two Wisconsin

SHWEC formulated the Southeast District Pollution Prevention Action Plan. With funds from USEPA and the Wisconsin Department of Natural Resources, SHWEC developed pollution prevention priorities for southeast Wisconsin and conducted targeted training and waste reduction demonstration projects for industries in the area.

SHWEC is currently researching the use of mercury in hospital and clinic settings.

SHWEC also conducts pollution prevention assessments for companies. Each assessment includes information on pollutants generated, costs associated with the pollution, and costs associated with alternatives to the pollution, including prevention, treatment, and disposal. These services are provided free of charge.

GREATER MILWAUKEE TOXICS MINIMIZATION TASK FORCE

*The Greater Milwaukee Toxics Minimization Task Force (recently renamed the “Pollution Prevention Partnership”) is a non-profit organization whose goal is to minimize toxic pollutants entering the environment. The Task Force includes representatives from industry, business, labor, educational institutions, and environmental organizations as well as state and local governmental agencies and elected officials. The Task Force began its activities in 1989 as an advisory committee to the Milwaukee Metropolitan Sewerage District (MMSD).

The Task Force prepared a list of 25 recommendations to reduce the release of toxic substances into the Greater Milwaukee sewerage system and the surrounding environment. This set of recommendations and the process used to develop it have been recognized by the USEPA as a model for other communities to follow in developing toxics reduction programs.

THE HOUSEHOLD POLLUTION PREVENTION EDUCATION PROGRAM

*The Household Pollution Prevention Education Program was developed by the Lake Michigan Federation with financial assistance provided by MMSD. The purpose of the program is to educate the Greater Milwaukee community about reducing its use of hazardous household products and disposing of those products in a proper manner.

WISCONSIN FISH CONSUMPTION ADVISORIES

The Wisconsin Division of Health publishes a Fish Consumption Advisory. This advisory contains guidelines on how often sport fish can be safely eaten. There are now 260 lakes and more than 350 miles of rivers in Wisconsin that have fish consumption advisories because of mercury.

Approximately one out of every three waterbodies tested is listed on the advisory due to high levels of mercury in the fish. About ten to twelve sites are added each year.

Mercury levels in Wisconsin walleye average 0.48 parts per million. Panfish, such as perch or bluegill, average 0.19 parts per million. A more detailed description of Fish Consumption Advisories in Wisconsin is available under the "Health Effects" chapter.

** = from A Review of Pollution Prevention Efforts Compared to Pollution Prevention Needs in The Lake Michigan Basin, prepared for the Lake Michigan Forum by Clean Sites, July 1995*

SUMMARY OF WISCONSIN MERCURY REGULATIONS

(From *Mercury in Wisconsin's Environment: A Status Report*)

Air Management Mercury Regulations in Wisconsin

Mercury emissions in Wisconsin are regulated three main ways:

- 1 Prevention of Significant Deterioration (PSD) program, implemented through Chapter NR 405, Wis. Admin. Code.
- 2 Wisconsin's Hazardous Air Pollutant Control Rule, Chapter NR 445, Wis. Admin. Code.
- 3 National Emission Standard for Hazardous Air Pollutant (NESHAP), implemented through Chapter NR 446, Wis. Admin. Code.

The PSD program applies to all new major stationary sources and all major modifications of such sources in areas meeting air quality standards. This program details procedures for reviewing and issuing air pollution control permits for these facilities. The program aims to ensure that new emissions of 18 pollutants greater than a specified amount are controlled by what is considered the best available control technology. Mercury is one of the 18 pollutants listed. The specific amount for mercury is 0.10 tons (200 pounds) per year.

Wisconsin's Hazardous Air Pollutant Control Rule, Chapter NR 445, Wis. Admin. Code, provides public health protection for both acute (based on 2.4 percent of the Threshold Level Value), and chronic (based on reference concentration) health impacts associated with mercury inhalation. In this rule, the owners of sources emitting more than specifically-established mercury amounts, ranging from 7 to 294 pounds per year, must show that the public is not exposed to levels above the health-based inhalation limits.

Chapter NR 446 incorporates the federal mercury National Emission Standards for Hazardous Air Pollutants (NESHAP) into state code. Sludge dryers and sludge burners are subject to this regulation. Again, this standard is based on protecting the public from unacceptable mercury exposure due to direct inhalation. The way Wisconsin statutes are structured, we cannot apply a state standard for a hazardous air pollutant if a federal NESHAP preceded or was promulgated prior to state law.

None of these programs explores the indirect health exposure route or considers the bioaccumulative effects of mercury. Thus, Wisconsin's people and other animals are not protected from mercury exposure that may build up through the food chain.

Mercury and Wastewater Effluents in Wisconsin

The WDNR Wastewater Program has been regulating mercury in wastewater effluents since the 1980s, using the same approach as for other toxic substances. This approach imposes effluent limits in Wisconsin Pollution Discharge Elimination System (WPDES) permits if, based on effluent testing, there is reasonable potential that surface water quality criteria for the substance will be exceeded. “Reasonable potential” has come to mean any detection of mercury in effluents using a standard approved commercial method, since calculated numerical effluent limitations are often far below the lowest level that can be detected in water by standard analytical tests.

Wastewater influent to municipal treatment plants contains significant quantities of mercury. Most of this mercury is concentrated in wastewater biosolids during treatment. Since most treatment plants dispose of generated solids by land spreading, mercury enters the terrestrial environment by this process. Some of this mercury spread on land may, over time, be volatilized to the atmosphere.

We estimate that wastewater treatment plants in Wisconsin take in about 195 kg of Hg/year. Probably less than 2 percent of this amount is discharged in effluents directly to surface waters. The rest is concentrated in sludges, as just discussed. A small fraction may also enter the atmosphere.

There are no known economically feasible treatment technologies (other than the biological treatment that most municipal and some industrial entities already practice) that can reduce mercury to the low levels necessary to meet water quality based limits. Since analytical errors have long been suspected as the main cause for effluent mercury detections, permittees have expended much effort and cost attempting to demonstrate that either effluent limits are unnecessary, or that variances to water quality standards should be allowed.

Thus, regulating mercury has been an extremely time-intensive process for the Wastewater Program, and an unnecessary financial burden for the permittees (in the form of meaningless effluent testing and consultants’ and attorneys’ fees to avoid limits). All this for little or no mercury reduction benefit to the environment. That’s why the Department set out to develop a “New Mercury Strategy” for regulating mercury in wastewater.

Water quality protection

Wisconsin’s Administrative Code contains water quality criteria that are not to be exceeded in surface waters to ensure the protection of aquatic life, wildlife and human health. The Administrative Code also contains the translation of those criteria into numerical effluent limitations for point source wastewater discharges. These codes are in the process of being revised in response to the Great Lakes Water Quality Initiative.

Wisconsin Proposed Criteria (In parts per billion)

Aquatic life (acute)	0.83
Aquatic life (chronic)	0.44
Wildlife	0.0013
Humans	
(fish & aquatic life)	0.0015
Humans	
(limited aquatic life water)	336

Procedures in NR 106 specify how effluent limitations, based on water quality criteria in NR105, are determined. Since many of the state’s surface waters currently do not meet the above wildlife criteria, end-of pipe effluent limitations (if they are determined to be necessary to protect water quality) are most commonly equal to the wildlife criteria. Background mercury concentrations of many surface waters in the state exceed the wildlife criteria. When this is the case, the limit is 1) the wildlife criteria if the source of the wastewater discharged is groundwater, or 2) the background concentration if the source of the wastewater discharged is from the surface water.

The New Mercury Strategy for Regulating Mercury in Wastewater

(below from Tom's Mugar's Executive Summary of the New Watershed Management Mercury Strategy)

As part of Wastewater Permit Streamlining Implementation, a policy team established a new mercury approach that emphasizes real environmental benefit and avoids unnecessary effort by WDNR and permittees.

The new approach sets up four levels of pollutant minimization programs for municipal entities, based on facility size (mass loadings), sludge mercury concentration, and sensitivity of receiving waters. Recommendations for industrial facilities are also provided. The approach focuses on source identification and pollution prevention rather than effluent limitations and monitoring, although there may still be some circumstances where traditional effluent limits are appropriate.

The benefits of this approach are that it:

- ◆ Directs Department and permittee attention towards achieving real reductions in mercury releases to the environment through pollution prevention techniques at the most important sources of mercury;
- ◆ Eliminates requirements for permittees to perform effluent testing for mercury using methods not sensitive enough to provide meaningful results; and
- ◆ Reduces Department and permittee effort and expense associated with permittee attempts to keep limits out of their permits or seek higher limits, yet continues to use the WPDES permit to require mercury source identification and reduction.

In addition to this strategy to limit mercury emissions, the Wisconsin Legislature passed two laws in 1993: One limits the mercury content in batteries and requires manufacturers to inform consumers of the need for proper disposal and to identify and publicize authorized sites to dispose of batteries containing mercury. The other bans the sale of toys containing toxic substances, including mercury. This was designed to stop the sale of a popular hand-held toy called "Quicksilver Maze" which contained elemental mercury as the maze medium. This same law prohibited the sale of tennis shoes with light-up heels containing mercury switches.

WHY IS IT IMPORTANT TO REDUCE MERCURY RELEASES TO WATER?

- ★ Because of mercury's bioaccumulation and cycling patterns in the environment, the reduction of any amount of mercury is important
- ★ Mercury emissions to water originate from sources that are largely preventable. It can be very expensive (EPA and EPRI estimates range from \$5,000 to \$174,000 per pound!) to install and maintain technologies to reduce mercury emissions that come from coal-fired plants. It is more cost-effective to eliminate mercury from processes where mercury is an optional ingredient, or where alternatives to mercury use exist.
- ★ Great progress can be made with source reduction efforts. For example, the Western Lake Superior Sanitary District has been able to reduce the mercury loadings to their plant by one half
- ★ Mercury reduction efforts clearly need to be a multi-media effort because of mercury's cycling patterns

BIBLIOGRAPHY

This document was designed to be a collaboration of the best mercury information available to date. We are gratefully indebted to the work of authors below, without whose innovative and ground-breaking research this report would not be possible. Please note that many of these sources were quoted directly:

Mercury in Wisconsin's Environment: A Status Report, WDNR, May 1996

Mercury, Power Plants and the Environment: Basic Facts about Mercury and Coal-fired Power Plants, the Environment, Fish and Wildlife, and Human Health, compiled by Steven Ugoretz, WDNR

Quantification of Total Mercury Discharges from Municipal Wastewater Treatment Plants the Wisconsin Surface Waters, by Thomas Muga, WDNR, May 1993

A Review of Pollution Prevention Efforts Compared to Pollution Prevention Needs in The Lake Michigan Basin, prepared for the Lake Michigan Forum by Clean Sites, July 1995

Wisconsin Strategy for Regulating Mercury in Wastewater, WDNR, December 1995

TARGET: THE GREAT LAKES

THE GREAT LAKES

Volume

Six quadrillion gallons of fresh water; one-fifth of the world's fresh surface water (only the polar ice caps and Lake Baikal in Siberia contain more); 95 percent of the U.S. supply. Spread evenly across the continental U.S., the Great Lakes would submerge the country under about 9.5 feet of water.

Total Area

More than 94,000 square miles/244,000 square kilometers of water (larger than the states of New York, New Jersey, Connecticut, Rhode Island, Massachusetts, Vermont, and New Hampshire combined, or about 23 percent of the province of Ontario). About 295,000 square miles/767,000 square kilometers in the watershed (the area where all the rivers and streams drain into the lakes).

Total Coastline

United States and Canada — 10,900 mi/17,549 km (including connecting channels, mainland and islands). The Great Lakes shoreline is equal to almost 44 percent of the circumference of the earth, and Michigan's Great Lakes coast totals 3,288 mi/5,294 km, more coastline than any state but Alaska.

- ★ Lake Erie
- ★ Lake Huron
- ★ Lake Michigan
- ★ Lake Ontario
- ★ Lake Superior

(Source: web site, Great Lakes Environmental Atlas, Environment Canada; Great Lakes Basin brochure, 1990, Michigan Sea Grant.)

The Great Lakes are an area of special concern with mercury pollution. The atmosphere is a significant pathway for mercury entering into these lakes. Loadings of atmospheric mercury most likely come from a large number and variety of sources, some of which are area sources and some are point sources. Although atmospheric source regions for air deposition to the Great Lakes extend as far west as Washington state, as far north as the Arctic, as far south as Florida, and as far east as Labrador (*Air Deposition of Pollutants in Water Bodies: Case Studies and Options Analysis Report, prepared for USEPA Water Policy Branch by Susan April, Kelly Lukins and Andrew Macdonald, Kerr and Associates, June 1994*), 60 percent of upper midwest deposition is regional (*Ed Swain, presenting at the Energy Efficiency Workgroup Meeting, February 1996*). Therefore reduced mercury emissions can have a regional impact.

MERCURY AND THE GREAT LAKES

(from GLNPO, Monitoring the Great Lakes: Metal Concentrations in Sediments, January 1996)

- ◆ Anthropogenic input of mercury is observable in sediments of the Great Lakes
- ◆ Build-up of anthropogenically derived metals in the Great Lakes started in the early 1800s.
- ◆ Lake Superior has been the least impacted by anthropogenic metal inputs, and Lake Ontario has been impacted the most.
- ◆ Lake Ontario sediments contain significantly more mercury than Lakes Superior and Michigan.
- ◆ The rate of anthropogenic input of mercury is decreasing in Lakes Superior, Michigan, and Ontario. The date of peak accumulation (ng/m²-yr) of mercury vary among the Lakes and are for Lakes Superior, Michigan, and Ontario, 1965, 1973, and 1967, respectively.
- ◆ Natural inputs of mercury account for less than 50% of the current input. In the case of mercury accumulation in Lake Ontario, natural input is very low (11%).
- ◆ The atmosphere is a significant source (>50%) for mercury in Lakes Superior and Michigan.

LAKE SUPERIOR

Length - 350 miles / 563 km.

Breadth - 160 miles / 259 km.

Average Depth - 489 ft. / 149 m.

Maximum Depth - 1,335 ft. / 407 m. maximum

Volume - 2,934 miles / 12,230 km. cubed

Water Surface Area - 31,700 sq. miles / 82,100 sq. km.

Drainage Basin Area - 49,300 sq. miles / 127,700 sq. km.

Shoreline Length (including islands) - 2,726 miles / 4,385 km.

Elevation - 600 ft. / 183 m.

Outlet - St. Mary's River to Lake Huron

Retention/Replacement Time - 191 years

Lake Superior is the largest of the Great Lakes in surface area and volume. Water flows into the lake from many small rivers and streams. Each year a small percentage of the lake's water flows out through the St. Mary's River, and it takes almost two centuries for the water to be completely replaced (retention time).

(Source: Web site, <http://www.great-lakes.net:2200/refdesk/almanac/lakes/supfact.html> Lake Superior brochure, 1990, Michigan Sea Grant.)

Mercury Loadings to Lake Superior

(Doug Knauer, presenting at the Energy Efficiency Workgroup Meeting, February 1996)

Atmospheric loading	800	kg/year
Watershed loading	354	kg/year
Direct Point Sources loading	<u>< 1</u>	kg/year
Total	1,155	kg/year

Effects of Pollution on Lake Superior

(Source: Lake Superior Lamp Vol. II, Stage I)

The Wisconsin Department of Natural Resources has issued consumption advisories for all Wisconsin waters within lake Superior for all lake trout, including siscowet, and for all walleyes. These advisories are based on levels of mercury and PCBs in these fish. The WDNR has also issued advisories to limit the consumption of walleyes for the St. Louis River because of high mercury levels.

The Michigan Department of Public Health has issued "no consumption" advisories for lake trout greater than 30 inches in length and all sizes of siscowet because of high levels of mercury and polychlorinated biphenyls (PCBs), chlordanes, and toxaphene (Michigan Department of Natural Resources 1995). However, the PCB consumption advisory was dropped in 1996.

The Minnesota Department of Health has issued consumption advisories for northern pike, white suckers, and walleyes in the St. Louis River as a result of high levels of mercury, PCBs, and dioxin (MNDH 1992).

In Thunder Bay, the commercial fishery for lake trout was closed in the early 1970s because of high mercury levels, and the Siscoewt fishery has been closed since 1978 because of mercury and PCBs. In Jackfish bay, lake trout consumption was historically restricted because of mercury and PCBs, but restrictions for mercury and PCBs were lifted in 1991 because levels of these contaminants had dramatically declined.

SPECIAL MERCURY REDUCTION EFFORTS IN THE LAKE SUPERIOR BASIN

(from web site: <http://www.great-lakes.net:2200/partners/LSBP/lspbintr.html>)

An Introduction to the Lake Superior Binational Program

In September 1991 at the International Joint Commission's (IJC) biennial meeting in Traverse City, Michigan, Canada, and the United States, as parties to the Great Lakes Water Quality Agreement, announced the Binational Program Resource and Protect The Lake Superior Basin. The program was developed by the governments of Canada and the United States in cooperation with Michigan, Minnesota, Wisconsin, and Ontario in response to the IJC's challenge in 1989 to use Lake Superior as a "zero discharge demonstration area" for persistent, bioaccumulative toxic substances. The program commits the governments to an action plan that recognizes the need to build upon partnerships and incorporate the expertise of industry, municipalities, universities, native groups, environmental groups, and other interested individuals. The goal of the Binational Program is to protect, and where necessary restore, the integrity of Lake Superior's ecosystem through pollution prevention, enhanced regulatory measures, and remedial programs. The parties have committed to working on joint binational incentives. **

Program Components of The Binational Program Task Force

The Task Force consists of senior agency representatives who make policy decisions related to Lake Superior. The Task Force serves as a steering committee and is responsible for program delivery.

Superior Work Group

The Work Group is comprised of technical experts who represent various agencies and organizations that manage Lake Superior water resources. The Work Group reports to the Task Force.

Binational Forum

The Forum is a group of Lake Superior citizen "volunteers" who make recommendations to the governments and provide governments with additional advice and input. The forum consists of stakeholders in the basin: representatives from environmental and native groups, industries, and municipalities.

Public

Public involvement is crucial to the success of the program. Members of the public are encouraged to become involved through the Forum and other groups, and as individuals.

A Sampling of Agencies and Organizations Participating in Superior Work Group Meetings

Lake Superior Binational Program

Binational

- International Joint Commission

Federal

Canadian Agencies

- Environment Canada
- Canada Department of Fisheries and Oceans
- Health and Welfare Canada

U.S. Agencies

- U.S. Environmental Protection Agency
- U.S. Fish and Wildlife Service
- U.S. Forest Service
- U.S. Geological Survey
- U.S. National Park Service

Provincial/State

Provincial Agencies

- Ontario Ministry of Environment and Energy
- Ontario Ministry of Natural Resources

State Agencies

- Michigan Department of Environmental Quality
- Minnesota Pollution Control Agency
- Minnesota Department of Transportation
- Wisconsin Department of Natural Resources

Tribal

- 1854 Authority
- Chippewa-Ottawa Treaty Fisheries Management Authority
- Great Lakes Indian Fisheries and Wildlife Commission

(<http://www.great-lakes.net:2200/partners/LSBP/zero/pollprev.html>)

Pollution Prevention Projects in the Lake Superior Basin

Since the governments announced the Lake Superior Binational Program, many pollution prevention projects have been initiated, including the following:

- ◆ A Binational Pollution Prevention Strategy (1995), with common goals and direction for P2 activities to reduce or eliminate nine identified toxic substances. Mercury is one of the toxic substances identified.
- ◆ “Twinning” (partnership) meetings between the cities of Duluth and Thunder Bay, to foster the exchange of P2 information, knowledge and expertise.
- ◆ P2 technical assistance provided by each jurisdiction to businesses and municipalities, via outreach materials, workshops and site visits.
- ◆ Collections of household hazardous waste and agricultural hazardous waste around the lake, in each of the three states and in Ontario.
- ◆ A mentoring program in which the Western Lake Superior Sanitary District (WLSSD) in Duluth, Minnesota helps other municipalities reduce toxic releases.
- ◆ Development and distribution of educational materials about PCBs (polychlorinated biphenyls) and mercury.
- ◆ Partnerships with industries, trade associations, building contractors and others to encourage the proper collection and disposal of mercury-containing products, and to promote the use of alternative products.
- ◆ A zero discharge demonstration pilot project by WLSSD, to test the concept that a discharger can achieve zero discharge/zero emission of mercury.
- ◆ A Virtual Elimination Project for mercury and PCBs, sponsored by the U.S. Environmental Protection Agency (USEPA), to see if current regulatory and non-regulatory structures are adequate to virtually eliminate these substances in the Great Lakes basin.
- ◆ The Lake Superior Pollution Prevention Strategy Implementation Plan (1995), by Michigan, Minnesota, Wisconsin and USEPA, recommending P2 activities that the governments could promote to help achieve the goals of the Binational Program.

