

Mercury Monitoring in Wisconsin

A Mature and Robust Program



Importance of Mercury as Pollutant

- Wisconsin is a water rich state and vulnerable to mercury contamination.
 - By area of water Wisconsin ranks 9th and for inland states Wisconsin is second behind Michigan.
 - USGS lists Wisconsin as 17.3% covered by water.
- Coastline, Rivers, Lakes, and Wetlands
 - Wisconsin has more than 1,000 miles of Great Lakes shoreline and more than 20 percent of the state's land area lies within the Great Lakes basin
 - Wisconsin DNR estimates in the state 84,000 river miles flow through 15,000 lakes and over five million wetland acres.
 - Includes Wetlands of international importance as designated by the Ramsar Convention
 - Door County Coastal Wetlands
 - Horicon Marsh
 - Kakagon and Bad River Sloughs

Wisconsin Mercury Regulations

- Mercury can be included as a regulated pollutant by a number of Air program rules including – NR404, 405, 406, 407, 408, 439, 445, and 446.
- Mercury is directly regulated by NR446, primarily affecting very large sources.
 - NR 446: **CONTROL OF MERCURY EMISSIONS**
 - No person may commence construction or modification of a stationary source that results in an increase in annual allowable emissions of mercury of 10 pounds with out a permit under NR 406.
 - No person may cause, allow or permit emissions of mercury in such quantity and duration as to cause the ambient air concentration to exceed 1 ug/m³, averaged over a 30-day period.
- Mercury monitoring in Wisconsin provides data for planning and to assess status. Monitoring is not as a tool of compliance.

Wisconsin Mercury Monitoring Program

Deposition Monitoring

- Collection of precipitation samples for laboratory analysis.
- Data used to assess the movement of the mercury from the atmosphere to the terrestrial and aquatic environment.

Ambient Monitoring

- Monitoring mercury concentration in the air.
- Typically done at remote sites.
- Measurements include gaseous elemental, gaseous oxidized and particle bound mercury.

Deposition Monitoring in Wisconsin

In 1985 Wisconsin Legislature passed Act 296 “Acid Rain Law”. Included in law was the establishment of the Acid Deposition Research Council which had funding and authority to support research.

Mercury monitoring started as an out-growth of Wisconsin Acid Rain monitoring and sites in NADPs NTN network.

Sampling started in late 1980s

First report on mercury monitoring issued in 1990. The report did not present much data instead reported that samplers were bad, collection techniques were bad and our analysis labs were contaminated.

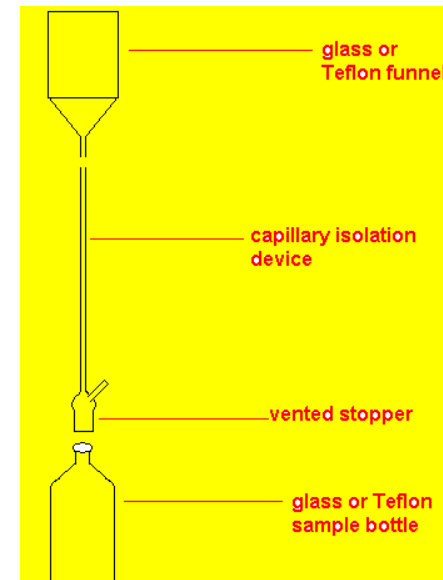
In 1993, Wisconsin began testing new samplers based on the Swedish IVL bulk sampler design.

IVL Mercury Sampler

- Developed in 1988 by the Swedish Institutet för Vatten- och-Luftvårdsforskning (Abbreviated IVL)
- Wisconsin purchased one IVL sampler and used that as a template for making additional samplers.
- Bulk sampler with no moving parts. Passive sampler using glass sampling train.
- Wisconsin DNR tested the sampler at a single site and then operated a network of sampler from 1993 to 1999.



