Chasing Quicksilver: From an Emperor's Tomb to the Global Environment

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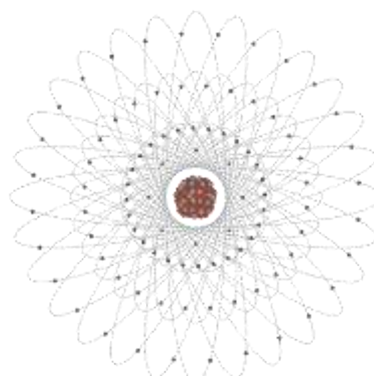
Quicksilver is metal mercury. Chemically, it is a heavy metal with a mild reactivity. Mercury is the only metal that exists in liquid form at room temperature. It is very heavy, nearly 14 times heavier than water. It looks pretty, very much like flowing silver, therefore the name “*quicksilver*.” The use of mercury dates back to 1500 BC. Historically, there have been myths and misunderstandings surrounding quicksilver. As an industrial material, there have been both misuses and beneficial uses. Environmentally, the US Environmental Protection Agency (EPA) regards it as one of the "priority" pollutants that we put into the air and water. Through global air and water circulation, it ends up in the fish and rice that we eat and causes other ecological problems. As a researcher, I have been working on the global movement, scientifically called global biogeochemical cycling, of quicksilver for more than 20 years. The more I work on it, the less I feel that I know. This is not surprising because mercury is supposed to be mercurial. Tonight, I want to share with you the story of mercury.



In nature, mercury exists primarily as cinnabar and a few other minor forms. Cinnabar is a mercuric sulfide (HgS) mineral of brick-red color. To extract liquid mercury, crushed cinnabar ore is heated to about 600 degrees Celsius (or 1100 degrees Fahrenheit). The rock is then decomposed to produce mercury vapor, which can be collected by cooling or condensation. Such a mining process in the old days was obviously very crude, poisoning mine workers and causing many premature deaths. The liquid metal has a lot of interesting chemical properties. It is heavy but has a very low viscosity; therefore, it flows readily and can be collected easily in liquid form for transportation. It is volatile and forms colorless and odorless vapor so it can enter the atmosphere easily without being detected. It has an extremely strong affinity to precious metals, particularly to gold and silver; therefore it has been extensively used for gold and silver extraction. It has a highly selective reactivity, only reacting with a few compounds under specific chemical or biochemical conditions. As a contaminant, it is regarded as an air pollutant because most of its release is into the atmosphere, but the real mercury pollution problems are mainly from its transformation in water. In the environment, it travels in the air and water and resides among air, water, dust, soil and even living vegetation in different chemical forms. Studies have shown that mercury released centuries ago still cycles in the global environment!


Cinnabar ore and crystal


Artisanal mercury mining

The toxicity of mercury depends on its chemical form, and its intoxication symptoms are also widely diverse. Elemental mercury vapor and the inorganic compounds of mercury have relatively mild toxicity. Organic mercury, particularly methylated and ethylated mercury compounds, is extremely toxic. Mercury is a potent neural toxin that can cause irreversible damage to the brain, central nervous system, kidneys, and lungs. Typical symptoms include impairment of vision, hearing and speech, and loss of body coordination. The type and degree of symptoms depend on the method, level, and duration of exposure.

The toxicity of methylmercury exposure is perhaps best illustrated by the tragic victims of Minamata disease in Japan since the 1950s. The episode started with the production of a series of specialty chemicals including vinyl chloride, the raw material of poly vinyl chloride (PVC) plastics, by Chisso Corporation. The manufacturing process used mercury compounds as catalysts and released waste streams containing methylmercury into Minamata Bay. Chisso had the most advanced industrial production in Japan before and after World War II. Unfortunately, we knew little of the environmental impact of mercury release in such a local marine environment. The released mercury initially caused significant reduction of fishing yield. From around 1950 onward, cats were seen having convulsions, going mad and then dying because they were the first food chain level up from seafood. The severity of the effect on the animal led to the name "dancing cat fever." Similar symptoms in body coordination and speaking problems were later observed in local human populations, the first case being in 1956. Unfortunately, it took almost a decade to identify the cause of the "unknown" disease. This single contamination episode caused thousands of human deaths. Even today, one of my Japanese colleagues, a specialized physician in Minamata, is treating remaining patients of Minamata disease.


