# Atmospheric Chemistry, Modeling, and Biogeochemistry of Mercury

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***Reprinted from**
*Mercury in the Environment: Pattern and Process* (Chapter 5) pp. 73-80

**Reprint 2012-8**

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## CHAPTER 5

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Mercury in the environment is of increasing concern globally because it can travel long distances through the atmosphere. For example, atmospheric transport and deposition of mercury from lower latitudes to the Arctic environment poses environmental and human health risks, despite few sources within the Arctic. On a more local scale, atmospheric chemical reactions and meteorologic processes can determine whether mercury deposits near sources or circulates globally. Understanding the chemistry and transport of atmospheric mercury is thus vitally important for managing mercury pollution.

There remain several critical uncertainties surrounding the behavior of mercury in the atmosphere. The global biogeochemical budget of mercury is not well constrained, particularly the magnitude of fluxes from land and ocean surfaces. The chemical reactions that control the transformation of mercury between its forms in the atmosphere are uncertain. However, some improvements in measurement techniques and the development of models at scales from local to global have provided important new insights into atmospheric mercury.

This chapter addresses the atmospheric chemistry and transport of mercury. It begins with an overview of the global biogeochemical budget of mercury, with particular attention to fluxes into and out of the atmosphere. It then surveys the different forms of atmospheric mercury and their distribution in the atmosphere. This includes the oxidation and reduction reactions that alter the form and properties of atmospheric mercury, and the wet and dry deposition processes that control its deposition to ecosystems. This is followed by a brief survey of atmospheric models that have been used in combination with measurements to further scientific understanding of atmospheric mercury. The chapter concludes by summarizing future challenges for atmospheric mercury research.

## Global Budget of Mercury

Prior to the onset of human industrial activities, the amount of natural mercury cycling through the land–ocean–atmosphere system was roughly one third of present levels. This represents the natural background level of mercury in the environment, which human activities have augmented. The origin of this natural background is geologic activity, including erupting volcanoes and emissions from the so-called global mercuriferous belts, where land is enriched with mercury (Fitzgerald and Lamborg, 2005).

The natural cycle accounts for about a third of present-day mercury entering the atmosphere; however, direct anthropogenic emissions are roughly comparable in magnitude. Anthropogenic activities that release mercury to the atmosphere include coal burning, industrial processes, waste incineration, and mining and metallurgical activities (Pacyna et al., 2006). The total amount of anthropogenic emissions to the atmosphere has remained relatively stable over the past decade; however, decreases in North America and Europe have been offset by increasing emissions in rapidly developing regions such as Asia (Pacyna et al., 2006).

The remaining third of emissions to the atmosphere is a result of the legacy of anthropogenic activity that has released mercury since industrialization. Human activities have taken mercury from its long-term storage in geologic reservoirs and transferred it to the atmosphere. While the lifetime of mercury in the atmosphere is about a year, cycling between the atmosphere and the land and ocean surface effectively lengthens the amount of time mercury circulates in the environment (Selin et al., 2008). Mason and Sheu (2002) estimate that it will take about 10,000 years for mercury to return to long-term sedimentary storage. Until then, this historical mercury continues to be released again to the atmosphere from land and ocean surfaces. The magnitude of these fluxes and the processes controlling them are not well constrained, but measurements have shown that fluxes can depend on temperature (Kim et al., 1995; Lindberg et al., 1995), solar radiation (Carpi and Lindberg, 1998; Gustin et al., 2002), or soil moisture (Gustin and Stamenkovic, 2005). Isotopic field studies have also shown that mercury recently deposited to ecosystems is more available for emission (Graydon et al., 2006; Hintelmann et al., 2002).

