

# Investigating Atmospheric Mercury with the U.S. Geological Survey Mobile Mercury Laboratory

Atmospheric mercury is thought to be an important source of mercury present in fish, resulting in numerous local, statewide, tribal, and province-wide fish consumption advisories in the United States and Canada (U.S. Environmental Protection Agency, 2007a). To understand how mercury occurs in the atmosphere and its potential to be transferred from the atmosphere to the biosphere, the U.S. Geological Survey (USGS) has been investigating sources and forms of atmospheric mercury, especially in locations where the amount of mercury deposited from precipitation is above average.

## Sources and Forms of Mercury in the Atmosphere

Mercury in the atmosphere is derived from both natural sources, such as emissions from volcanoes, and anthropogenic sources, such as combustion of mercury-bearing fossil fuels (fig. 1). Mercury exists in several different forms, which remain in the atmosphere for different lengths of time before being deposited on the land surface, or in rivers, lakes, or the ocean. Most of the mercury in the atmosphere occurs in the gaseous state. Three forms of mercury are recognized:

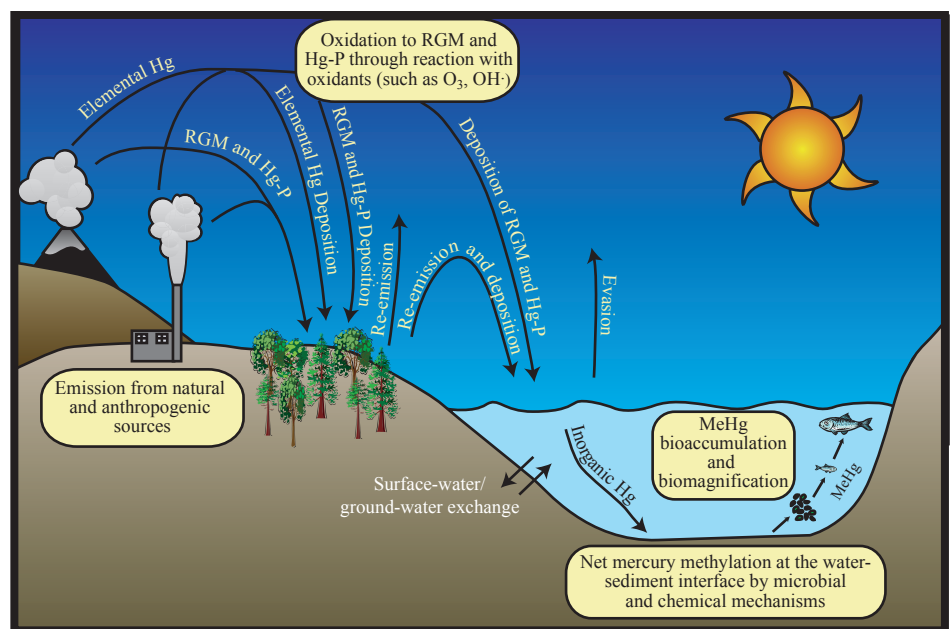
- **Elemental mercury ( $Hg^0$ )** makes up most of the mercury in the atmosphere.  $Hg^0$  can exist in the atmosphere for up to a year. During this time,  $Hg^0$  can travel around the globe, far from its source, before being deposited.
- **Particulate mercury ( $Hg_p$ )** is mercury that is attached to atmospheric aerosols (solid or liquid fine particles suspended in the atmosphere).
- **Reactive gaseous mercury (RGM)** is charged (ionic) gaseous mercury that is bound to other elements and is chemically reactive. The properties of RGM cause it to be deposited rapidly from the atmosphere. Compared to  $Hg^0$ , RGM has a much shorter lifetime in the atmosphere (days or weeks). As a result, RGM is much more likely than  $Hg^0$  to be deposited near the source.

