

Atmospheric mercury: How much do we really know?

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Abstract: Mercury in the environment is of concern because of its toxic effects on humans and other organisms. The introduction of mercury into the environment from anthropogenic sources coupled with natural sources has compelled governments on national and international levels to address the need for its control. Regulations have been directed at mercury emitting industries such as power generation plants that consume fossil fuels, smelters, incinerators, chlor-alkali industries, and many others. However, mercury continues to be found in fish at levels of a few mg/kg. Elevated levels of mercury have also been found in air and water samples in regions far from industrial or other man-made sources. Despite mercury's importance and history, its environmental mass balance is uncertain, its long range atmospheric transport and fate are not fully understood, and its collection and measurement continues to be difficult.

Introduction

Among the vast number of chemicals known to mankind, mercury is one of the most unique due to its long history, its toxicity, and its chemical and physical properties. It was known to the ancient Chinese and Hindus, and has been found in Egyptian tombs from 1500 B.C. The Phoenicians traded cinnabar (HgS, used as the pigment vermilion) from around 700 B.C. and the medicinal use of 'liquid silver' (*Hydrargyrum* in Latin) is described by Aristotle. Mercury's ability to separate precious metals such as gold and silver from their ores by amalgamation was known as early as 500 B.C. and is still employed today for gold extraction in the Amazon region. Through the Middle Ages, alchemists regarded the metal as the key to transforming base metals into gold.

Mercurialism as an occupational disease was recognized by the Romans who sentenced slaves and prisoners to work the mines of Almaden in Spain. Mercury poisoning, either acute or chronic, affects the central nervous system, with early signs ranging from tingling in the hands and feet, slurring of speech, loss of coordination, and difficulties in vision and hearing. In the organic form (methyl mercury, CH₃Hg⁺) mercury can pass through the blood/brain barrier and through the placenta (1). With the increased use of mercury and its compounds in crafts, industry and for the treatment of such ailments as syphilis, the toxic effects of mercury became more common. The expression "mad as a hatter" stems from the use of mercuric nitrate in the making of hat felts from rabbit fur. Mercuric chloride (the corrosive sublimate HgCl₂) was used as an antiseptic, but its toxicity was further employed as a violent poison through the Middle Ages.

The modern realization of mercury as a public health hazard came about because of the Minamata disaster of 1953-1956. Fifty-two deaths and over seven hundred poisonings resulted that year (and many more over the next several years) when the fish which were the staple of the local community's diet became contaminated with dimethyl mercury sulfide (CH₃HgSCH₃). It was not until 1958 that the mercury was found to be the source of the poisonings and to have originated from a local chemical works where mercury salts were used inefficiently as a catalyst and discharged into the shallow Minamata Bay in an inorganic form (2). The use of mercury containing fungicides has also caused numerous deaths world wide when treated seeds meant for planting were inadvertently consumed directly. The most notable case here occurring in rural Iraq in 1971 when 459 deaths resulted from alkyl mercury poisoning.

It is consumption of mercury contaminated fish as in Minamata which continues to keep mercury pollution a matter of scientific interest, public concern, and government regulation. The general airborne concentration of mercury is extremely low, well below any level where it might be considered a direct hazard. However, once the mercury reaches open waterways, it enters a complex web of chemical reactions and microbial activity where it may eventually be transformed into methyl mercury. In this form, mercury is ingested and retained by aquatic organisms. In fish, the mercury accumulates preferentially in the muscles with proportionately much less in neural tissues than in birds or mammals. Traveling up the food chain, through the process of bioaccumulation the concentration of mercury in large fish can reach several micrograms per gram or ppm (the fish which caused acute poisonings at Minamata contained an average of 50 ppm mercury). The death of at least one Florida panther has been attributed to the consumption of raccoons who in turn consumed mostly fish (3).

Consumption of fish with this level of mercury constitutes a significant health risk to humans, especially small children and developing fetuses. Game fish in many areas exceed state, national, and international public health guidelines for mercury levels. The U.S. Food and Drug Administration removes fish from stores if its mercury level exceeds one ppm. It is somewhat surprising though fortunate that this is the general public's only source of exposure to hazardous levels of mercury.

