MERCURY USE: CHEMICAL MANUFACTURERS/USERS

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Mercury compounds are used in a wide variety of settings by chemical manufacturers. Chemical uses of mercury may occur in catalysts, cosmetics, explosives, fireworks, livestock and poultry remedies, packaging, pharmaceuticals, pigments and dyes, poisons, preservatives, and special paper coatings. Commonly used mercury compounds include mercuric oxide (cathode material in batteries), mercuric chloride (pharmaceuticals), phenylmercuric acetate (used in paints and pharmaceuticals) mercuric sulfide (used in red pigment and other pharmaceuticals), and thimerosal (contact lens solutions) [ross and associates].

Most of the mercury- containing products listed above will be covered in specific sector listings (eg., livestock remedies will be detailed in the "Veterinary Clinic" section; pharmaceutical uses will be covered in the "Hospital and Clinic" section or in the "Household Uses" section; the "Laboratory" section will provide information about laboratory reagents. This chapter will discuss the use of mercury-containing compounds by the chemical industry, or industries that may use caustic soda (sodium hydroxide) in their facility.

ABOUT THIS HANDOUT

This is one chapter of the "Wisconsin Mercury SourceBook." The Sourcebook was written as a guide for communities to help identify and reduce the purposeful use of mercury. The SourceBook contains background information on mercury contamination and provides a seven-step outline for drafting a mercury reduction plan.

This handout is one of the nineteen sectors that were highlighted in the SourceBook as a potential contributor of mercury in any given community.

What you will find in this handout:

- ★ Information on mercury-containing products and that are unique to the chemical industry
- ★ Information on mercury-containing products that are found both in the chemical industry and in a wide variety of other sectors (e.g., fluorescent lamps, switches)
- ★ Case studies that describe the source substitution experiences of businesses in the chemical industry
- ★ Action ideas that describe pollution prevention, recycling, and management practices for a mercury reduction plan for a business in the chemical industry. This provides a good overview of the types of mercury-containing products and alternatives that may exist in the chemical industry.
- ★ Current mercury projects in the chemical industry

For more information, please contact:

WHY SHOULD I BE CONCERNED ABOUT MERCURY?

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 in 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.

Because mercury is very dense, expands and contracts evenly with temperature changes, and has high electrical conductivity, it has been used in thousands of industrial, agricultural, medical, and household applications.

It is estimated that half of the anthropogenic mercury releases in Wisconsin are the result of the purposeful use of mercury. The other half of mercury emissions originate from energy production.

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.

The good news is that the majority of products that use mercury purposefully have acceptable alternatives. For example, electric vacuum gages, 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 so easily transfer from air to soil to water.

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.

HEALTH EFFECTS OF ELEMENTAL MERCURY

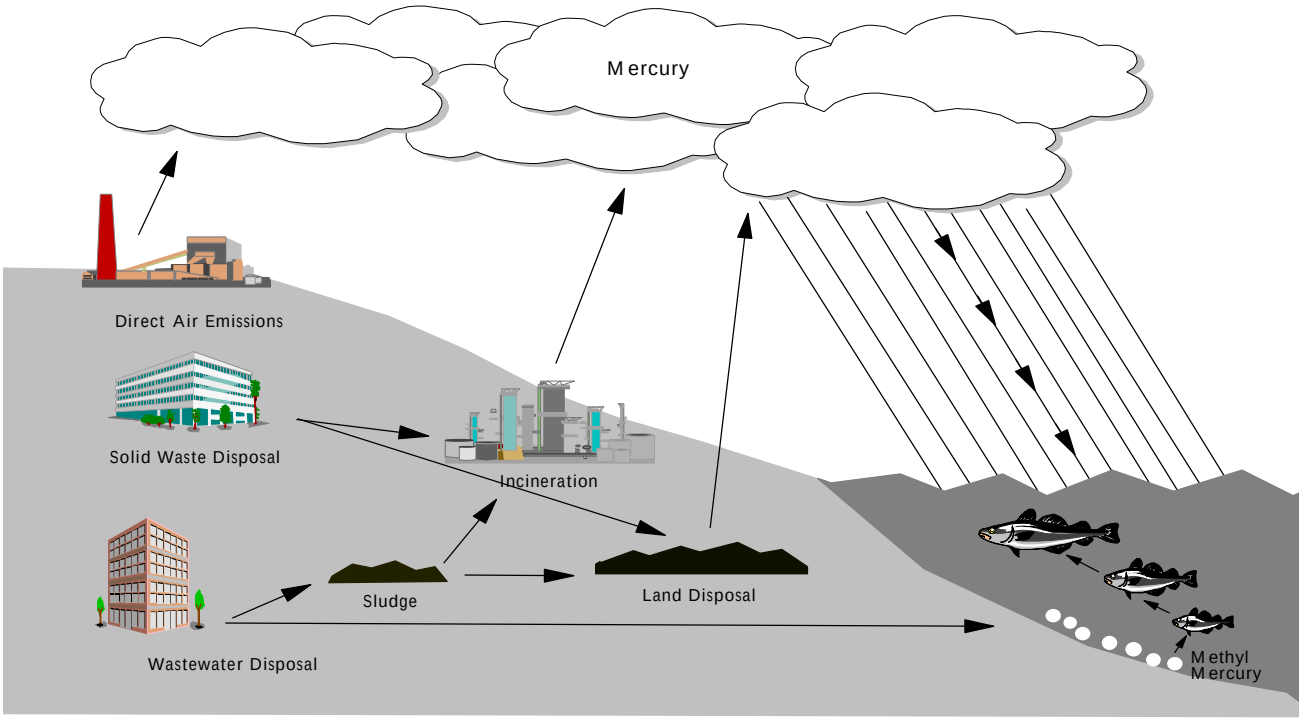
The toxicity of mercury has long been known to humans. Hat makers during the 19th century developed symptoms of shaking and slurring of speech from exposure to large amounts of inorganic mercury, which was used to give a metallic sheen to felt hats. This gave rise to the term "mad as a hatter."