WIVL at field site

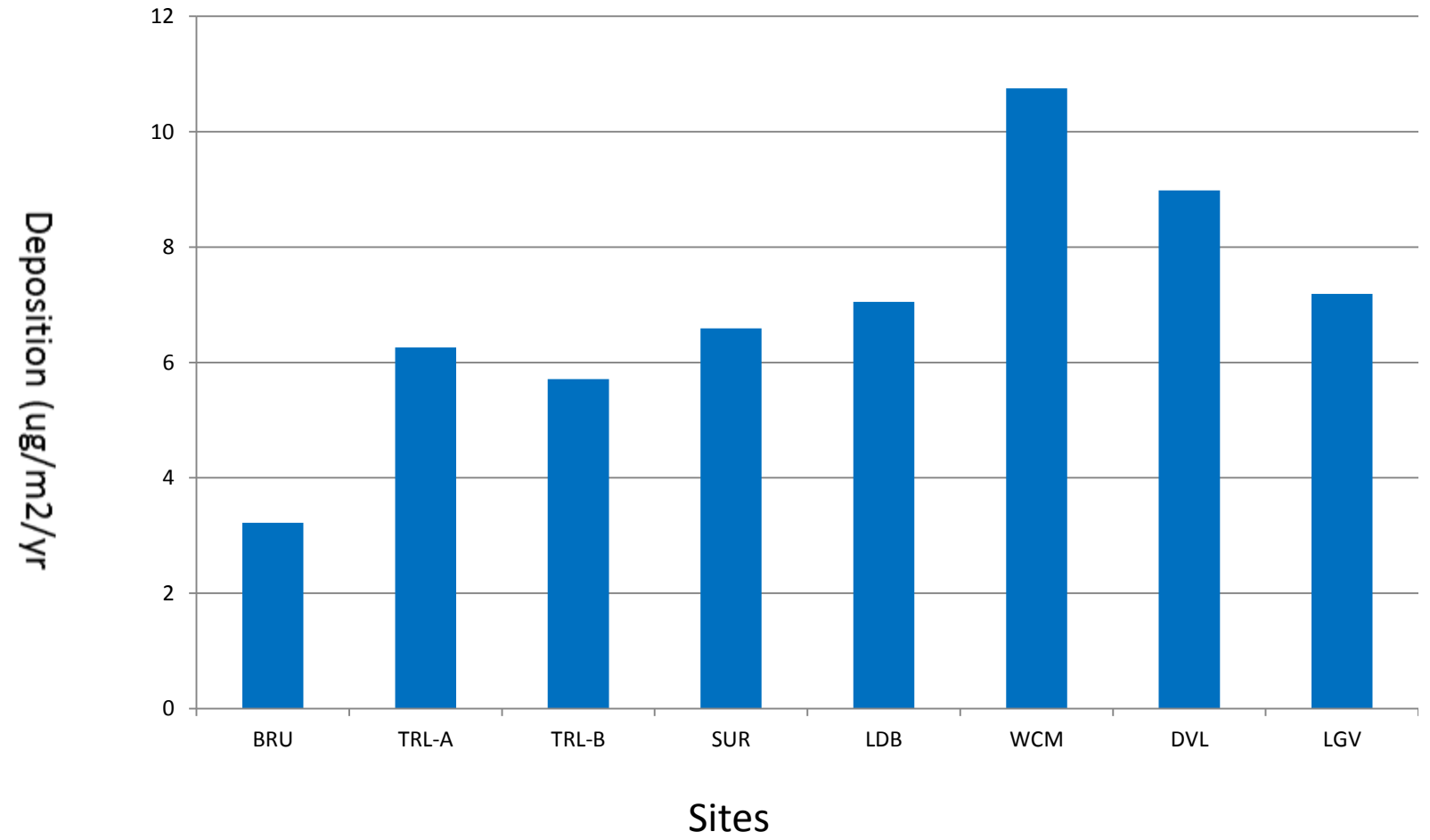


Sampling train

Wisconsin
IVL Mercury Sampling
Network



Wisconsin IVL Network Summary 1997



From: MONITORING MERCURY DEPOSITION IN WISCONSIN 1996-1997
MARK K. ALLEN AND BART SPONSELLER1
1998 International Symposium on Measurements of Toxic and Related Air Pollutant (Sept.1998)

Mercury Deposition Network (MDN)

- Beginning in 1996 Wisconsin staff began deploying MDN wet only samplers to field sites.
- Wisconsin would have eventually deploy a network of 6 WDNR sites and two tribal sites.
 - Including a site on Lake Superior, an urban site, and one site with event sampling.
- MDN provided consistent sampling and analysis of deposition samples for mercury.