## Forms and Distribution of Mercury in the Atmosphere

In the atmosphere, mercury exists in three major forms. The majority of mercury in the atmosphere is in the form of gaseous, elemental mercury, which is termed Hg(0) (Mason and Sheu, 2002; Schroeder and Munthe, 1998). Typical concentrations of Hg(0) in the atmosphere are about 1.6 ng $m^{-3}$ at the surface. Hg(0) has a Henry's law constant of 0.11 M $atm^{-1}$ at 298 K (Lin and Pehkonen, 1999), which makes it less soluble than other forms of atmospheric Hg, and therefore more likely to be present in the gas phase in the atmosphere. Hg(0) has a lifetime of between 0.5 and 2 years in the global atmosphere, which means that it has the ability to transport globally. The two other forms of mercury are both shorter-lived. Divalent mercury [Hg(II)] is more soluble than Hg(0), which means that it is more likely to deposit to the surface through wet deposition and also dry deposition (which is enhanced for more soluble species). Because it deposits so readily, its lifetime in the atmosphere is shorter than that of Hg(0)—on the order of days to weeks. Typical concentrations of atmospheric Hg(II) vary between 1 and 100 pg $m^{-3}$. It is thought that most divalent mercury in the atmosphere is in the form of $HgCl_2$ (Lin et al., 2006). Mercury can also be associated with atmospheric particulate matter, termed Hg(P). Atmospheric concentrations of Hg(P) are of the same order of magnitude as Hg(II). Depending on particle size, it will also be deposited to the surface through wet and dry deposition on timescales of days to weeks. Mercury can also exist in organic forms in the atmosphere (e.g., methylmercury), though concentrations are more than an order of magnitude smaller than inorganic forms (Hammerschmidt et al., 2007).

Measurements of Hg(0) in the atmosphere are available at a number of land-based stations and from some ocean cruises and aircraft missions. Most land-based measurements are from the northern midlatitudes. Measurements from the Southern Hemisphere at Cape Point (Baker et al., 2002), from Antarctica (Ebinghaus et al., 2002) ,and from ocean cruises (Lamborg et al., 1999; Laurier et al., 2003; Temme et al., 2003) have generally reported lower concentrations than in the Northern Hemisphere, which indicates that most mercury sources are in the Northern Hemisphere. The interhemispheric gradient of Hg(0), in combination with the balance of sources between the Northern and Southern hemispheres, provides constraints on the atmospheric lifetime of Hg(0), as the interhemispheric exchange time for air is about a year (Jacob et al., 1987). The longer the atmospheric lifetime of mercury, the smaller the interhemispheric gradient is expected to be, since mercury would have an opportunity to mix between the hemispheres before it is removed from the atmosphere.

Seasonal variation of Hg(0) is consistent at most sites in the Northern Hemisphere (Kellerhals et al., 2003; Selin et al., 2007), with a maximum in winter and minimum in late summer. This behavior has been measured, for example, at a network of stations in Canada (CAMNet) (Kellerhals et al., 2003), and the seasonal variation is statistically significant for available sites in the northern midlatitudes (Selin et al., 2007). This suggests a photochemical sink of Hg(0), which is oxidation to Hg(II). However, the dominant atmospheric oxidant of Hg(0) is at present uncertain, as discussed below. Seasonal variation of Hg(0) in the Southern Hemisphere is more puzzling. Hg(0) measurements at Cape Point observatory in South Africa (Slemr et al., 2008) are maximum in summer and minimum in winter, opposite what would be expected from photochemical oxidation in this hemisphere. Slemr et al. suggest, based on the Cape Point data, that the seasonal behavior of mercury is driven by its sources rather than its sinks. Obrist (2007) reviewed the seasonal data from mercury measurements and suggested that the spring and summer declines in atmospheric mercury could be driven by the uptake of mercury by vegetation rather than its oxidation sink. This is a subject of continuing scientific investigation and discussion.

Measurements of Hg(II) and Hg(P) are fewer, though the number of measurements of these species are increasing. Hg(II) is measured in the atmosphere as reactive gaseous mercury (RGM) using an operationally defined method. Typically, Hg(II) measurements are made by collecting the species on KCl-coated denuders and reducing it to Hg(0) before measurement (Landis et al., 2002).