The hat makers were suffering from neurological damage from the inhalation of mercury fumes. Exposure to elemental mercury vapors can cause acute respiratory problems, which are followed by neurologic disturbances and general systemic effects. Acute exposure to inorganic mercury by ingestion may also cause gastrointestinal disturbances and may effect the kidneys.

SO WHAT'S THE BIG DEAL?

Mercury is a bioaccumulative, persistent, toxic substance that threatens the health of humans and wildlife throughout North America. The USEPA, Environment Canada, the International Joint Commission, the Commission for Environmental Cooperation and many state and provincial governments have identified mercury as one of the most critical pollutants for significant elimination and/or reduction.

Mercury Transport and Bioaccumulation



Mercury can enter the environment from a number of paths. For example, if a mercury-containing item is thrown into the garbage, the mercury may be released into the atmosphere from landfill vapors or leachate, or the mercury may vaporize if the trash is incinerated. If mercury is flushed through a wastewater system, the mercury will likely adhere to the wastewater sludge, where it has the potential to volatilize and be deposited elsewhere. Mercury can enter the atmosphere through these various means because it evaporates easily. It then travels through the atmosphere in a vaporized state.

Once mercury is deposited into lakes and streams, bacteria convert some of the mercury into an organic form called *methylmercury*. This is the form of mercury that humans and other animals ingest when they eat some types of fish. Methylmercury is particularly dangerous because it *bioaccumulates* in the environment. Bioaccumulation occurs when the methylmercury in fish tissue 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.

These concentrations are significant when one considers the potential toxic effects of methylmercury. 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, high levels of methylmercury consumption 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.

Fish Consumption Advisories

There are currently 260 lakes and more than 350 miles of rivers in Wisconsin that have fish consumption advisories because of mercury. Approximately 1 out every 3 sites that is tested is listed on the advisory; no sites have ever been removed. Forty-eight states now issue fish consumption advisories to protect human health. Most of these warnings are related to mercury contamination.

Keeping Mercury Out of Wastewater

There are a number of ways mercury can enter the wastewater stream of a chemical manufacturing facility. When a mercury-containing product such as a thermometer is broken over a sink or improperly cleaned up after a spill, the mercury could get flushed down the drain. Mercury may also be present in a chemical facility's sewer pipes and traps from historical use of mercury.

Once mercury enters a wastewater treatment plant, most of it concentrates 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. This mercury may then be deposited into lakes and streams, methylated, and ingested by fish, eventually reaching wildlife and humans.

To prevent such occurrences, it is important to have effective spill response measures. Instruments containing mercury should be labeled and proper procedures should be followed when cleaning or refilling instruments that contain mercury. Instrument cleaning or refilling should take place in a well ventilated area, and, if possible, over a tray to contain any spills.