Minamata, Japan





Minamata disease

More recently, the killing of a renowned toxicologist at Dartmouth College made national headlines. In 1996, Prof. Karen Wetterhahn ran toxicity measurements using dimethylmercury. She spilled one or two drops of liquid dimethylmercury from the tip of a pipette onto her latex gloved hand. Not recognizing the immediate danger, she proceeded with the standard procedures of spill cleanup and protective clothing removal. Unknown at her time, later tests showed that the dimethylmercury can penetrate through latex glove within seconds. Despite aggressive chelating therapy for months, she fell into a coma and tragically died because of methylmercury intoxication. Her passing was not in vain though. Her colleagues tested various safety gloves against dimethylmercury. As a result, it is now recommended that one wear selected resistant gloves when handling dimethylmercury and other similarly dangerous chemicals. In the earlier days of chemical synthesis, there have also been documented cases of death due to dimethylmercury poisoning.


Prof. Karen Wetterhahn (1948-1997)

In modern days, the exposure to inorganic mercury is primarily through inhalation of elemental mercury vapor or accidental ingestion, while the exposure to methylmercury is mainly through the consumption of fish. In fact, the US EPA has been issuing fish advisories since 1990s warning against the excessive consumption of fish. The affected freshwater and marine fish contain low levels of methylmercury that can gradually accumulate in the human body with continuous fish consumption. In this case, expectant mothers and children are most vulnerable. Studies have shown that such low yet continuous exposure can significantly reduce the IQ of newborns. In contaminated sites, the consumption of rice is also an exposure pathway because methylmercury in contaminated soils climbs up to the fruit of rice plants. How does mercury get into fish and rice that we consume? That is a more complicated question that we will answer later on. But mercury poisoning has a long history, including the suspected killing of the first emperor in ancient China.


"Before you do something you may regret, I think you should know that I contain six parts of mercury per million."

Mercury exposure pathways

USEPA Fish Consumption Advisory

One of the earliest documented episodes of mercury poisoning is probably the death of the first emperor of China more than 2200 years ago, Qin-Shi-Huang (259BC－210BC). At that time, China was separated into seven different nations. Each had its own word characters, language, and standards of weights and measures. Qin-Shi-Huang became the emperor of the nation of Qin at the age of 13. He grew up during numerous wars, fostering great ambition. He was smart, disciplined and eloquent. His troops strategically invaded the other six nations, and his regime took over their territories in 221 BC. After that, he named himself the supreme emperor, implemented the first legal system, and unified the language and measurement systems in China. To achieve this, he ordered his troops to burn much literature and to kill the scholars of other nations. This action was strongly criticized and arguably destroyed this ethnic identity and heritage in some historians' views. He was also the first emperor to begin the project of building the Great Wall of China to prevent the enemy in the North from invading China. He had a cruel and determined character that was not at all popular at his time. However, his policies had profound influence on the development of Chinese culture.


Qin-Shi-Huang (259BC－210BC)

But even the strongest and smartest person has a weakness. He longed for the impossible – eternal life. He assigned a group of people to go abroad to search for a medicine for gaining eternal life. It was cited in Chinese historic literature that those people became the ancestors of the Japanese. In his palace, he had alchemists who created medicines to extend life for him. According to ancient Chinese historical literature, he took pills made of liquid mercury and jade powder that eventually killed him at the age of 39. Obviously, it did not work out for him. During the final days of his legacy, he was characterized by being hot tempered and uncontrollable behavior, descriptive of the symptoms of mercury poisoning.

He started building his own tomb early on with a workforce of 720 thousand people. His tomb is located in the city of Xian, China. There have been major archeological projects funded by the Chinese government attempting to understand the construction and myth of his tomb. Modern sensors determined that his tomb is more than 100 feet deep, and larger than five football stadiums. It was said that his tomb contained rivers of flowing mercury on a model of the land he ruled. The use of mercury was to preserve his body and to deter thieves of tomb treasures. Interestingly, using modern sensing technology, archeological investigations have detected also high levels of mercury vapor on the ground above his tomb, making the myth more conceivable.