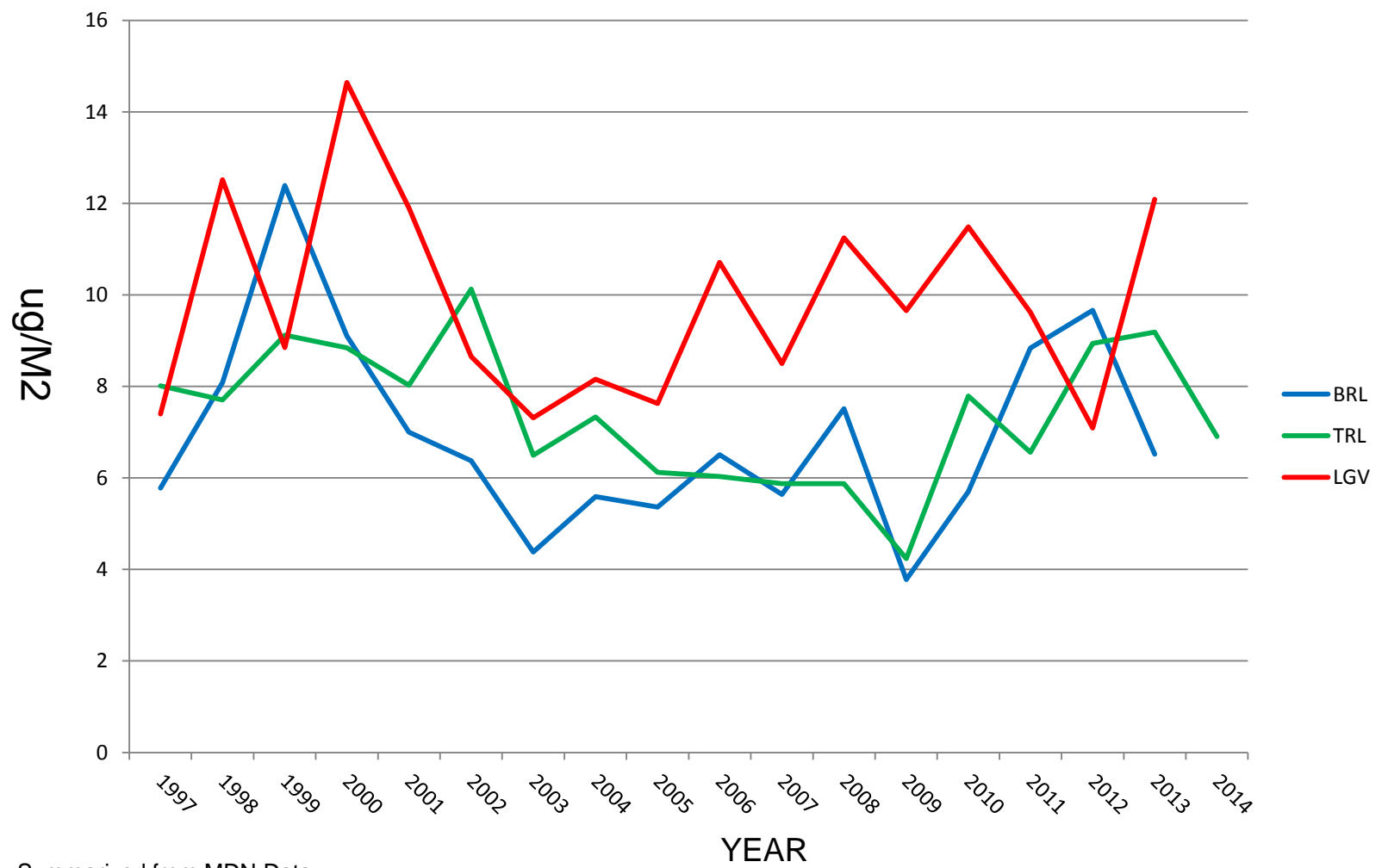


Wisconsin MDN Monitoring Sites

- WDNR Sites
- Tribal Sites

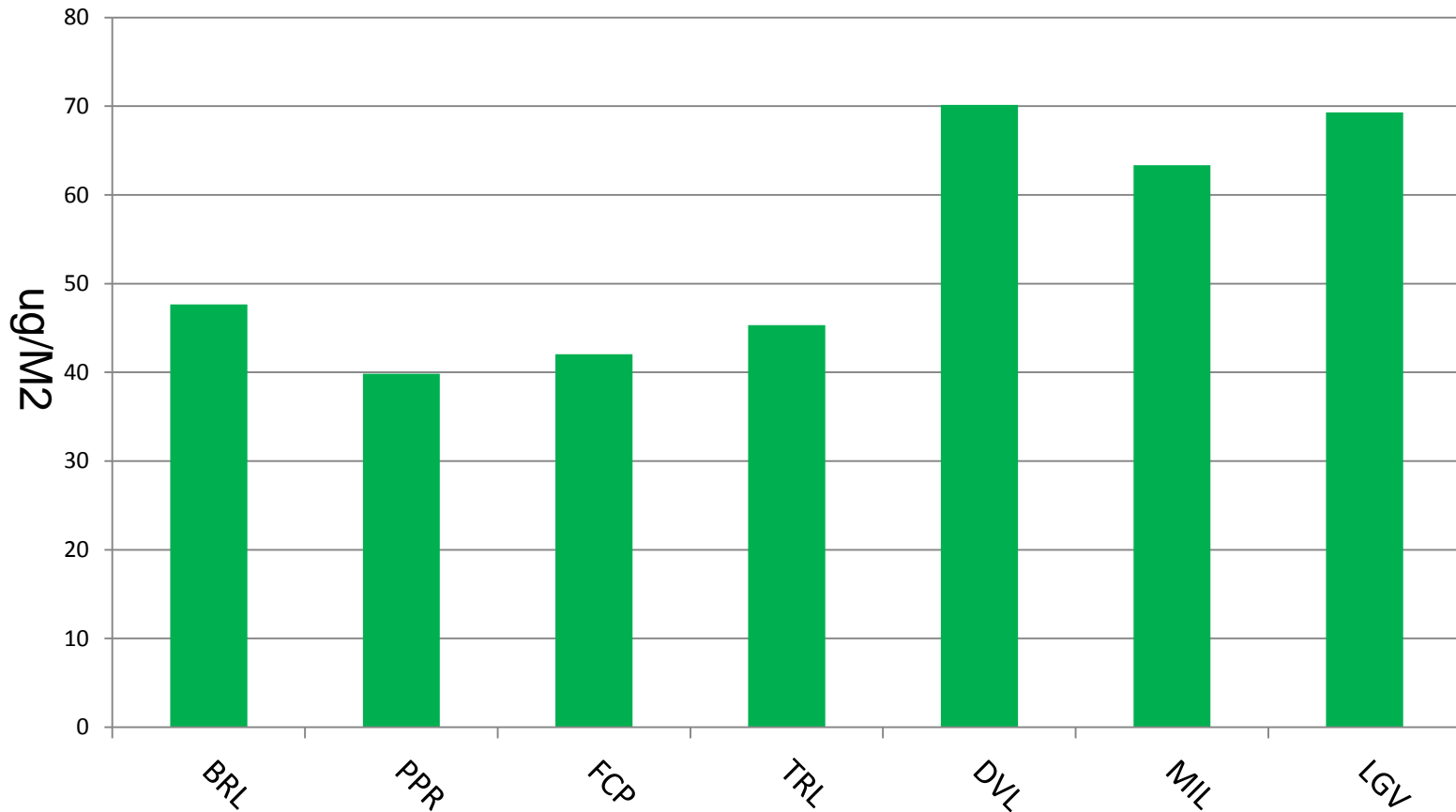


Mercury Deposition by Year 1997 to 2013

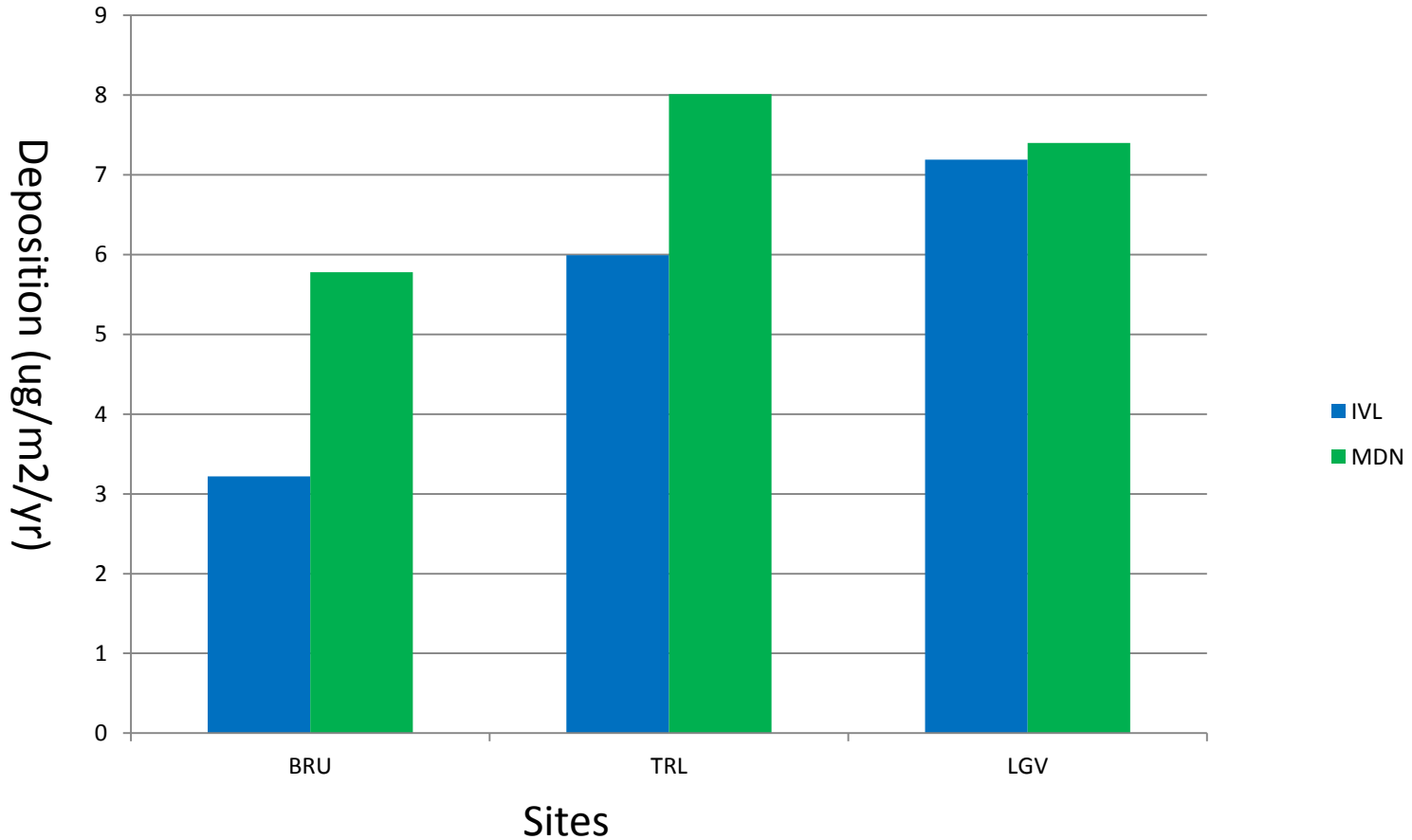


Summarized from MDN Data

Mercury Deposition 2006-2012



Comparison of WIVL & WMDN 1997



Funding Mercury Deposition Monitoring

1. Work started under a number of funding sources
 1. IVL network and initial MDN sites were funded by Acid Deposition Research Council (ADRC)
 1. ADRC established by Wisconsin Acid Rain Legislature and funded by assessment on utilities.
 2. Additional MDN Site were started with EPA and USGS grant.
2. Eventually all sites in MDN were funded by Focus On Energy (FOE)
 1. FOE operates under Wisconsin DOA and is funded by the state's investor-owned energy utilities as well as participating municipal and electric cooperative utilities.
 2. FOE funded research including MDN network and other Wisconsin monitoring projects.
 3. Recently FOE mission changed moving them program away from research.

