

CASE STUDY

Mercury Emissions from Power Plants

Overall, about one-third of airborne mercury results from natural, geological sources on land and water. Of the other two-thirds, half are new emissions from point sources such as power plants, and the other half are recycled anthropogenic emissions that were temporarily deposited on land and water. Because the direct emission of mercury-containing wastes into natural waters and onto land has largely ceased in developed countries, environmental concentrations of mercury have fallen substantially from their levels in the 1960s and 1970s. However, the levels are apparently not continuing to fall rapidly toward natural concentrations. This paradox is resolved by the realization that one important source of anthropogenic mercury has

not yet been tackled globally: the deposition onto water and soil from the air, into which it is released largely from the burning of coal to produce electricity.

Large amounts of mercury are released into the air from the unregulated burning of coal and fuel oil, both of which always contain trace amounts of the element (reaching levels of several hundred ppm in some coals), and from incinerating waste. Currently, coal-fired power plants, and municipal and medical waste incinerators, are the largest sources (40%) of mercury emissions to the atmosphere in the United States. In Canada, primary base metal and iron and steel industries also contribute significantly to the load.

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What You Can Do

1. Dispose properly of any mercury-containing batteries, fluorescent bulbs, thermometers, etc.
2. Discuss the regulation of mercury emissions from coal-fired power plants with local politicians.
3. Avoid eating fish that are known to contain higher levels of mercury.
4. Don't use lead sinkers and jigs when sport fishing, or lead ammunition to hunt game.
5. Avoid pottery that may have been glazed improperly with lead salts.
6. Avoid using nicad batteries, and promote the use of alternatives to them. Dispose of nicad batteries properly if you do use them.
7. Have your water supply tested for arsenic if you use well water.
8. Remove CCA-treated lumber from play areas, etc. where children may encounter it.

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Mercury Emissions from Power Plants (*continued*)

Mercury occurs in coal in the form of the Hg^{2+} ion, which is present naturally in the inorganic *pyritic* component of the fuel. Mercury is present in coal at a level of about 0.2 ppm (corresponding to the fraction 0.2×10^{-6}) on average. During combustion of the coal, much of the mercury is liberated into the air rather than becoming part of the ash. About 4 billion tonnes of coal are currently combusted globally per year. Consequently, the annual emission of mercury to the atmosphere from coal burning is as much as $(0.2 \times 10^{-6}) \times (4 \times 10^9) = 800$ tonnes, which amounts to about 40% of global air emissions of the element.

Data for the mid-1990s indicate that atmospheric mercury emissions in North America from incineration of waste at that time were also large, due to the presence of mercury in products such as batteries, and amounted to more than 50% of the emissions from fossil-fuel combustion. Since then, however, the use of mercury in batteries has been almost completely eliminated, so incineration should now be a smaller source. Ironically, because there are restrictions on the placing of mercury-containing hazardous waste in landfills in the United States, much mercury waste now is burned, releasing most of the element into the air!

The global anthropogenic emissions into the air of mercury from all other sources combined are of about the same magnitude as that from coal combustion, yielding a total output of about 2000 tonnes/year. Eastern North America, western and central Europe, central and South Africa, China, Japan, India, and parts of Russia have many high-emission sites. The many large-emission sources for North

America in 2002 shown in Figure 1 are located in the United States just below the Great Lakes; in most cases, they are coal-fired power plants, although the largest single sources are metallurgical operations in the western states and Canada.

Asia is now the largest source of mercury to the atmosphere, contributing more than half the total. Emissions from developing countries have risen as those from developed ones have fallen: China, for example, has increased its emissions by over 50% in the last decade, and India by over 25%. Indeed, China is now the world's largest consumer of coal, accounting for 28% of the global total in 2003. Europe and North America have decreased their emissions over the past 20 years, and now each account for about 10% of the total. Overall, however, the reductions in mercury emissions achieved by the United States and Canada have been offset by increased airborne emissions from outside North America, especially from Asia, so there has been little change in the total emission rate and global atmospheric concentration of the element over the last three decades.