Site of Qin-Shi-Huang’s Tomb (Xian, China) and Visualization of its Internal Structure

The use of mercury as an industrial material has a long history. Ancient Egyptians and Romans used mercury in cosmetics, which can deform the face. By 500BC, mercury was used to make amalgams, a special mercury alloy with other metals. The early commercial demand for mercury was mainly due to its strong affinity to precious metals such as gold and silver. Mercury has the unique property of “picking up” gold from the ore that contains large amounts of impurities. The process mixes liquid mercury with the ore in water using a pan. When the small gold particles are brought in touch with mercury, they are absorbed by mercury, forming mercury-gold amalgam that can be easily separated from sand and silt. To obtain the pure gold, the amalgam is heated to evaporate mercury into the atmosphere. It takes about 1 Kg of mercury to produce 1 Kg of gold using the amalgam method. Around 1550, the process of using mercury for extracting silver from ore was developed. This led to a large consumption of liquid mercury by Spanish colonist in the Americas. In those old days, there were obviously not any environmental control measures to capture the mercury. This resulted in a large quantity of mercury emission into the atmosphere. The 19th century’s gold rush also contributed to a large release of mercury vapor extending into the early 20th century. Until now, there have been many small scale gold mining operations in developing countries using this crude method to extract gold, resulting in large amount of mercury release into the atmosphere.

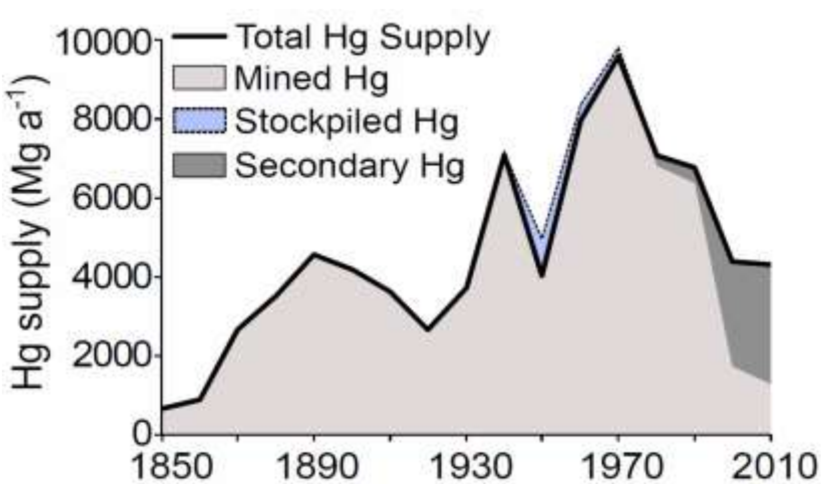
Artisanal gold mining using mercury

Other early industrial applications of mercury included dental amalgam, which was first documented in an early Chinese medical book in 695 and then became the mainstream dental filling material in the 18th century worldwide. The dental amalgam is an alloy of mercury, silver and tin that consists of 50% mercury. It has excellent ductility and strength, making the alloy easy to be filled into small cavities and long lasting. Beginning in the 17th century in France, mercuric nitrate was extensively used as a softening agent for fur processing in the felt hat industry. During the felt production, workers were often confined in small working areas filled with mercury fumes. The industry caused many intoxication cases called “mad hatter disease.” The neurological disorder symptoms of mercury poisoning, including slurred speech, tremors, irritability, shyness and depression, that these victims exhibit have been documented extensively.

Since the 20th century, the use of mercury and mercury products in several large-scale industries and commercial products has had important impacts on our daily lives. For example, mercuric chloride is an excellent catalyst in the production of vinyl chloride that makes water pipes and many plastic products. Liquid elemental mercury is used electrochemically in the chloralkali industry that makes chlorine bleach (e.g., Clorox) and caustic soda (sodium hydroxide), both are essential in drinking water production and in many other industries. The manufacturing process using mercury electrochemical cells is considered the most efficient one. However, compared to other alternatives, these processes using mercury are more polluting, and therefore have been gradually phased out by cleaner manufacturing methods in the US and Europe. In developing countries, they remain predominant because of their cost competitiveness. In the present day, of course, the disastrous release of mercury such as that in the Minamata episode is much less likely because of the previous lessons learned.

