Low Level Mercury:
Importance of Clean Sampling

Presented by:
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Sponsored by the MWOA & CSWEA Laboratory Committees:

Mercury

The droplet of mercury shown in this slide is about 1 gram; the same amount that is in a standard mercury thermometer and the total amount that is deposited annually on a lake in northern Wisconsin with a surface area of 27 acres.

http://water.usgs.gov/wid/FS_216-95/FS_216-95.html

Forms of Mercury

- **Hg (mercury zero)**
  - Elemental form, silver liquid at room temperature
  - Easily volatilizes; persists 3-24 months
  - Not very water soluble, thus it does not readily wash out of the atmosphere during rainfall
  - Removed from the atmosphere very slowly after converting mostly to HgII
- **Hg (II) (mercury two)**
  - Ions known as mercury salts
  - Water soluble and easily attached to particles
  - Readily washes out of the atmosphere
- **MeHg (methylmercury)**
  - The organic form of mercury
  - Volatile
  - Very water soluble
  - Readily washes out of the atmosphere
  - Bioaccumulative

http://dnr.wi.gov/org/caer/cea/mercury/element.htm

Mercury: Health Effects

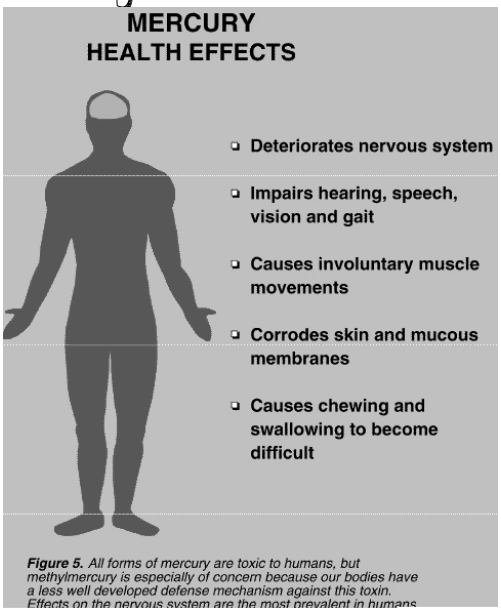


Figure 5. *All forms of mercury are toxic to humans, but methylmercury is especially of concern because our bodies have a less well developed defense mechanism against this toxin. Effects on the nervous system are the most prevalent in humans.*

http://water.usgs.gov/wid/FS_216-95/f5.gif

Mercury Toxicity

Effects depend on chemical form and exposure route.

- **Methylmercury [CH3Hg]** is the most toxic form.
  - It affects the immune system,
  - alters genetic and enzyme systems, and
  - damages the nervous system, including coordination and the senses of touch, taste, and sight.
  - particularly bad for developing embryos, (5-10X > sensitive than adults).
  - Exposure usually by ingestion, and it is
  - absorbed more readily & excreted more slowly than other forms
- **Elemental mercury, Hg(0)** *[broken thermometers]* when vapors inhaled over a long period of time, causes:
  - tremors,
  - gingivitis, and
  - excitability
  - If ingested, it is absorbed relatively slowly and may pass through the digestive system without causing damage.
- Ingestion of other common forms, e.g., **salt, HgCl2**,
  - damages GI tract & causes kidney failure
  - is unlikely from environmental sources.

http://www.usgs.gov/themes/factsheet/146-00/

Methyl-Mercury Exposure

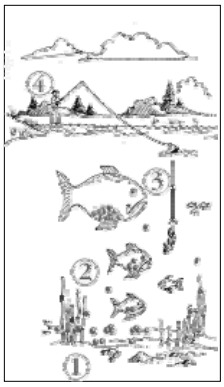
People are exposed to methylmercury almost entirely by eating contaminated fish and wildlife that are at the top of aquatic foodchains.

Japan, 1956: Minimata Disease

- USEPA (1997) Mercury Study Report to Congress: concluded that mercury also may pose a risk to some adults and wildlife populations that consume large amounts of fish that is contaminated by mercury.
- The National Research Council, (2000) estimated that more than 60,000 children are born each year at risk for adverse neurodevelopmental effects due to in utero exposure to methylmercury.