Target Areas for Pollution Prevention

Action Areas for Pollution Prevention in the Binational Pollution Prevention Strategy include education, substitution, product stewardship, conservation, and bans and phase-outs. Recommended P2

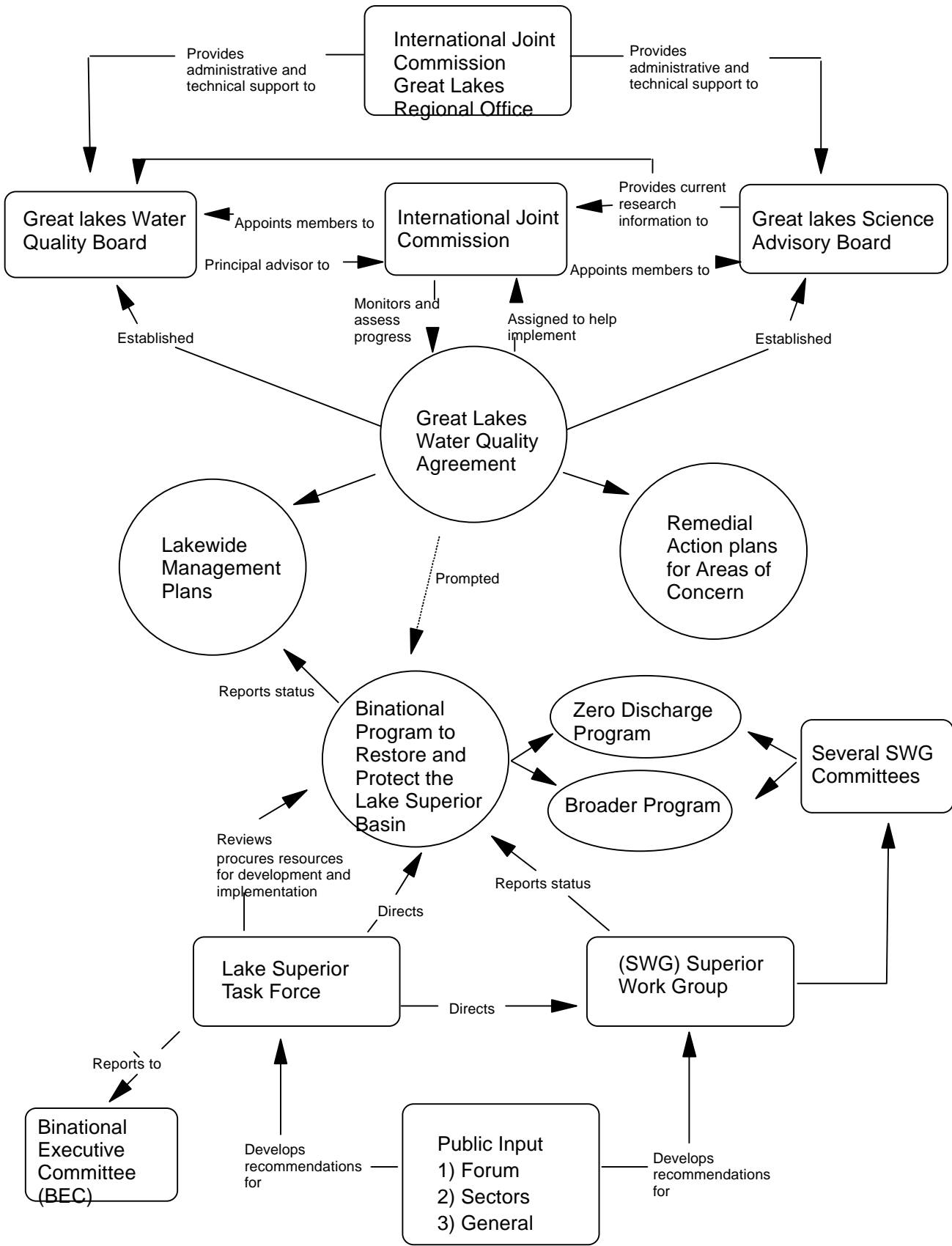
activities that need funding include the following:

- ★ Ambient (background) and precipitation monitoring for mercury, to support current monitoring of mercury emissions from basin smokestacks.

- ★ Consumer education and awareness about mercury-containing products and their proper disposal.

- ★ Curricula for elementary education.

- ★ An evaluation of programs designed to reduce energy usage in the basin.



LAKE MICHIGAN

Length - 307 miles / 494 km.

Breadth - 118 miles / 190 km.

Ave. Depth - 279 ft. / 85 m

Max. Depth - 925 ft. / 282 m.

Volume - 1,180 miles / 4,920 km. cubed

Water Surface Area - 22,278 sq. miles / 57,750 sq. km.

Drainage Basin Area - 45,598 sq. miles / 118,100 sq. km.

Shoreline Length (including islands) - 1,659 miles / 2,670 km.

Elevation - 581 ft. / 177 m.

Outlet - Straits of Mackinac to Lake Huron

Retention/Replacement Time - 99 years

★ Lake Michigan is the third largest Great Lake and the sixth largest freshwater lake in the world.

★ Because Lake Michigan is joined to Lake Huron at the Straits of Mackinac, they are considered one lake hydrologically.

★ Lake Michigan's cul-de-sac formation means that water entering the lake circulates slowly and remains for a long time (retention) before it leaves the basin through the Straits of Mackinac.

★ The northern part of the Lake Michigan watershed is covered with forests, sparsely populated, and economically dependent on natural resources and tourism, while the southern portion is heavily populated with intensive industrial development and rich agricultural areas along the shore.

★ The world's largest freshwater dunes line the lakeshore.

(References : Lake Michigan brochure, 1990, Michigan Sea Grant. Maintained by Bonnie Bouman bouman@glc.org <http://www.great-lakes.net:2200/refdesk/almanac/lakes/michfact.html>)

Pollution Prevention Projects in the Lake Michigan Basin

*With funds from the lake Michigan Federation and Citizens for a Better Environment, SHWEC developed the Greater Milwaukee and Southeast Wisconsin Pollution Prevention Information Exchange. The Exchange provides a forum for companies to exchange information about pollution prevention technologies.

SHWEC formulated the Southeast District Pollution Prevention Action Plan. With funds from USEPA and the Wisconsin Department of Natural Resources, SHWEC developed pollution prevention priorities for southeast Wisconsin and conducted targeted training and waste reduction demonstration projects for industries in the area.

*The Greater Milwaukee Toxics Minimization Task Force is a non-profit organization whose goal is to minimize toxic pollutants entering the environment. The Task Force includes representatives from industry, business, labor, educational institutions, and environmental organizations as well as state and local governmental agencies, and elected officials. The Task Force began its activities in 1989 as an advisory committee to the Milwaukee Metropolitan Sewerage District (MMSD).

Pollution Prevention Projects in the Lake Michigan Basin, continued

The Task Force prepared a list of 25 recommendations to reduce the release of toxic substances into the Greater Milwaukee sewerage system and the surrounding environment. This set of recommendations and the process used to develop it have been recognized by the USEPA as a model for other communities to follow in developing toxics reduction programs.

*The Household Pollution Prevention Education Program was developed by the Lake Michigan Federation with financial assistance provided by MMSD. the purpose of the program is to educate the Greater Milwaukee community about reducing its use of hazardous household products and disposing of those products in a proper manner.

* = from *A Review of Pollution Prevention Efforts Compared to Pollution Prevention Needs in The Lake Michigan Basin*, prepared for the Lake Michigan Forum by Clean Sites, July 1995

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This document was designed to be a collaboration of the best mercury information available to date. We are gratefully indebted to the work of authors below, without whose innovative and ground-breaking research this report would not be possible. Please note that many of these sources were quoted directly:

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Lake Superior Brochure, web site: <http://www.great-lakes.net:2200/refdesk/almanac/lakes/supfact.html>, Michigan Sea Grant, 1990

Lake Superior Lakewide Area Management Plan, Vol. II, Stage 1

Lake Superior Pollution Prevention Strategy, Lake Superior Pollution Prevention Team, October 1993

Monitoring the Great Lakes: Metal Concentrations in Sediments, GLNPO, January 1996

A Review of Pollution Prevention Efforts Compared to Pollution Prevention Needs in The Lake Michigan Basin, prepared for the Lake Michigan Forum by Clean Sites, July 1995

Organizations and Agencies -- Current Mercury Work

Chicago Metropolitan Sewerage District (proper name?)

Council of Great Lakes Governors

Detroit Water and Sewerage Department

EPA (Environmental Protection Agency)

Electric Utilities

GLNPO (Great Lakes National Program Office)

Honeywell

IDEM (Indiana Department of Environmental Management)

IL DNR (Illinois Department of Natural Resources)

MDEQ (Michigan Department of Environmental Quality)

MN (Minnesota) **Department of Agriculture**

MPCA/OEA (Minnesota Pollution Control Agency/Minnesota Office of Environmental Assistance)

Michigan Technical University - Houghton

MnTAP (Minnesota Technical Assistance Program)

Monroe County Health Department

NW (Northwest Wisconsin) **Regional Planning Commission**

NWF (National Wildlife Federation)

Northern Michigan University - Marquette

Northland College

Potlatch Corporation

Public Service Commissions

SHWEC (Solid and Hazardous Education Center - Wisconsin)

Terrene Institute

University of Minnesota - Duluth

University of Michigan

WDNR (Wisconsin Department of Natural Resources)

WI DATCAP (Wisconsin Department of Agriculture, Trade, and Consumer Protection)

WLSSD (Western Lake Superior Sanitary District)

Current Mercury Work

Business Outreach/Research	
<p>Project: <i>Lake Superior Partnership</i></p> <p>Description: Multi-Media compliance and pollution prevention inspections in the Lake Superior Basin</p> <p>Agencies working on this project: MPCA/OEA WLSSD</p>	
<p>Project: <i>Minnesota Very Small Quantity Generator Program</i></p> <p>Description: Provide pollution prevention information for very small quantity hazardous waste generators in Minnesota</p> <p>Agencies working on this project: MPCA/OEA</p>	
<p>Project: <i>Pollution Prevention Opportunity Assessment and Database Needs Survey</i></p> <p>Description: Target pollution prevention for small and medium sized businesses</p> <p>Agencies working on this project: University of MN - Duluth</p>	
<p>Project: <i>RCRA Hazardous Waste Great Lakes Initiative</i></p> <p>Description: Technical assistance and multimedia pollution prevention audits of hazardous waste generators in Lake Superior and Lake Michigan Basins</p> <p>Agencies working on this project: WDNR</p>	
<p>Project: <i>Small Business Technical Assistance Model</i></p> <p>Description: Technical Assistance strategy for the Lake Superior Basin</p> <p>Agencies working on this project: MPCA/OEA WLSSD</p>	
<p>Project: <i>Technical Assistance Audits for Municipalities and Industries</i></p> <p>Description: Target industries to provide training on basic pollution prevention concepts; perform free, non-regulatory pollution prevention audits and demonstration projects</p> <p>Agencies working on this project: MDEQ SHWEC</p>	

Current Mercury Work

Collection Programs	
<p>Project: <i>Button Battery Collection</i></p> <p>Description: Battery collection through recycling programs, retain establishments, and public education</p> <p>Agencies working on this project: WLSSD</p>	
<p>Project: <i>Clean Sweeps of Waste Pesticides</i></p> <p>Description: Minnesota, Wisconsin and Michigan all run pesticide collection programs</p> <p>Agencies working on this project: MN Department of Agriculture WI DATCAP</p>	
<p>Project: <i>Household Hazardous Waste Collection Program</i></p> <p>Description: Collection, transportation and disposal of agricultural and household hazardous wastes in MI, MN, and WI in 1995</p> <p>Agencies working on this project: MDEQ MPCA/OEA WDNR</p>	
<p>Project: <i>Mercury and PCBs: Outreach and Collection</i></p> <p>Description: Outreach and collection program with a pilot collection program in the Lake Superior Basin</p> <p>Agencies working on this project: MPCA/OEA</p>	
<p>Project: <i>Minnesota Pilot Project for the Management of Hazardous Waste</i></p> <p>Description: Honeywell collects used mercury thermostats through merchants, who will not be regulated as hazardous waste generators</p> <p>Agencies working on this project: Honeywell MPCA/OEA</p>	
<p>Project: <i>Minnesota-Wisconsin Household Hazardous Waste Collection</i></p> <p>Description: WLSSD will run a permanent household hazardous waste collection facility for WI and MN residents</p> <p>Agencies working on this project: WLSSD</p>	
<p>Project: <i>NW Wisconsin Permanent Household Hazardous Waste Collection Center</i></p> <p>Description: Mobile collection service for northwest Wisconsin counties</p> <p>Agencies working on this project: NW (WI) Regional Planning Commission</p>	

Current Mercury Work

General Outreach/Research	
<p>Project: <i>Grand Calumet River Districts Project</i></p> <p>Description: Addresses sources that directly discharge cooper, lead, and mercury into the Grand Calumet River and Nearshore Lake Michigan Area of Concern. Provides pollution prevention training to indirect dischargers and industrial users</p> <p>Agencies working on this project: IDEM</p>	
<p>Project: <i>MercAlert</i></p> <p>Description: Mercury education and waste reduction program focusing on dentists and the general public</p> <p>Agencies working on this project: WLSSD</p>	
<p>Project: <i>Mercury Reduction Reduction for Tribes</i></p> <p>Description: EPA is in the proces of finalizing an \$85,000 grant award under the Environmental Justice through Pollution Prevention grant program to a group in Minnesota to work on mercury reduction for tribes in MN, WI, MI</p> <p>Agencies working on this project: MPCA/OEA</p>	
<p>Project: <i>Mercury and PCBs: Outreach and Collection</i></p> <p>Description: Outreach and collection program with a pilot collection program in the Lake Superior basin</p> <p>Agencies working on this project: MPCA/OEA</p>	
<p>Project: <i>Public Awareness Campaign for Lake Superior and Lake Michigan</i></p> <p>Description: Unified pollution prevention public awareness campaign; developed literature</p> <p>Agencies working on this project: IDEM MDEQ MPCA/OEA WDNR</p>	
<p>Project: <i>Public Education/Awareness</i></p> <p>Description: As part of Detroit’s Mercury minimization Program, DWSD is implementing community awareness programs that encourage proper disposal of contaminants. P² program for households.</p> <p>Agencies working on this project: Detroit Water and Sewerage Department</p>	

Current Mercury Work

Science/Technology	
<p>Project: <i>Data Acquisition: Emissions from Landfills</i></p> <p>Description: Air Quality Division and Ground Water/Solid Waste Division are testing total and methylmercury levels in gases and leachate</p> <p>Agencies working on this project: MPCA/OEA</p>	
<p>Project: <i>Household Hazardous Waste Stream Assessment</i></p> <p>Description: Establishes an indicator system for tracking mercury used in products</p> <p>Agencies working on this project: MPCA/OEA</p>	
<p>Project: <i>Other Current Mercury Monitoring Activities</i></p> <p>Description: Regional air monitoring network; monitoring and mass balance study of Lake Michigan; Doug's computer mass balance work (title? lead?)</p> <p>Agencies working on this project: GLNPO University of Michigan</p>	
<p>Project: <i>Regional Air Pollution Database (RAPIDS)</i></p> <p>Description: Inventory of toxic pollutants of concern to the Great Lakes</p> <p>Agencies working on this project: EPA IL DNR MDEQ MPCA/OEA WDNR</p>	
Specific Outreach/Research	
<p>Project: <i>Rochester Embayment Watershed Mercury Pollution Prevention Program</i></p> <p>Description: Focus on hospital mercury sources and alternatives</p> <p>Agencies working on this project: Monroe County Health Department</p>	
Sector: Chemicals and Chemical Preparations	
<p>Project: <i>Mercury Reduction through Treatment Chemical Selection</i></p> <p>Description: Study of caustic soda, ferric chloride, and sulfuric acid use to determine levels of mercury from different manufacturing processes</p> <p>Agencies working on this project: MPCA/OEA</p>	

Current Mercury Work

Specific Outreach/Research	
Sector: Colleges, Universities, and Professional Schools	
<p>Project: <i>“Cool It” Program</i></p> <p>Description: National campus outreach program focusing on transportation and campus procurement policies</p> <p>Agencies working on this project: MWF</p>	
<p>Project: <i>Groundwater Education in Michigan Program</i></p> <p>Description: Initiating pollution prevention strategies for batteries, fluorescent tubes, and chemicals on campus</p> <p>Agencies working on this project: Michigan Technical University - Houghton</p>	
<p>Project: <i>Northern Michigan University Waste Flow Reduction and Consolidation Project</i></p> <p>Description: Reduction and consolidation of waste flows from main campus and university medical facility</p> <p>Agencies working on this project: Northern Michigan University - Marquette</p>	
<p>Project: <i>Northland College - Zero Discharge Campus</i></p> <p>Description: Education, pollution prevention, and sustainable development for reducing and eliminating toxic substances</p> <p>Agencies working on this project: NWF Northland College</p>	
Sector: Dairy Farms	
<p>Project: <i>Mercury at Dairy Farms</i></p> <p>Description: A fact sheet establishes a baseline for the amount of mercury currently used in the dairy industry. Further efforts will analyze the efficiency of non-mercury gauges, prepared outreach material, and training workshops</p> <p>Agencies working on this project: MnTAP</p>	
Sector: Dentists	
<p>Project: <i>Lake Superior Pollution Prevention Pilot</i></p> <p>Description: A focus area of dentist and hospital outreach and product education/collection was targeted for 1996 projects</p> <p>Agencies working on this project: WDNR</p>	

Current Mercury Work

Specific Outreach/Research	
Sector: Dentists	
Project:	<i>MercAlert</i>
Description:	Mercury education and waste reduction program, focusing on dentists and the general public
Agencies working on this project:	WLSSD
Project:	<i>Targeted Initiative: Dentists</i>
Description:	Outreach effort and study of recycling/disposal procedures; best management practice document
Agencies working on this project:	WLSSD
Project:	<i>Lake Superior Implementation Plan Team</i>
Description:	A focus area of dentist and hospital outreach was targeted for 1996 projects
Agencies working on this project:	MPCA/OEA WDNR
Project:	<i>Study of Dentist Mercury Use and Alternatives</i>
Description:	A section of the M ² P ² Task Force examined sources and alternatives for mercury use in dental settings. Includes a table of amalgam alternatives, collection of bulk mercury from dentist offices, and research
Agencies working on this project:	MDEQ
Project:	<i>Mercury Minimization from Dental Facilities</i>
Description:	As part of Detroit's Mercury Minimization Program, DWSD is establishing collaborative voluntary efforts with the ADA, the MDA, and the Detroit District Dental Society. Task Force of 20 members. Bulk mercury collection.
Agencies working on this project:	Detroit Water and Sewerage Department
Sector: Food Preparations	
Project:	<i>Targeted Initiative: Food Industry</i>
Description:	Study of production of organic chemical use (malic acid and fumaric acid) for the food industry. Potassium hydroxide may be the potential mercury source
Agencies working on this project:	WLSSD