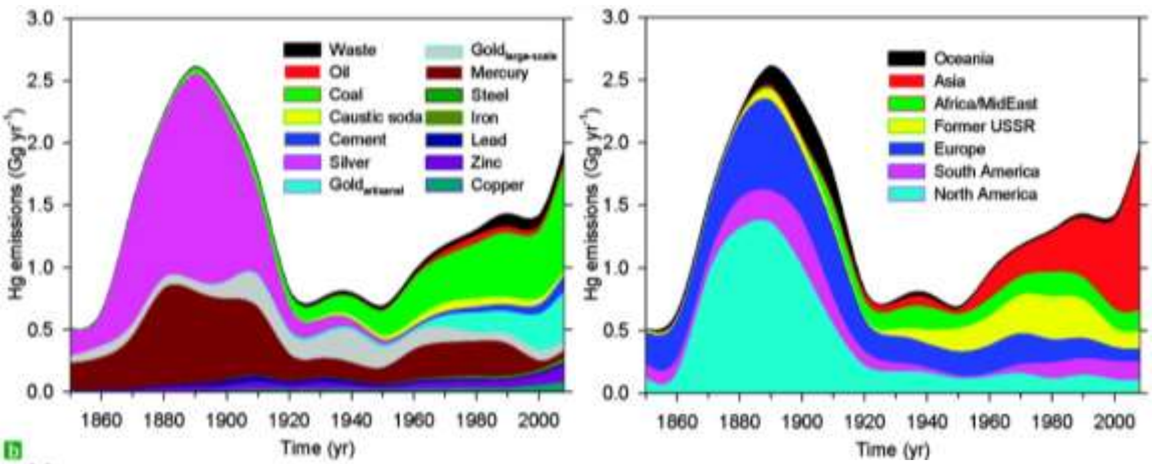
Commercial products that contain mercury

Perhaps you have noticed that products containing mercury have been surrounding us in our daily lives. Lamps, thermostats, batteries, meters, paints, pesticides – you name it! The use of mercury in these commercial products has been steadily decreasing in developed countries because of more stringent environmental regulations, however. For example, the worldwide supply and consumption of mercury peaked in 1970 (nearly 10,000 tons per year) and has decreased by half to about 5,000 tons per year today. Nevertheless, mercury is still irreplaceable in certain areas, for example, as a light source. Lamps containing mercury vapor give a very specific light spectrum with long-lasting stable light intensity that is rarely matched by other light sources. In addition to the wide application in the energy-saving fluorescent lights, such characteristics are particularly favorable in research equipment that needs stable light sources. Most of the time, these commercial products are either broken or end up in landfills, releasing mercury vapor into the atmosphere. The good news is that modern processes have procedures to recover mercury vapor during manufacturing; therefore, the demand for mining mercury has been decreasing since 1970.

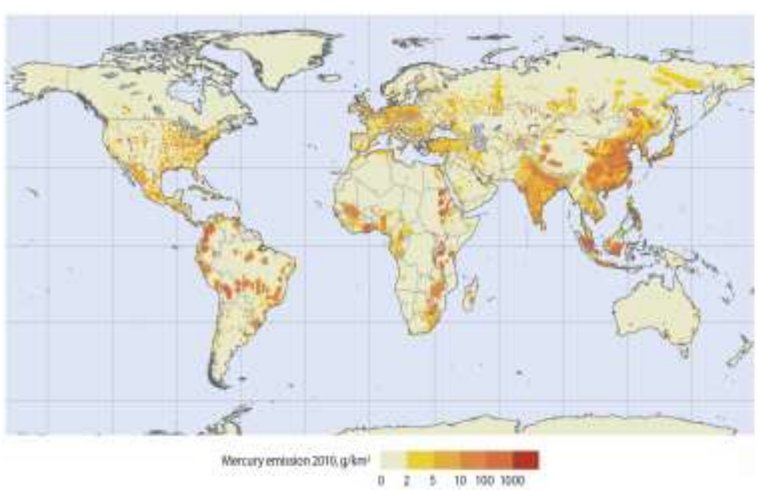


Global mercury supply/consumption (Horowitz et al., 2014). Secondary Hg refers to the mercury recovered from modern process using mercury.