Thus it is mercury emitted from coal-fired power plants and waste incinerators that is the residual problem with the element today in developed countries, rather than direct discharges into water or soil from industrial or waste-disposal sites. The question of how far this airborne mercury travels—whether deposited locally or regionally or globally dispersed—is important and controversial. To understand this issue, we must first consider the different forms of mercury that exit from the stacks of power plants and incinerators.

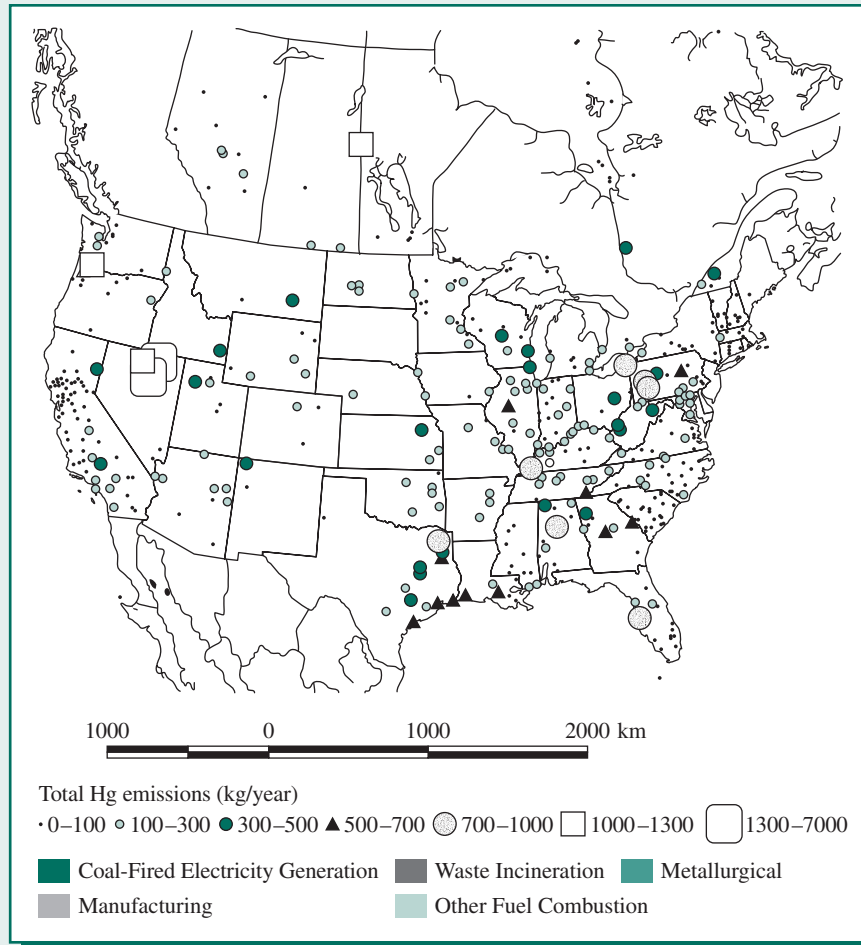


FIGURE 1 Geographic distribution of the largest anthropogenic mercury sources in the United States (1999) and Canada (2000). [Source: M. Cohen (NOAA), Presentation to Mercury Workshop, International Commission on the Great Lakes Biennial Meeting, Kingston, Ontario, Canada; June 9, 2005.]

The Nature of Airborne Mercury

One important form of emitted mercury is the gaseous, free, neutral atoms, Hg^0 . This elemental

mercury is formed in the combustion process by the chemical reduction of the Hg^{2+} that was present in the fuel. The element is emitted

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Mercury Emissions from Power Plants (*continued*)

mainly as a gas—rather than condensing to a liquid—since the temperatures in the combustion process and in the exhaust gases greatly exceed 357°C , the boiling point of the element, although some Hg^0 is adsorbed onto particulates in the stack emissions. In contrast to the behavior of organic pollutants that undergo long-range atmospheric transport, mercury vapor does not condense in cool climates. In addition, it is not water-soluble. It circulates in air until it is eventually oxidized back to Hg^{2+} , following which it is rained out relatively soon thereafter. The average lifetime of this *gaseous elemental mercury*, GEM, in air is a year or perhaps a bit less. Consequently, no significant amount of the GEM emitted by a power plant or incinerator is deposited in the region of its emission.