Current Mercury Work

Specific Outreach/Research	
Sector: General Medical and Surgical Hospitals	
Project: Description: Agencies working on this project:	<p><i>Data Acquisition: Emissions from Medical Waste Incinerators</i></p> <p>Two year study of emissions from three rural hospital completed in 1991</p> <p>MPCA/OEA</p>
Project: Description: Agencies working on this project:	<p><i>Mercury Health Care Outreach</i></p> <p>“The Case Against Mercury: Diagnosis, Treatment, Alternatives,” a regional educational/outreach brochure for hospitals, nursing homes, and doctor’s offices</p> <p>EPA</p>
Project: Description: Agencies working on this project:	<p><i>Mercury Pollution Prevention in the Medical Waste Stream</i></p> <p>Targeted education and outreach, promoting awareness, partnerships, and recycling</p> <p>EPA MEQ MPCA/OEA Terrene Institute WDNR</p>
Project: Description: Agencies working on this project:	<p><i>Mercury Pollution Prevention Education and Technical Assistance for Medical Facilities in Wisconsin</i></p> <p>EPA-funded grant for SHWEC to distribute information to hospitals; develop hospital task forces, assessment programs, and workshops</p> <p>SHWEC</p>
Project: Description: Agencies working on this project:	<p><i>Grant and Working Partnership to Reduce Health Care Mercury Emissions</i></p> <p>EPA (GLNPO) funded grant to reduce/eliminate mercury use in health care establishments. Will produce a plan for reduction and will educational activities and workshops</p> <p>NWF</p>
Project: Description: Agencies working on this project:	<p><i>Study of Healthcare Sources and Alternatives</i></p> <p>A section of the Michigan Mercury Pollution Prevention Task Force examine sources and alternatives for mercury use in health care settings. Includes 6 case studies.</p> <p>MDEQ</p>
Project: Description: Agencies working on this project:	<p><i>Outreach to Medical Waste Incinerators</i></p> <p>“MDEQ-EAD received an EPA grant to do education outreach to medical waste incinerators in southeast Michigan</p> <p>MDEQ</p>

Current Mercury Work

Specific Outreach/Research
Sector: General Medical and Surgical Hospitals
<p>Project: <i>Mercury Minimization for Hospitals</i></p> <p>Description: As part of Detroit's Mercury Minimization Program, DWSD is establishing a pilot program to determine the effectiveness of voluntary reduction efforts. Three hospitals are participating in the pilot.</p> <p>Agencies working on this project: Detroit Water and Sewerage Department</p>
Sector: Golf Courses
<p>Project: <i>Green Thumb Project</i></p> <p>Description: Highlights ways in which non-point source run-off from the use of toxic-containing products can affect wastewater treatment plants. Examines use of unused stock of mercury-containing pesticides</p> <p>Agencies working on this project: WLSSD</p>
Sector: Industrial Launderers
<p>Project: <i>Industrial Laundry Study</i></p> <p>Description: Found measurable levels of mercury in liquid bleaches with assistance from Chicago</p> <p>Agencies working on this project: WLSSD</p>
<p>Project: <i>Mercury Minimization for Laundries</i></p> <p>Description: As part of Detroit's Mercury Minimization Program, DWSD is establishing a pilot program to determine chemicals used in the laundry that contain mercury (two were found). One facility is participating in the pilot.</p> <p>Agencies working on this project: Detroit Water and Sewerage Department</p>
Sector: Miscellaneous Business Services - Commercial Testing Laboratories
<p>Project: <i>Mercury Minimization for Laboratories</i></p> <p>Description: As part of Detroit's Mercury Minimization Program, DWSD is investigating mercury use in their analytical laboratory to eliminate contributions from chemicals, reagents, and equipment. Did audit; developing list of alternatives</p> <p>Agencies working on this project: Detroit Water and Sewerage Department</p>
Sector: Miscellaneous Manufacturing Industries
<p>Project: <i>Mercury Audit Fact Sheet</i></p> <p>Description: Mercury reduction audit fact sheet for manufacturing facilities</p> <p>Agencies working on this project: SHWEC</p>

Current Mercury Work

Specific Outreach/Research	
Sector: Motor Vehicles and Moter Vehicle Equipment	
Project:	<i>Auto Industry Pollution Prevention Project</i>
Description:	Partnership between MDNR, Chrysler, Ford, and General Motors to promote voluntary reduction of persistent toxic chemicals in the Great Lakes region. Coordinated by the American Automobile Manufacturers Association.
Agencies working on this project:	MDEQ
Sector: Motor Vehicles - Truck and Bus Bodies	
Project:	<i>Monitoring Programs: Automobile Salvage Yard Issues</i>
Description:	1991 Task Force gathered information, developed list of applicable environmental regulations, and developed best management practices. Also grant program to examine alternative management for shredder residue
Agencies working on this project:	MPCA/OEA
Sector: Paper Mills	
Project:	<i>Potlach Mercury Pollution Prevention Project</i>
Description:	Identification of mercury sources in pulp mill wastewater; source reduction pilot at Potlach
Agencies working on this project:	Potlach University of MN - Duluth
Sector: Sanitary Services - Sewerage Systems	
Project:	<i>Blueprint for Mercury Elimination</i>
Description:	Production of a document, similar to this SourceBook, that will detail reduction opportunities for wastewater treatment plants
Agencies working on this project:	WLSSD
Project:	<i>Pollution Prevention Training for Major Dischargers to Lake Superior</i>
Description:	Certification program and pollution prevention training for industrial and municipal wastewater treatment plant operators
Agencies working on this project:	MDEQ
Project:	<i>Study on Disinfection Alternatives</i>
Description:	Study of the efficiency and impact of chlorine-free wastewater treatment plant disinfection
Agencies working on this project:	WLSSD

Current Mercury Work

Specific Outreach/Research	
Sector: Sanitary Services - Sewerage Systems	
Project:	<i>Toxics Pollution Prevention Mentoring</i>
Description:	Providing pollution prevention training for Wastewater Treatment Plant personnel in MN, MI, and WI
Agencies working on this project:	WLSSD
Project:	<i>WLSSD Plant Balance for Mercury</i>
Description:	Plant balance examines inputs and emissions for a wastewater treatment plant that incinerates their sludge
Agencies working on this project:	WLSSD
Project:	<i>Minimization Plans for Michigan WWTPs</i>
Description:	Mercury Minimization Plans are required for all WWTPs when mercury is detected in influent, effluent, or sludge at levels of concern. May allow for POTWs to require similar plans in the permits of industrial users.
Agencies working on this project:	MDEQ
Workgroups	
Project:	<i>Federal Mercury Research and Regulations</i>
Description:	Mercury emission studies
Agencies working on this project:	EPA
Project:	<i>Green Lights Program</i>
Description:	Encourages voluntary light bulb replacement, and promotes use of energy-efficient lighting
Agencies working on this project:	EPA
Project:	<i>Lake Superior Pollution Prevention Team</i>
Description:	Published Lake Superior Pollution Prevention Strategy, 1993 and Implementation Plan 1995. Focus on mercury education/awareness, legislation improvements, financial tools, special projects
Agencies working on this project:	EPA GLNPO MDEQ MPCA/OEA SHWEC WDNR WLSSD

Current Mercury Work

Workgroups	
<p>Project: <i>Mercury Reduction Legislative Roundtables</i></p> <p>Description: Establishes one or two meetings for staff from MI, WI and MN about legislative approaches to mercury reduction in Lake Superior Basin. First meeting took place September 1995</p> <p>Agencies working on this project: MPCA/OEA</p>	
<p>Project: <i>Michigan's Mercury Pollution Prevention Task Force</i></p> <p>Description: Identification of sources of anthropogenic mercury and development of effective pollution prevention strategies and other sector specific targeted public education campaigns</p> <p>Agencies working on this project: MDEQ</p>	
<p>Project: <i>National Mercury Task Force</i></p> <p>Description: Task force focusing on long-term mercury elimination and reduction strategies nationwide</p> <p>Agencies working on this project: EPA</p>	
<p>Project: <i>Transition Economics Project</i></p> <p>Description: Established from the Binational Forum to recognize barriers to achieving zero discharge and to examine economic incentives for reduction measures in the pulp and paper and mining and mineral industries, wastewater, and general</p> <p>Agencies working on this project: Michigan Technical University - Houghton</p>	
<p>Project: <i>Virtual Elimination Project</i></p> <p>Description: Identification and modification of governmental actions which contribute to the elimination of releases of bioaccumulative chemicals of concern in the Great Lakes basin</p> <p>Agencies working on this project: EPA</p>	
<p>Project: <i>Wisconsin's Ad Hoc Committee on Mercury</i></p> <p>Description: Provides information on mercury sources and levels in Wisconsin's environment. Also provides a comprehensive listing of research activities and current legislation in Wisconsin</p> <p>Agencies working on this project: WDNR</p>	

Current Mercury Work

Workgroups	
Sector: Electric Services	
Project:	<i>Lake Superior Energy Efficiency Workgroup</i>
Description:	Partnership to reduce mercury emissions in the Lake Superior Basin through investigations of demand-side management, control technology, generation efficiency, renewables, recyclables/offset programs, fuel strategy
Agencies working on this project:	
Electric Utilities MDEQ MPCA/OEA Public Service Commissions WDNR	
Sector: Paper Mills	
Project:	<i>Targeted Initiative: Paper Mills</i>
Description:	Study of increased mercury discharge from a recycling plant. Identified plastics as a possible source of mercury
Agencies working on this project:	
WLSSD	

Information compiled from

Lake Superior Pollution Prevention Strategy Implementation Plan: Recommendations for Achieving Zero Discharge in Wisconsin, Minnesota, and Michigan, Lake Superior Pollution Prevention Team, September 1995;

A Review of Pollution Prevention Efforts Compared to Pollution Prevention Needs in The Lake Michigan Basin, prepared for the Lake Michigan Forum by Clean Sites, July 1995;

Strategies for Mercury Control in Minnesota, MPCA Mercury Task Force, July 1994

MERCURY SPECIES

Mercury can exist in a variety of forms and oxidation states. Mercury's behavior in the environment depends heavily on the state it is in, so it is important to have at least a basic understanding of the different species of mercury and how they behave in the environment. It is also important to note that scientists do not fully understand this process. We have included a list of uncertainties at the end of this section.

Mercury is an unusual element in that it is a metal that sometimes has the characteristics of an organic compound. Since it is an element, it is like other metals in that it is persistent in the environment, being destroyed neither by combustion nor bacterial degradation. Mercury is like some organic compounds because it has an ability to bioaccumulate through food chains due to its tendency to associate with organic matter.

Know your mercury species

Hg⁰: "Metallic" or "Elemental" Mercury

- ◆ Appears in its pure form as a silvery liquid
- ◆ Has no charge
- ◆ Is not water soluble
- ◆ Does not readily wash out of the atmosphere; contributes to global pollution
- ◆ Comprises 95 - 99% of mercury in the atmosphere

Hg(II): "Mercuric ion, mercury two, divalent mercury"

- ◆ Ionized
- ◆ Easily associates with particles and water in the atmosphere
- ◆ Readily washes out of the atmosphere; contributes to local/regional pollution

MeHg: "Methylmercury"

- ◆ The organic form of mercury
- ◆ Form most available to biota (zooplankton, insects, fish, humans)
- ◆ Bioaccumulates in tissue
- ◆ Volatile
- ◆ Water soluble

Mercury in the atmosphere

- ★ Consists of 95-99% elemental mercury

Elemental mercury can remain in the atmosphere for a long time (residence time is three months to two years). Elemental mercury (Hg⁰) leaves the atmosphere when it is oxidized by ozone or other oxidants to Hg(II). After it is in its ionic, mercury-two state, it can form an organic or inorganic compound.

Mercury in water, soil, and sediments

- ★ Typically in the form of inorganic mercury salts or organomercurics

Inorganic mercury salts
HgCl₂ (the predominant inorganic form)
Hg(OH)₂
HgS (cinnabar)

Organomercurics
(Methylmercury compounds)
CH₃HgCl (the predominant organic form - methylmercuric chloride)
CH₃HgOH (methylmercuric hydroxide)

Approximately 10 percent of the mercury in water is methyl-mercury or its compounds; the rest is Hg(II) and its compounds. Mercury content in soils consist of approximately 2 percent methylmercury/compounds; the remainder is Hg(II) and its compounds. Organo-mercury compounds and mercury salts [Hg(II)] are toxic to microbial activities, growth, and reproduction.

SPECIAL FOCUS: MERCURY SPECIES

Mercury (Hg): refers to any of the different chemical forms that mercury can take, including methylmercury, Hg^0 , and $\text{Hg}(\text{II})$. These three forms can be converted to each other and back again. The oxidation state of mercury that will occur in the atmosphere, in sediments, or in a water body depends on the redox potential and the pH of that environment.

Hg^0 : “mercury zero” is the elemental form of mercury, and it appears in its pure form as a silvery liquid. However, for it to appear in its liquid form it must remain contained. Hg^0 can volatilize to the atmosphere at normal temperatures, so it is rarely found in the environment as a pure, silvery liquid. Because it partitions so strongly to the air, mercury zero that is in lakes and soils tends to volatilize back into the atmosphere as it is formed.

Over 90% of mercury in the atmosphere is Hg^0 , although other forms can be considerably higher than 10% near point sources. Chemically, Hg^0 has no charge and is not very water soluble, so it does not adsorb to particles. Therefore, it does not wash out of the atmosphere readily during a rainfall; instead it is removed from the atmosphere very slowly, mostly after conversion to $\text{Hg}(\text{II})$. Elemental mercury has a long residence time in the atmosphere, on the order of three months to two years, averaging about one year.

Hg^0 liquid or amalgam is not absorbed during digestion, but the vapor is readily absorbed by the lungs.

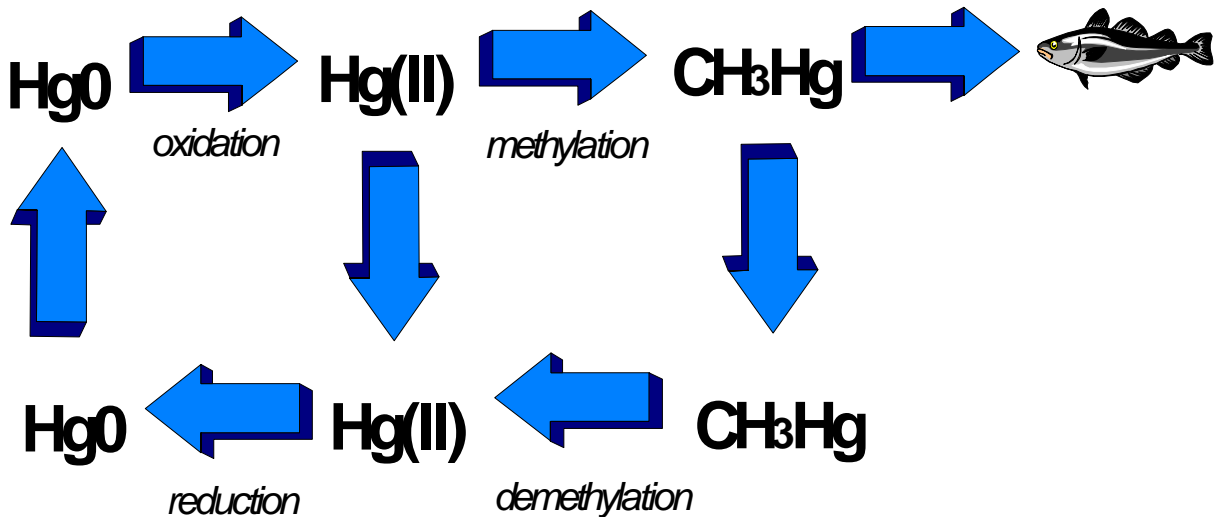
Hg^{2+} : “mercury two” is the mercuric ion. It may also be referred to as “mercury salts.” Because it is water soluble and associates with particles, atmospheric deposition of $\text{Hg}(\text{II})$ occurs relatively fast, either as dry deposition or in precipitation. Combustion sources can emit both Hg^0 and $\text{Hg}(\text{II})$. $\text{Hg}(\text{II})$ is produced in the atmosphere by the oxidation of Hg^0 by ozone or other oxidants.

Hg_2^{2+} : “mercurous ion; monovalent mercury; mercury one.” This ion is rarely stable under normal environmental conditions. It typically breaks down to one atom of elemental mercury and one atom of $\text{Hg}(\text{II})$.

Methylmercury (sometimes abbreviated MeHg): can be produced by “methylating bacteria” or by chemical methylation in association with dissolved humic substances. Mercury will generally not bioaccumulate unless it is converted to its organic form.. Methylmercury is water soluble and volatile, so it is readily washed out of the atmosphere. Only a small proportion (less than 10%) of mercury entering a lake becomes methylated, and that proportion is not constant from lake to lake. The amount of biomethylation that occurs in a water body seems to depend on pH, alkalinity, state of anoxia, sulfur sources, dissolved organic material, and other factors within the aquatic environment. The half-life of methylmercury is on the order of 1 to 3 years.

Virtually all of the mercury in fish is methylmercury. Methylmercury is readily absorbed during digestion.

Mercury Cycles



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Mercury, Power Plants and the Environment: Basic Facts about Mercury and Coal-fired Power Plants, the Environment, Fish and Wildlife, and Human Health, compiled by Steven Ugoretz, WDNR

Mercury Atmospheric Processes: A Synthesis Report, prepared by the Expert Panel on Mercury Atmospheric Process, convened March 1994

Quantification of Total Mercury Discharges from Municipal Wastewater Treatment Plants the Wisconsin Surface Waters, by Thomas Mugan, WDNR, May 1993

Strategies for Mercury Control in Minnesota, MPCA Mercury Task Force, July 1994

MERCURY TRANSPORT

Transportation of Mercury through the Environment

Mercury cycling through the environment is an extremely complicated process that is not entirely understood. The various forms of mercury can be converted from one to another and back again; the conversion process that has the most direct effect on animal and human life is the conversion to methylmercury (CH_3Hg^+).

The distance mercury will travel in the atmosphere before deposition is dependent on the form when emitted. $\text{Hg}(\text{II})$ and methylmercury are more likely to be deposited from the atmosphere than elemental mercury (Hg^0) because they are water soluble and are more easily scavenged by precipitation. Although only a small proportion of mercury emitted from a point source is thought to be associated with particles, it is this fraction of $\text{Hg}(\text{II})$ or methylmercury that will be deposited closest to that source because it easily washes out of the atmosphere through dry deposition or scavenging by precipitation. It is estimated that 10% of all mercury emitted from an emission source is deposited within 10 kilometers of that source. Little information has been collected concerning the proportion of the various species emitted by different sources, but it

is an important issue in determining local reduction strategies. (*Strategies for Mercury Control in Minnesota*, MPCA Mercury Task Force, July 1994)

Atmospheric deposition can occur directly to the lake's surface or to the soils in a watershed that drain to the lake. Organic matter in soils has a high affinity for mercury, so that only 10% to 30% of mercury deposited to a lake's watershed is transported to the lake. (*Strategies for Mercury Control in Minnesota*, MPCA Mercury Task Force, July 1994) The source of mercury to most aquatic systems (with the exception of isolated cases of known point sources) is deposition from the atmosphere, mainly from rainfall. Once mercury enters the aquatic system, it can be brought into the sediments by particle settling and then later released by diffusion or resuspension. It can enter the food chain, or it can be released back to the atmosphere by volatilization.

(*Mercury Contamination of Aquatic Ecosystems*, U.S. Geological Survey, web site address: http://h2o.usgs.gov/public/wid/FS_216-95/FS_216-95.html, December 1995)

deposition is dependent on the form when emitted. Elemental mercury (Hg^0) remains in the atmosphere a long time (from three months to two years) and contributes to global pollution. (*Strategies for Mercury Control in Minnesota*, MPCA Mercury Task Force, July 1994) Elemental mercury only deposits when converted to $\text{Hg}(\text{II})$.