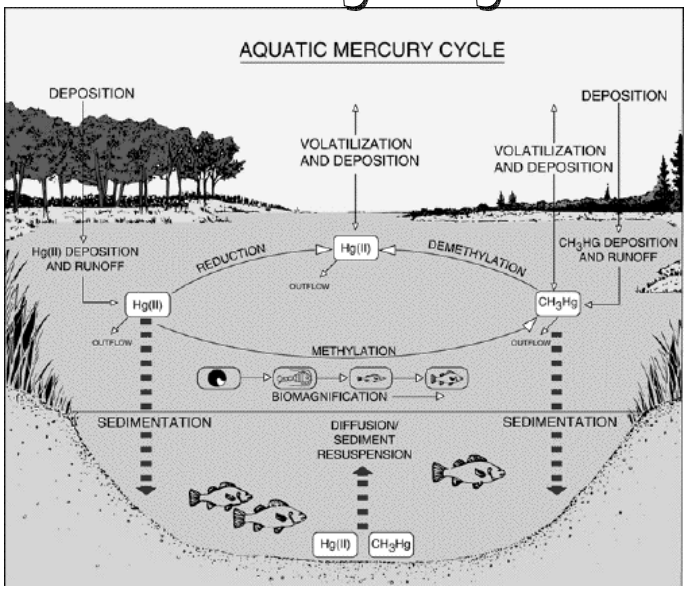
MeHg: the 2 "B"s

Methylmercury is very toxic to living organisms. Although only 10% of the mercury in water is methylmercury, it is very soluble, mobile, and bioaccumulative.



- ***Bioaccumulation*** is the process by which organisms take up a contaminant more rapidly than their bodies can eliminate it. Thus, mercury accumulates in the body over time. If mercury is continually ingested it can build up to toxic levels. Mercury becomes even more hazardous to organisms higher in the food chain because it biomagnifies.
- ***Biomagnification*** is the incremental increase in a contaminant's concentration at each level of the food chain. For example, humans eat large fish, which eat lots of small fish, which eat lots of plants. Mercury bioaccumulates in every organism along the way, and the human will ingest all of the mercury accumulated during each step

Mercury Cycle



http://water.usgs.gov/wid/FS_216-95/f6.gif

Overview: Mercury Issues in wastewater

Mercury History: California

Burning fossil fuels (coal) releases naturally occurring mercury into the air. Incineration of municipal & medical waste releases mercury from wastes. Combustion & incineration = US's largest contributors of mercury pollution

During the Gold Rush, the cinnabar deposits from the coast were mined, and mercury was shipped to the Sierra Nevada Range to extract gold from gold-containing ore.

The legacy of this era is that many rivers, creeks, lakes, and reservoirs of both eastern and western California contain mercury, and mercury-laden sediments continue to flow downstream into San Francisco Bay.

The San Francisco Bay Regional Water Quality Control Board has identified sources of mercury in San Francisco Bay:

- ~ 45%: Sacramento/San Joaquin River Delta, (runoff from historic mines).
- ~ 37%: Sediment remobilization
- ~ 3%: Bay Area wastewater treatment plants

Mercury: Environmental Sources

2000: Estimated Annual Mercury Releases
from Common Mercury-Containing Products to Wisconsin's Environment (lbs)

PRODUCT	AIR	WATER	LAND	TOTAL
Dental	420	10	1110	**1540**
Fluorescent lamps	200	0	380	**580**
HID & other lamps	20	0	40	**70**
Bulk liquid Hg	90	10	30	**130**
[1] Relays & Switches	700	10	1200	**1910**
[2] Measurement & control devices	450	10	1060	**1520**
TOTALS	**1880**	**40**	**3820**	**5750**
Products included above:				
Auto Switches [1]	100	0	150	**240**
Thermostats[1]	250	0	810	**1050**
Fever thermometers [2]	150	0	440	**590**

This table is taken from a computer model prepared for WDNR by the Barr Engineering Company of Minneapolis, MN. Numbers are estimates based on the best available info.

http://dnr.wi.gov/org/caer/cea/mercury/sources.htm

Products containing Hg

Table 2-2. Mercury Containing Products

Residential	Commercial	Industrial	Medical/Laboratory
Appliance Keyboards (mercury switches)	Chemicals (trace amounts)	Chemicals (trace amounts)	Dental Amalgam
Thermometers	Thermometers	Thermometers Thermostats (mercury switches)	Thermometers
Thermostats (mercury switches)	Thermostats (mercury switches)	Barometers/Manometers	Reagents (trace contaminant)
Camera and Watch batteries	Mercury Vapor Lamps	Mercury Vapor Lamps	Barometers/Manometers
Mercury Vapor Lamps			