Mercury is one of only eight hazardous air pollutants for which the EPA set emissions standards under the initial Clean Air Act of 1970, and it is among the 189 hazardous air pollutants requiring maximum achievable control technology (MACT) under Title III of the CAAA (4). This is where a better understanding of mercury transport and fate is essential. Knowing the significant sources of atmospheric mercury and identifying the areas which have become contaminated is not enough. What is needed is to link the two so that emissions reductions will indeed result in reduced human exposures.

Further complicating the need for a cradle to grave understanding of atmospheric mercury however are uncertainties in determining its concentration. Historically, analytical errors and contamination of samples have meant that many mercury measurements were of questionable merit. Stack emissions quoted by the EPA in 1989 for bituminous coal plants varied by a factor of one hundred (5). Measurements in natural waters during the 1970's range from zero to one thousand nanograms per liter (1). Previous to 1985, anthropogenic emissions to the atmosphere were thought to be small compared to natural sources based on measurements of pre-industrial Greenland ice cores whose values turned out to be too high by a factor of ten (1). Even though there is currently a much better appreciation of the need for clean sampling and analytical protocols, the anthropogenic contribution to the atmosphere is perhaps only known to within a factor of two (6).

Mercury contamination in remote regions can occur through long range atmospheric transport. Existing in the air as an atomic vapor, mercury's high vapor pressure and low solubility give it an atmospheric lifetime of up to one year. The concentration in ambient air is however extremely low, and elevations above the natural background level are small (Table 1). This makes the measurement and analysis of ambient atmospheric mercury troublesome.

Table 1. Vapor and Particulate Phase Atmospheric Mercury Concentrations

	Vapor-phase (ng/m ³)	Particulate (pg/m ³)	Reference
North Pacific	1.77	< 2	Fitzgerald et al. (7)
Wisconsin	1.57	22	Fitzgerald et a. (7)
Tennessee	2.15	30	EPRI Report (6)
Nordic	2.5 - 2.8	60	Iverfeldt, (8, 9)
Florida	1.64	1.5 - 8	Landing et al. (10)
New York	2.1 - 2.7	37 - 62	This work (11)

Current Methods for Mercury Analysis

Mercury which is initially in the vapor phase can be absorbed by a number of materials including: activated carbon both plain and treated, magnesium oxide or magnesium-copper oxide, lead sulfide, and liquid impingers (12-17). Owing to mercury's unique alloying properties it may also be collected by amalgamation with gold or silver (18-20). Because particulate mercury is also of importance in the atmosphere, several sampling and analytical procedures have also been developed to determine the concentration of mercury in this form. Aerosol collection is more straight forward than gas-phase, and is performed routinely by passing air through a suitable filter.

The two methods for the release of mercury vapor from charcoals and from particulates and filters are wet digestion and pyrolysis. Acid digestion is usually performed in a Teflon pressure vessel followed by a reduction-aeration vessel. Reduction of ionic mercury species collected in sorbants or in impingers is carried out using either SnCl_2 or NaBH_4 . Problems associated with this digestion are the long times required to completely digest the samples, the possibility of incomplete digestion, and the relatively large and sometimes variable blank values present in the digestion and reduction reagents. Pyrolysis is more efficient and straight forward, but the organics which may also be collected and which result from the destruction of the filter can cause serious interference and need to be removed from the analytical stream (21).

In order to shorten the release time of mercury into the actual detection device and to purify it from such interfering species a gold amalgamation stage is commonly inserted between the sample collection media and the detector. Fitzgerald and Gill (20) actually employ a two-stage gold amalgamation technique using gold-coated glass beads, where the initial field mercury is collected on one column and then the mercury released by controlled heating to 500°C and absorbed by a second analytical column.

Once the mercury is appropriately vaporized it can be detected by atomic absorption or atomic fluorescence, the former being simpler and more commonly available, and the latter being more sensitive but also more complex and expensive. These analytical techniques are more usually performed by atomizing a sample and introducing it into a flame, but because mercury has such a high vapor pressure it can be analyzed without the use of an ionizing flame. Thus the methods are referred to as cold vapor atomic absorption spectroscopy and cold vapor atomic fluorescence spectroscopy (CVAAS and CVAFS respectively).