## Relation Between Mercury in the Atmosphere and Human Exposure

At the miniscule concentrations at which it is present in the atmosphere, mercury poses no direct health hazard. However, deposition of mercury from the atmosphere into water bodies, together with the input of mercury from the surrounding land, can result in its accumulation in aquatic sediments, where it may be converted by bacteria to an organic form, such as methylmercury (MeHg) (U.S. Geological Survey, 2000). Bacteria containing methylmercury are consumed by organisms higher in the food web, or adsorbed onto plankton, which are also consumed. Because

methylmercury tends to be retained in the bodies of organisms, concentrations increase at each higher level of the food web. As a result of this process, known as biomagnification, high-end consumers such as fish, fish-eating wildlife, and people potentially can be exposed to harmful concentrations of methylmercury even at locations that are far from mercury sources and in areas with very low rates of atmospheric mercury deposition. Most humans are exposed to mercury primarily through the consumption of fish, especially those species that are high in the food web.

Studies conducted in the Experimental Lakes Area of northwestern Ontario, Canada, by scientists from the



**Figure 1.** Diagram of mercury cycling in the atmosphere showing major sources and pathways. (Hg, mercury; RGM, reactive gaseous mercury; Hg-P, particulate mercury; MeHg, methylmercury)

USGS and various other organizations are investigating the connection between the deposition of mercury and its uptake in ecosystems by tracing known amounts of mercury added to a watershed ecosystem. Results of the experiment, known as METAALICUS (U.S. Geological Survey, 2007), show that recently added mercury is more likely to be converted to methylmercury and taken up in organisms than mercury that is already present in the ecosystem. This finding indicates that a

reduction in the input of anthropogenic mercury to the atmosphere could decrease the occurrence of fish consumption advisories in some environments. In an effort to reduce atmospheric emissions of mercury in the United States, the U.S. Environmental Protection Agency (USEPA) has adopted a plan to limit mercury emissions from coal-fired utility power stations, the largest unregulated anthropogenic mercury source in the United States. The plan, consisting

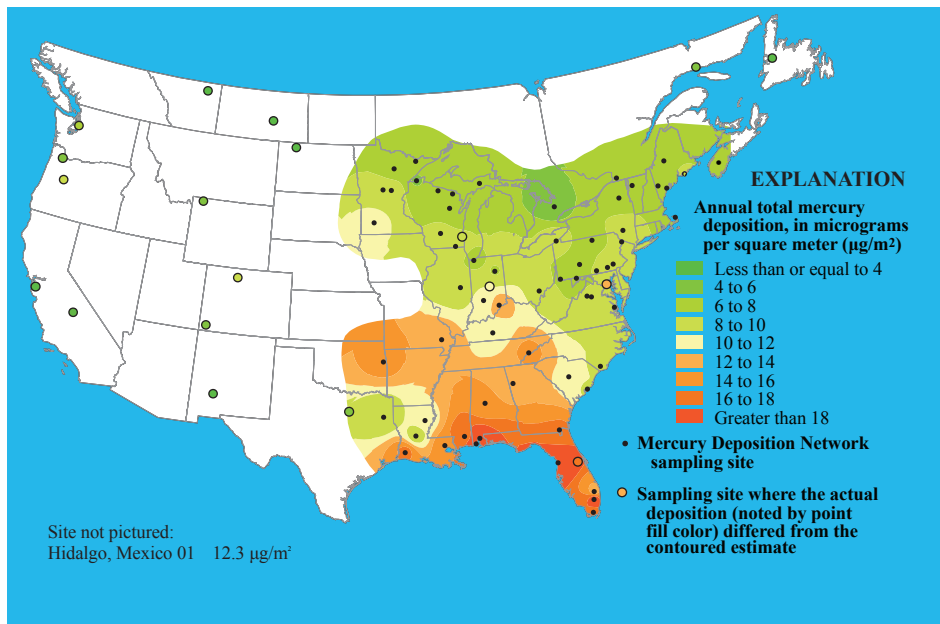
of the USEPA Clean Air Interstate Rule (U.S. Environmental Protection Agency, 2007b) and the USEPA Clean Air Mercury Rule (U.S. Environmental Protection Agency, 2007c), would ultimately result in a 70-percent reduction in mercury emissions from this source by 2018.