Table 2-3. Common Medical Products Containing Mercury

Equipment	Mercury Use
Sphygmomanometer	mercury is used to measure pressure
Sphygmomanometer Service Kit	contains reserve mercury
Esophageal Dilators (Bougies) and Feeding Tubes	mercury is used as a weight for tubes and dilators
Gastro/Esophageal Tubes	mercury is used as a weight for tubes
Barometers in Respiratory Therapy	mercury is used to measure pressure
Thermometers	mercury is used to measure temperature
B-5 Fixative	product is used to fix cells to slides for histological examination

http://www.ecologic-eng.com/rio_vista/images/rv_msrp_workplan.pdf

How much Hg in these products?

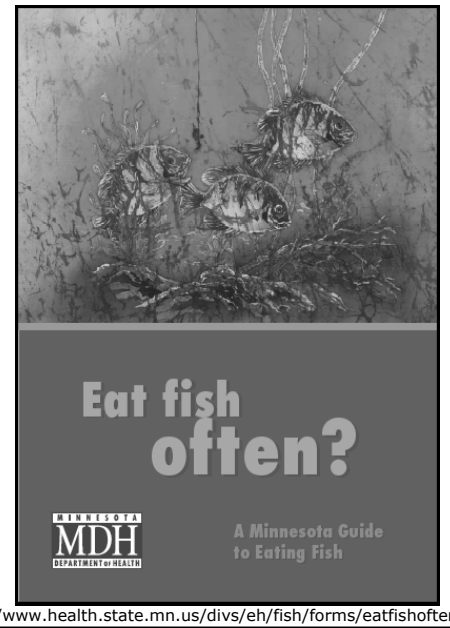
Table 3-1. Amounts of Mercury Contained in Products

Product	Mercury Amount
Household thermometers	0.5 - 1 gram
Laboratory thermometers	3 grams
Dairy manometers	355 grams
Gas range pilot light switch	2 grams
Switch from one freezer (thermostat)	1 gram of mercury
Household thermostat (50 million nationally)	2 - 4 grams
Fluorescent bulbs	41.6 milligrams

How much Hg is in our waters?

- All municipal wastewater contains some level of mercury.
- The concentration of mercury in influents to municipal wastewater treatment plants can vary widely depending on the size and types of discharges to the sewer system.
- Based on information collected several years ago, concentrations ranged from 100 to 800 ηg/L (0.1 to 0.8 micrograms per liter).
- Sources include dental and medical waste, some consumer products (for example, broken thermometers), human wastes (e.g. urine), rainwater infiltration, flush-out of historical deposits in sewers, among others.
- Due to its behavior, an extremely high percentage of mercury contained in wastewater becomes concentrated in treatment plant bio-solids or sludge. Thus, bio-solids concentration data are good predictors of what plants have elevated mercury loadings.
- As detection limits have decreased, we have discovered just how prevalent mercury is in the environment.
- It is not uncommon to find concentrations of 3 to 5 ηg/L in Wisconsin lakes or rivers, significantly above the 1.3 ηg/L MN & WI water quality criterion for the Great Lakes Basin. We have even found mercury in some of the most pristine lakes in the state.
- In Lakes Michigan and Superior, mercury concentrations are less than 1 ηg/L.

MN Fish Advisories



http://www.health.state.mn.us/divs/eh/fish/forms/eatfishoften.pdf

MN Mercury Reduction Program Summary

Focus: "MPCA's reduction programs focus on finding, disposing of, and reducing mercury used in products."

Since 1999, in addition to implementing the voluntary agreement program (described in Section 5, below), the MPCA and the OEA have continued or initiated a number of mercury-reduction programs. These include:

- the Mercury-Free Zone Program, in which a specially trained detector dog is used to search schools and other facilities for spills and other "hidden" mercury;
- a project to reduce and recover mercury in automotive switches;
- a statewide mercury thermometer ban and swaps;
- health care program;
- community mercury-reduction projects;
- improved estimates of releases from mercury in products;
- ongoing labeling law enforcement;

MN Mercury Reduction Program Summary

- ongoing efforts to recover mercury at demolition sites;
- waste incinerator and combustor regulations;
- integrated state/federal Internet pilot project;
- the Minnesota/North Dakota Fish Consumption Survey;
- low-level monitoring for wastewater discharges; and
- continued monitoring of, and research into, mercury releases and deposition.