All of the above sampling and analytical techniques have some common requirements and difficulties. Because of the low concentrations typically measured, contamination is by far the greatest problem during sampling, handling, transfer or analysis. Mercury loss, which produces the opposite result of contamination, is also a problem through all stages of measurements.

Because instrumental neutron activation analysis (INAA) does not require any pre-analysis sample preparation and is non-destructive, most of these difficulties do not arise. Samples for mercury analysis are placed directly into acid cleaned polyethylene vials which are sealed shut, labeled and further sealed into polyethylene bags. Several features of the analysis are worth noting. First, there are no chemical additions or extractions involved. The mercury remains largely unchanged within the sample, greatly reducing the chance of sample contamination or mercury loss. Because the samples are transferred to unirradiated containers for gamma ray detection, no blank correction is needed. The instrumental nature of the methodology also permits the analysis of samples that are difficult to dissolve or digest, such as atmospheric particulate material, coal, and minerals. Another unique advantage of INAA in environmental mercury analysis is the determination of additional elements (tracers) in the sample that can be used for source identification. The necessity of a reliable mercury sampling and analysis technique is highlighted in a recent publication by Nott, et. al (22). Simultaneous collection of gas phase mercury was performed in a coal-fired utility stack gas at six ports in the duct between the electrostatic precipitator outlet and the stack. Sampling was performed for 4 h on eight consecutive days. The samples from each day were analyzed for total gas phase mercury by six different groups using different methods. The particular sampling ports used were rotated among the groups in order to eliminate any bias. Although all of the methods used are considered to be acceptable, the measured mercury concentrations of simultaneously collected samples ranged from 26 to 167 percent of the average (total mercury concentrations were on the order 10^3 of ng/m^3). In light of the large variability reported in this carefully performed

intercomparison of well recognized analytical techniques, one has to be exceptionally critical and careful in evaluating results reported at levels of a few nanograms, or lower.

Sources:

As there is a significant abundance of mercury, both crustal and aquatic, there is of course a natural amount of mercury in the atmosphere as well. The mercury content of typical crustal material range from a few up to several hundred parts per billion, with some common mineral ores as high as a few hundred parts per million. The levels near the sites of active mercury mines such as those near Almaden Spain are as high as 20% (23). The general worldwide distribution of mercuriferous belts tend to follow regions of geological activity. Natural waters, including the oceans and inland fresh waters have on the order of 0.5 to 5 nanograms per liter with the mercury in ocean waters being stabilized as HgCl_4^{2-} (1). The natural vaporization and evasion of these large mercury pools result a globally averaged atmospheric mercury concentration of 1.6 nanograms per cubic meter (ng/m^3). The flux of mercury to the atmosphere is driven by its availability at the surface since at 20°C its equilibrium vapor concentration is $\approx 20 \text{ ng}/\text{m}^3$.

It is somewhat misleading however to consider this the natural concentration level for atmospheric mercury because anthropogenic emissions over the past one hundred years greatly outweigh the pre-industrial abundance of available mercury. It is estimated that since 1890 two hundred thousand tons of mercury have been emitted to the atmosphere (6), whereas the current atmospheric burden is perhaps only five thousand tons (the troposphere is $3.1 \times 10^{18} \text{ m}^3$). Thus a great deal of what may appear to be natural emissions of mercury especially from the oceans is actually the re-emission of anthropogenically produced mercury. An estimate of the present 'natural' global emission rate is one thousand tons from land and two thousand tons from the oceans annually (24).

Anthropogenic sources can be categorized in a variety of ways, the first being to divide them into diffuse and point sources. Point sources constitute the largest mercury emissions, are the easiest to measure, and the most likely to be addressed by regulation. World-wide mercury consumption is on the order of ten kilotons (metric) per year; up to one half of this is lost to the environment through source estimates vary by as much as a factor of two (6).

Globally, the largest source component is fossil fuel combustion for industrial applications, which contributes about 1200 tons per year. Waste incineration accounts for 600 tons and electricity production about 300 tons annually (about 60 tons from U.S. plants) (3). The concentration of mercury at the outlet of a 500 MW coal fired power plant is on the order of a few micrograms mercury per cubic meter, which corresponds to about 200 kilograms of mercury per year. Industrial sources include chlor-alkali production, metal ore roasting, refining and processing are also significant in some areas.