Sewer Pipes

Mercury was used extensively in chemical settings in the past. Often times the mercury may have found its way into the pipes of a chemical facility during manufacturing, or when mercury-containing items were broken, disposed of, or spilled. This mercury can settle at a low point such as a sump or trap and remain in the pipes of a chemical facility for many years. Often the slow dissolution of the mercury in a sump, trap, or pipe is enough to cause violations of wastewater discharge standards even after poor management practices have been eliminated. Hot spots in a chemical facility's piping may appear where equipment maintenance areas were located. Whenever traps or sumps are moved or cleaned, the solid contents should be treated as a hazardous waste unless proven otherwise. For more information, please see the excerpts from the MWRA/MASCO Infrastructure Subcommittee Maintenance Guidebook that appear in the "Resources" section of this sourcebook.

Mercury-Containing Compounds

Chemical reagents, used with regularity in a wide range of laboratory testing, are likely sources of mercury contamination. The difficulty of identifying which chemicals and reagents contain mercury is compounded by the fact that Material Safety Data Sheets (MSDS) are not required to list the hazardous components of a product unless that component is present at a level of $\geq$1% (0.1% for carcinogens). This means that a particular product *could* contain up to 10,000 parts per million of mercury before the manufacturer would have to alert users of that fact. *(MWRA operations subcommittee final report)*

Work by the MPCA

John Gilkeson of the Minnesota Pollution Control Agency has compiled an extensive list of all mercury-containing compounds that are currently available for research and scientific purposes. He has developed a list of all mercury-containing compounds with a CAS number. These charts are attached at the end of this chapter.

A number of facilities have discovered that mercury is present in very low levels in some of their products. However, because the mercury was added as a preservative, not as an active ingredient, its low level may be below the reporting threshold and thus not included in the Material Safety Data Sheets (MSDS) sheets. *(gilkeson + butterworth, Metpath)*

Mercury-Containing Chemicals and Alternatives

Compiled from City of Detroit, Gilkeson, Terrane, Michigan M2P2

Chemical	Alternative
Mercury (II) Oxide	Copper catalyst
Mercury Chloride	None Identified
Mercury (II) Chloride	Magnesium Chloride/Sulfuric Acid or Zinc Formalin, Freeze drying
Mercury (II) Sulfate	Silver Nitrate/Potassium/Chromium-(III) Sulfate
Mercury Nitrate (for corrosion of copper alloys) for antifungal use (mercurochrome)	Ammonia/Copper Sulfate Neosporin, Mycin
Mercury Iodide	Phenate method
Sulfuric Acid (commercial grade; mercury as impurity)	Sulfuric acid from a cleaner source
Zenker's Solution	Zinc Formalin

Work by The Massachusetts Water Resources Authority

Reagents: The Mercury Products Database

The Massachusetts Water Resources Authority (MWRA), in conjunction with MASCO (a consortium of Longwood Medical and Academic Area Institutions), has been working with their area hospitals and academic institutions to identify and address the problem of mercury contamination in hospital and medical waste streams. The Operations Subcommittee of this group set out to identify mercury in reagents. As part of this process, a database worksheet was developed to capture the wide range of information known to contain mercury. Next, a letter was sent to 153 major reagent vendors to elicit supplier support in identifying the trace levels of mercury contained in their products. The letters also requested that suppliers provide verification of product mercury content via the submission of a state certified laboratory report.

Using all available inputs, a total of 5,504 products were identified and inventoried into the master database using both vendor and member responses to requests for information. The statistics for their findings are as follows:

Total number of products inventoried: 5504

Number of records that contain mercury data: 781

Number of records that contain mercury concentrations below detection (BD): 166

Number of records with mercury concentrations BD - 1 ppb: 43

Number of records with mercury concentrations 1 -5 ppb: 53

Number of records with mercury concentrations 5 - 10 ppb: 19

Number of records with mercury concentrations > 10 ppb: 469

Number of records under review of concentration data: 31

Due to the size of the overall Mercury Products Database, only that portion of it which contains chemicals and products that have been verified, as of 8/21/95, to contain mercury at some level, have been included in the attached report.

75 Priority Samples

In an attempt to maximize the value of the database, MWRA selected seventy-five (75) of the most commonly used products by member hospitals and institutions and tested these for mercury content.

The analysis results for these 75 priority samples are shown on the table to the right.

Please see the "Laboratory" chapter of the Wisconsin Mercury Sourcebook for more information.