In addition to the emission caused by commercial products and gold and silver mining, mercury is also released into the atmosphere from the consumption of fossil fuels (particularly coal), smelting production of industrial metals (zinc, copper, lead, iron and mercury, etc.), waste incineration, cement production, and burning of agricultural and natural biomass. The quantity and pattern of global mercury emissions reflect important historical periods such as the gold/silver rush, the depression after World War I and the rapid economic development after Second World War. It also shows the shift of economic growth rates in different regions. From the late 19th to the early 20th century, the Americas and Europe contributed to more than 90% of anthropogenic mercury emission globally. Today, Asia is responsible for more than 50% of the global mercury emission, while the emission from Americas and Europe constitutes less than 20 % of the global release because of better emission control measures. Coal and waste combustion, the metal extraction processes and cement production release about 2000 tons of mercury into the atmosphere every year. Adding that to the accidental release of commercial products and the evaporative release from landfill operations, the global anthropogenic emission of mercury is about 4000 tons per year. Being the largest economy in the world, the US emits fewer than 100 tons of mercury per year into the atmosphere, mostly from coal fire power plants and smaller industrial boilers that use fossil fuels.



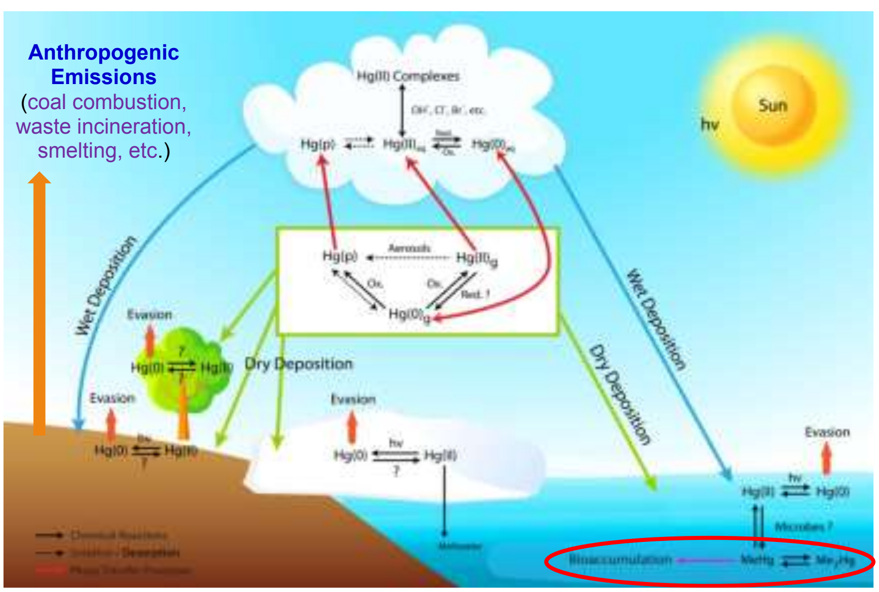
Global anthropogenic mercury emissions from 1850 to 2010 excluding the release from commercial products (Streets et al., 2010)



Global distribution of anthropogenic emissions (UNEP, 2013)

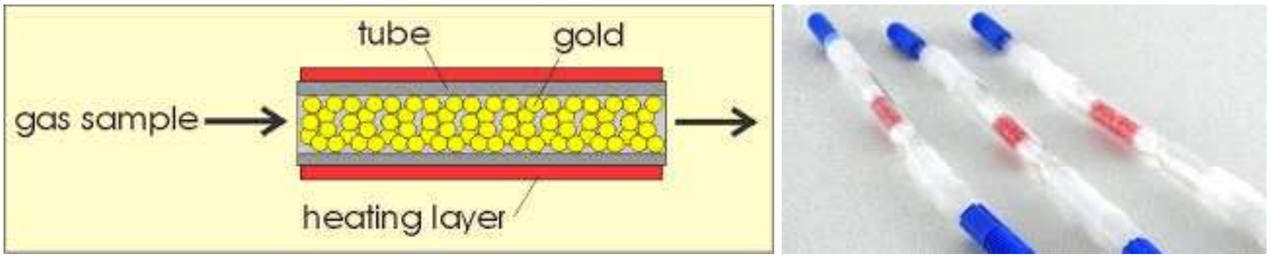
But the emission picture does not stop here because the quantity of mercury released from natural surfaces such as soils, water, and even vegetative canopy, is comparable to the quantity of emissions from human activities. Recent estimates suggest that the mercury release from earth's surface ranges from 3000 to 7200 tonnes per year. Adding this release to the emissions from volcanic sources and occasional large-scale forest fires, both liberate trace quantities of naturally bound mercury; the atmospheric release from these so-called natural sources can rival or even exceed the emissions from all modern anthropogenic sources combined.