A fraction (roughly 50%, though the exact amount is uncertain and controversial) of the mercury emitted from power plants and incinerators occurs in an oxidized form, since some of the atomic mercury vapor released during coal combustion is oxidized in the exhaust gas. Some of the oxidized mercury called *particulate mercury*, or PM (or TPM), consists of Hg^{2+} ions that are bound to particles. The actual compound here may well be mercuric oxide, HgO . Since airborne particles tend to deposit within a few weeks, most particulate mercury is deposited regionally, downwind of the power plant.

The other emitted form of oxidized mercury is called *reactive gaseous mercury*, or RGM. It is probably gaseous mercuric chloride, HgCl_2 , a molecular compound of oxidized mercury, which is formed when Hg^0

reacts with chlorine gas also released by the coal. In particular, Hg^0 may react with atomic chlorine to form HgCl , which subsequently reacts with atomic or molecular chlorine or HCl to form HgCl_2 . However, most of the reactions to form oxidized mercury may be heterogeneous and may occur on surfaces. The lifetime of RGM in air is relatively short (about 1–10 days) since it is highly water-soluble and so is readily deposited by wet precipitation. For this reason, RGM is mainly deposited locally and regionally downwind of its source.

Some recent controversial, industry-sponsored research indicates that much of the oxidized mercury emitted from coal-fired power plants may be quickly reduced in air to the elemental (GEM) form—by mechanisms as yet unknown—rather than deposited. If this is true, then very little of the U.S. power-plant mercury emissions would be deposited locally, regionally, or even nationally; it would instead join the mass of Hg^0 traveling around the world for upward of a year or so on average before being deposited in a random location. The resolution of whether or not this reduction of Hg^{2+} to Hg^0 occurs has important political, economic, and environmental consequences: Power plant operators could argue against tightening controls on their emissions if most of the mercury simply joins the global pool of the element in the air, the great majority of which is it emitted by countries having no emission controls.

The various forms of airborne mercury, and their lifetimes, are summarized in the following table:

Form of the Mercury	Chemical Formula	Estimated Atmospheric Lifetime
Gaseous elemental mercury (GEM)	$\text{Hg}^0(\text{g})$	months–year
Particulate mercury (TPM)	Hg^{2+} (adsorbed, possibly as HgO , on solid); some adsorbed Hg^0	few weeks
Reactive gaseous mercury (RGM)	$\text{HgCl}_2(\text{g})$	days–week

The concentration of mercury in air is so small—about 2 ng/m^3 on average, although wintertime levels in some Chinese cities are more than 10 times that high—that it usually will not directly affect human health, even though mercury vapor is a very toxic form of the element. However, once mercury is deposited and enters the aquatic environment, it can be transformed by microorganisms to the very toxic and bioavailable **methylmercury**, which bioconcentrates and can contaminate fish to levels unhealthy to humans who consume them. Indeed, fish consumption is the main route of mercury exposure to humans, and most U.S. states have issued fish consumption advisories for that reason. About 8% of American women currently have mercury levels in their bodies that exceed those thought to be safe. As a consequence, it is estimated that more than half a million babies born annually in the United States have some degree of neurological deficit owing to their exposure to mercury in the womb. At its current levels in the environment, mercury poses its greatest health risk to people whose diet is largely local fish and

game, to others whose fish consumption exceeds the average, and to young children and pregnant women. Indeed, the number of water bodies—both rivers and lakes—in North America having fish advisories due to mercury contamination is actually increasing, not falling.

Mercury Emission Control by Power Plants

To date it has proven to be virtually impossible to keep all or most mercury vapor from being emitted from coal-fired power plants, since the gas is so inert. It has resisted chemical attempts—such as adding catalysts to exhaust gases to make it react—to trap it completely. Powdered activated carbon injection into the exhaust gas stream can be used to adsorb and thereby trap mercury vapor; the powder subsequently is captured by a fabric filter or an electrostatic precipitator. Partially brominating the carbon leads to higher capture efficiency. Indeed, adding elemental bromine gas to the flue gas from the power plant oxidizes much of the elemental mercury, allowing it to be captured by techniques discussed below.