## Measuring Deposition of Mercury from the Atmosphere

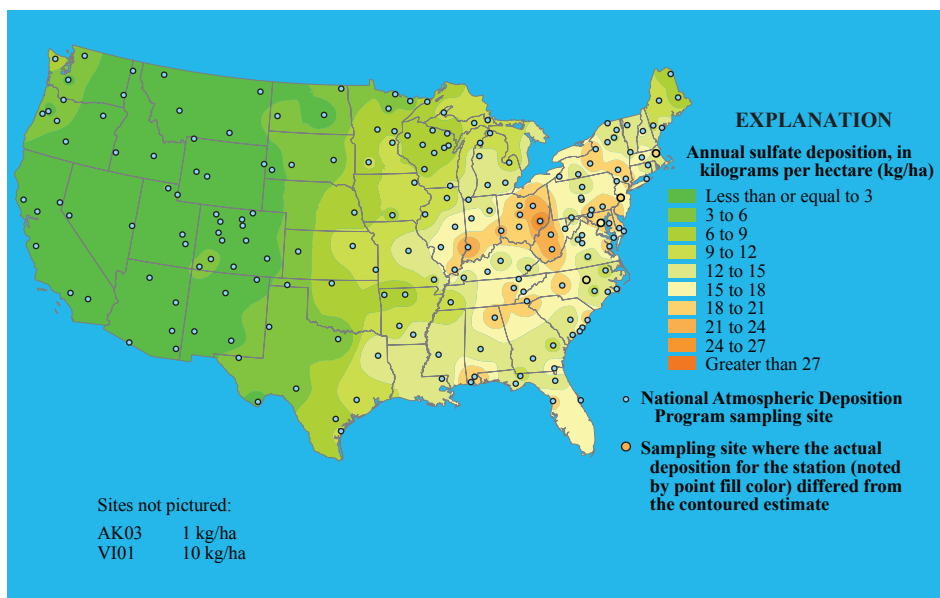
In the mid-1990s, the Mercury Deposition Network (MDN) of the National Atmospheric Deposition Program was begun to provide weekly estimates of the amount of mercury deposited in the United States from precipitation and the concentration of mercury in that precipitation (National Atmospheric Deposition Program, 2007). The MDN, a cooperative effort of many agencies and participants, consists of nearly 100 sampling stations concentrated primarily in the eastern United States, where rainfall amounts, and the proportion of mercury-emitting point sources, are high. Recent MDN results (fig. 2a) show that wet deposition is greatest in the southeastern United States and the Gulf Coast states; however, the density of coal-fired utility power stations and the proportion of atmospheric contaminants derived from coal combustion, such as sulfur dioxide, are greatest in the Ohio Valley, Mid-Atlantic, and northeastern states (fig. 2b). Possible explanations for this discrepancy include (1) the MDN does not measure mercury that is deposited when there is no rainfall (dry deposition); (2) reactions may be occurring in coal-fired power plant plumes that convert most of the mercury to the elemental form, which is less easily deposited; and (or) (3) there may be unique conditions or sources of mercury in the southeastern states, or near coastal settings, that contribute to high rates of mercury deposition there.

## Deployment of the USGS Mobile Mercury Laboratory to Measure Atmospheric Mercury

In order to improve understanding of the pattern of mercury wet deposition, especially in the southeastern United States, the USGS mobile mercury lab was deployed to sites in Alabama and South Carolina in 2005 and 2006, respectively (fig. 3). These sites were chosen to study the interaction of atmospheric mercury from sources on land with air masses



**Figure 2a.** Map showing location of Mercury Deposition Network sampling sites and contours of 2005 total annual mercury wet deposition. Map shows that wet deposition of mercury is greatest along the Gulf Coast and in Florida. (From National Atmospheric Deposition Program, 2007)