Results from 75 Priority Samples

Information from The Massachusetts Water Resources Authority (MWRA), in conjunction with MASCO (a consortium of Longwood Medical and Academic Area Institutions)

Product Sampled	Mercury Content (ppm)
Seven Deionized Water Samples	<0.0010
Periodic Acid	<0.0010
Acetone	<0.0010
Sodium Iodate	<0.0010
Acetonitrile	<0.0020
Aluminum Potassium Sulfate	<0.0010
Boric Acid	<0.0010
Butter Solution pH -7	<0.0010
Fixer	0.0049
Formaldehyde	0.012
Glutaraldehyde	<0.0010
Herpes Buffer	<0.0010
Phosphate Buffered Saline	<0.0010
Potassium Carbonate	<0.0010
Sodium Carbonate	<0.0010
Sodium Sulfate	0.010
Sodium Bisulfate	<0.0010
TDX	<0.0020
TRIS	<0.0010
Triton X-100	<0.0010
Oxalic Acid	<0.0010
Sodium Phosphate Dibasic	<0.0010
3%, 30% Hydrogen Peroxide	0.0012
Isopropyl Alcohol	<0.0010
Nitric Acid	<0.0019
Potassium Chloride	<0.0010
Silver Nitrate	<0.0010
Sodium Bicarbonate	<0.0010
Sodium Chloride	<0.0010
Trizma Buffer	<0.0010
Sodium Phosphate Monabasic	<0.0010

CAUSTIC SODA

Manufacturing plants may use chlorine, caustic soda, or muriatic acid to treat water or to assist in the production of paper products, cosmetics, pharmaceuticals, or food products. Manufacturing plants may dilute sodium hydroxide or potassium hydroxide and use it to regenerate ion exchange resin, adjust the pH of water or process feedstocks, or in their intermediate or final processes. Additionally, caustic soda may be used to treat "cooling" water used in power plants and boilers.

The Chlorine Institute, the trade association of chlor-alkali manufacturers, has recently supported an initiative set forth by the Virtual Elimination Project to reduce mercury emissions from mercury-cell chlor-alkali manufacturing by 50% by the year 2005. The Institute has also supported a 50% reduction in the deliberate use of mercury (purchases or consumption) in chlor-alkali manufacturing by 2005.

These significant commitments are an important step in reducing mercury emissions in the US. We applaud the efforts set forth by the Institute, and support their voluntary actions of environmental leadership.

From a memo addressed to Ms. Elizabeth LaPlante of the USEPA from Robert Smerko, president of the Chlorine Institute, dated September 19, 1996.

Chlorine Production and the Mercury Cell Process

(taken directly from November 21, 1994 C&EN)

The mercury process is one of three electrolytic systems that convert sodium chloride in brine into chlorine and sodium hydroxide, which is referred to as caustic soda. In the US, about 75% of chlorine is made in diaphragm cells, 13% in mercury cells, and 11% in ion-exchange membrane cells. The remainder is formed as a by-product of other chemical reactions.

In mercury cells, liquid mercury forms the cathode, gathering sodium ions from brine to form a mercury-sodium amalgam. Chlorine gas is released at the anode. The amalgam, when transferred to a "decomposer" and reacted with water, produces sodium hydroxide solution, hydrogen gas, and mercury, which is returned to the electrolytic cell.

As US chlorine production is consolidated, small mercury-based plants are the most likely to close. In Europe, most chlorine production is based on mercury cells, but the European Union plans to phase out their use by 2010. And Japan already has replaced most mercury cells, says Roger E. Shamel, president of consulting Resources Corp., Lexington, Mass., because of incidents of mercury poisoning.

Diaphragm cells produce chlorine, hydrogen gas, and sodium hydroxide solution in one cell, with no mercury involved. Brine flows into an anode compartment, which is separated from the cathode by a diaphragm. Chlorine forms at the anode, and the sodium ions and dilute brine traverse the diaphragm. Hydrogen is released at the cathode, and the sodium hydroxide-salt solution is removed. The effluent is concentrated by evaporation, and salt precipitates.

Ion-exchange membrane cells, the newest method, allow nearly one-step chlor-alkali production. As in the diaphragm cells, brine flows into the anode compartment, where chlorine is formed. But the membranes selectively allow only the sodium ions to pass into a water-filled cathode compartment. The cathode solution is removed from the cell and concentrated.