How did this happen? The reasons can still be traced back to human activities. First of all, mercury vapor is only moderately reactive in the atmosphere and is not removed efficiently by the cleaning process of the atmosphere except near a large emission source such as a power plant or metal smelter. On average, the emitted mercury vapor can stay in the air for 6-12 months. Such a time scale is more than sufficient to distribute the vapor relatively evenly in the global atmosphere. Once in the atmosphere, mercury slowly reacts with other trace gases and with the pollutants emitted by human activities. These reactions take place in the air, in cloud, and even on the surface of suspended dust and move the mercury vapor back to earth's surface, typically through rainfall and snowfall. After these chemical reactions and subsequent atmospheric deposition, mercury gets accumulated in soils, in vegetation, and in surface water. In these environmental media, microorganisms and photochemical reactions can convert the deposited mercury back to mercury vapor, causing the "re-emission" of mercury back the atmosphere. Such a biogeochemical cycle goes on for tens to hundreds of years. Because human activity is responsible for artificially putting mercury into the air, the mercury level has gradually accumulated in air and on earth's surface. Studies have shown that mercury concentration in the atmosphere has tripled since the Industrial Revolution and that the mercury released during the gold rush era still cycles in the global environment! In other words, much of the natural emission of mercury is derived from the "re-emission" of deposited anthropogenic emission; and the emission from a region or country can cause mercury pollution problems in remote regions such as the Arctic and in other countries. Model studies have shown that the emitted mercury can undergo intercontinental transport in 7-10 days given the right meteorological conditions.



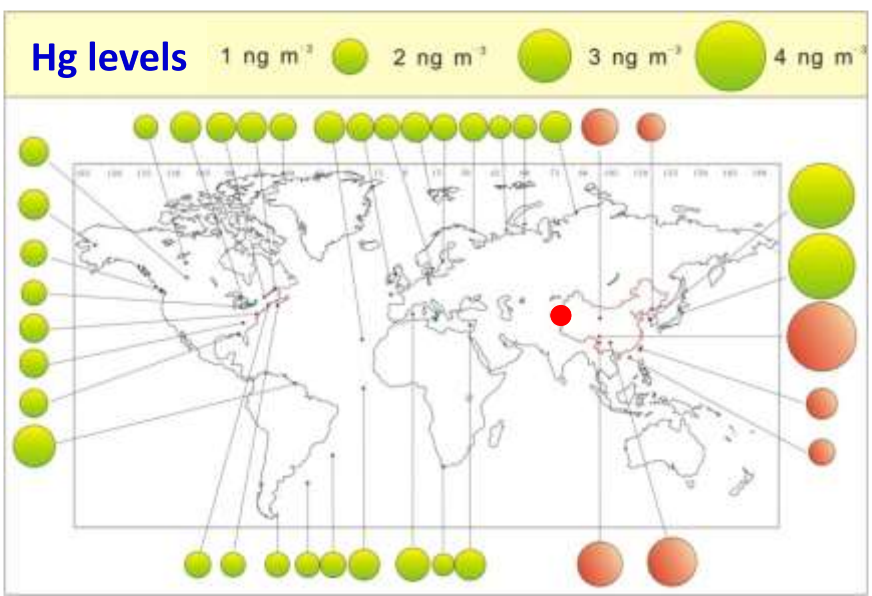
Global biogeochemical cycle of mercury (Lin et al., 2011)