**Figure 2b.** Map showing 2005 contours of sulfate-ion ( $\text{SO}_4^{2-}$ ) deposition, which reflect the distribution of sulfur-emitting sources such as coal-fired utility power stations. This distribution is distinctly different from that for total wet mercury deposition (shown in figure 2a). (From National Atmospheric Deposition Program, 2007)



**Figure 3.** USGS Wisconsin Water Science Center mobile mercury laboratory deployed at Weeks Bay National Estuarine Reserve, Alabama. Instruments on mast at left rear of the trailer include the front end of the mercury speciation unit (large box) and meteorological sensors. Instrument on rooftop tripod collects fine particulate matter ( $\leq 2.5$  micrometers in diameter), whose mass per unit volume of air is determined by an instrument inside the trailer.

coming off the Gulf of Mexico or the Atlantic Ocean. In addition, wet deposition of mercury is high or moderately high at these sites, and coastal ecosystems are known to be highly sensitive to the input of atmospheric mercury.

The mobile mercury lab is equipped with instruments not available at most MDN sites. These instruments

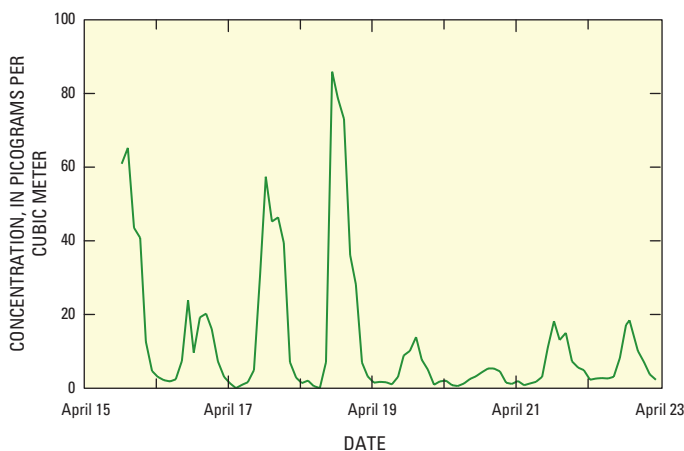
continually measure the amounts and proportions of  $Hg^0$ ,  $Hg_p$ , and RGM in the atmosphere. The mobile mercury lab also measures important atmospheric components such as sulfur dioxide, ozone, nitrogen oxides, and the mass of fine particulate matter, while making continuous meteorological measurements. In addition to the

mobile mercury lab, separate particulate samplers were set up in each study area to determine the proportion of mercury and trace metals bound to particles larger than  $2.5 \mu m$  (micrometers) in diameter—particles missed by the mercury sampling unit in the mobile lab because of its upper particle-size limit of  $2.5 \mu m$ .

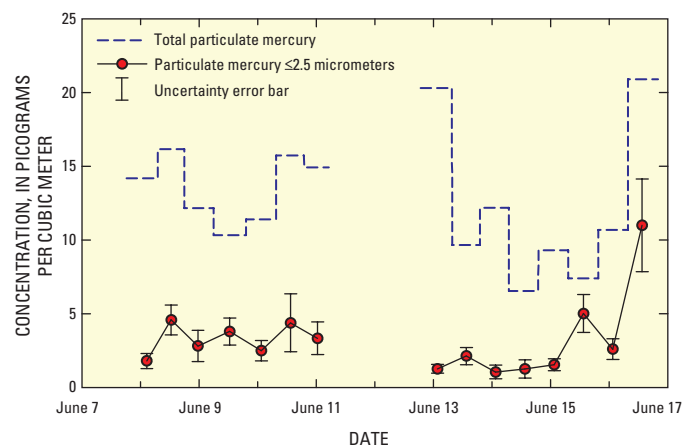
### Model for Enhanced Mercury Deposition at Coastal Sites

Daily results for the Weeks Bay sampling site in southern Alabama are shown in figure 4. Figure 4a shows the results of continuous sampling for RGM, with daily elevation of RGM concentrations during the afternoon hours, when sunlight and ozone levels are greatest. These conditions favor formation of RGM by sunlight-induced oxidation of  $Hg^0$  derived from natural and anthropogenic sources on land. A similar pattern of afternoon maximum RGM concentration, but with less prominent highs, was found in Cape Romain, South Carolina, in 2006.