Aqueous redox reactions appear to be the most important pathway for removal of elemental mercury from the regional atmosphere. Ozone is currently considered to be the most important oxidant, while SO_3^{2-} and complexing ligands such as Cl^- and particulate matter (soot) are thought to control the reduction reactions. Important controlling factors include the cloud droplet pH. (*Mercury Atmospheric Processes: A Synthesis Report*, prepared by the Expert Panel on Mercury Atmospheric Process, convened March 1994)

Regional deposition of mercury reflects the presence of ionic $\text{Hg}(\text{II})$ and particulate mercury species in emissions. It is estimated that 10% of all mercury emitted from an emission source is deposited within 10 kilometers of the point source. There is currently little information about the different species of mercury emitted from various sources. (*Strategies for Mercury Control in Minnesota*, MPCA Mercury Task Force, July 1994)

3 Much of the mercury deposited to oceans and other

waters is re-emitted to the atmosphere because of conversion to Hg^0 , which is not water soluble. This is sometimes known as the “ping-pong” effect of mercury cycling, and it may prolong the impact of anthropogenically derived mercury on aquatic systems. (*Biogeochemical Cycling of Mercury: Global and Local Aspects*, William F. Fitzgerald, as published in *National Forum on Mercury in Fish: Proceedings*, USEPA Office of Water, June 1995. EPA 823-R-95-002)

4 Organic matter in soils has a high affinity for mercury, so that only 10 -30% of mercury deposited to a lake’s watershed is transported to the lake. (*Strategies for Mercury Control in Minnesota*, MPCA Mercury Task Force, July 1994) Surface soils contain most of the mercury pollution released over the last 100 years. In fact, recent estimates indicate that of the approximately 200,000 tons of mercury emitted to the atmosphere since 1890, about 95% resides in terrestrial soils, about 3% in the ocean surface waters, and 2% in the atmosphere. (*Mercury Atmospheric Processes: A Synthesis Report*, prepared by the Expert Panel on Mercury Atmospheric Process, convened March 1994)

5 Not all mercury entering aquatic systems is taken up by fish; most enters the sediment pool. Small amounts (approximately 5-10%) is methylated and enters the biotic pool.

Elemental mercury can be produced from $\text{Hg}(\text{II})$ through reduction by humic acids. Once the mercury is reduced, it is re-released into the atmosphere because it is no longer water soluble. (*Quantification of Total Mercury Discharges from Municipal Wastewater Treatment Plants the Wisconsin Surface Waters*, by Thomas Mugan, WDNR, May 1993)

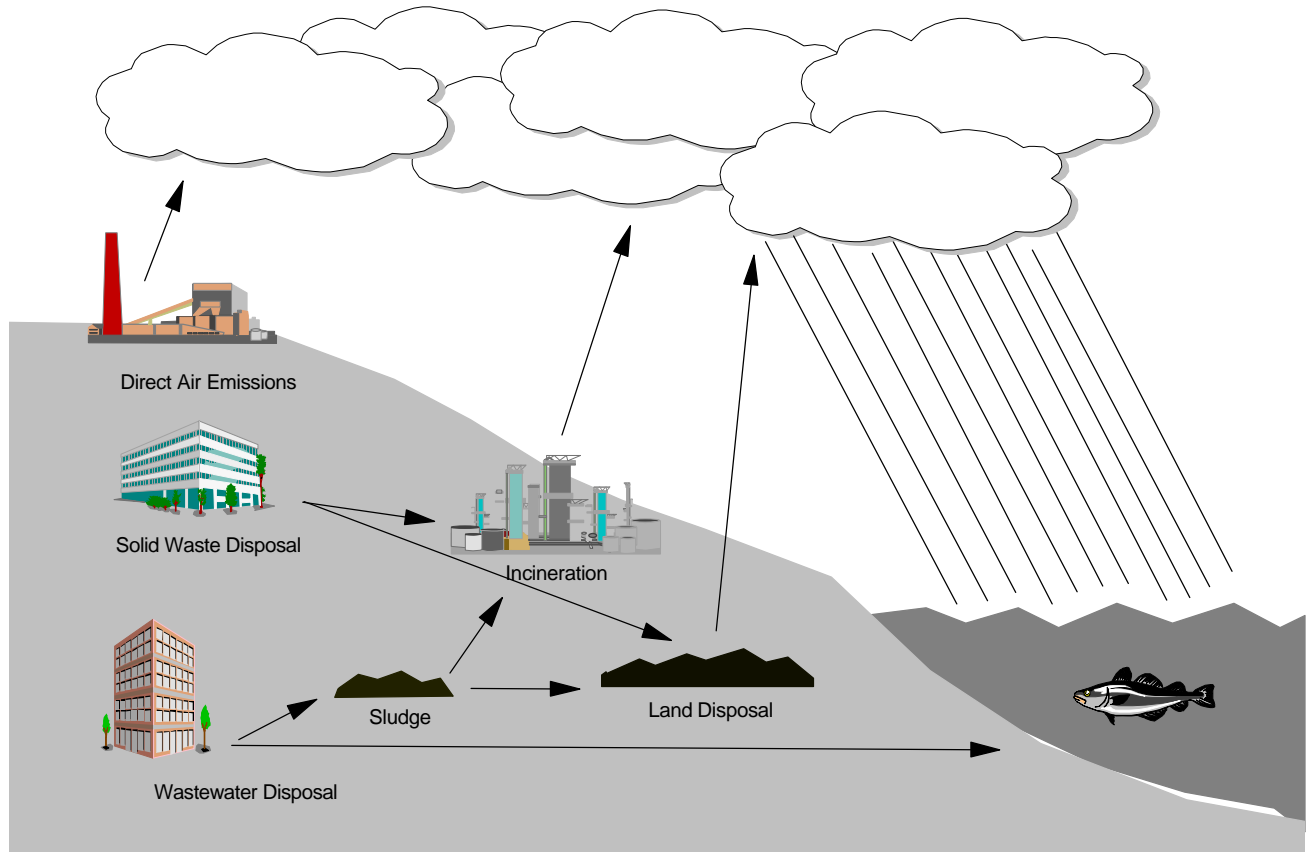
6 Methylmercury accounts for less than 10% of total mercury in lakes with out point sources. Several factors can increase the methylation rate in lakes. Positive correlations have been associated with water color (dissolved organic compounds) and sulfate, and negative correlations have been associated with alkalinity, pH, and phosphorus. (*Strategies for Mercury Control in Minnesota*, MPCA Mercury Task Force, July 1994)

7 Benthic organisms may take up mercury and make it available for other biota.

8 Dimethyl mercury is assumed to have no charge, and it easily volatilizes to the atmosphere.

MERCURY TRANSPORTATION TO THE ATMOSPHERE

Mercury Transport



The volatility of mercury implies that mercury introduced anywhere into the environment, including landfills, soil application, and surface water discharges, has the potential to volatilize and be deposited elsewhere. Therefore, land and water disposal of mercury can be considered as potential air emission sources.

Mercury can be directly emitted to the air through the burning of coal, oil, gasoline, or wood, or through industrial processes like metal smelting or chloralkali production. Mercury that is thrown into the

garbage and enters the solid waste stream can potentially enter the atmosphere through two paths. If the waste is incinerated, the mercury will volatilize and enter the atmosphere because the metal evaporates at low temperatures. There are few economically practical control measures that can control this emission. If the mercury-containing product is disposed of in a landfill, the mercury may volatilize out of a landfill with methane gas. It may also appear in the leachate from landfills.

If the mercury is flushed through a wastewater system, only a small

portion of it will be directly emitted to surface waters. Instead, mercury adheres to the sludges produced in wastewater treatment plants and can volatilize to the atmosphere when these sludges are incinerated. New research from Anthony Carpi and Steve Lindberg of the Oak Ridge National Laboratory indicates that inorganic mercury vapor levels are elevated over lands where municipal sewage sludge was applied (*see sidebar*).

Key aspects to the environmental context of mercury: It is mobile and nondegradable

(from *Great Lakes Virtual Elimination Project*, Frank Anscombe, as published in *National Forum on Mercury in Fish: Proceedings*, USEPA Office of Water, June 1995. EPA 823-R-95-002)

◆ **Mercury is mobile.** It is a volatile fluid at room temperatures and reaches a gaseous state at 300°C. Any mercury released to the environment can be a “grasshopper pollutant,” volatilizing from land to be redeposited again and revolatilized again. When it enters water, it can be converted to methylmercury.

◆ **Mercury does not decay.** If the volume of mercury that humans use and release exceeds the earth’s capacity to rebury it, then mercury levels will rise in the atmosphere and the earth’s waters. In general, this rise has been going on for the last 150 years, as evidenced in bog and sediment cores. Some people believe the only way to stop this outcome is to convert unused mercury and mercury waste to a non-soluble form - such as its sulfide phase or cinnabar, and dispose of this, perhaps by reburial.

New research from the Oak Ridge National Laboratory indicates that inorganic mercury vapor levels are elevated over lands where municipal sewage sludge was applied. Beneath a forest, sludge application increased total daytime mercury emissions from ~2ng/m²/h over background soils to 15-40 ng/m²/h over sludge amended soils. On open-field soils, daytime mercury emissions increased from ~5 ng/m²/h to over 500 ng/m²/h after sludge application. By comparison, mercury emissions from spoils contaminated with elemental mercury averaged about 90 ng/m²/h. (*Lindberg et al., Environmental Science Technology 28, 1995*)

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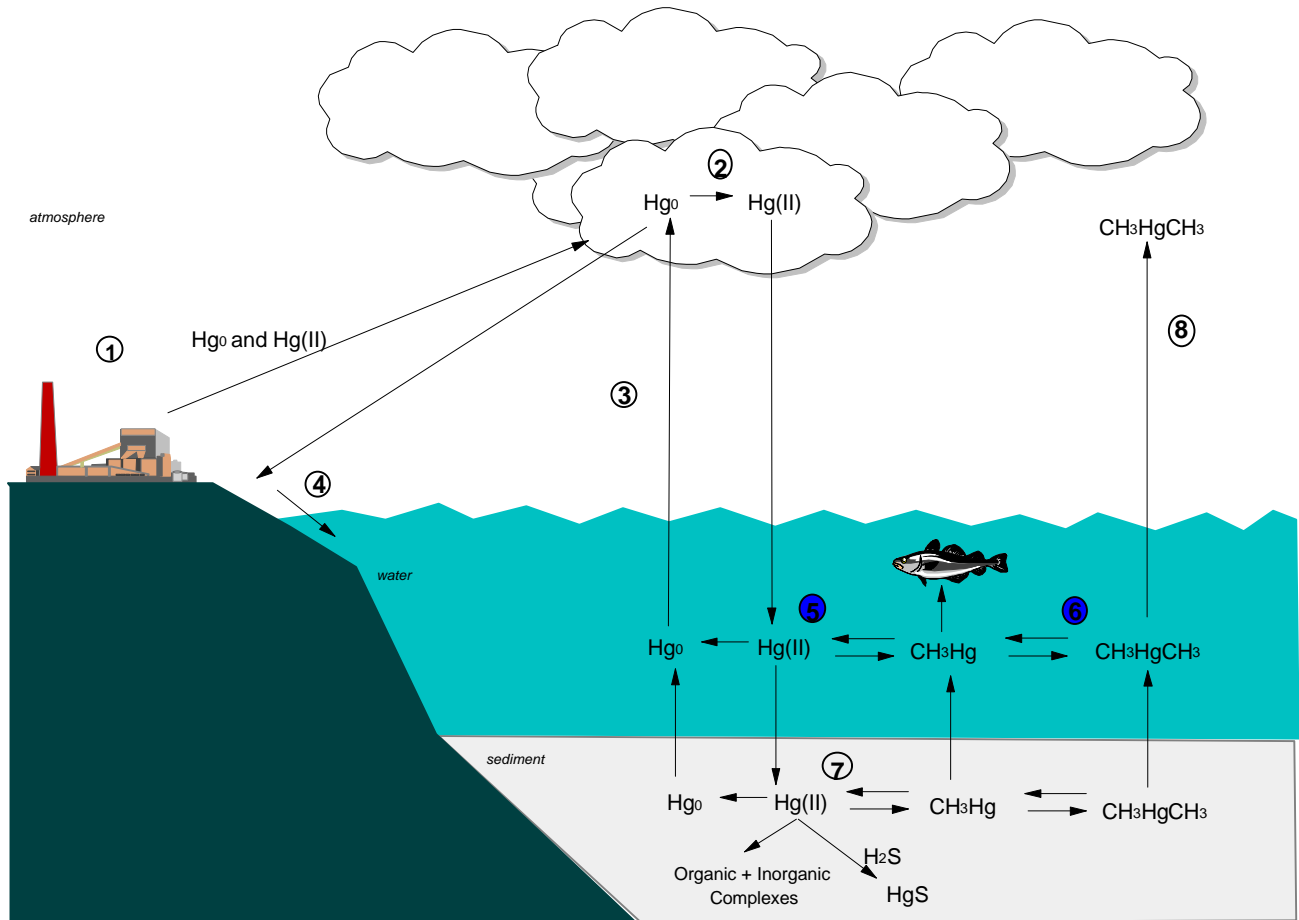
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Strategies for Mercury Control in Minnesota, MPCA Mercury Task Force, July 1994

Mercury Species Transportation



Adopted from Winfrey & Rudd, 1990

1 Mercury enters the air from a variety of sources that include both natural and anthropogenic emissions. It has been estimated that 70-80% of mercury emissions are related to human activities, although this is a difficult estimate to calculate. The source of human emissions vary over location and time, but could include waste incinerators, fossil fuel combustion, chloralkali plants, ore extraction, and precious metal extraction, among others. See the chart

“Mercury Transport to the Atmosphere” for a more complete description of how mercury enters the air from a variety of sources.

Mercury emissions in the Upper Midwest have increased 3.4 times in the last century. (Strategies for Mercury Control in Minnesota, MPCA Mercury Task Force, July 1994) Current calculations for air emissions to Wisconsin’s atmosphere are estimated at 5,600 pounds per year. Estimates for

annual amounts of mercury released to the air by human activities globally range between 3,600 and 4,500 tons.

(Biogeochemical Cycling of Mercury: Global and Local Aspects, William F. Fitzgerald, as published in National Forum on Mercury in Fish: Proceedings, USEPA Office of Water, June 1995. EPA 823-R-95-002)

2 The distance mercury will travel in the atmosphere before

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MEASURING MERCURY LEVELS IN WISCONSIN'S AIR AND WATER

From *Mercury in Wisconsin's Environment: A Status Report*, WDNR, May 1996

ATMOSPHERE

Trout Lake Studies

Atmospheric mercury in particles, gases and precipitation has been measured near Trout Lake in north central Wisconsin since 1988. These activities have been part of an Electric Power Research Institute/WDNR-funded research project.

Since 1993, Dr. William Fitzgerald of the University of Connecticut has operated an atmospheric sampling tower under WDNR subcontract at a remote site in northern Vilas County. In addition to mercury, other parameters such as meteorology, sulfate and aerosol mass are monitored. Seventy-two hour back trajectories and upwind precipitation data are used to connect time-related variations in concentration of all mercury forms to possible removal processes and potential source regions.

Mercury in precipitation has been measured at several other sites near Trout Lake. The mercury concentration in rain from the area between 1988-1994 averaged 7.86 nanograms per liter (ng/L); the methylmercury concentration 0.03 ng/L. During the project's first three years (1988-1991), the atmospheric wet deposition for total mercury was 6.8 (micrograms per square meter per

year) ug/m²/yr, and 0.03 ug/m²/yr for methylmercury. Atmospheric and depositional measurements continued through 1995.

In 1994, three different methods for collecting atmospheric mercury deposition were compared (Morrison et al., 1995): (1) manual event sampling, (2) automated wet-only collector, and (3) IVL bulk collectors. The potassium dichromate preservative used in the automated wet-only sampler produced very high mercury blanks (2 to 55 percent of the measured Hg). The IVL bulk sampler is probably most suitable for mass balance studies. Thoroughly sampling each depositional event is important to accurately determine the depositional flux to a region.

Air Monitoring Section Activities

The Air Monitoring Section in the Bureau of Air Management has conducted atmospheric mercury monitoring in wet and dry deposition:

1 In 1993, a new type of sampler was deployed to collect wet samples for total mercury analysis. The sampler is

based on a Swedish Environmental Institute (IVL) design used in measuring mercury deposition in northern European countries. Wisconsin currently has a network of seven IVL monitoring stations; Brule River, Trout Lake, Suring, Lake DuBay, Wildcat Mountain State Park, Lake Geneva and Devil's Lake State Park. Weekly integrated samples are collected using clean sampling techniques and are shipped to Brooks-Rand, Inc., in Seattle, Washington, for analysis. Funding guarantees this network for another six years.

2 In February 1994, mercury sampling began at the Brule River Toxic Loading Station near Lake Superior. This sampler is a modified aerochemMetrics design by the Mercury Deposition Network (MDN) of the National Atmospheric Deposition Program (NADP). This sampler also collects a weekly integrated wet sample that is analyzed for total mercury. An ideal sampler would be a passive sampler, meaning the collection funnel would be continuously exposed during week-long sampling. This would allow particulate dust to settle on the glass collection surfaces during dry periods. The dust would then wash into the collection bottle during precipitation. The MDN sampler

glassware, however, is only open during precipitation. A sensor detects precipitation, opens the device to collect the sample, then closes it when precipitation stops. Since February 1994, MDN and IVL collocated sampling has been performed at Brule River to compare the two sampling techniques.

Two additional MDN sampling stations were deployed at Trout Lake in Vilas County and at Popple River in Florence County in May 1995. MDN and IVL samples will also be collected at Trout Lake.

Air monitoring staff have converted three additional aerochemMetrics samplers to the MDN design. These samplers were placed with IVL sampling stations at Devil's Lake State Park, Lake Geneva and Wildcat Mountain State Park Stations in summer 1995.

MDN mercury network samples are submitted to Frontier GeoSciences Incorporated (Nicolas Bloom) for weekly analysis. Sufficient funding will cover operation of Wisconsin's MDN stations for another five years.

3Dr. Jerry Keeler at the University of Michigan School of Public Health is the lead researcher for the Atmospheric Mercury Monitoring Network. The network has equipment deployed throughout the upper Midwest to measure mercury deposition. A wet deposition sampling station was operating at Chiwaukee

Prairie in southern Kenosha County from June 1994 through October 1995. An MIC wet-only sampler collected and "separated" event samples at the Chiwaukee Prairie site. These samples were analyzed for total mercury at Dr. Keeler's laboratory.

A dry deposition mercury sampling station has been operating at Wildcat Mountain State Park in Vernon County since December 1994. This background monitoring station uses equipment developed by Dr. Keeler. These samples are also analyzed for total mercury at Dr. Keeler's lab. Funding for the site will cease December 31, 1996.

LAKES AND RIVERS

Lakes

Since 1988, the Bureau of Research has conducted a program to examine the biogeochemical fate of mercury in a suite of north central Wisconsin lakes. Before significant work could begin, new "ultra-clean" sampling protocols had to be either adopted from oceanographic work in this field or newly developed. In addition, a new method had to be developed to measure low concentrations of methylmercury in water. Once these tasks were accomplished, the mercury cycle in a group of northern Wisconsin seepage lakes was studied. These results are summarized from a paper by Watras et al., 1994:

The direct depositional total mercury load (wet and dry) from the atmosphere to these lakes was approximately 10 ug/m²/yr, mainly from rain and snow. The atmospheric loading of methylmercury to these lakes is estimated to be 1 percent of total mercury inputs. Although the direct atmospheric deposition and sediment accumulation of methylmercury roughly balanced, the atmospheric influx of methylmercury was much lower than annual rates of methylmercury bioaccumulation. This suggests that in-place production is an important source of methylmercury. Most of the methylmercury in these lakes was stored in fish tissue.