Network Future

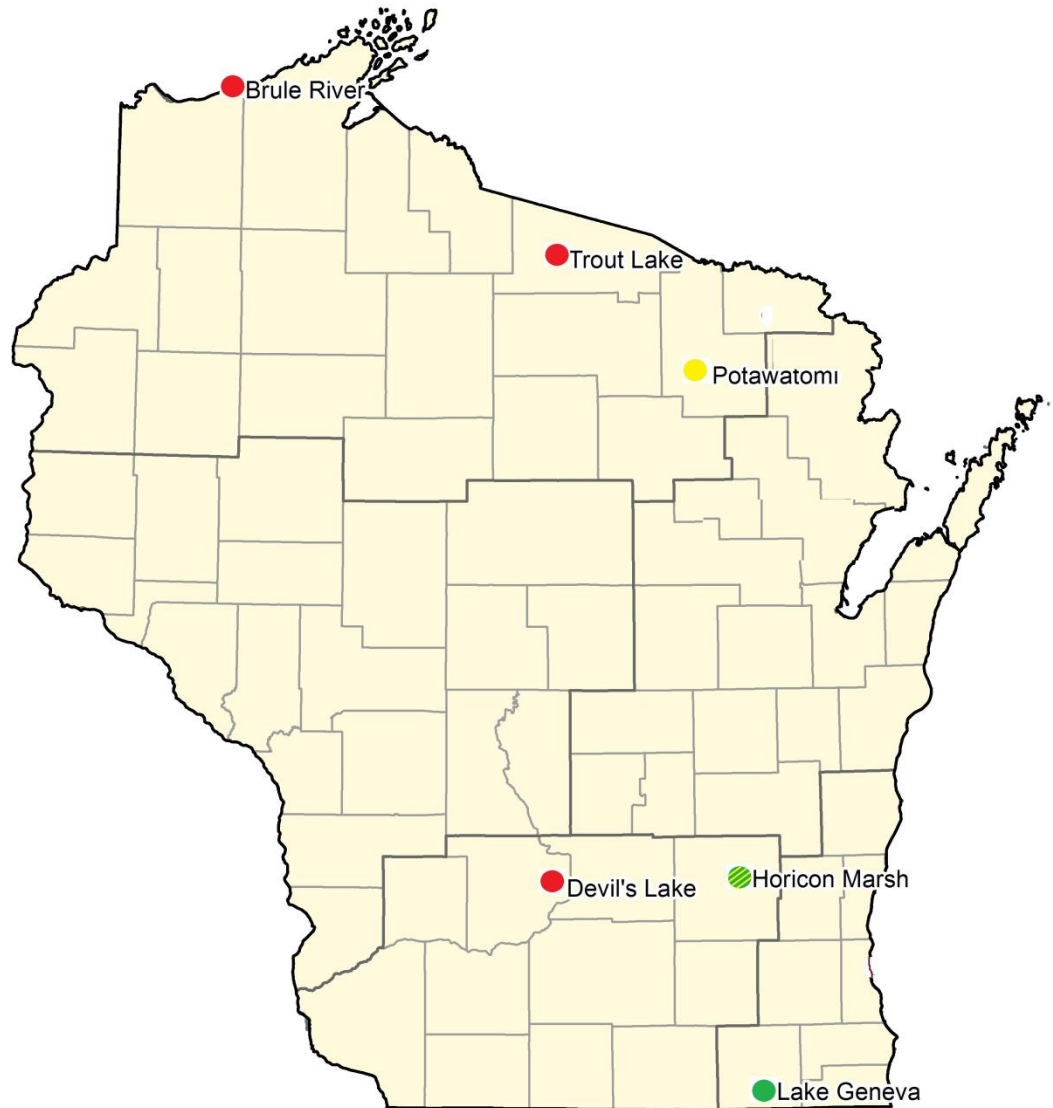
1. Beginning in late 2012 Wisconsin FOE informed the Wisconsin DNR that funding would end after 2013. This provided time for review and planning for the network's future.
2. Ad Hoc group in Air Program was charged with developing a plan for future funding of the network.
 1. Group did a review of the Wisconsin network following method used by Kenski, Gay and Risch.
 2. Included USGS models of areas susceptible to mercury methylation.
 3. Develop a priority list for the Wisconsin sites.
 4. Developed scenarios for funding from 1 contingency site to a full network of sites.
3. Monitoring Section Chief presented these scenarios to Bureau of Air Management's managers and secured long term funding for three sites.

Wet Deposition Site Priority Ranking

^{1.}

Site Name	Priority Ranking	Reason for Ranking
Devil's Lake	1	Site covers a large area and affected population. This long term monitoring site has been used in several important mercury studies. Site is also near several significant mercury sources in the middle of the state. Maintaining the operation of this site should be the highest priority.
Trout Lake	2	Area includes the UW Trout Lake Station, a long term mercury and lake research center. Identified as a Wisconsin site in a proposed regional mercury deposition network.
Brule River	3	Only site in the Lake Superior watershed. Site affected by a significant number of out of state mercury sources. Located in an area of higher methylation potential.
Lake Geneva	4	Identified as a Wisconsin site in a proposed regional mercury deposition network. Long term mercury monitoring site and located in an interstate area.
Popple River	5	Site location is near to and redundant with the Potawatomi site. Current plans are to discontinue monitoring at the site after 2013.
Milwaukee	6	Urban sites are not a focus of the national network. Site location is being redeveloped and this will necessitate a site move. Current plans are to discontinue monitoring at the site in late 2013.