RGM has been shown to vary diurnally in the atmosphere, with a peak around midday and at a minimum at night. Jaffe et al. (2005) measured RGM at Okinawa, Japan, and found that levels peaked in the afternoon and were at a minimum at night. RGM at this site did not correlate with Hg(0), indicating that RGM results here from oxidation of Hg(0) and is not directly emitted from anthropogenic sources. It is thought that this reflects production of Hg(II) via oxidation of Hg(0). Laurier and Mason (2007) measured RGM at two sites in Maryland and on an Atlantic cruise and reported diurnal variation in RGM consistent with in situ photochemical production at background sites. At more urban sites in Baltimore, Maryland, they reported that local sources contributed to RGM concentrations. While these measurements of RGM suggest the influence of photochemical production, the major oxidation reactions producing RGM remain uncertain. The details and uncertainties surrounding mercury oxidation and reduction reactions are discussed further in the next section.

Some aircraft measurements of Hg(0) show relatively constant levels as altitude increases (Banic et al., 2003), while others show depletion of Hg(0) with increasing altitude (Friedli et al., 2004; Talbot et al., 2007). A number of measurements of RGM at altitudes above the surface (Landis et al., 2005; Sillman et al., 2007; Swartzendruber et al., 2006) have shown that RGM is higher there than at sea level. Swartzendruber et al. (2006) measured RGM at Mt. Bachelor, Oregon (2.7 km), and observed RGM enhancements up to 600 pg $m^{-3}$ at night, associated with downslope flows of free tropospheric air. Sillman et al. (2007) reported aircraft measurements in the free troposphere (up to 4 km) between 10 and 250 pg $m^{-3}$, with concentrations increasing with higher altitudes. As total mercury is expected to be conserved, RGM increases with higher altitudes are consistent with aircraft measurements that show depletion of Hg(0) with increasing altitude, such as the measurements of Talbot et al. (2007) of near-total depletion of Hg(0) in the stratosphere. Single-particle measurements have measured mercury attached to particles around the tropopause (Murphy et al., 2006). Mercury is thought to adsorb to elemental carbon (soot) particles (Seigneur et al., 1998), but the dynamics of gas-particle exchange for mercury are not well understood. The influence of high-altitude mercury on the surface is uncertain, but this question has been explored with models as discussed below.

## Oxidation and Reduction Processes

Hg(0) is converted to Hg(II) by oxidation in the atmosphere, which is thought to be a photochemically driven process. Based on laboratory data, it was previously thought that $O_3$ (Hall, 1995) and OH radicals (Pal and Ariya, 2004; Sommar et al., 2001) were the primary oxidants of mercury in the global atmosphere. However, more recent theoretical research has demonstrated that the reactions with $O_3$ and OH are unlikely to occur under atmospheric conditions (Calvert and Lindberg, 2005). At present, it is thought that Br could be the dominant global oxidant of mercury (Holmes et al., 2006; Seigneur and Lohman, 2008) and measurements have established kinetic parameters for its reaction with Hg(0) (Donohoue et al., 2006).

In polar regions, observations of Hg(0) and RGM have shown that these species exhibit unusual behavior in springtime. Shortly after Arctic sunrise, a series of so-called Atmospheric Mercury Depletion Events (AMDEs) have been observed to occur, in which Hg(0) levels show a very rapid decline, accompanied by concurrent increases in RGM. Hg(0) is depleted and recovers in a series of such events, which have been measured throughout the Arctic, sub-Arctic, and Antarctic coasts (Steffen et al., 2008). These depletion events are highly correlated with depletion events of tropospheric ozone in the Arctic (Simpson et al., 2007), which are caused by reactions involving halogen chemistry. It is thus thought that halogens, specifically Br, are responsible for AMDEs. At present, it is unknown how much of the depleted mercury remains in the ecosystem, and how much is revolatilized to the atmosphere, during AMDEs. Some measurements have indicated that much of the deposited mercury is revolatilized, but this remains a topic of active scientific interest. In particular, this is because mercury is of concern in Arctic ecosystems because of its accumulation in sensitive food chains (Arctic Monitoring and Assessment Programme [AMAP], 2002). Mercury deposition during the springtime period of productivity could thus contribute to these levels.