Key to Success of the Mercury Reduction Program: The support from organizations, both public and private.

MN strategy for Hg

Appendix E

Outline of the Interim Mercury Water Quality Strategy for Existing Discharges

Municipal/Industrial existing facility permit reissuance – statewide

Monitoring (method 1631 and perhaps method 245.7 in the future) and sampling (method 1669)

- Majors: minimum quarterly for life of the permit.
- Minors (>0.2 mgd): minimum semi-annual monitoring for life of permit concurrent with lab availability, sampling training, and evaluation of MPCA collected pond data.
- *Ponds: once each discreet discharge event*
- Storm-water: Case-by case; 4 times/year for "representative" discharge points
- List of exclusions (e.g., non-contact cooling water)
- List of inclusions because of anticipated mercury levels in effluent

Mercury Contamination Reduction Initiative (MCRI)

- Marketed to all dischargers for the initial 5 year permit cycle.

Sampling Considerations

Are "clean techniques" really required for sampling?

Does "clean sampling" matter?

All results in μg/L

Metal	Copeland & Ayers (1972)	Rossman 1984	Shafer & Armstrong (1995)
Ag	**0.3**	**0.057**	**0.0004**
Cd	**0.42***	**0.044**	**0.009**
Cr	**1.7**	**0.68**	**0.5**
Cu	**5**	**0.39**	**0.4**
Hg	**0.027**	**0.045**	**0.0003**
Pb	**4.8***	**0.25**	**0.02-0.08**
Zn	**16**	**0.59**	**0.5**
	Conventional Sampling		"Clean Hands-Dirty Hands"

* Gara and Hawley (1974)

Hg Contamination Potential

1669- sec 4.1.2

- Potential sources of trace metals contamination during sampling:
  - metallic or metal-containing sampling equipment, containers, reagents, deionized water, and labware
    - (e.g. talc gloves that contain high levels of zinc)
  - improperly cleaned and stored equipment, labware, and reagents;
  - atmospheric inputs such as dirt and dust from automobile exhaust, cigarette smoke, nearby roads, bridges, wires, and poles.
  - Even human contact can be a source of trace metals contamination.
    - For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples that are directly exposed to exhalation.

Controlling Contamination During Sampling

- Efforts necessary to control contamination increase significantly as detection limits and concentrations decrease.
- Mercury tends to "stick" to surfaces so pumps and tubing used for composite sampling can be reservoirs of contamination.
- Equipment exhaust and dust can also be contributors.
- Even the sampling crew themselves can be a source of mercury contamination (hands, clothing, even breath).
- it is possible to obtain a reliable sample for low level mercury by paying attention to hygiene.
- EPA method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels (EPA 821-R-95-034) describes an effective "**clean hands-dirty hands**" procedure.
- How rigorously you need to follow this procedure depends on
  - the type of sample being collected,
  - the sensitivity or detection limits desired, and
  - the environment in which the sample is being collected.

http://www.dnr.state.wi.us/org/es/science/lc/info/Mercury/Contamination.htm

Sampling for low level mercury

Sampling Locations

- Get as close to outfall as possible
- Must be a grab
- Possible sampling points:
  - Outfall-hold bottle under outfall
  - After dechlorination-after bisulfite addition
  - Mercury can be a by-product of chlorine production. Regulators recommend collecting samples after chlorination
  - Manhole-with a pole sampler (must be trace metals clean)
- Other advice:
  - Gloves are the best bang for the buck
  - Avoid having smokers collect samples
  - Wearing Tyvek during sampling is a plus

Why Tyvek?

Clean Hands -Dirty Hands basics

"Clean Hands"

shoulder-length polyethylene gloves
PVC gloves
precleaned wind suits

All operations involving contact with the sample bottle and with transfer of the sample from the sample collection device to the sample bottle (*if the sample is not directly collected in the bottle*)

"Dirty Hands"

precleaned wind suits
PVC gloves

responsible for all activities that do not involve direct contact with the sample.

Although the duties of "clean hands" and "dirty hands" would appear to be a logical separation of responsibilities, in fact, the completion of the entire protocol may require a good deal of coordination and practice.