The distribution of mercury chemical species in the study lakes was characterized by very dilute pools that varied seasonally and spatially. Waterborne mercury species had concentrations in the picomolar to femtomolar range, with parts per million to parts per billion concentrations in the sediments and organisms. Average waterborne total mercury and methylmercury concentrations correlated negatively with lake water pH and positively with dissolved organic carbon. Epilimnetic total mercury concentrations ranged from 1 to 3 ng/L (nanograms per litre) and methylmercury concentrations 0.05 to 0.5 ng/L. Higher mercury concentrations were observed with increasing depth in stratified lakes (total mercury 45 ng/L and methylmercury 10 ng/L) and total mercury maxima were observed near microbial layers in the water

column. In anoxic, sulfidic plankton layers, 50 percent of the mercury may be in the methyl form (versus 2 to 15 percent in the epilimnion). Methylmercury was biomagnified in the Little Rock Lake food chain, but evidence showed that non-methylmercury species became more dilute at higher trophic levels. The bioconcentration factors for methylmercury increased threefold for each trophic level, approaching 107 in fish. The mercury in fish was almost all methylated (95%), while the mercury in sediments was primarily non-methylmercury (97%).

Since most methylmercury in the study lakes appeared to be sequestered by fish biomass, fish contamination could be significantly enhanced by small increases in net rates of methylmercury production, recycling or loading.

An environmental model of mercury cycling in lakes is available for use with IBM®-compatible PCs. The mercury research effort on lakes has produced more than 50 publications (see references). An additional mercury research effort for Devil's Lake in southern Wisconsin is just beginning.

Rivers

Using recent advances in trace-metal clean sampling and analytical techniques, the Bureaus of Research and Water Resources Management have repeatedly sampled 39 selected river sites around the state for mercury and other trace metals. (Hurley et al.,

1995) Mean unfiltered total mercury was higher in the spring (7.94 ng/L) than fall (3.45 ng/L). Using a Geographic Information System, watersheds were delineated by both their unique and homogeneous physical characteristics. Major differences in total mercury yields were observed among various land-use groupings. In wetland/forest watersheds, elevated total mercury fluxes were associated with the filtered phase, while in agricultural watersheds, increased total mercury fluxes were due to particle loadings. Methylmercury yields from wetland/forest sites were higher than agricultural/forest sites, with percent wetland surface area positively correlated with methylmercury yield.

These results identify the importance of land use and land cover in influencing mercury concentrations, speciation and transport in rivers.

The Bureaus of Research and Water Resources Management are measuring mercury in selected tributaries to Lake Michigan. Their work is part of a larger Lake Michigan Mass Balance Model. Preliminary results indicate that mean unfiltered total mercury concentrations range from 1-2 ng/L in the Manistique and Muskegon rivers (Michigan) to 10-30 ng/L in the St. Joseph (Michigan) and Fox (Wisconsin) rivers. Elevated mercury concentrations were generally associated with increased particle loads.

Lake Sediments

The concentrations of mercury in surface sediments of northern Wisconsin lakes range from 10 to 190 ng/g (dry wt) (Rada et al. 1989, Rada, 1991). There are similar concentrations found in lakes in northeastern Minnesota (Swain, 1989). The uppermost 15 cm of sediment contains the greatest Hg concentrations in comparison with observed background as measured from the deeper sediments in lakes, indicating recent enrichment (Rada, 1989).

TESTING FOR MERCURY

Recent breakthroughs in the analytical determination of methylmercury and the advent of very low detection limits, along with “ultra-clean” sampling protocols developed in the late 1980s have allowed accurate measurements of mercury in water, air and precipitation. Because mercury amounts in air and water are relatively minute, measurements made before the use of ultra-clean sampling and analytical protocols are considered inaccurate. The early inaccuracies were caused more by contamination than by inadequate detection limits.

emission (AE). Sensitivity improvements may be achieved through use of preconcentration steps, such as gold amalgamation trapping.

In most aquatic environments, total mercury ranges in concentration from approximately 0.5 to 5 ng/l, while the fish living in those waters might contain from 100 to 2,000 ng/g. The methylmercury content of natural waters is generally about 5-20 percent of the total.

Although great improvements have been made in testing and analyzing mercury, problems still exist for certain forms, especially Hg(II) and some ambient conditions. Mercury sampling programs have typically suffered from relatively short periods of record (a month or less) and longer sample durations (days to months) than those designed for criteria pollutants. Many recent and ongoing mercury studies are avoiding these shortcomings with improvements in measuring techniques and program design.

The last decade has brought great improvements in the testing and analysis of mercury in ambient environmental media. Ultra-clean techniques typically apply to aqueous samples; biota samples contain concentrations 10^5 to 10^7 times higher and do not need to be tested with such rigor.

Ultra-clean sampling for mercury begins with the processing of

equipment in a low mercury environment. Particulates are controlled by passing air through high efficiency (HEPA) filters. If total gaseous mercury is under 10 ng/m³, then the lab is clean for low-level work; if the lab has levels greater than 100 ng/m³ it is considered unacceptable for low-level work. Ultra-clean sampling also mandates that the mercury concentrations of all reagents, gases, water, and room air be known at all times.

Water samples are typically taken in hot-acid-cleaned Teflon®, borosilicate glass, or quartz; soft plastics such as polyethylene and Tygon® are avoided. Field collection of water samples is accomplished with the “clean hands-dirty hands” technique to avoid any contamination. Mercury is typically detected in the lab by one of three cold vapor atomic spectroscopic methods - atomic absorption (AA), atomic fluorescence (AF), or atomic

In the early 1960s, the limit of detection of many substances was in the parts per millions, which is equivalent to about 2 1/2 ounces of a substance in enough water to fill a 20,000-gallon railroad tank car. Now chemists can detect trace amounts of most contaminants in the parts per trillion, which is equivalent to about 2 1/2 ounces of material in enough water to fill one million 20,000-gallon railroad tank cars. This many tank cars would make a train long enough to stretch from the east coast to the west more than three times.

(from *A Review of Fish Consumption Advisories*, Robert Reinert, as published in *National Forum on Mercury in Fish: Proceedings*, USEPA Office of Water, June 1995. EPA 823-R-95-002)

Table below from *Considerations in the Analysis of Water and Fish for Mercury*, Nicolas Bloom, as published in *National Forum on Mercury in Fish: Proceedings*, USEPA Office of Water, June 1995. EPA 823-R-95-002

Analytical Detection Limits for Mercury Speciation				
	Water (ng/L)		Biota (ng/g)	
	Total	Methyl	Total	Methyl
(typical level)	0.5-5	0.01-0.5	0.01-2	0.01-2
Gold Amalgamation Atomic Absorption Spectroscopy (Au Amalgamation/ AAS)	0.05	---	0.001	---
Direct Atomic Absorption Spectroscopy (Direct/AAS)	50	---	0.005	0.005
Direct Atomic Fluorescent Spectroscopy (Direct/AFS)	1	---	0.001	---
Cold Vapor Atomic Fluorescent Spectroscopy (CVAFS)	---	0.01	0.005	0.001
Ethylation/ Cold Vapor Atomic Absorption Spectroscopy (Ethylation/CVAAS)	---	1	0.05	0.01
Gas Chromatography/ Electron Capture Detection (GC/ECD)	---	0.1	---	0.001
Headspace/ Cold Vapor Atomic Fluorescent Spectroscopy (Headspace/CVAFS)	---	0.5	---	0.01
Liquid Chromatography/ Cold Vapor Atomic Fluorescent Spectroscopy (LC/CVAFS)	---	1	---	---

Analytical Method Requirements

(From *Considerations in the Analysis of Water and Fish for Mercury*, Nicolas Bloom, as published in *National Forum on Mercury in Fish: Proceedings*, USEPA Office of Water, June 1995. EPA 823-R-95-002)

- ★ Sensitive

	Water	Fish
Total Hg	0.1 ng/L	0.01ng/L
Methyl Hg	0.01 ng/L	0.01 ng/L
- ★ Accurate (±10%)
- ★ Precise (±10%)
- ★ Generalizable (water, sediment, tissue)
- ★ Chemically Specific (Hg(II), MMHg, DMHg)
- ★ Interference Free
- ★ Non-Contaminating
- ★ Economical

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UNCERTAINTIES

There are scientific uncertainties about a number of issues relating to the transportation of mercury through the environment. The following list details some of the important areas that need further research:

Point source emissions/Local deposition

- What percentage of Hg(II) is emitted to the atmosphere from point sources?
- What atmospheric reactions contribute to local deposition?
- What is the capture efficiency of pollution control equipment?

Atmospheric reactions

- What becomes of Hg(II) (chemically and physically) once it enters the atmosphere?
- What affects the rate of wet and dry deposition?

Measurement

- A reliable method of testing for Hg(II) is needed (specifically: subpicogram per cubic meter concentration in atmosphere)

Modeling

- The predictive capacities of atmospheric mercury models need to be evaluated and improved
- The accuracy of local and regional models needs to be tested

Movement from soils to waterbodies

- What are the rates of emissions/uptake from terrestrial ecosystems?
- What are the soil-mercury turnover processes and time constraints?

Revolatilization

- What are the rates of emissions/uptake from oceanic environments?
- How much mercury volatilizes from landspread sludge?
- How much mercury is leaking from landfills?

Methylation rates

- What factors increase or decrease methylation rates in different types of waterbodies?
- What factors contribute to increased methylation levels in fish?
- How much methylation occurs in landfills?
- How much methylation occurs in wastewater treatment plants?

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Strategies for Mercury Control in Minnesota, MPCA Mercury Task Force, July 1994

HEALTH EFFECTS: METHYLMERCURY

Direct exposure to elevated concentrations of mercury vapor can be hazardous, but this is only likely to occur in enclosed spaces where mercury is handled without adequate ventilation. The most damaging contact for humans and other mammals is with mercury in its methylated form. Most of the methylmercury that is in fish is thought to be formed from the oxidized form, Hg (II), that is present in the water body.

Methylmercury is the most hazardous form of mercury for birds, mammals, and aquatic animals. It is highly stable, has a strong affinity to sulfur containing organic compounds like proteins, and its ionic properties allow it to penetrate membranes in living organisms, including blood-brain barriers and the placenta.

especially affects top-predators in aquatic food chains (eg., walleyes and northern pike) as well as fish-eating wildlife (eg., hawks, eagles, loons). (*Mercury Contamination of Aquatic Ecosystems*, U.S. Geological Survey)

Bioaccumulation results in situations where the ambient water levels of mercury are safe to drink but it may be unsafe to eat the fish. For example, the average concentration of mercury in a northeastern Minnesota lake is about 2 nanograms per liter (ng/L), but the average concentration of a 22-inch northern pike is about 450 nanograms per gram, a bioaccumulation factor of 225,000. Added together, the total amount of mercury in a million of these pike would be just a pound. (*Strategies for Mercury Control in Minnesota*)

BIOACCUMULATION

Methylmercury levels in fish multiply because of a process called *bioaccumulation*. Bioaccumulation is the process by which organisms (including humans) take up contaminants more rapidly than their bodies can eliminate them; thus, the amount of mercury in their bodies accumulates over time. If, for a period of time, an organism does not ingest mercury, its body burden of mercury will decline. If, however, an organism continually ingests mercury, its body burden can reach toxic levels. The rate of increase or decline in body burden is specific to each organism. For humans, about half the body burden of mercury can be eliminated in 70 days if no mercury is ingested in that time. (*Mercury Contamination of Aquatic Ecosystems*, U.S. Geological Survey) The estimated half retention time of

methylmercury in fresh water fish is 0.5 to 2 years. Some studies have found no measurable excretion of methylmercury from fish. (*Bioaccumulation of Mercury in Fish*, James Wiener)

Biomagnification is the incremental increase in concentration of a contaminant at each level of a food chain. Mercury biomagnifies from the bottom to the top of the food chain. This occurs because the food source for organisms higher on the food chain contains progressively more concentrated mercury and other contaminants, thus magnifying bioaccumulation rates at the top of the food chain. The bioaccumulation effect is generally compounded the longer an organism lives, so that larger predatory game fish will likely have the highest mercury level. Therefore, bioaccumulation

Methylmercury

- ★ Most toxic form of mercury
- ★ Soluble & mobile
- ★ Quickly enters aquatic food chains
- ★ Biomagnifies in aquatic ecosystems

HOW MERCURY IS METHYLATED

The methylmercury content in atmospheric deposition is quite low, only 1-2% of the total amount of mercury deposited. (*Watershed Effects on Background Mercury Levels in Rivers*, James Hurley) However, almost all of the mercury in fish tissue is methylmercury. This led scientists to conclude that mercury is processed or biotransformed in the aquatic environment.

Methylation of inorganic mercury takes place through both nonenzymatic and enzymatic processes, primarily in freshwater and marine sediments. Methylation is the result of microbial activity; the most probable reaction involves nonenzymatic methylation of mercuric mercury ions by methylcobalamine compounds produced as a result of bacterial synthesis. In addition to anaerobic sulfur reducing bacteria, aerobic bacteria and fungi, including yeasts that thrive in acidic conditions such as *candida albicans* and *saccharomyces cerevisiae*, methylate mercury. (It is also believed that these yeast may reduce ionic mercury to elemental mercury.) Furthermore, fulvic and humic material may abiotically methylate mercury. (*Mercury in Michigan's Environment: Environmental and Human Health Concerns*, 1993)

The conversion rate of mercury to methylmercury in a lake or watershed is dependent on the characteristics of the lake and its surrounding watershed. The rate of methylmercury formation is determined by the concentration of methyl cobalamine compounds,

inorganic mercuric ions, and the oxygen content of the water (rates of methylation also increase as conditions become anaerobic). In addition, if there is a high degree of erosion or large amounts of suspended particulate loads (especially particulate organic carbon in soil) or if the waterbody is near a wetland area, the methylation rate may increase. (*Mercury in Michigan's Environment: Environmental and Human Health Concerns*, 1993)

Methylmercury is also incorporated into terrestrial environments, but bioaccumulation factors do not reach the same scale as aquatic environments.

Factors Contributing to Increased Methylation Levels in a Waterbody:

- ★ water color - high dissolved organic carbon (DOC)
 - ★ increased water sulfate levels
 - ★ low pH levels
 - ★ reservoir formation or newly formed reservoir
 - ★ near wetland ecosystems
- (Sources: Wiener, Gilmour in *National forum on Mercury in Fish*, June 1995)

Three different terms are used to describe the way a contaminant accumulates in living organisms.

Bioconcentration

Is the uptake of a chemical *directly* from an organism's surrounding medium. This type of concentration occurs solely from body contact; it could happen in a fish as water passes through its gills. It does *not* include the ingestion of food that contains a contaminant.

Bioaccumulation

Is the net uptake of a pollutant by an organism through *all* exposure pathways, including direct exposure (bioconcentration) or through the consumption of contaminated food.

Biomagnification

Refers to the concentrated increase of a pollutant that occurs as organisms of a high trophic level ingest contaminated organisms at lower trophic levels. Mercury is one of the few metals that is known to biomagnify in aquatic food webs.

Uptake of methylmercury occurs through all of these phenomena, although bioaccumulation has been demonstrated to be the primary mode of accumulation in the upper trophic levels.

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HUMAN HEALTH EFFECTS

The toxicity of mercury has long been known to humans. Hat makers during the 19th century developed symptoms of shaking and slurring of speech from occupational exposure to large amounts of inorganic mercury, which was used to give a metallic sheen to felt hats. This gave rise to the term “mad as a hatter.” (*Mercury, Power Plants and the Environment*, compiled by Steven Ugoretz, WDNR)

Although the inhalation of elemental mercury fumes can be toxic to humans, human exposure to mercury almost always occurs through the consumption of methylmercury in fish tissue. Most of the data about the human health effects of exposure to methylmercury is based on studies from Minamata, Japan and Iraq. The individuals in these cases were exposed to very high levels of methylmercury, much higher than is currently found in freshwater or marine fish.

Subtle health effects (especially prenatal effects) are difficult to measure, and long-term health effects may appear later in life. (*Strategies for Mercury Control in Minnesota*, MPCA Mercury Task Force, July 1994) This uncertainty has led to a national debate over the health effects of low levels of methylmercury consumption.

Health effects of exposure to inorganic mercury

Exposure to elemental mercury vapors cause acute respiratory problems, which are followed by neurologic disturbances and general systemic effects. Acute exposure to inorganic mercury by ingestion will also cause gastrointestinal disturbances and will effect the kidneys.

There are several studies currently underway that address subtle central nervous system damage from low levels of methylmercury exposure that might be occurring in the absence of obvious clinical disease. These studies are addressing questions such as the following:

(from *An Overview of Human Studies on CNS Effects of Methylmercury*, Roberta White, Philippe Grandjean, and Pal Weihe, June 1995. EPA 823-R-95-002)

1. Does exposure to methylmercury at levels that are not associated with obvious clinical disease produce target organ system changes in the central nervous system that are subtle but measurable using sophisticated testing?
2. What levels of exposure are required to produce behavioral effects?
3. What are the relationships between the age at exposure, expression of behavioral changes, and persistence of cognitive deficit? Do different kinds of behavioral changes appear at different ages?

Effects of methylmercury poisoning at levels great enough to cause clinical disease and/or death

Much of the information on the human health effects of methylmercury was derived from the 1971-1972 accidental consumption in Iraq of bread that was prepared from wheat treated with a mercury fungicide. In this unfortunate incident, over 6,000 people were admitted to hospitals and over 400 people died. (*Strategies for Mercury Control in Minnesota*, July 1994) The Iraq incident demonstrated the alarming sequence of events that occurs with severe methylmercury poisoning. During the intake period of about six weeks, no signs or symptoms of poisoning were experienced. In fact, some victims ingested what would ultimately result in a fatal dose without any effects, not even stomach irritation, during the intake period. After intake had stopped, the first symptom, paresthesia (a loss of sensation in fingers and toes), did not appear for another month or so. This was followed by a series of more serious effects such as ataxia, slurred speech, and the constriction of visual fields. (*Mercury Toxicity: An Overview*, Tom Clarkson, EPA 823-R-95-002)

On a cellular level, methylmercury combines with the amino acid cysteine to form a complex that has a structure very similar to the large essential amino acid, methionine. It therefore gets a "free ride" on amino acid carriers and penetrates all mammalian cells. It easily crosses the blood-brain barrier and enters the

interstitial tissue of the brain, where it affects the central nervous system. (*Mercury Toxicity: An Overview*, Tom Clarkson, June 1995. EPA 823-R-95-002)

Methylmercury is believed to interfere with neuronal migration, so that high exposure can produce massive disruption of the developing brain. Young children and infants are most at risk because methylmercury effects the development process by disturbing cell division. Effects in prenatally exposed children appear at intakes 5 to 10 times lower than intakes associated with adult effects. In general, the younger the exposed individual, the greater the impact on the central nervous system. Neuropathological damage and the number of sites within the brain that are affected also increase when exposure occurs at a very young age. (*An Overview of Human Studies on CNS Effects of Methylmercury*, Roberta White, Philippe Grandjean, and Pal Weihe, June 1995. EPA 823-R-95-002)

Prenatal exposure to methylmercury of sufficient severity to produce clinical disease or death has been demonstrated to produce widespread brain damage extending to the cerebral cortex and cerebellum with reduction in brain size and changes in the cytoarchitecture of the brain. Prenatal exposure has also been associated with intellectual deficits in multiple cognitive domains. In addition, children prenatally exposed to methylmercury at

levels insufficient to develop obvious disease might exhibit changes in general cognitive function on a delayed basis (i.e., they might later show deficits that are not obvious at birth). (*An Overview of Human Studies on CNS Effects of Methylmercury*, Roberta White, Philippe Grandjean, and Pal Weihe, June 1995. EPA 823-R-95-002)

Children exposed to methylmercury have shown significant neuropathological abnormalities in the cerebellum and cerebral cortex with widely distributed focal cerebral lesions and some reduction in brain size. However, brains were less reduced in size than those of children exposed prenatally and brain architecture was not disturbed. Methylmercury exposure in children has also been associated with multiple cognitive deficits, which are known to persist. (*An Overview of Human Studies on CNS Effects of Methylmercury*, Roberta White, Philippe Grandjean, and Pal Weihe, June 1995. EPA 823-R-95-002)

Adults exposed to methylmercury have shown cerebellar changes, mild atrophy, and focal cortical lesions at autopsy. Exposure also produces a variety of deficits, which have been less intensively studied than those associated with childhood exposure but seem to include prominent visuospatial and motor impairment. (*An Overview of Human Studies on CNS Effects of Methylmercury*, Roberta White, Philippe Grandjean, and Pal Weihe, June 1995. EPA 823-R-95-002) Other symptoms affected by organic mercury are

the renal and cardiovascular systems, while the liver seemed to be spared. Additionally, high levels of methylmercury exposure have been associated with an increase in the incidence rate for heart attacks and cardiovascular disease. *(Charlene Drumm)*

Generalized pathologic findings in corresponding regions of the brain:

- ★ Occipital lobe
 - visual center
- ★ Pre- and post central cortex
 - motor and sensory centers
- ★ Temporal cortex
 - auditory center

(Health Effects of Exposure to Methylmercury Presentation Notes, Brian Delaney, Toxicologist, Wisconsin Division of Health, 1995)

Symptoms of Methylmercury Poisoning:

Acute/Subacute Cases of Methylmercury Poisoning:

- ◆ Paresthesia (loss of sensation in fingers and toes, numbness/tingling around mouth and lips)
- ◆ Headache
- ◆ Memory loss
- ◆ Hearing loss
- ◆ Visual and speech disorders
- ◆ Lack of coordination
- ◆ Spasticity
- ◆ Paralysis
- ◆ Stupor
- ◆ Coma
- ◆ Death

Congenital Cases of Methylmercury Poisoning (studies from Minimata, Japan):

- ◆ There was a 42.9% incidence of miscarriage/stillbirth in 1963 (compared to 4.2% before World War II) Effects frequently not observed until several months after birth
- ◆ Increase in Cerebral Palsy There was a 9% incidence in rural fishing villages (compared to 0.2 - 2.3% national average)
- ◆ Mental retardation
- ◆ Cerebellar ataxia
- ◆ Dysarthria
- ◆ Limb deformity
- ◆ Hyperkinesia
- ◆ Hypersalivation
- ◆ Strabismus

Chronic Cases of Methylmercury Poisoning:

- ◆ Sensory disturbances
- ◆ “Glove and stocking” symptoms (dullness of feeling in hands and feet)
- ◆ Increase or decrease in taste sensations

(Health Effects of Exposure to Methylmercury Presentation Notes, Brian Delaney, Toxicologist, Wisconsin Division of Health, 1995)

FIVE IMPORTANT METHYLMERCURY-HUMAN HEALTH EFFECT STUDIES

Minamata

Principal Investigator:

Minamata Bay, Japan, 1957 study of poisoning by methylmercury that was directly discharged into Minamata Bay by Chisso Company, Ltd. “Strange phenomena” first discovered as cats, fish, and birds developed unusual symptoms and died. Fifty-four people died from methylmercury poisoning in this incident. Minamata Bay brought the dangers of methylmercury poisoning into international focus. The health effects of high levels of methylmercury consumption were analyzed (see box below).