Current MDN Network Sites



- WDNR Sponsored/Operated
- Tribal Sponsored/operated
- LADCO Sponsored/Operated
- LADCO Sponsored/ WDNR operated

Ambient Mercury Monitoring

1. First Tekran 2537 Analyzers were produced in 1993.
2. Wisconsin's use of these analyzer started with the development of the Mobile Mercury Monitoring Trailer (M3T)
 1. A three state proposals were submitted to the EPA under the Great Lakes Atmospheric Deposition (GLAD) National Priority 105 Funds.
 1. Funded in 1999 with additional funds in 2000.
 2. Michigan DEQ lead the project .
 2. The project developed Mobile Mercury Monitoring Trailer (M3T).
 1. Mobile laboratory with on-board power generator.
 2. Trailer equipped with two Tekran 2537 elemental analyzers.
 3. Project also funded two LUMEX analyzers for survey work.

Mobile Mercury Monitoring Trailer (M3T)



TEKRAM 2537 Elemental Mercury Analyzer



Air samples concentrated on gold traps and then analyzed by AF.

Allows ambient monitoring for 5 minute periods at ambient background concentrations.

LUMEX RA915 Portable Hg Analyzer



Atomic absorption spectrometry with Zeeman background correction.

Used for surveys and preliminary monitoring for Tekran studies.

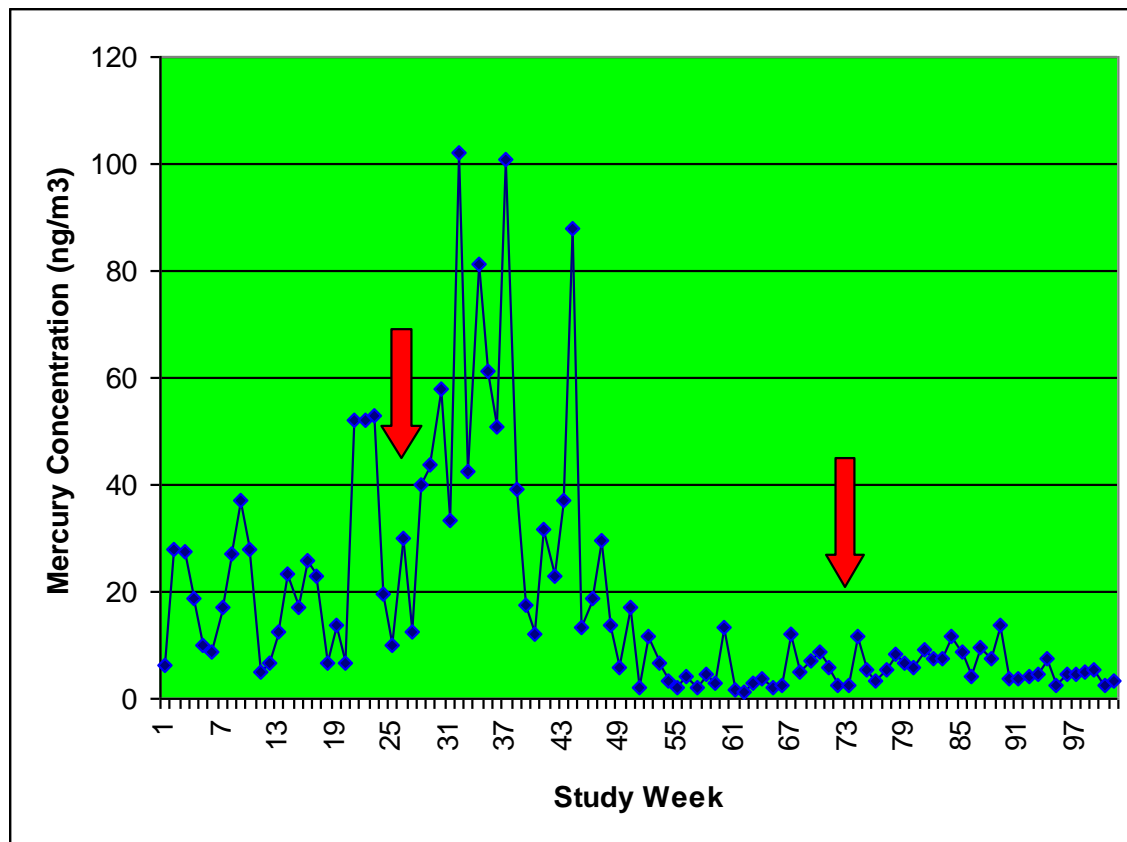
Early Mercury Studies

- Small sources studies through surveys or short term deployments.
 - mercury recycling facility
 - metal recycling facilities
 - landfills with gas extraction systems
 - lamp recycling facilities
 - neon lamp manufacturers
- Mercury Flux Study 2003-2005
 - FOE 2003 funded study looking at mercury concentrations at five Wisconsin sites, including large sources.
 - Power generating facilities
 - Chemical plant

Monitoring Near a Chlor-Alkali Chemical Manufacturing Facility (2008 to 2011)

In 2007, a Wisconsin Chemical Manufacturer committed to converting mercury cells at its Chlor-Alkali Chemical Manufacturing plant to a new non-mercury process. Prior to this time, the facility was responsible for about 20% of the annual mercury emissions reported in Wisconsin.

The Wisconsin DNR partnered with the company to monitor ambient air through the conversion. Monitoring results are plotted as weekly average mercury. Red arrows indicate the approximate start and approximate completion of the conversion.