Diffuse sources are, in general, much harder to quantify, but some mass balance based estimates are possible and it appears that the global sum of these many small sources is up to 1000 tons per year. The EPA estimates from the emissions inventory, an annual U.S. release of 8.8 tons from the breakage of fluorescent and other lamps, 4.4 tons from latex paints where mercury has been used as a bio-cide, and one tone from dental uses including the release of mercury used in fillings of people who are cremated (25). Other common small scale sources include the disposal of dry cell batteries and other electrical equipment. (Mercury levels in both paints and batteries have been decreasing over the past years, partly through regulation and partly through consumer preference.) The use of mercury compounds in agricultural and lumber fungicides, and its use in primitive gold extraction in the Amazon are possibly large but diffuse semi-industrial sources (26). Finally the small amount of mercury present in motor fuel and lubricating oils may be a significant and wide spread source (27). The physical size of the sources is not as critical in determining the fate of the mercury emissions as the chemical and physical form of the emissions. While many of the difficulties associated with measuring total mercury have been solved, the speciated measurements of mercury sources continues to be problematic and rare despite the fact that this information is critical in determining mercury's short and long range fate. Part of the difficulty in making speciated measurements is the volatility of mercury creates problems of inter-species conversion during sampling periods. Generally speaking, sources emit mostly gaseous elemental mercury. If significant chlorine is present such as in incinerators, paper mills, and chlor-alkali plants a sizable fraction of mercury can

be emitted as HgCl_2 which is volatile, but also highly soluble. The amount of soluble mercury present in a plant's emissions is important both in terms of the mercury's ultimate fate, and in terms of the ability of current clean-up technologies to remove it from flue gasses. A pilot scale coal plant run by EPRI had almost total capture of ionic mercury using an electrostatic precipitator followed by wet limestone flue gas desulfurization (5), though only a small fraction of the elemental mercury was removed. The proportion of ionic to elemental mercury however varies with coal type, plant design and operation, and location along the flue gas path. Central sewage facilities may be a significant source of organic mercury such as CH_3HgCl and $(\text{CH}_3)_2\text{Hg}$ (28). The mercury likely enters the facilities as inorganic mercury having been previously ingested and excreted by humans. The emission levels vary widely and are dependent on the specific biological activity present and the population load on the facility.

The other important characteristic concerning mercury emissions from a specific source is the percent mercury associated with airborne particulates and also the size distribution of those particulates. An aerosol's size drastically affects its atmospheric range (i.e., coarse particles settle locally, while fine ones can travel hundreds of miles). Measurements very close to the stack of a coal-fired power plant near Oak Ridge Tennessee indicate that mercury particulate emissions may be as high as 9% of the total, but drop to 3% and then 1% at seven and twenty-two kilometers respectively (29). 1- 2% particulate mercury is a usual ambient level. The fraction of mercury associated with particulates is also important because of the role of particulates in source attribution studies and selection of control strategies. Emissions of particulates from coal plants for example are usually controlled through the use of electrostatic precipitators (ESP) and/or fabric filters which effectively reduce trace metal concentrations in the plant's effluent. The reduction in the mercury emissions for these systems varies widely (0 - 60%) depending on the flue gas conditions, coal type, fly ash, and gas compositions, temperature, placement of control systems, etc.

Upstate New York Study

A two year study is conducted to collect and analyze ambient aerosol samples and vapor phase mercury at five rural sites in New York State. The objective of this program was to explain probable sources and their contributions for trace element concentrations. Some of the pertinent findings from this study are given below:

- Source attribution and apportionment suggest that at least ten different source groups affect the sites individually, including U.S. Regional (defined as high temperature combustion emissions originating in the Midwestern U.S.), Canadian Regional (which presents aged and homogenized mixed industrial emissions from eastern Canada), wind-blown dust, smelters & precious metal works. This is the first study that identifies the source region referred to in this work as the Canadian Regional with specific trace elements markers.
- Seasonal variation of particulate and vapor phase mercury was observed, with higher values of both forms obtained for winter months. In addition a summer peak was also observed for particulate mercury.
- Lower concentration of fine particulate mercury were observed at all five sites beginning in February, 1993 and continued for the remainder of the sampling period.
- The large data set allowed us to estimate the current receptor background concentrations using the most frequently measured values at the sampling locations.
- There is an inverse relationship between ambient ozone and vapor phase mercury concentrations.