Iraq

Principal Investigator:

Study of 1972 incident when seed grain treated with methylmercury was used to bake bread. Over 6,000 people were admitted to hospitals and over 400 people died in this unfortunate incident. Health effects were studied in detail; our current reference concentration was based on studies at this incident.

Seychelles Islands

(An Overview of Human Studies on CNS Effects of Methylmercury, Roberta White, Philippe Grandjean, and Pal Weihe, as published in National Forum on Mercury in Fish: Proceedings, USEPA Office of Water, June 1995. EPA 823-R-95-002)

Principal Investigator: T. Clarkson

This is a longitudinal study of children evaluated at 6, 19, and 29 months of age who are now being retested at about age 5.5 years. Physical, neurological, and psychological examinations were completed at each evaluation. Results are pending.

Faroe Islands

(An Overview of Human Studies on CNS Effects of Methylmercury, Roberta White, Philippe Grandjean, and Pal Weihe, as published in National Forum on Mercury in Fish: Proceedings, USEPA Office of Water, June 1995. EPA 823-R-95-002)

Principal Investigator: P. Weihe

This investigation examines the relationship between prenatal exposure to methylmercury and measures of central nervous system function 7 years later. Results: Year one data suggest that some neurobehavioral dysfunction is related to maternal seafood intake during pregnancy, but full investigation of potential confounders has not yet been completed.

Canadian Study of 40,000

(Exposure of Canadian Aboriginal Peoples to Methylmercury, Brian Wheatley and Sylvain Paradis, Water Air and Soil Pollution 80: 3-11, 1995.)

Principal Investigators: Brian Wheatley and Sylvain Paradis

This investigation studies 38,571 indigenous people in 514 native communities across Canada. Methylmercury levels were tested during a twenty-year time period, 1970 to 1992. No definite diagnosis of methylmercury poisoning was made for individuals with greater than 100 ppb in blood. Over the twenty-year time period, there was a general downward trend of methylmercury concentration in individuals with over 20 ppb in their blood or hair equivalent. Further analysis will be done to assess temporal trends by community and individuals, relationships between maternal and fetal levels of methylmercury, and, if possible, a re-assessment of potential risk.

TO WHAT EXTENT IS THE POPULATION AT RISK? WHAT FACTORS RESULT IN ELEVATED EXPOSURE?

Overview

(From Mercury in Michigan's Environment: Environmental and Human Health Concerns, Michigan Environmental Science Board, April 1993)

Potential sources of exposure to mercury for the general population include inhalation of the compound in ambient air, ingestion of contaminated water and food, and dental and medical treatments.

A multi-media analysis of exposure to mercury in Canada has demonstrated that food consumption appears to be the most significant route of exposure to both methylmercury and Hg (II). Fish and shellfish are the single greatest contributor of methylmercury. This study also indicated that dental amalgams are the most significant source of exposure to total mercury, contributing 17 to 42% of total mercury absorbed for age groups greater than or equal to 5 years of age. However, the levels of mercury found in urine and other tissues of the body likely

associated with an average number of filled teeth does not approach levels associated with toxic effects.

Fish Consumption

(from Charlene Drumm:)

The most common route for methylmercury to reach humans is through consumption of contaminated fish products. Even though levels in some fish populations are high (>1 ppm), repeated consumption is required to dramatically elevate human blood levels to the point of toxicity. This requirement narrows the adult risk group substantially to include only those who eat a lot of fish for ethnic and/or economic reasons. For example, one study on Chippewa Indians found that fish consumption was highest in unemployed males and tried to correlate human blood levels to the species of fish consumed.

Fish and wildlife are a vital component to the diet of many native people. They are also an integral part of the culture, lifestyle, and socio-economic well

being of these individuals, and the impact of levels of methylmercury and the perceived risk should not be taken lightly.

Workplace Exposure

From Mercury in Michigan's Environment: Environmental and Human Health Concerns, Michigan Environmental Science Board, April 1993

In 1980 and 1983, The National Institute for Occupational Safety and Health (NIOSH) indicated that 67,551 workers, including 21,153 women, in 2,877 workplaces were potentially exposed to mercury in the workplace in 1980. Most of the exposed workers were employed in the health services, business services, special trade contractors, and in chemical and allied products industries as chemical technicians, science technicians, registered nurses, and machine operators. The use of fluorescent tube compactors may also expose workers in adjacent areas or those working the compactors to increased levels of mercury if proper filters, scrubbing devices, and ventilation are not used. These estimates were derived from observations of the actual use of mercury (97% of total estimate) and the use of trade-name products known to contain the compound (3%).

Workplace environments presenting the largest potential sources of occupational exposure to mercury include chlor-alkali production facilities, cinnabar mining and processing operations, and the manufacture and use of instruments containing liquid mercury. Previous estimates of occupational exposure identified clinical laboratory technologists and technicians, machine operators, stock handlers, grinding machine operators, autobody repairmen, and miscellaneous mechanics and repairmen as the largest potential sources of occupational exposure to mercury exposure.

The principal route of occupational exposure to mercury is vapor phase inhalation of mercury from

workplace atmospheres. Exposure of mercury may result from mercury transported to the home on clothes from individuals occupationally exposed to mercury. Increased exposure to mercury has also been reported in children of occupationally exposed workers. Children whose parents work in facilities that use mercury but do not wear protective uniforms or footgear are most at risk because the mercury may be transferred to the worker's home on clothing or shoes.

Other Exposure Factors

From *Mercury in Michigan's Environment: Environmental and Human Health Concerns*, Michigan Environmental Science Board, April 1993

Persons using skin lightening creams and soaps containing mercury are exposed to higher levels of mercury than the general populations. The use of other products containing mercury, such as laxatives and antimicrobial agents, can also lead to increased exposure. Two cases of chronic mercury exposure have been reported from laxative abuse. Increased exposure to mercury has also been reported from accidental causes, such as broken thermometers and the misuse of mercury as a cleaning agent.

Human Health Effect Studies in Wisconsin

from *Mercury in Wisconsin's Environment: A Status Report*, WDNR, May 1996

The mean fish consumption by adults in the United States is about 15 g/day, or approximately 36 fish meals per year. Fiore et al. (1989) conducted a study of Wisconsin residents who purchased fishing licenses and found a mean consumption of 42 fish meals per year. In a study of consumption rates among Wisconsin Chippewa, Peterson et al. (1994) reported a mean consumption rate of 1.2 meals per week or 62 meals per year, slightly above the mean for the general population. Five Wisconsin Chippewa tribes participated in the study: Lac du Flambeau, Lac Courte Oreilles,

St. Croix, Red Cliff and Bad River. Fish consumption varied seasonally, with the highest consumption following spearfishing season. Blood analyses showed an increase in mercury concentration correlating with an increase in the number of walleyes eaten over two months.

A recent study of a Wisconsin family that consistently ate 4-5 fish meals per week (Knobeloch et al., 1995), revealed their blood mercury concentrations to be between 37-58 ug/L. Their hair samples ranged from 10-12 ug mercury per gram dry weight. The fish were purchased from a local

seafood market and included Lake Superior whitefish, Lake Superior trout, farmed-raised trout and salmon, and imported seabass. Analysis of these fish found that only one group, the imported seabass, contained significant mercury levels. After the family eliminated seabass from its diet, analyses of sequential blood samples confirmed that their mercury levels had significantly decreased. (Elimination followed first-order kinetics with a half-life of approximately 60 days.)

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WILDLIFE HEALTH EFFECTS

As we have just learned, the bioaccumulation of mercury occurs as the organic form of mercury, methylmercury, concentrates in higher trophic levels of the aquatic environment. The process of bioaccumulation of mercury contrasts with the behavior of other trace metals whose concentrations remain constant or decrease with increasing levels in the aquatic environment.

Although the full implications of mercury contamination on wildlife are not fully understood, there is more certainty regarding the health effects of mercury bioaccumulation on wildlife than on human beings. In fact, mercury contamination is considered to be the most serious environmental threat to the well being of fish and wildlife in the southeastern United States. The US Fish and Wildlife Service have found that both freshwater and marine species, including various species of reptiles, birds, and mammals, have been impacted. (*Impacts of Mercury Contamination in the Southeastern United States*, Water, Air, and Soil Pollution, 80: 923 - 926, 1995.)

Scientists in Wisconsin have concluded that the reproductive ability of loons in Wisconsin is affected by high mercury levels. (*Mercury, Power Plants and the Environment*) Elevated mercury levels have been documented in Minnesota's mink and otter populations. Extremely high levels of mercury can permanently damage the central nervous system and impair muscular coordination and vision. This could have serious implications for predators, who rely on speed and coordination to catch their food. (*Strategies for Mercury Control in Minnesota*, 1994)

Embryos and very young animals have the most potential for mercury damage. This is because mercury passes through the placenta to the offspring and can affect cell division.

The wildlife health effects of methylmercury contamination were first studied in 1957 in Minamata Bay, Japan. "Strange phenomena" were reported as cats began to salivate excessively, run in circles, go into convulsions, and die. Fish swam in continuous rotation or floated belly up, and birds went blind and fell out of the sky. In 1959, The Minamata Disease Research Group attributed these "strange phenomena" to methylmercury poisoning that was occurring because a manufacturing plant was discharging methylmercury directly into Minamata Bay.

The levels of methylmercury found in the fish in Minamata Bay (50 parts per million) far, far exceed the levels found in fish today (maximum recorded in Wisconsin: 3 parts per million). However, the studies of the Minamata Disease Research Group have provided us with data about the toxic health effects of methylmercury.

From *Health Effects of Exposure to Methylmercury Presentation Notes*, Brian Delaney, Toxicologist, Wisconsin Division of Health, 1995

Mercury levels that produce sublethal effects in wildlife

Mink	0.1	part per billion
Loons	0.5	part per billion

Mercury levels that produce acute toxicity in wildlife

Pheasant	12	parts per billion
Mink	3-5	parts per billion
Otters	>2	parts per billion

- Mike Meyers, 1997

EFFECTS OF MERCURY ON FISH

Concentrations of methylmercury in fish accumulate through dietary consumption, or through bioconcentration as the methylmercury passing over the gills is assimilated. Although most of the methylmercury in a fish accumulates in the muscle, methylmercury concentrations reach the highest levels in the blood, spleen, kidney, and liver of fish. Fish do not readily eliminate methylmercury. Estimated half-lives are on the order of 0.5 to 2 years; some studies have shown that there is no measurable excretion of methylmercury from fish. (*Bioaccumulation of Mercury in Fish*, James Wiener)

Piscivorous fish usually contain higher levels of methylmercury than co-existing fishes of lower trophic levels. Mercury concentrations in a fish species within a given water body generally increase with increasing age or body size, partly because the rate of uptake greatly exceeds the rate of eliminations. (*Bioaccumulation of Mercury in Fish*, James Wiener)

Fish appear to be highly resistant to the toxic effects of methylmercury. The levels in fish - about 10 times what a human can tolerate - seem not to effect the performance of a fish. Selenium has been suggested as a possible aid in this resistance factor, but it is not greatly understood. (*Mercury Toxicity: An Overview*, Tom Clarkson)

Some studies, however, have indicated that the fish at the top of the food chain, such as walleye

and northern pike, are negatively affected by methylmercury. (*Mercury in Wisconsin's Environment: A Status Report*, WDNR, May 1996)

For example, one study (Whitney 1991) found that the hatching success of walleyes from two Wisconsin lakes was negatively correlated with mercury concentrations in eggs ($r = -0.76$, p) and that the survival of embryos was negatively correlated with egg concentration ($r = -0.7$, $p 0.02$). Growth, survival and behavior were not correlated with egg concentrations. Water column concentrations at both lakes were 0.7 to 2.1 ng/L total mercury and 0.05 to 0.33 ng/L methylmercury. Egg concentrations were 0.002 to 0.058% g/g (micrograms per gram) wet weight eggs. Filet concentrations were 0.14 to 0.57 %g/g wet weight, respectively.

[Following section from *Mercury in Wildlife*, Charles F. Facemire, as published in *National Forum on Mercury in Fish: Proceedings*, USEPA Office of Water, June 1995. EPA 823-R-95-002]

HEALTH EFFECTS OF MERCURY CONTAMINATION ON WILDLIFE

Mercury bioaccumulation occurs when animals consume mercury at levels faster than their bodies can eliminate it. The half-life of mercury in birds appears to be in the range of 35-90 days; the half-life of methylmercury in mammals is extremely variable, ranging from about 3.7 days in mice to as much as 74 days in humans.

As mercury accumulates, toxic effects may appear.

Methylmercury is among the most potent known inhibitors of mitotic cell division; it can also produce chromosomal aberrations, polyploidy, and somatic cell mutations. Therefore, at the cellular level, there appears to be no threshold for methylmercury.

Mortality has been reported in birds with total mercury concentrations in liver tissue ranging from 17 (red tailed hawk) to 752 ppm (grey heron). Sublethal effects reported by Eisler in 1987 include adverse effects on growth, development, reproduction, blood and tissue chemistry, metabolism, and behavior. Other outward clinical signs of methylmercury poisoning include incoordination, vertigo, anorexia, paralysis, convulsions, and abnormal vocalization. Some of these effects have been noted at dietary concentrations as low as 0.5 ppm dry weight (dw) methylmercury. Mercury concentrations ranging from 5 to 40 ppm dw in feathers of adult birds have been linked to reproductive impairment.

Mortality from mercury toxicosis was reported for a Florida panther with mercury residues in hair and liver of 130 and 110 ppm, respectively. A fox (liver tissue methylmercury concentration 30 ppm) and an otter (liver tissue methylmercury concentration 96 ppm) were observed staggering and running in small circles - similar behavior to what was found in the Minamata cats. Death in most mammals appears when mercury concentrations in the brain approach 20 to 30 ppm.

There are a few factors, such as the bioaccumulation of selenium, and internal demethylation of methylmercury to elemental mercury, which may alter the toxicity of mercury in mammalian species.

Mercury and Loons

Loons are at risk to elevated mercury exposure in Wisconsin because they often nest in acidified, low alkalinity lakes. Fish in these lakes bioaccumulate methylmercury to a greater extent than biota from neutral pH lakes. Loons are top predators on these lakes, consuming fish which weigh 10 to 250 grams, and are therefore at risk due to increased mercury exposure.

There is evidence that increased mercury exposure can reduce common loon reproduction. Wisconsin loons may be consuming prey with levels of mercury that are impairing their reproductive capabilities. It appears that methylmercury levels of 0.3 ppb affect loon reproduction and methylmercury levels of 0.4 ppb lead to total loon reproductive failure. (*Mike Meyers, Mercury in the Midwest Conference*) The hatching and fledgling rate of loons with high levels of methylmercury is approximately one half of loons without high methylmercury levels.

The Wisconsin LoonWatch volunteer loon monitoring network and the Wisconsin DNR have identified 80 study lakes (40 "high mercury," low pH lakes, and 40 "low mercury," neutral/alkaline pH lakes) in Ashland, Bayfield, Iron, Vilas, Oneida, and Forest counties.

(*Common Loons Nesting on Low pH Lakes in Northern Wisconsin Have Elevated Blood Mercury Content, Water, Air, and Soil Pollution*, 80:871 - 880, 1995.)