Reduction of Hg(II) to Hg(0) is an uncertain process in the atmosphere. Hg(II) is known to be reduced to Hg(0) in natural waters, and this process has been observed to occur in rainwater. It has been hypothesized that an aqueous reaction could reduce Hg(II) in the atmosphere, though its exact mechanism remains unknown. Hg(II) can also be reduced in power plant plumes (Vijayaraghavan et al., 2008). The extent to which reduction of Hg(II) occurs in the atmosphere is important both for the global budget (Lin et al., 2007) as well as for regional chemistry. As reduction produces the longer-lived Hg(0), it can lengthen the lifetime of mercury, and/or reduce regional deposition of anthropogenically emitted Hg(II). Thus, better constraints on the oxidation and reduction reactions of mercury are critical for policy.

## Deposition Processes

Processes of wet and dry deposition bring mercury from the atmosphere to the surface. Measurements are available for wet deposition of mercury through the U.S. Mercury Deposition Network (MDN) (National Atmospheric Deposition Program, 2009), which was established in 1996. The MDN measures wet deposition of mercury in weekly precipitation samples at over 100 sites in the United States, Canada, and Mexico. This is the most extensive network of wet deposition monitoring data for mercury that is available, although some stations in Europe also measure mercury wet deposition as part of the Co-Operative Programme for Monitoring and Evaluation of the Long-Range Transmissions of Air Pollutants in Europe (EMEP, 2009). In the United States, wet deposition of mercury varies both regionally and seasonally. The highest measurements of wet deposition are in the southeastern United States, and an additional area of elevated deposition has been measured near Hg(II) sources in the Midwest (e.g., the Ohio River Valley region, which has a high concentration of coal power). Deposition can vary seasonally, and is generally highest in the summer months in the eastern United States.

Dry deposition could be more important than wet deposition to many ecosystems, though few measurements are available. Methods for mercury dry deposition are not well developed (Lyman et al., 2009), and thus the total global magnitude of dry deposition is unknown. Measurements of the deposition velocity of Hg(II) to forest canopies and wetlands are very high (Lindberg et al., 1998; Poissant et al., 2004), as expected for a species of high solubility. The importance of dry deposition of Hg(0) is unknown. Uptake of Hg(0) by vegetation is thought to occur at the leaf interior, controlled by gas exchange at the stomata (Lindberg et al., 1992). While measured deposition velocities for Hg(0) are much slower than those for Hg(II) (Lindberg et al., 1995; Poissant et al., 2004), the significantly higher concentrations of Hg(0) in the atmosphere mean that this could be an important atmospheric sink. However, as the Hg(0) land–atmosphere and ocean–atmosphere flux is bidirectional, measurements and models must take this into account in estimating the net flux. Because the total amount of deposition of mercury is roughly equal to its source to the atmosphere, the total amount of dry deposition in particular is a key constraint in the global biogeochemical budget of mercury.

## Atmospheric Models and Applications

Atmospheric models can help to constrain uncertainties in the global mercury cycle, evaluate the importance of various chemical reactions, and assist in policy-making applications. A variety of atmospheric models have been applied to mercury at scales from regional to global (Bullock et al., 2008). In addition, modeling applications have been used to estimate the global biogeochemical budget of mercury.

Lamborg et al. (2002) used a simple, multibox model of mercury to estimate the present-day and preindustrial global biogeochemical budgets of mercury, constrained by the interhemispheric gradient and the enhancement of deposition since the preindustrial era. Mason and Sheu (2002), in contrast, scaled up from individual measurements to estimate preindustrial and present-day cycles. Sunderland and Mason (2007) used an ocean cycling model to assess preindustrial and present ocean fluxes, and Selin et al. (2008) constructed preindustrial and present-day cycles using a coupled three-dimensional land–ocean–atmosphere model. Estimates of global mercury fluxes vary, with the largest uncertainties in fluxes to and from the ocean and land (Selin, 2009).