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Mercury Emissions from Power Plants (*continued*)

Particulate mercury can readily be captured by power plants—such as many of those in the United States and Europe but few of those in developing countries—that have electrostatic precipitators or fabric filters installed to efficiently remove particles. Since RGM is water soluble, it is efficiently removed from exhaust gases if they are scrubbed to remove other pollutants such as sulfur dioxide. Most of the mercury captured by these technologies is the ionic Hg^{2+} form, which would deposit locally and regionally if not removed. However, none of the existing technologies is efficient in removal of atomic mercury vapor.

About 25 new technologies are under development for mercury emission control. In one, called *Chem-Mod*, Hg^0 is captured by a liquid adsorbent material that either oxidizes it to Hg^{2+} or traps it on its surface. Another technology in development irradiates the exhaust gases with UV light (ironically using a mercury lamp), ionizing the mercury atoms into the oxidized Hg^{2+} state, which then reacts with HCl already present in the gases to produce HgCl_2 . This compound is water-soluble and can be removed efficiently by water-based scrubbing for other pollutants, thereby converting them to aerosols that can be collected by electrostatic precipitators.

Mercury Emissions in the Great Lakes Region

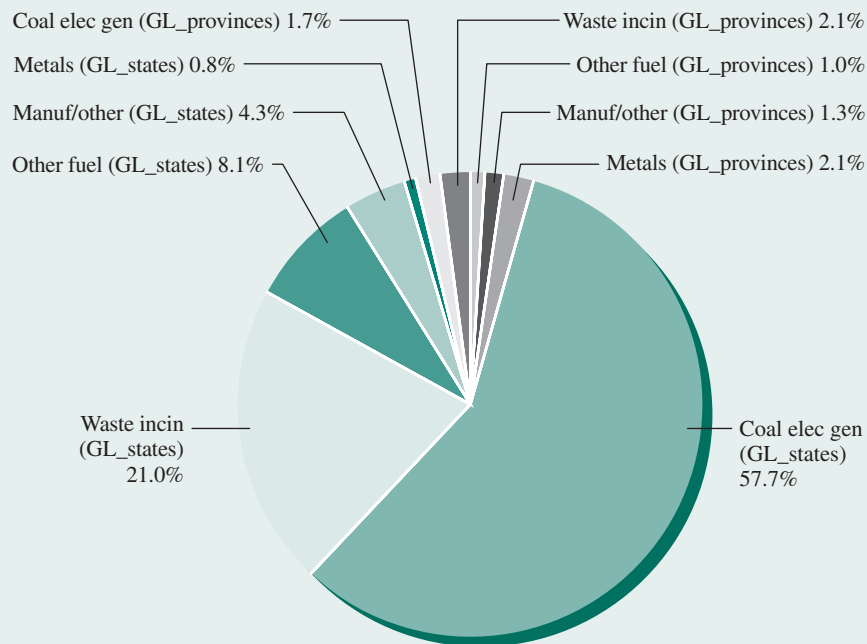
As an example of the effects of airborne deposition, consider the estimates of the important current sources of mercury emissions that eventually deposit within the Great Lakes region that separates the United States and

Canada. Power plants that burn coal are the most important source of mercury in the region (42%). Combustion of diesel fuel in heavy-duty vehicles provided about 15% of the emissions (with only 1% originating with gasoline-fueled vehicles) and was the second most important source as of 1999. Another combustion source, the incineration of refuse, was responsible for 8%. Collectively, combustion-based emissions into the air provided about two-thirds of mercury emissions within and into this region in the late 1990s. The pie chart in Figure 2 shows the distribution of emission sources *within* the Great Lakes for RGM—the form of mercury most likely to deposit locally; in decreasing order of importance we have

coal-fired electricity generation > waste
incineration > combustion of other fuels
> manufacturing (mainly chlor-alkali)
> metallurgical operations

Emissions from U.S. sources dominate Canadian ones in all categories except metal operations.