Carri Lohse-Hanson at the Minnesota Pollution Control agency has undertaken a project of "Mercury Reduction Through Treatment Chemical Selection." She has researched mercury levels in caustic soda and has also found that other feedstock chemicals may have high levels of mercury. For example, sulfuric acid produced at a lead smelter was found to have significantly higher levels of mercury than sulfuric acid made from a copper smelter.

The Mercury Reduction Through Treatment Chemical Selection project is collecting information on sources and characteristics of feedstock chemicals, including the prices of various grades, and will identify likely users of these materials. The second phase of the project will distribute information and request switching to low mercury feedstocks.

The table below from the MPCA provides preliminary information on characteristics of different grades of caustic soda:

Characteristics of Different Grades of Caustic Soda

Properties*	Mercury Cell	Membrane Cell	Rayon Grade	Diaphragm Grade	Purified
sodium hydroxide	50%	50%	50%	50%	50%
sodium chloride	400 ppm	100 ppm	100 ppm	11000 ppm	300 ppm
sodium chlorate	3 ppm	5 ppm	3 ppm	3000 ppm	10 ppm
sodium carbonate	1000 ppm	1000 ppm	1000 ppm	2000 ppm	1000 ppm
sodium sulfate	100 ppm	250 ppm	250 ppm	500 ppm	500 ppm
iron	3 ppm	3 ppm	3 ppm	10 ppm	5 ppm
nickel	--	0.3 ppm	0.3 ppm	3 ppm	4 ppm
copper	--	0.3 ppm	0.3 ppm	0.2 ppm	0.2 ppm
mercury	0.25 ppm	0.001 ppm	0.2 ppm	0.001 ppm	--
heavy metals	1.5 ppm	5 ppm	15 ppm	10 ppm	10 ppm
silica	17 ppm	10 ppm	15 ppm	50 ppm	80 ppm

** Maximum values*
Information from The Minnesota Pollution Control Agency

The table below shows the estimated mercury concentration (ppb) in wastewater given the usage of caustic (in tons per day) and the average wastewater discharge (in gpm).

Mercury in Wastewater (ppb)				
	Wastewater Flow (gpm)			
Caustic Used (tons per day)	100	500	1,000	5,000
1	0.017	0.003	0.0016	0.0003
2	0.033	0.007	0.0033	0.0007
10	0.17	0.033	0.016	0.0033
20	0.33	0.066	0.033	0.0066
Table from Vulcan Chemicals				

REDUCTION WORKS!

Case study: Potlatch Corporation - Tracking Down Mercury in Feedstock Chemicals

Potlatch Corporation is a pulp and paper manufacturing facility in Cloquet, Minnesota. The plant changed its bleaching process to Elemental Chlorine Free (ECF) in March, 1994, which required the introduction of new feedstock chemicals.

The facility discharges into the Western Lake Superior Sanitary District, which recently imposed a local limit for mercury. Prior to the development of this limit, the company and the District were aware that Potlatch effluent was typically low in mercury, but occasional peaks were of concern to both parties. The two facilities began an examination of possible mercury sources in feedstock chemicals.

Caustic soda feedstock was tested and eliminated because the company was no longer using mercury grade caustic soda. However, the testing of sulfuric acid revealed that some shipments had low mercury levels, while other shipments were higher. The use of high mercury sulfuric acid correlated with the mercury peaks in Potlatch effluent. Further investigation revealed that the low and high mercury sulfuric acids were from different manufacturing processes. the company then took the step of informing suppliers that the company had to be assured of low mercury content on all its feedstock chemicals.

"Worst Month" vs. "Best Month" reductions were about 7.5 pounds of mercury for this facility!

(From "Mercury Reduction Through Treatment Chemical Selection," a handout for the Lake Superior Basin Energy Efficiency Workgroup Meeting, 2/27/96)

ACTION IDEAS TO CONSIDER:

- ✔ Send a letter to users of caustic soda and sulfuric acid asking them to request low-mercury grade materials.

BIBLIOGRAPHY

The information included in this pamphlet is essentially a compilation of the best mercury pollution prevention work to date. Information was gathered from the documents below; some material may have been quoted directly from these sources:

"Business Waste Reduction and Recycling: A Guide For The Workplace," Wisconsin DNR, 1995

"Chlorine Industry Running Flat Out Despite Persistent Health Fears," Bette Hileman, Janice R. Long, and Elisabeth Kirschner, C&EN, November 21, 1994

"Medical Waste Pollution Prevention: Keep Mercury Out of the Wastewater Stream," USEPA Region 5, September 1995

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