Clean hands - Dirty hands

"Clean hands"	"Dirty hands"
	"Dirty hands" must open the cooler or storage container, remove the double-bagged sample bottle from storage, and unzip the outer bag.
"Clean hands" opens the inside bag containing the sample bottle, removes the bottle, and reseals the inside bag.	
	"Dirty hands" then reseals the outer bag.
"Clean hands" unscrews the cap and, (holding the cap upside down), discards the dilute acid solution from the bottle.	
"Clean hands" submerges the sample bottle, and allows the bottle to partially fill with sample.	
"Clean hands" fills the bottle 3 times, shaking & rinsing Then "clean hands" fills the bottle. After the bottle has filled (and while the bottle is still inverted so that the mouth of the bottle is underwater, "clean hands" replaces the cap of the bottle. In this way, the sample has never contacted the air.	
	Once the bottle lid has been replaced, "dirty hands" reopens the outer plastic bag (8.2.5.6)
"Clean hands" opens the inside bag, places the bottle inside it, and zips the inner bag.	
	"Dirty hands" zips the outer bag.


Dirty
Clean


POURING
Dirty
Clean
PRESERVING
Clean
RETURN TO INNER BAG
Dirty
Clean
RETURN TO OUTER BAG
Dirty
Clean


PREPARING TO SAMPLE
Dirty
Clean
TAKING SAMPLE BOTTLE
Dirty
Clean
Dirty
Clean
RINSING
Dirty
Clean
COLLECTING GRAB