WILDLIFE MOST IMPACTED BY HIGH MERCURY LEVELS

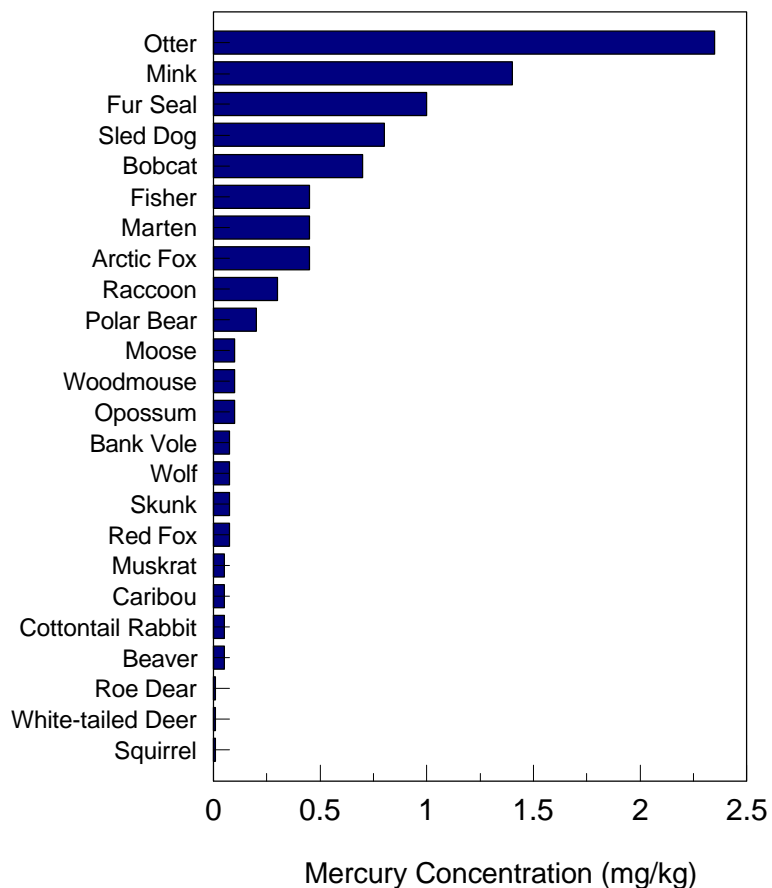
Elevated mercury levels have been found in virtually all wildlife species. Each species tends to handle methylmercury a little differently, but some generalities can be made. (*Mercury in Wildlife*, Charles F. Facemire)

sustained on a diet containing 5.0 ppm methylmercury showed clinical signs of mercury toxicosis within 24 days and died within 30 days. (*Mercury in Wildlife*, Charles F. Facemire)

The bioaccumulation and biomagnification of methylmercury occurs at more intense levels in aquatic systems than in terrestrial environments. This may be due in part to the fact that aquatic chains typically have more trophic levels, and thus more chance at magnification. It also may be attributed to the way different species store their methylmercury burden. Birds and mammals tend to concentrate methylmercury in their feathers and fur, which are not easily digestible. In contrast, methylmercury accumulates in the tissue of fish, which is completely digested. (*Mercury in Wildlife*, Charles F. Facemire)

The lowest concentrations of methylmercury are typically found in herbivores. The highest levels of methylmercury concentration are found in the top predators in aquatic food chains. These animals include fish, fish-eating birds such as eagles and ospreys, raccoons, otters, mink, and the endangered Florida panther (who eat raccoons). There has been one death of a Florida panther attributed to mercury poisoning. Mink seem to be the mammalian species most sensitive to methylmercury poisoning. Mink

Mercury Concentrations in Mammals



From Wren, 1986 (as quoted in Facemire, 1995)

MERCURY CONCENTRATIONS IN WISCONSIN WILDLIFE

From *Mercury in Wisconsin's Environment: A Status Report*, WDNR, May 1996

Mercury concentrations have been determined in several Wisconsin wildlife species. The first study was conducted in the early 1970s on upland game. Average liver concentrations were very low for white-tailed deer (0.01 mg/kg, n=18) and cottontail rabbits (0.02 mg/kg, n=20) (Kleinert and Degurse 1972). This was representative of low exposure for herbivorous, terrestrial mammals. The first analysis of carnivore tissues, in 1978, revealed high average mercury concentrations in piscivorous (fish-eating) species: Mink were 2.08 mg/kg, n=39; and otter 3.34 mg/kg, n=49. These were directly related to mercury contamination in sediments, crayfish and fish along the Wisconsin River (Sheffy and St. Amant 1982). In 1985 and 1986, furbearer carcasses from other Wisconsin basins were analyzed for mercury (Amundson 1986). All mink, otter and fisher livers had detectable concentrations (mink: 0.47 mg/kg, n=8; otter: 2.08 mg/kg, n=6; fisher: 0.17 mg/kg, n=4), while 50 percent of raccoon and bobcat livers sampled were above the minimum detection limit (MDL) for mercury (raccoon: 0.43 mg/kg, n=32; bobcat: 0.06 mg/kg, n=3).

Subsequent sampling has focused on piscivorous mammals. Mink collected in 1990 and otter in 1994 indicate that, while mercury exposure and bioaccumulation are

ubiquitous, there is variation in the level of contamination by area. Hot spots^a have been identified in Marathon and Adams/Juneau Counties on the Wisconsin River. Tissue concentrations here were 20 and 17 ppm, respectively. For the northern section of the river (i.e., Vilas, Oneida, and Lincoln Counties), mercury concentrations have not changed appreciably over 20 years. In some southern counties along the river, mink and otter have lower mercury burdens than were found in earlier surveys. Mink and otter from northern lakes and river systems draining into Lake Superior have consistently higher mercury burdens than animals from southern lakes and river systems draining into Lake Michigan, Green Bay, and the Mississippi River.

As previously discussed, fish and other aquatic prey items have accumulated mercury from water and sediments. While whole fish analysis is not available for sites where carcasses have been analyzed, analyses from other river basins and lakes throughout the state indicate that consumption of fish as 50 percent of a mink or otter's diet would likely exceed proposed daily exposures protective for mammals (0.016 mg/kg/day) (Bradbury et al. 1993). This observation suggests that individual animals in contaminated areas may be experiencing toxic effects, and that populations in

highly contaminated ecosystems may be reduced or even extirpated. Unfortunately, reliance upon trapper-harvested, frozen carcasses has prevented biochemical and histological evaluations of tissues for potential mercury-induced toxic effects, as well as an unbiased estimation of population sizes. Therefore, it is unknown whether mink or otter health and productivity are impaired at mercury-contaminated sites.

Similar to mammals, piscivorous birds are at risk for elevated mercury exposure in Wisconsin. This relationship is evident when average tissue mercury levels of Wisconsin birds are compared between species occupying various feeding niches (all samples reported as mg Hg/kg tissue, wet weight):

Muscle Tissue - Wild turkey (0.04 mg/kg, n=2), ring-necked pheasant (0.04 mg/kg, n=10), woodcock (0.04 ± 0.01 mg/kg, n=14), ruffed grouse (0.04 mg/kg, n=9), Canada geese (0.04 mg/kg, n=5), mallard (0.05 ± 0.02 mg/kg, n=11); common merganser (0.38 ± 0.26 mg/kg, n=5), bald eagle (1.28 ± 1.14 mg/kg, n=13), common loon (3.22 ± 3.37 mg/kg, n=7)
Liver tissue - Wood duck (0.04 mg/kg, n=2), mallard (0.24 ± 0.20 mg/kg, n=42), bluewing teal (0.53 ± 0.08 mg/kg, n=6), bald eagle

(2.81 ± 1.72 mg/kg, n=22), osprey (5.3 ± 3.1 mg/kg, n=3), common loon (16.53 ± 25.5 mg/kg, n=12) (WDNR unpubl. data).

Eggs of piscivorous birds (bald eagles, ospreys, loons, herring gulls, cormorants, etc.) are often used to monitor temporal and spatial trends of bioaccumulating contaminants. The total mercury content of Wisconsin bald eagle eggs has not declined [(1976-79) 0.17 ± 0.02 mg/kg, n=37; (1983-87) 0.18 ± 0.02 mg/kg, n=36]. Egg mercury content ranged from 0.02 to 0.62 mg/kg fresh wt. Twenty Wisconsin bald eagle eggs collected in 1990-94 underwent mercury analysis at the Wisconsin State Lab of Hygiene. Mercury content in Wisconsin bald eagle eggs has not declined: Content was 0.17 ± 0.02 mg/kg, n=37, from 1976 to 1979; 0.18 ± 0.02 mg/kg, n=36, from 1983 to 1987; and 0.23 ± 0.10 mg/kg, n=13, from 1990 to 1994.

The mercury content of common loon eggs collected in Wisconsin has remained stable over the past 10 years [(1985-87) 0.68 ± 0.23 mg/kg, n=15; (1991-93) 0.87 ± 0.27 mg/kg, n=21) (WDNR unpubl. data). Notably, Wisconsin common loon eggs contain four times as much mercury concentrations than Wisconsin bald eagle eggs.

The mercury exposure levels of live birds can be determined by collecting feather and blood samples. WDNR is collaborating with the University of Minnesota and Northern Michigan University to compare common loon feather and blood mercury levels in

Wisconsin, Minnesota, and Michigan. Preliminary analysis (1991-94) indicates that similar blood and feather levels are found in loons sampled in all three states (adult feathers 2.8 - 49.0 mg/kg fw; adult whole blood 0.5 - 4.2 mg/L; nestling whole blood 0.1-0.5 mg/L fw). The Wisconsin sampling effort is stratified and more intensive as WDNR is interested in examining the relationship between mercury exposure and lake pH. Fish from these lakes bioaccumulate methylmercury to a greater extent than biota from neutral pH lakes. A significant negative linear relationship exists between adult loon blood clot mercury and lake pH ($r^2=0.38$, $F=15.27$, P). This indicates that loons nesting on low pH lakes (pH 6.3) receive greater mercury exposure than loons nesting on neutral pH lakes. The relationship was greater for adult males ($r^2=0.56$) than for adult females ($r^2=0.36$) (Meyer et al. in press).

Nestling bald eagle feathers were also collected in Wisconsin, Michigan and Minnesota (1985 to 1989.) The average mercury content of Wisconsin nestling feathers (10.2 ± 4.4 mg/kg, n=43, range 2.7-23.0) (WDNR unpubl. data) was similar to that found in nestling feathers collected in the Michigan Upper Peninsula (8.2 ± 3.4 mg/kg, n=47, range 3.5-16.0) and Lower Peninsula (9.0 ± 2.7 mg/kg, n=30, range 4.6-15.0). The content was also less than that found in nestling feathers from Voyageurs National Park in Minnesota (17.7 mg/kg, n=11, range 4.6-27.0), but greater

than feathers collected from nestlings on Ohio's Lake Erie shoreline (4.7 ± 3.3 , n=7, range 1.5-11.1) (Evans, 1993).

Researchers are measuring the impact of elevated mercury exposure on common loon reproduction on northern Wisconsin lakes. Fish in many of these lakes have total mercury concentrations exceeding 0.4 ppm. Furthermore, the total mercury content of livers of three adult loons collected in Iron and Vilas Counties exceeds that of reproductively impaired common loons in Ontario. Many adult loons nesting on low pH lakes have elevated blood mercury levels, as do all of the chicks produced on those lakes. Preliminary results indicate that reproduction in loons nesting on low pH lakes is impaired, but we do not know whether this is due to elevated mercury exposure or to other habitat variables (Meyer, 1994). An epidemiological approach is being used to test whether reduced breeding success is related to elevated mercury exposure, habitat variables, or a combination of both.

A recent study investigated the relationship between bald eagle reproduction and mercury exposure in the Great Lakes region. Bowerman et al. (1994) tested the relationship between logarithmic mean concentrations of mercury in adult feathers among breeding areas and mean five-year reproductive measures using general linear regression methods. The study found that mercury does not currently affect bald eagle reproduction in the Great Lakes

region. A more rigorous test of this relationship would be to compare adult and nestling feather mercury levels and the reproductive output at individual territories. Fish mercury levels are a function of individual lake chemistry, thus exposure within a given region (i.e. northern Wisconsin) can differ by a factor of 10 (WDNR unpubl. data).

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ANTHROPOGENIC USE OF MERCURY

Historical Perspective

From The Historical Background of Chemistry, Henry M. Leicester; Discovery of the Elements, Mary Elvira Weeks and Henry M. Leicester; M2P2

The human relationship with mercury reaches far back into history. Mercury has been found in Egyptian tombs dating back to 1500 or 1600 B.C., and there are vague references to it in early greek literature. By the first century A.D., its preparation by roasting cinnabar was well known. It was also during this time that Pliny the Elder (A.D. 23-79) noted that mercury was poisonous. Mercury’s liquid nature caused it to be classified as a “water” for hundreds of years; it was not until 500-700 AD that it was considered a metal.

Mercury was especially interesting to ancient alchemists, who regarded it as a distinctive substance. Arabian alchemists believed that all metals were formed from a combination of mercury and sulfur.

It is likely that cinnabar was the only mercury compound known to the ancients, who used it both as a pigment and as a source of the metal. At times, cinnabar was more highly regarded than gold as a medicine for prolonging life. It has been reported that several Chinese emperors died after drinking mercury compounds in an attempt to secure immortality. The mercury mines in Almadén, Spain, were known to have been

worked since 492 B.C. to send cinnabar to Rome. A visitor to the mines in 1717 was surprised to find “the crops, trees, and inhabitants were not injured by the fumes, and the springs near the mine yielded good potable water.” Unfortunately, the slaves who worked and ate in the mines did not fare as well; they suffered

severely from mercury poisoning and died by the thousands.

In the 1800s, the term “mad as a hatter” was coined to describe the physical symptoms of inorganic mercury poisoning that hat makers experienced from spending hours with their hands immersed in open vats of mercury as they shaped felt hats and breathed in mercury fumes.

Did Newton suffer from mercury poisoning?

J.R.M. Seitz (Harvard) and J.Y. Lettvin (MIT) argue that Newton’s problems around the age of 50 were not psychic trauma following his mother’s death but mercury poisoning: Newton’s “Optiks” describes in detail how he worked in closed rooms exposed to kilograms of mercury. They estimate that the vapor level exceeded by a 1000 fold factor that necessary for mercury poisoning. This was also the time that Newton’s handwriting became tremulous. The researchers also cite Newton’s fondness for crimson rooms which at the time were likely painted with vermilion pigment (ground up cinnabar ore).
- *New Scientist*, 52, 274, (1971).

“It is a fluid but does not moisten, and runs about, though it has no feet”

- *Paracelsus the Great, Medical Alchemist, sixteenth century*

ANTHROPOGENIC EMISSIONS OF MERCURY

below from Mercury Sources and Regulations: background Information for the Virtual Elimination Pilot Project, Ross & Associates, September, 1994.

Mercury is emitted from a variety of human activities. It is emitted when coal is burned; when metals such as copper and lead are mined or smelted; when garbage or medical waste containing used mercury-containing products is incinerated; or when lime, cement, chlorine, or caustic soda is manufactured.

Estimated United States emissions of mercury total approximately 263 tons/year. Combustion point sources, including utility, commercial, and industrial boilers, as well as Municipal Solid Waste (MSW) incineration and medical waste incinerators, account for 85% of anthropogenic mercury emissions.

Anthropogenic mercury releases to the environment are usually classified into two categories:

Purposeful Use

Describes the intentional or deliberate introduction of mercury into a manufacturing process or consumer goods.

In this situation, mercury can be potentially released through:

- ◆ Production or supply of mercury
- ◆ Use in manufacturing
- ◆ Waste Disposal

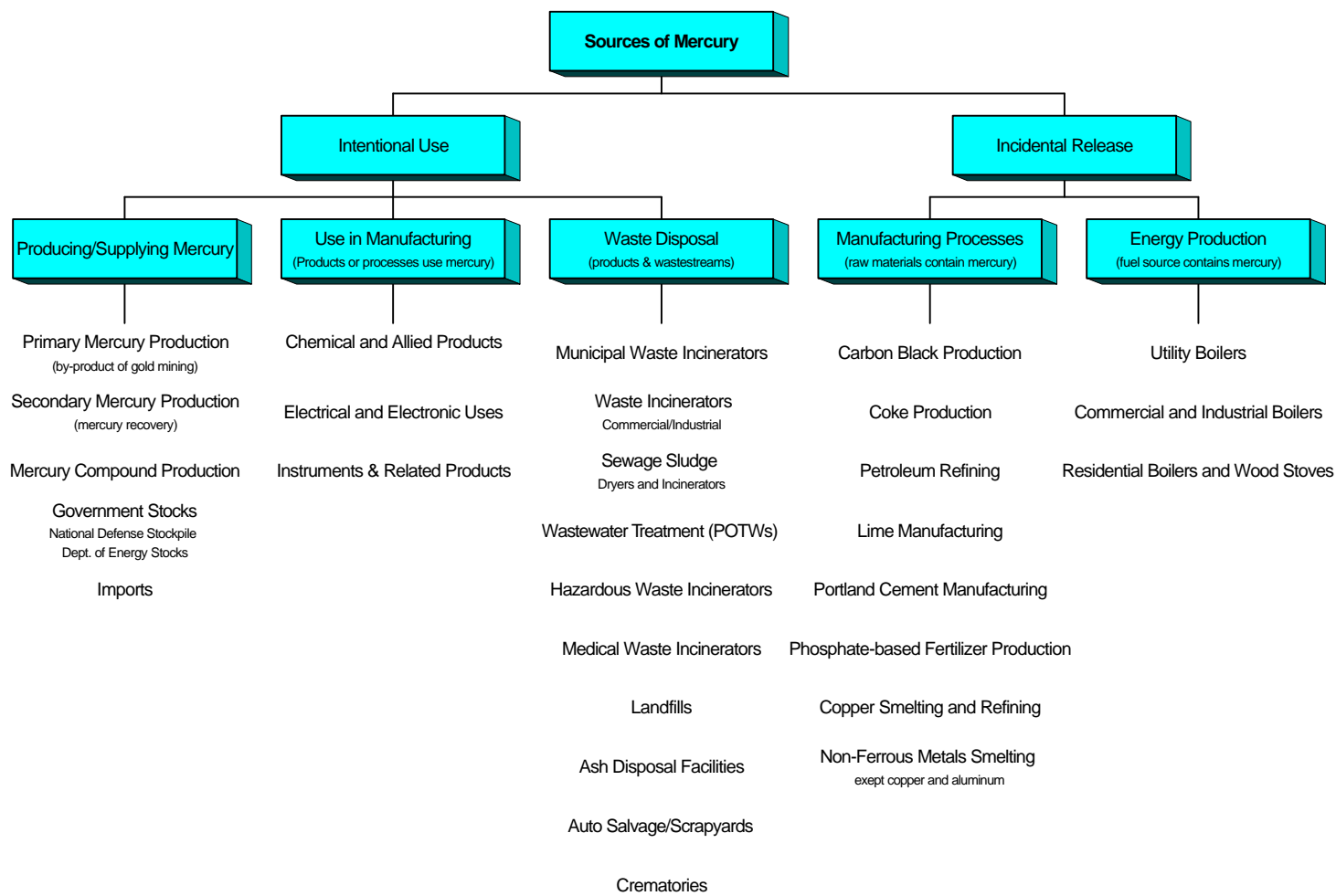
Incidental Release

Because mercury is a naturally occurring element that is present in ores and fuels, and because mercury is easily vaporized at low temperatures, it is released when some raw materials are heated. This is called *incidental release* because mercury plays no role in these processes.

Incidental release is typically broken into two categories:

- ◆ Manufacturing Processes (whose raw materials or fuel supplies contain mercury)
- ◆ Energy Production (whose fuel sources contain mercury)

Sources of Mercury - Purposeful Use

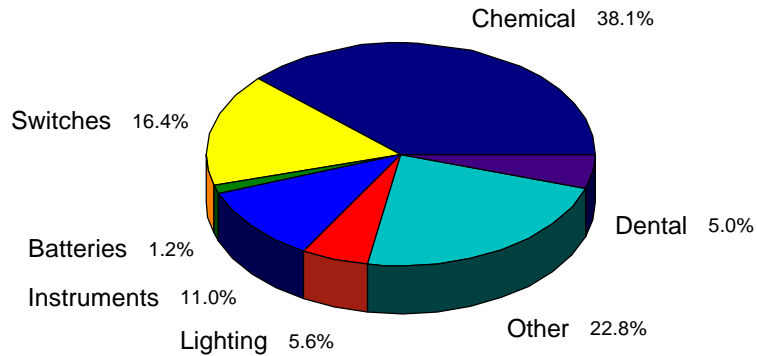


PURPOSEFUL USE OF MERCURY: GLOBAL AND NATIONAL DEMAND

Mercury use in both the United States and Europe has fallen dramatically in recent years. Between 1980 and 1992, US consumption fell by about 70 percent. Chlorine and caustic soda manufacturers remain the largest consumers with 1994 consumption of 135 metric tons. However, these manufacturers were able to reduce their consumption of mercury by 45 metric tons from their 1993 level by increasing the recovery of their mercury sludge and by converting several production plants to non-mercury technologies.

The use of mercury in battery production has fallen dramatically. In 1980, batteries accounted for 40 percent of mercury demand in the US; by 1992, this had declined to only 2 percent of domestic consumption.