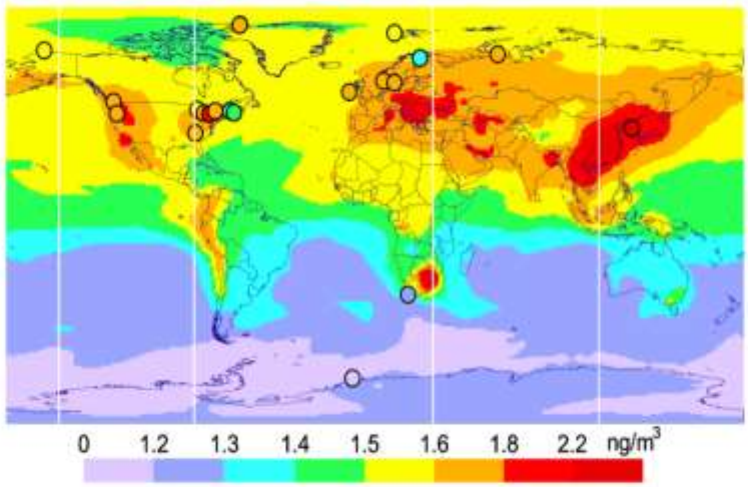
The threefold increase in air mercury concentration may sound a little scary, but the air concentration is never an environmental or health concern because the concentration is so small. Since the late 1980s, data of air mercury measurement on ground-based monitoring stations, in ship cruises and on aircrafts have been reported. Because the concentration is so small, scientists need to concentrate the mercury in the air before the measurement. So we borrowed the technique that our ancestors used hundreds of year ago – gold traps. The concentrated mercury is heated up to 600 degrees Celsius, like the gold miners did in the early days but in a precisely controlled fashion, and detected by cold vapor fluorescence or atomic absorption techniques.



Gold trap samplers of mercury

Using "trap-and-detect" methods and modern atmospheric dispersion models, we now know relatively well, thanks to many hard working scientists, the global distribution of mercury concentration in the atmosphere: 1 to 4 nano-gram per cubic meter. In heavy mercury-emission regions such as East Asia, the concentration is 2-3 times greater than the levels in the US and Europe. Such a concentration range is 10 to 100 thousand times lower than typical air pollutants such as ozone and nitrogen oxides, and hundreds of millions times lower than the most important greenhouse gas, carbon dioxide. Using a similar measurement scheme, the mercury levels in natural water have been also determined to be a few tens of nano-grams per liter. Because these environmental concentrations are so low, we were able to reliably measure these levels only about 30 years ago.





Global air concentration of mercury (Feng et al., 2013; Travnikov, Lin et al., 2010)

Ironically, the low mercury concentration in air and water, as well as the relatively recent analytical advancements also means that the hidden dangers of mercury pollution have gone undetected for decades. Once atmospheric mercury is deposited in freshwater or seawater, it can be converted to the highly toxic methylmercury by specific microorganisms in the anoxic zone of water or in the sediments where little dissolved oxygen exists. The methylated mercury is then gradually bio-accumulated as it moves up through the food chain. From the level of microorganisms to the fish that we consume, the concentration is already amplified by about one million times for species such as bass and tuna. For rice in contaminated soils, mercury is also methylated in the rice paddy, and the methylmercury moves upward into the fruit and contaminates the rice. Although the concentration of methylmercury is considered small, in the range of several to a few hundred parts per billion (ppb) levels, the chronic exposure to such a low level of methylmercury damage developing nervous systems in humans and decrease the IQ of newborns. This is the primary reason why USEPA and state agencies issue fish consumption advisories to the public, particularly to pregnant women and young children. Different impacts by methylmercury in the form of reduced population of fish-consuming birds are also reported. This is a unique and classic contamination route: an extremely low-concentration pollutant in the air ends up polluting fish and rice that we consume, and it has affected human health for a long time without being known until the 1990's.