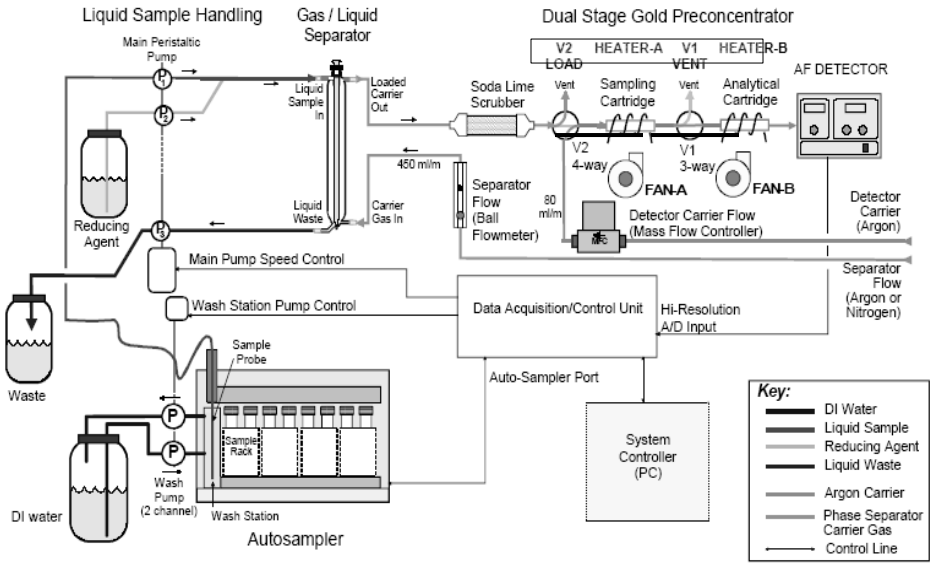
RE-CAPPING SAMPLE

RETURN TO INNER BAG

Alternate sampling techniques

Overview: low-level mercury analysis

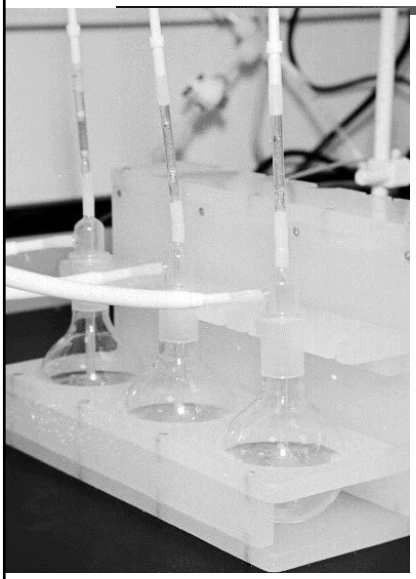
1631 analysis scheme



1631 Summary

- **2.1** A 100- to 2000-mL sample is collected directly into a cleaned, pretested, fluoropolymer or glass bottle
- **2.2** For dissolved Hg, the sample is filtered through a 0.45-:m capsule filter prior to preservation.
- **2.3** The sample is preserved by adding either pretested 12N hydrochloric acid (HCl) or bromine monochloride (BrCl) solution.
- **2.4** Prior to analysis, all Hg in a 100-mL sample aliquot is oxidized to Hg(II) with BrCl.
- **2.5** After oxidation, the sample is sequentially
  - reduced w/ $NH_2OH@HCl$ to destroy the free halogens, then
  - reduced w/ $SnCl_2$; converts Hg(II) to volatile Hg(0).
- **2.6** The Hg(0) is separated from solution either
  - by purging with nitrogen, helium, or argon, or by
  - liquid separation.

  The Hg(0) is collected onto a gold trap.
- **2.7** The Hg is thermally desorbed from the gold trap into an inert gas stream that carries the released Hg(0) to a second gold (analytical) trap. The Hg is desorbed from the analytical trap into a gas stream that carries the Hg into the cell of a cold-vapor atomic fluorescence spectrometer (CVAFS) for detection.



1631 & 245.7 Comparison

	Method 1631	Method 245.7
Digestion	BrCl / Sn^2Cl / $NH^2OH^{\bullet}HCl$	BrCl / Sn^2Cl / $NH^2OH^{\bullet}HCl$
Separation	Purge Gold Trap	Liquid Gas Separator Dryer Tube
Detection	CVAFS	CVAFS
MDL	0.2 ng/L (validated in 12 labs)	0.3 – 3.3 ng/L (observed in 3 labs)
Range	0.5 – 100 ng/L (validated in 12 labs)	1 – 100 ng/L (interlaboratory study underway)
Time	15 - 30 minutes	10 - 15 minutes

Tips for selecting a lab to perform low level mercury

What to look for in a lab

- Make sure the lab is certified to perform low-level mercury testing.
  - Check list at the MDH website (list here)
  - Does the lab have a "clean" room or clean zones?
- Make sure the laboratory can obtain a detection that will meet your permit level.
- Ask if the lab provides:
  - Ultra-clean preservatives (generally HCl)
  - Ultra-clean bottles
  - Ultra-pure water for field and trip blanks
- Does the laboratory charge separately for field and trip blanks
- Ask the lab for field and trip blank data.
  - Are the blanks typically below the MDL low or do they bounce around?
  - Does the lab offer instructions for collecting the samples?

What to look for in a lab

- Laboratories must demonstrate their ability to meet the performance criteria and be recognized for their low-level mercury
  - A copy of your SOP that includes
    - make and model of instrument used and
    - any method modifications from the published procedure.
  - Procedures the laboratory uses to ensure that contamination is not introduced into samples,
    - including any carry-over studies performed
  - Initial Demonstration of Capability (IPR) Results .
    - LCS (fortified reagent water) recoveries _____ (must fall between 79 and 121%).
    - For method 1631, the LCS concentration is set at 5 ng/L
  - Method Detection Limit (MDL)
    - Reagent Water Result: _____
    - Wastewater Result: _____
      - Wastewater source: _____

Additional Information About MPCA's Mercury Programs

- MPCA mercury reduction projects and initiatives. You are invited to send your comments, questions and suggestions to Ned Brooks at 651-296-7242.
- Visit the following websites:
  - www.mnmercuryinfo.org
  - www.pca.state.mn.us/air/mercury.htm
  - www.pca.state.mn.us/air/pubs/mercury-policy01.pdf
  - www.health.state.mn.us
  - www.epa.gov/mercury

Information and contracts

Where do I find more information?

To find out more about these topics related to mercury monitoring, call the MPCA at (651) 296-6300 or toll-free/TDD (800) 657-3864. Or, contact the staff listed below on specific issues.

Topic	Contact and/or Web site
Mercury strategy, voluntary reduction of mercury	John Wachtler, MPCA (651) 297-8333
Mercury in lakes	Jeff Jeremiason, MPCA, (651) 296-7215
Mercury in fish	Hillary Carpenter, MDH (651) 215-0928
Public information or media contact on mercury	Sam Brungardt, MPCA (651) 282-6410
Certified laboratories	Susan Wyatt, MDH (612) 676-5674

MPCA Web site: http://www.pca.state.mn.us