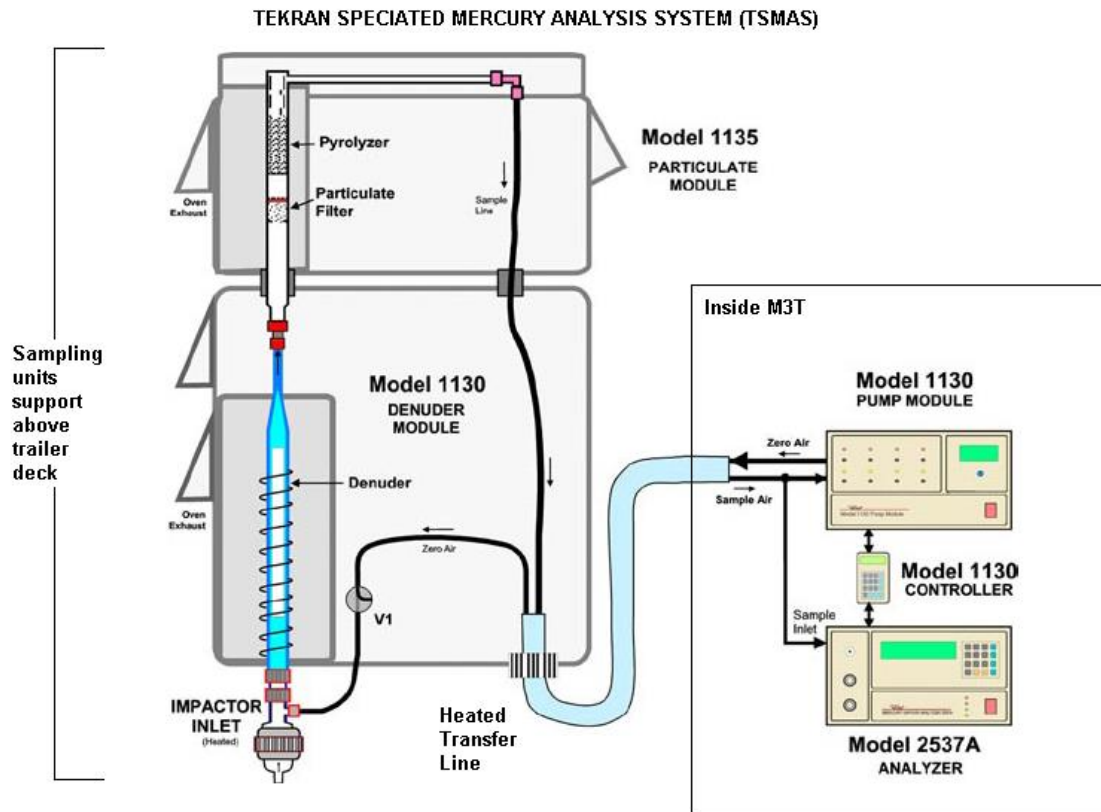
Speciated Mercury Monitoring

The Mercury Flux Study included sites in close proximity to a number of power plants including monitoring sites that have historically been impacted by the power plants.

A statistical analysis of the monitoring data suggested that monitoring data from the elemental analyzer was unable to detect any impacts from the power plants.

Detecting a power plant signal would require greater sensitivity and monitoring for mercury species.

Tekran Speciated Mercury Measuring System (TSMAS)



Wisconsin DNR's First Speciated Monitoring Site

1. Monitoring was started with equipment loaned to Wisconsin DNR from USGS. This work was facilitated by Dr. James Schauer of UW-Madison.
2. Speciation start-up
 1. In 2009, Wisconsin DNR began speciation monitoring at Mayville, WI where David Grande working with Mark Olson installed a USGS system to monitoring mercury species.
 2. The speciation system was transferred to Horicon in 2010.
 3. Wisconsin purchased a TSMAS in 2010 installing the system at the Horicon site. Monitoring has been on-going at the Horicon site since its start-up in late 2010.

Mercury Trailer Up Grade

1. The success of the trailer, the success of speciation monitoring, and the limits of the elemental analyzer led to a new three state proposal to upgrade the mercury trailer to include a capacity for speciated mercury monitoring.
 1. In 2009 EPA funded the upgrade through a GLAD grant administered by GLC.
2. Trailer upgrade included purchases of a Tekran 1130 and Tekran 1135 sampling units to convert an existing 2537b to a TSMAS.
 1. Installation included trailer upgrades including the fabrication of a folding mount system for the external samplers.
3. Grant included training at a multistate mercury monitoring workshop lead by Mark Olson.
4. Wisconsin used the new system for several short-term monitoring studies at Chiwaukee, Manitowoc, Eau Claire, and Odanah.
 1. During these deployments Wisconsin DNR liaison chemist reviewed data daily.
 2. Local site operators performed glass ware and gas replacements.