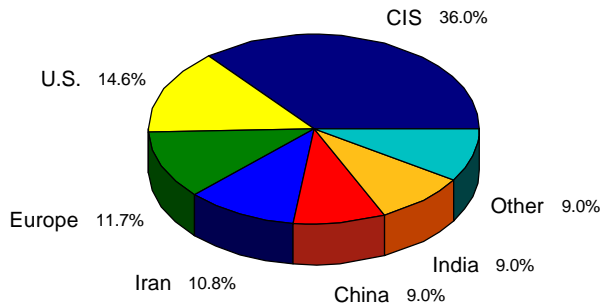
1994 U.S. Purposeful Mercury Use



Total: 483 Metric Tons

Source: DoD memo, November 1995, quoting Bureau of Mines

1993 Global Mercury Consumption



Total: 3,834 Metric Tons

Source: DoD memo, November 1995, quoting Bruce Lawrence, "Mercury," E&MJ, March 1994

Mercury's Unusual Properties

Mercury's unusual chemical properties have led to its widespread use in industry. Mercury is very dense (13.5 g per cc, compared to water at 1 g/cc) and does not readily react with nonoxidizing acids. It is the only heavy metal that is a liquid at room temperature, although it vaporizes easily. Simply exposing the metal to air or blowing air through it will release it in a gaseous state. Fluorescent lights and mercury-vapor lamps rely on mercury's high vapor pressure (it vaporizes quickly when current is applied), high electrical conductivity, and its ability to emit UV light when it is excited (phosphors in the lamps convert this invisible light to visible light). Mercury alloys easily with almost any metal (except iron, which is sometimes used for mercury containers) and forms amalgams. Mercury amalgamates with sodium in sodium chloride (ordinary salt) to release chlorine gas that can be used for purification of public water supplies and production of bleached paper. Amalgams are also used to extract precious metals or for dental uses.

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This document was designed to be a compilation of the best mercury information available to date. We are gratefully indebted to the work of authors below, without whose innovative and ground-breaking research this report would not be possible. Please note that many of these sources were quoted directly:

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Mercury in Michigan's Environment: Environmental and Human Health Concerns, Michigan Environmental Science Board, April 1993

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Mercury in Minnesota Slide Show Script, Western Lake Superior Sanitary District, November 1995

Mercury Pollution Prevention In Michigan: Summary of Current Efforts and Recommendations for Future Activities, The Michigan Mercury Pollution Prevention Task Force, April 1996

Mercury, Power Plants and the Environment: Basic Facts about Mercury and Coal-fired Power Plants, the Environment, Fish and Wildlife, and Human Health, compiled by Steven Ugoretz, WDNR

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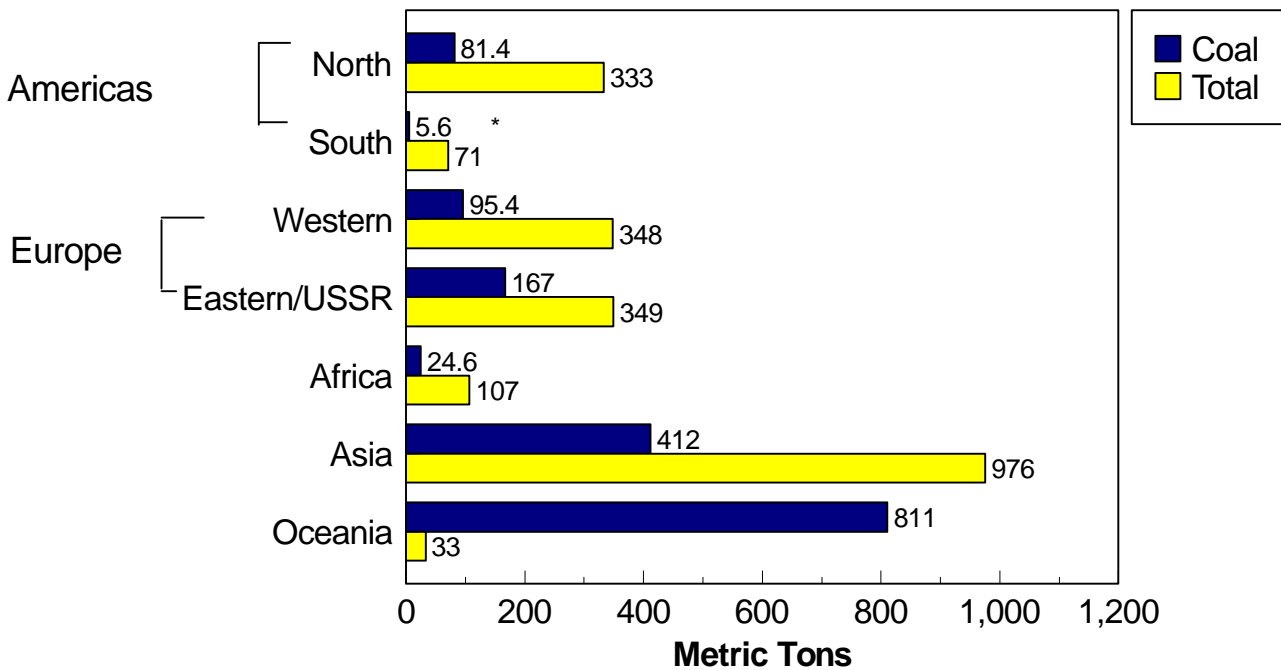
Strategies for Mercury Control in Minnesota, MPCA Mercury Task Force, July 1994

The Historical Background of Chemistry, Henry M. Leicester, Dover Publications, New York, 1956.

The Hunt for Quicksilver, presented at AERB's Wastewater Discharge Compliance Conference, November 17, 1992 by Frank Altmayer, Scientific Control Labs, Inc.

US AND GLOBAL MERCURY EMISSIONS

Worldwide Annual Mercury Emissions



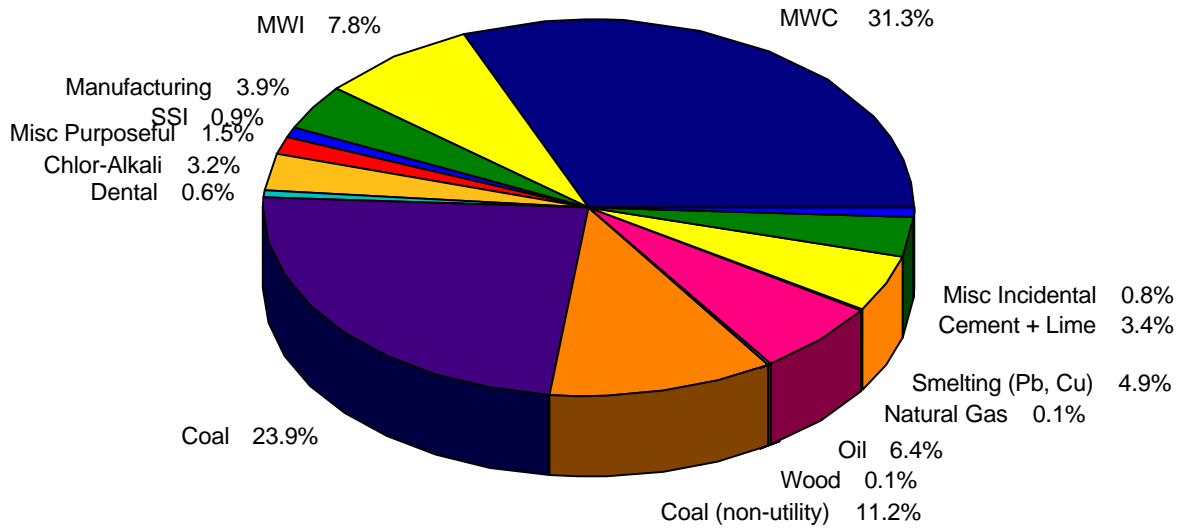
Total Coal: 794 Mg
 Total Combined: 2217 Mg

Don Porcella, Presenting at "Mercury in the Midwest" Conference, October 22, 1996

* = add 100 tons for gold mining

1990 US Mercury Emissions

Draft EPA Report to Congress



Intentional Mercury Use - 49%; Energy Production 42%; Incidental Release 9%

Data arrangement by Ed Swain, MPCA

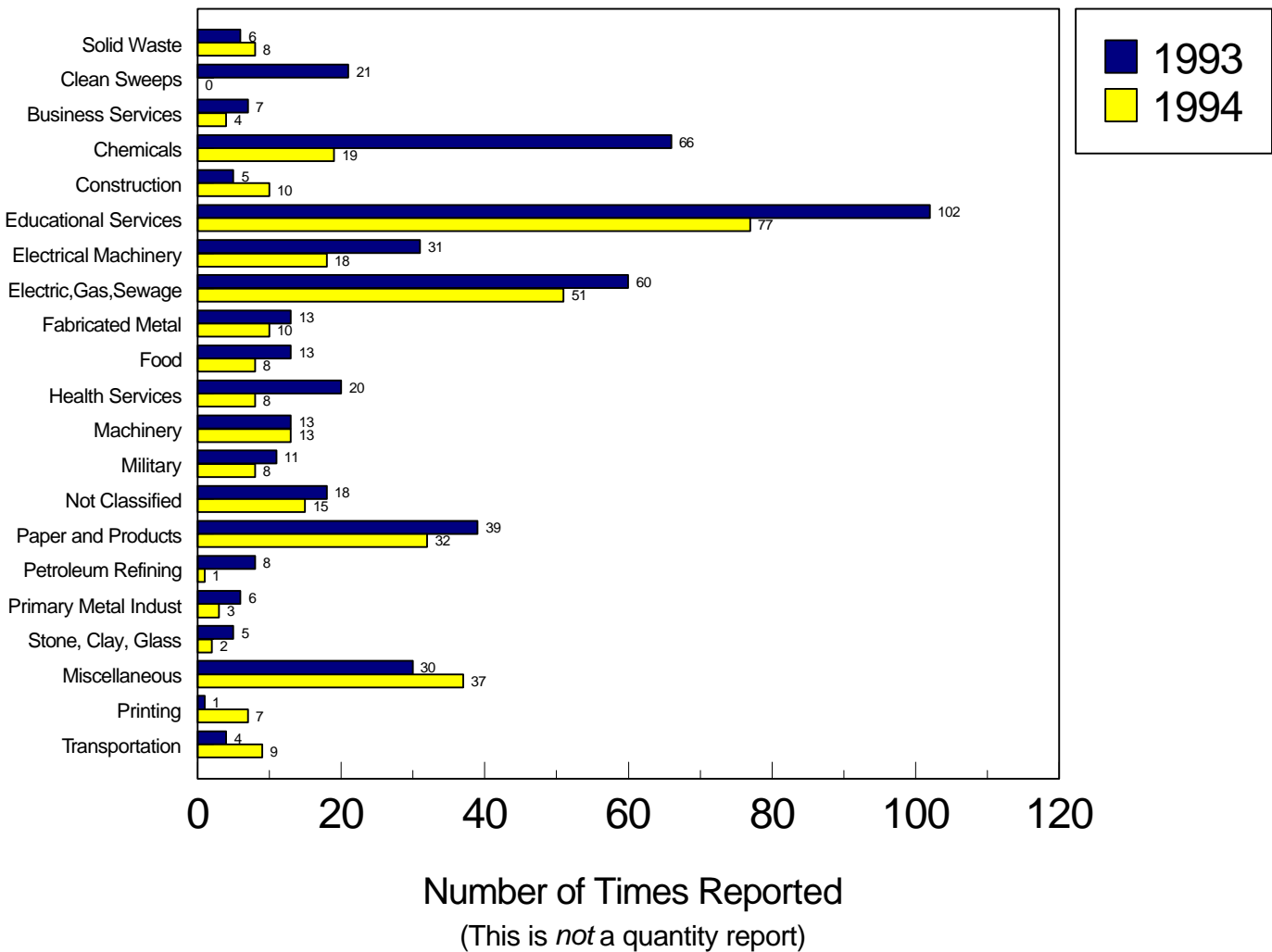
WISCONSIN MERCURY EMISSIONS

ITRS DATA

The Integrated Toxics Reporting System (ITRS) includes information from The Hazardous Waste Annual Report, The Hazardous Waste Manifest, the Air Emissions Inventory, The Wastewater Industrial Discharge Report, and the Toxics Release Inventory (TRI).

This information is valuable in identifying sources of mercury, but it has its limitations. The following charts identify the number of reports that were filed for each category; this does not reflect the number of facilities reporting for that category (e.g., one facility could report three times), nor does it reflect the amounts of mercury emitted for each category. It is useful for source identification only. All of the information has been sorted according to SIC codes.

Number of Wisconsin Reports of Mercury Use or Emissions 1993 & 1994
Data from the Integrated Toxics Reporting System



WISCONSIN AIR EMISSIONS

Wisconsin mercury emission estimates are also broken into three basic categories: energy production, incidental release, and purposeful use.

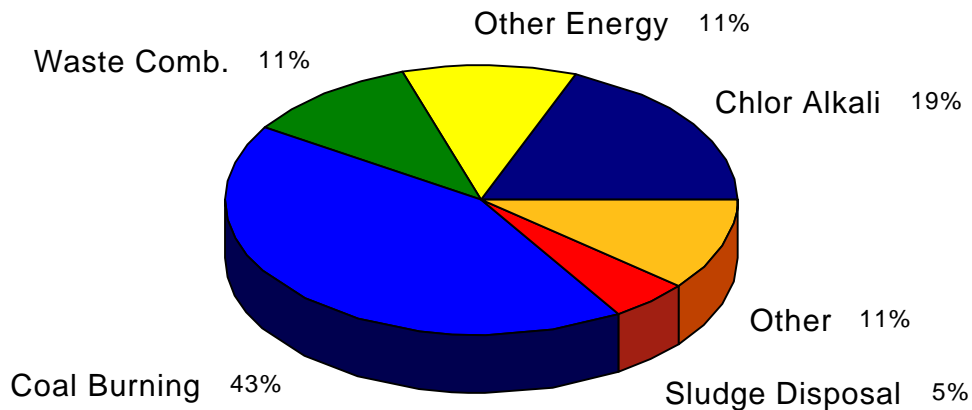
We estimate that energy production accounts for about 60 percent of mercury air emissions in Wisconsin. This includes the burning of coal, oil, gasoline, and wood.

About 20 percent of mercury air emissions in Wisconsin comes from processes like chlor-alkali production or lime production that incidentally release mercury as part of their manufacturing process. There is one chlor-alkali facility in Wisconsin that uses a mercury cell process to convert brine (sodium chloride) into caustic soda (sodium hydroxide).

About 20 percent of mercury air emissions in Wisconsin originate from the purposeful use of mercury in products.

“Estimated Air Emissions in Wisconsin” data was provided by Kurt Hansen of the Air Management Bureau in the WDNR.

Annual Hg Air Emissions 1994 Wisconsin



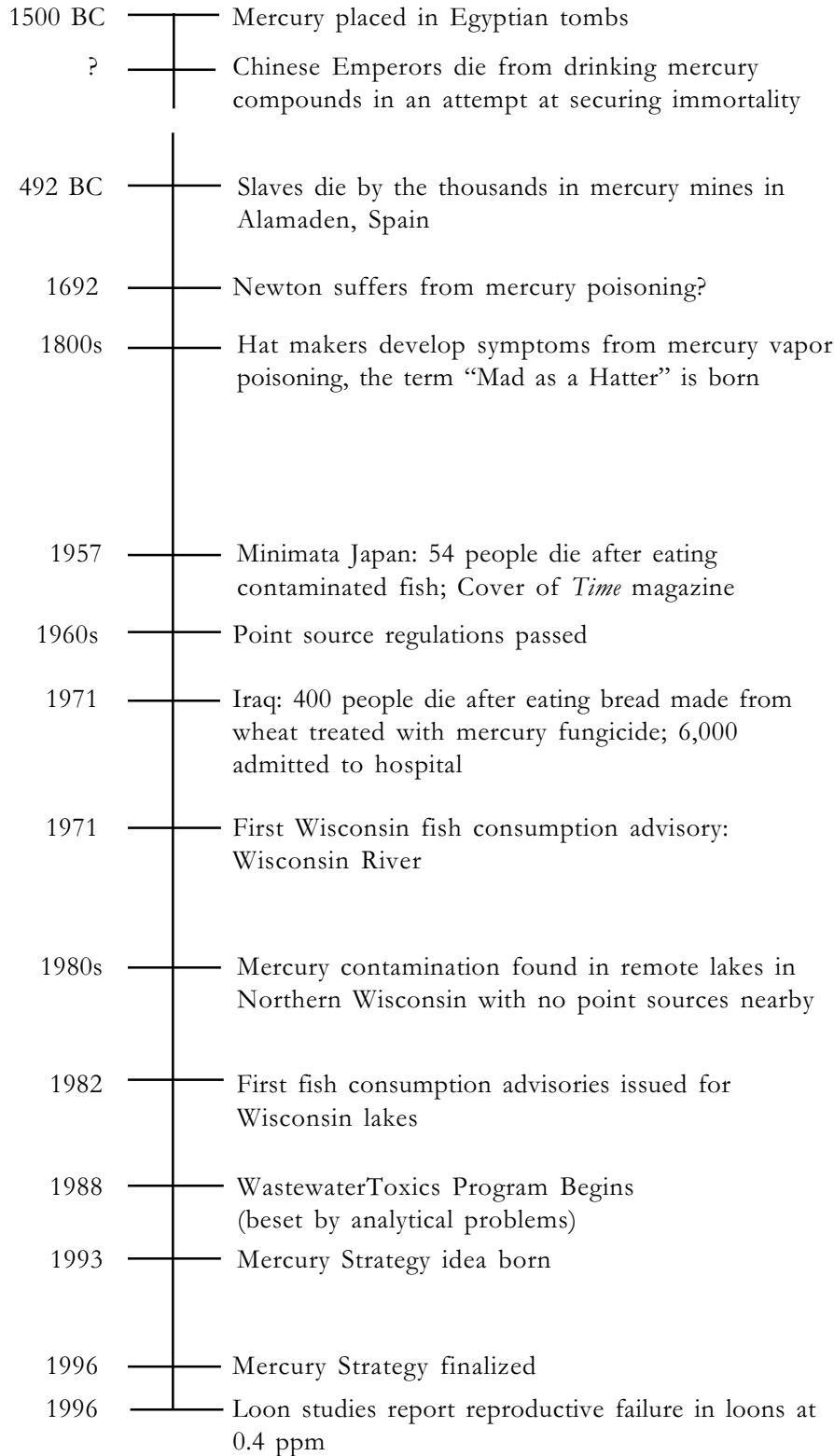
Source: Kurt Hansen , WDNR

**Estimated Mercury Air Emissions-
Wisconsin 1994**

	Mercury Emissions (lbs/yr)	% of State Total
Originating from ENERGY PRODUCTION		
Coal - Utility	2,076	37.00 %
Industrial/Commercial	382	6.80 %
Oil - Industrial/Commercial	200	3.60 %
Residential	170	3.00 %
Gasoline and Diesel - Mobile Sources	220	3.90 %
Wood	27	0.50 %
<i>Subtotal</i>	3,075	54.80 %
Originating from PURPOSEFUL USE		
Medical Waste Incineration	313	5.60 %
Municipal Waste Incineration	243	4.30 %
Wastewater Sludge Incineration & Land Spreading	286	5.10 %
Electric Lamp & Mercury Switch Breakage	274	4.90 %
Laboratory and Dental Use	64	1.10 %
Hg-Containing Apparatus Manufacturing	42	0.70 %
Secondary Metal Smelting	37	0.70 %
Cremation	16	0.30 %
Battery Production	2	0.00 %
<i>Subtotal</i>	1,277	22.80 %
Originating from INCIDENTAL RELEASE		
Chlor-Alkali Production	1,141	20.30 %
Lime Production	118	2.10 %
<i>Subtotal</i>	1,259	22.40 %
<i>Total</i>	5,611	100 %

*Notes: Only Anthropogenic categories which are quantifiable have been included.
Mercury emissions from landfill volatilization have not been quantified.
Mercury is no longer used in paints, pigments, or turf products in the US.
Significant digits of inventory values are not indicative of the accuracy of the values.*

MERCURY THROUGH THE AGES



1500BC - 1800s:
Toxicity of Elemental Mercury Understood

1957-1971:
Methylmercury Hazards in Forefront; Point Source Regulations Passed

1980 - Present:
Studies of Mercury Transport in Environment Begin

1993 - Present:
New Regulatory Era