As scientists continue to understand the adverse human health and ecological impacts of environmental mercury, efforts have been undertaken to reduce the emissions. Because it is essentially not possible to “control” natural emission, initial efforts have been targeted to the large point sources such as coal fire power plants, waste incinerators, cement plants, and metal smelters. Fortunately, many conventional emission reduction technologies designed for removing nitrogen oxides and sulfur dioxide have a co-benefit of removing mercury. New absorption technologies using new-generation, chemically treated activated carbons were also developed to capture mercury leaving the emission stacks. However, every emission reduction effort bears a cost that someone, either the emitters or very often the customers, will need to pay. In 2005, the USEPA first introduced the “Clean Air Mercury Rule” that established a “cap and trade” system to limit the total amount of mercury emission and allowed the emitters to “sell” their unused emission credits. The rule was challenged by the utility companies and later dropped by the US Court of Appeals in 2008. It did not work out too well. In 2011, the EPA again proposed Mercury and Air Toxics Standards for coal-fired power plants, and the final rule was signed into law by President

Obama in 2013. This new rule is a stringent one – it requires that coal-fired power utilities prevent more than 90% of mercury naturally contained in coal from emitting, and they have only four years to implement the control measures. Although EPA considers the law a success for curbing mercury emission, the affected companies are now preparing to challenge the rule by stating that it is too costly.

In addition to source reduction in the US, the United Nations Environment Program (UNEP) initiated an internationally coordinated mercury emission reduction effort in February 2009. The ultimate goal was to develop a global legally binding instrument on mercury similar to the Kyoto Protocol for greenhouse gases. The idea is that by cutting mercury emission from human activities, the anthropogenic input will be reduced and the accumulation of mercury in air, water and surface soils will then be slowly decreased over time, therefore reducing the accumulation of methylmercury in fish. Our assessment using multiple sophisticated atmospheric models supported the same outcome: if all anthropogenic emission of mercury is eliminated, the level of mercury concentration will go back to the pre-industrial revolution level eventually, with the greatest benefits taking place in 10 to 15 years.

Since June 2010, five intergovernmental negotiations were carried out to discuss the agenda for cutting anthropogenic emissions of mercury. The negotiation process has been interesting and delicate because of the emission characteristics and history. If the natural emission of mercury is as large as or larger than the anthropogenic emission, does emission control at anthropogenic sources make sense? Also, if the developed countries once contributed to 90% of global mercury emission in the past, which may still be cycling in the global environment, is it fair to target the emission reduction effort to the developing countries that contributed to the majority of modern day emission? These are certainly not easy questions to answer. But the world seems to agree that mercury emission control is needed and achievable. On January 19, 2013, after long sessions late into the night, the negotiations concluded with 147 governments agreeing to the draft convention text. It mainly includes implementing the best available technology for mercury emission control, eliminating mercury use in commercial products, and providing assistance to developing countries for emission control. The legal-binding international convention was signed in October 2013 in the place that suffers the most from mercury pollution – Minamata, Japan. The “Minamata Convention on Mercury” is now formally adopted by the European Union and 91 other countries in the world, including the biggest emitter in the world, China.

The final (5th) intergovernmental negotiation of the Minamata Convention

Today, it is unlikely that we will see major mercury contamination events on the scale of Minamata disease. But the story of the use and pollution of mercury remind us of the potential consequences of a highly useful material in our daily life. The international agreement of the Minamata Convention also demonstrates the power of knowledge and human race working together to solve challenging problems faced in our time.

So why am I still chasing quicksilver? Because there are still plenty of unanswered questions. First of all, there is still much uncertainty in estimating of anthropogenic and natural mercury release into the atmosphere. The long-term monitoring at pristine locations suggests that we have not accounted for all the sources and sinks of environmental mercury just yet. Particularly, we do not have very good understanding of the process of mercury vapor exchanges in forest ecosystems. Secondly, we know inorganic mercury in the atmosphere deposits into water and soils; the deposited mercury can be converted into the highly toxic methylmercury, but we know very little regarding the relationship between the deposition and methylation. Thirdly, we recently found that the physical and chemical conversions of mercury can force significant changes in the distribution of mercury isotopes. This finding provides exciting new tools for us to better understand where the detected mercury in a given location may originally come from. Finally, the movement and transformation of mercury is simply “mercurial” and interesting. Its environmental quantity is very low, and it can show up or disappear unexpectedly. I have many more stories I could tell about mercury, and I am not sure how much more I can learn about quicksilver. But I know I will just keep on chasing it.

Thank you very much for your presence. Have a great evening!