The fluxes via air, water, and sediments of mercury in and out of the water of Lake Ontario have been studied and are summarized in Figure 3. Nominally, the biggest source is sediment (1800 kg), although settling of mercury-containing solid particles onto sediments (1100 kg) offsets about two-thirds of that released from it, giving a net addition of 700 kg. Mercury contained in incoming waters exceeds that flowing out to the St. Lawrence by about 600 kg. Of the subtotal increase of 1300 kg, about 800 kg is



Total RGM emissions = 13.4 metric tonnes/year.

FIGURE 2 Emissions of ionic mercury (RGM) from different anthropogenic source sectors in Great Lakes states and provinces (1999–2000). [Source: M. Cohen (NOAA), Presentation to Mercury Workshop, International Commission on the Great Lakes Biennial Meeting, Kingston, Ontario, Canada; June 9, 2005.]

lost by “evasion” (evaporation) to the air, giving a net increase from water sources of 500 kg. However, atmospheric input of 360 kg almost doubles this source, resulting in an overall *increase* in mercury content of about 860 kg/year to the water of the lake. The largest sources of airborne mercury to the lake are two waste incinerators in New York State, two coal-fired power plants in Pennsylvania, and the Nanticoke power plant and an energy-from-waste incinerator in southern Ontario on the Canadian side.

Point to Ponder

Whereas pollution of soil and water by liquid discharges of mercury from industry and waste dumps were a local or regional problem, this is not necessarily true of emissions into the air by power plants. If the conventional wisdom—that about half the emissions from such plants are deposited locally and regionally—is correct, then it is in the self-interest of the local population that power plant emissions be efficiently cleansed of the element before it can

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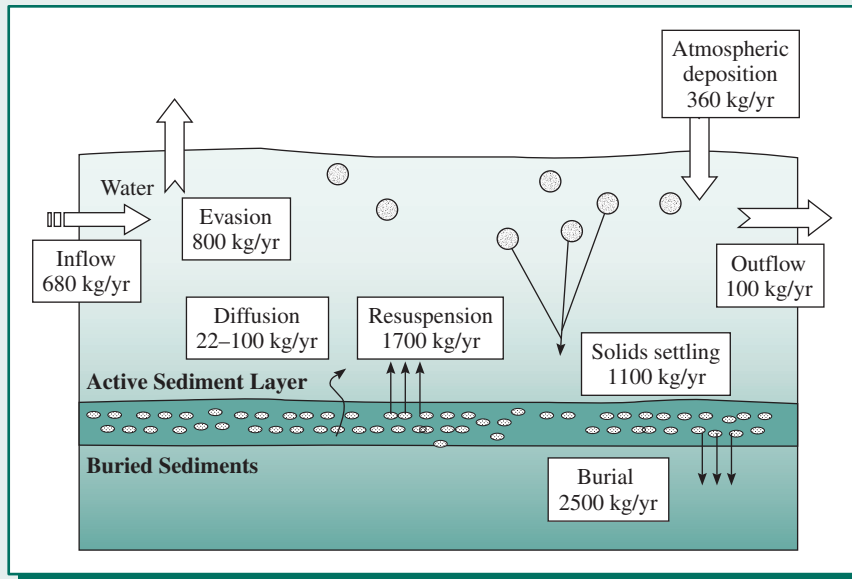


FIGURE 3 Total mercury fluxes for Lake Ontario. [Source: R. Ambrose, J. M. Johnston, C. D. Knightes, and E. M. Sunderland (U.S. EPA), Presentation to Mercury Workshop, International Commission on the Great Lakes Biennial Meeting, Kingston, Ontario, Canada; June 9, 2005.]

enter their food chain. However, if it turns out that through atmospheric chemistry most of the emissions are or quickly become Hg^0 and therefore circulate globally rather than being

deposited in the region, it can be argued that mercury is similar to carbon dioxide in that international, rather than national, controls are more appropriate.