REFERENCES

1. O. Lindqvist, *Tellus*, **37B**, 136-159, (1985).
2. L. T. Kurland, S. N. Faro, and H. Seidler, *World Neurology*, **1**, 370, (1960).
3. J. Douglas, *EPRI Journal*, April/May, (1994), 14-21.
4. BNA (The Bureau of National Affairs), *The Clean Air Act Amendments: BNA's Comprehensive Analysis of the New Law*, (1991).
5. T. Moore, *EPRI Journal*, January/February, (1994), 6-15.
6. EPRI, Electric utility trace substances synthesis report EPRI TR-104614 (1994).
7. W. F. Fitzgerald, R. P. Mason, and G. M. Vandal, *Water Air Soil Pollut.* **56**: 745-768, (1991).

8. Å. Iverfeldt, Ph.D. Thesis, Department of Inorganic Chemistry,, University of Goteborg, Goteborg, Sweden, (1990).
9. Å Iverfeldt, *Water Air Soil Pollut.* **56**:251-266 (1991).
10. W. M. Landing, J. L. Guentzel, G. A. Gill, and C. D. Pollman, *Water Air Pollut.*, (in press. (1994)).
11. I. Olmez, M. R. Ames, G. Gullu and J. Che, *Upstate New York Trace Metals Program Report*, Volume 1, Mercury (1995).
12. W. H. Schroeder, and R. A. Jackson, *International Journal of Environmental Analytical Chemistry*, **22**, 1-18, (1985).
13. M. E. Kitto, D. L. Anderson, and W. H. Zoller, *J. of Atmospheric Chemistry*, **7**, 241-259, (1988).
14. BITC, (Bureau International Technique du Chlore) *Analytica Chimica Acta*, **108**, 1-11, (1979).
15. SKC, *Comprehensive Catalog and Guide, Summer 1992*, SKC Inc., Eighty-four, PA, (1992).
16. S. Alexandrov, *Fresenius' Zeitschrift für Analytische Chemie*, **321**, 578-580, (1985).
17. M. S. DeVito, and N. Bloom, *Proceedings: Second International Conference of Managing Hazardous Air Pollutants, 1993*, Electric Power Research Institute, VII-39-68, (1993).
18. M. Taylor, *Analysit*, **108**, 265-276, (1983).
19. P. Schierling, and K. H. Schaller, *Atomic Spectroscopy*, **2**, 3, 91-92, (1981).
20. W. F. Fitzgerald, and G. A. Gill, *Analytical Chemistry*, **51**, 11, 1714-1720, (1979).
21. R. R. Dumarey, R. Heindryckx, R. Dams, and J. Hoste, *Analytica Chimica Acta*, **107**, 159-167, (1979).
- 22/ B. R. Nott, K. A. Huyck, W. Dewlees, E. Prestbo, I. Olmez and C. W. Tawney, *AWMA 87th Annual Meeting*, Cincinnati, OH. June 19-24 (1994).
23. F. M. D'Itri, *The Environmental Mercury Problem*, CRC Press, (1972).
24. R. P. Mason, W. F. Fitzgerald, and F. M. M. Morel, *Geochimica et Cosmochimica Acta*, **58**, 15, 3191-3198, (1994).
25. J. Raloff, (2), *Science News*, **145**, 10, 142, (1994b).
26. W. C. Pfeiffer, and L. Drude de Lacerda, *Environmental Technology Letters*, **9**, 325-330, (1988).
27. I. Olmez, X. Huang, and M. R. Ames, *AWMA 88th Annual Meeting*, San Antonio, TX, June 18-23. (1995).
28. B. A. Soldano, P. Bien, and P Kwan, *Atmospheric Environment*, **9**, 941-944, (1975).
29. S. E. Lindberg, *Atmospheric Environment*, **14**, 227-231, (1980).