Wisconsin Air Monitoring Studies using the M3T



M3T Deployed for Field Study



Bad River Tribal site at Odanah

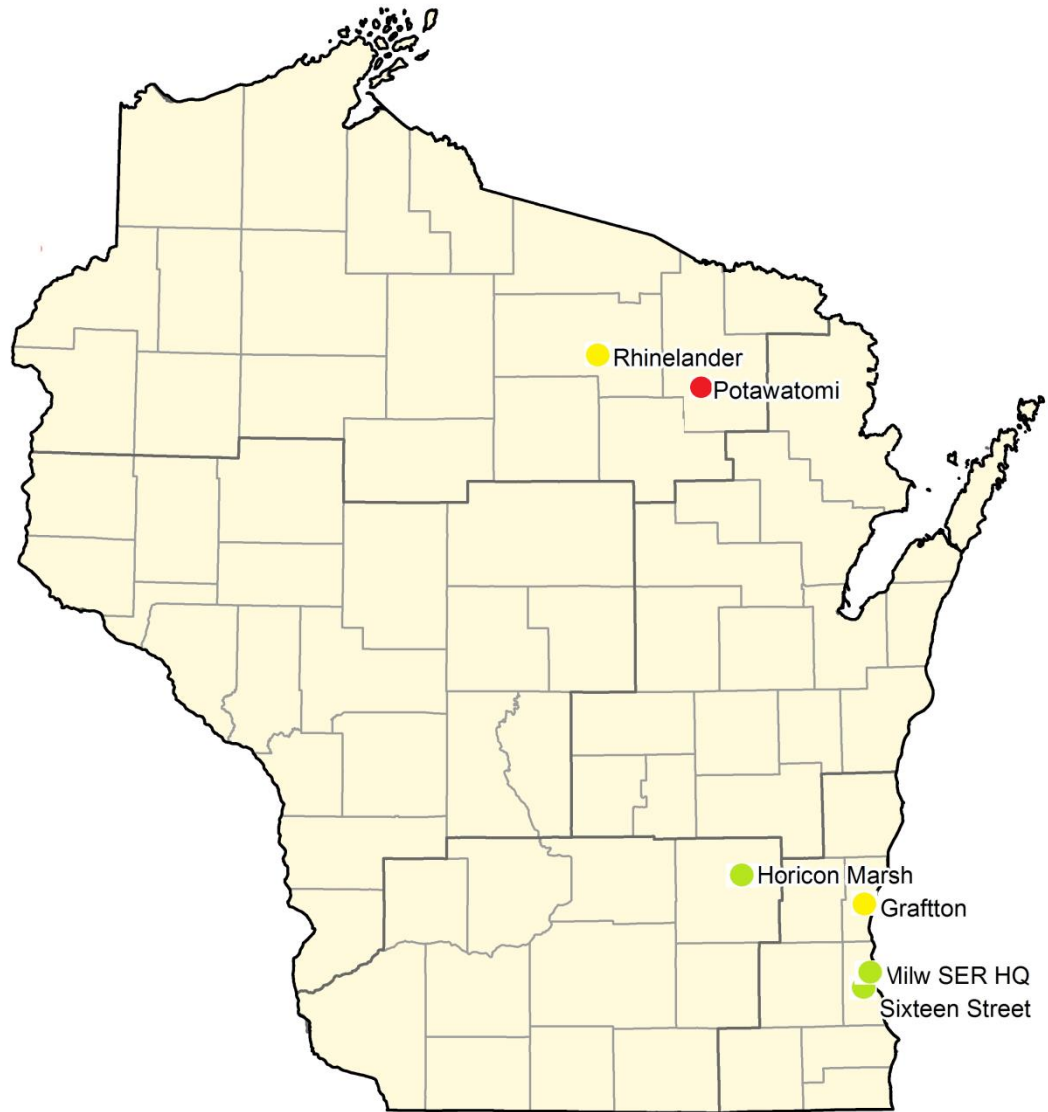
Summary Data for Speciated Mercury Monitoring Study

	Start	End	GEM 5 min (ng/m ³)		GOM 120 min (pg/m ³)		PBM 120 min (pg/m ³)	
			Avg	Max	Avg	Max	Avg	Max
Chiwaukee Prairie	04/06/10	06/08/10	1.63	7.31	3.11	60.73	7.56	306
Woodland Dunes	04/21/11	06/30/11	1.4	2.59	3.62	48.93	3.6	35.23
Eau Claire	08/29/11	11/22/11	1.16	4.63	0.99	14.61	5.57	18.22
Odanah (Typical)	03/27/2012	04/02/2013	1.29	4.45	1.06	37.9	4.01	48.67
Odanah (Dynamic)	03/27/2012	10/10/2012	1.17	3.44	1.38	22.1	40	146.8

Monitoring at 4 sites we have logged over 589 days of monitoring.

Current and Future Ambient Mercury Sites

- Currently operating WDNR
- Future WDNR
- Currently operating tribal



Mercury Data

Wisconsin has SOPs for Tekran operation.:

- final draft for SOPs for operation of Tekran analyzer and the TSMAS.
- finalized SOP for processing mercury data.

In-house our data is managed and stored in stand alone ACCESS databases. Analyzer data is polled daily for review.

Elemental data is sent to the EPA's AQS system

- Included Port Edwards and Milwaukee data

Horicon speciated mercury data is now submitted to NADP's AMNet network.

- AMNet data submittal started 2011.

All deposition data is available from NADP's MDN site.

Summary

Wisconsin has been monitoring Mercury for over 20 years. Over this period Wisconsin staff have developed and documented a high level of expertise in operation of mercury analysis systems. Wisconsin plans will continue to provide high quality mercury measurements.

Importance of Funding

Initial funding supported early work and established the values of Wisconsin's monitoring. This early monitoring work's value supported requests for and resulted in continued funding.

Importance of Cooperation

Much of the early success on Wisconsin's monitoring program was the result cooperation with other programs.

Importance of WDNR staff

Key staff like Bruce Rodger overseeing the deposition monitoring program and David Grande working to maintain ambient monitoring operations has been crucial to Wisconsin success program.