Despite the uncertainties in modeling mercury, substantial insights can nevertheless be gained from their application in combination with measurements. Most mercury models show reasonable agreement with data on atmospheric Hg(0) and wet deposition (although, as suggested by Lin et al. [2006], it should be recognized that model uncertainties could be compensating for each other). For example, Shia et al. (1999) reported agreement with spatial and seasonal trends for the Chemical Transport Model for Mercury (CTM-Hg) model, and Selin et al. (2007, 2008) showed that GEOS-Chem agreed with mean concentrations at land-based sites as well as spatial variations. A large number of models have also been compared with constraints from MDN measurements (Bullock et al., 2009; Seigneur et al., 2004; Selin and Jacob, 2008).

Lin et al. (2006, 2007) have used the CMAQ mercury model in an extensive evaluation of the sensitivity of the atmospheric behavior of mercury to different model assumptions about chemistry and deposition processes. They suggested that chemical speciation and kinetics introduce the greatest uncertainties in atmospheric mercury modeling. Bullock et al. (2008) conducted a model intercomparison of the regional mercury models CMAQ (Bullock and Brehme, 2002), Regional Modeling System for Aerosols and Deposition (REMSAD) (ICF, 2005), and the Trace Element Analysis Model (TEAM) (Pai et al., 1997). They found significant differences among the models, driven both by initial and boundary conditions and by model processes. In their study, initial and boundary conditions were supplied by three different global models, CTM-Hg (Shia et al., 1999; Seigneur et al., 2001), GEOS-Chem (Selin et al., 2007), and the Global/Regional Atmospheric Heavy Metals (GRAHM) Model (Dastoor and Larocque, 2004). For some mercury species, monthly average boundary conditions varied by over an order of magnitude, especially at higher altitudes. Bullock et al. (2009) compared wet deposition measurements to output from these models, and found that adjusting for errors in precipitation data improved the agreements between models and observations.

One application of mercury modeling that is of particular interest to policy makers involves diagnosing and attributing the sources of mercury in deposition. Seigneur et al. (2004) used CTM-Hg to calculate that on average 25–32% of deposition to the United States is from North American sources, but at some locations their contribution was as high as 81%. They also estimated that Asian sources contributed 5–36%. Cohen et al. (2004) used the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model to investigate the sources of mercury to the Great Lakes, and found that coal combustion was the largest contributor. Selin and Jacob (2008) estimated, using the GEOS-Chem model, that North American sources contributed 20% on average to U.S. deposition, exceeding 50% in the industrial Midwest and Northeast. They also estimated that high-altitude RGM contributed over 50% to U.S. deposition, in particular contributing to high levels of deposition in the U.S. Southeast in summertime from convective scavenging.

## Future Challenges

Though concentrations of mercury in the atmosphere are low, it is atmospheric transport that makes mercury a global pollution concern. Understanding the pathways by which mercury travels long distances in the environment thus requires a better understanding of the reactions and processes that mercury undergoes in the atmosphere.

Despite increasing attention to mercury in the atmosphere, there remain several scientific uncertainties that limit our understanding of mercury chemistry, transport, and global biogeochemical cycling.

First, constraining the global budget of mercury, and in particular the interactions between land and ocean surfaces and the atmosphere, is a priority. From the atmospheric perspective, this will require improved measurements of land and ocean fluxes as well as dry deposition measurements, and comparison of these measurements with atmospheric models. Improved knowledge of land–atmosphere fluxes will also help to address the influence of historical mercury that continues to reside in these reservoirs, and its interactions with processes such as land-use and climatic changes.

Second, as Hg(II) is the predominant form depositing to ecosystems and Hg(0) represents the majority of emissions, understanding the oxidation and reduction reactions that control the speciation of mercury is necessary to better constrain where and when deposition is most likely to occur. Better understanding of where and under what conditions Hg(II) is formed can help to trace pollutants from source to receptor as well as identify gaps in measurements in potentially impacted ecosystems.

Finally, to support policy applications, better integration and analysis of the fate of atmospheric mercury across local, regional, and global scales is necessary. Deposition to ecosystems comprises mercury from anthropogenic sources nearby and faraway, in combination with historical mercury loadings as well as natural background. These source attributions vary spatially and temporally in ways that are only beginning to be understood. Effective controls on mercury pollution will thus likely require coordinated policy actions at a variety of scales (Selin and Selin, 2006).

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