Particulate mercury ( $Hg_p$ ) concentrations measured in Weeks Bay atmospheric aerosol particles were significantly lower for particles equal to or less than  $2.5 \mu m$  in diameter than for aerosol particles of all sizes (fig. 4b), indicating that a large fraction of  $Hg_p$  is bound to coarse particles. During sampling for  $Hg_p$  at Weeks Bay, some air masses came directly off the land; others came onshore from over the ocean; and still others came off the land, spent time over the ocean and returned

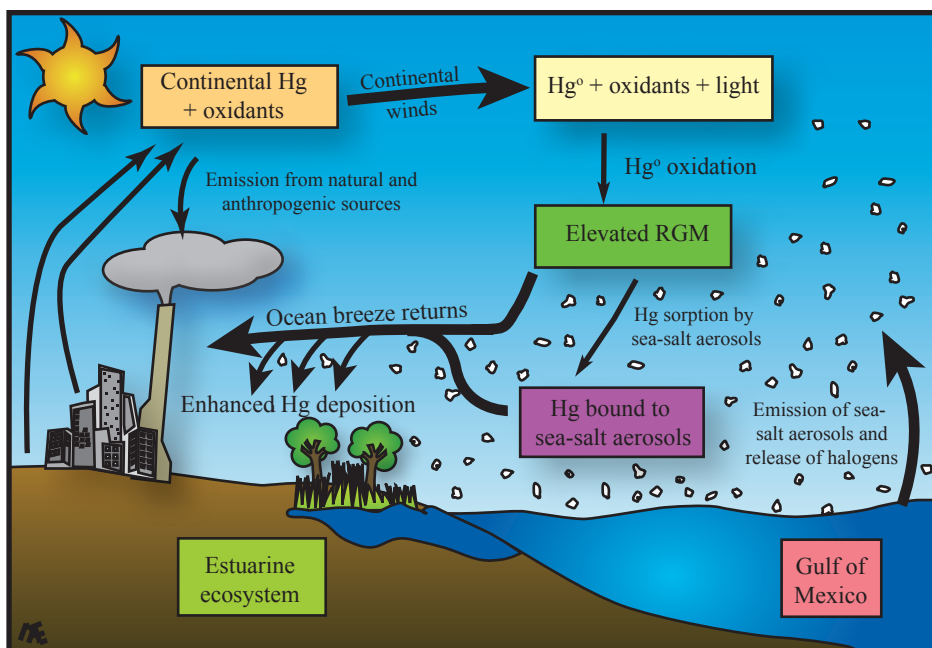


**Figure 4a.** Plot showing continuous daily variation in the concentration of reactive gaseous mercury at the Weeks Bay, Alabama, site during an 8-day period in April 2005.



**Figure 4b.** Plot showing concentrations of particulate mercury (particles  $\leq 2.5$  micrometers in diameter) measured by the mobile mercury lab and total particulate mercury measured in samplers with no size limitation. The difference between the two values equals the concentration of particulate mercury missed by the mobile lab analyzer. The plot shows that a large proportion of particulate mercury is bound to particles larger than 2.5 micrometers in diameter.





**Figure 5.** Conceptual model for enhanced mercury (Hg) deposition along the Alabama Gulf Coast, based on results from atmospheric sampling with the USGS mobile mercury lab and separate aerosol samplers. Model shows formation of sea-salt aerosols, primarily by action of wind on the ocean, and release to the atmosphere of halogen elements such as chlorine, a major component of sea salt. Wet deposition of mercury in coastal areas may be enhanced by formation of reactive gaseous mercury (RGM) from elemental mercury ( $Hg^0$ ) and oxidants derived from sources on land, and return of mercury onshore as RGM and mercury adsorbed onto sea-salt aerosols that are easily dissolved.

onshore as ocean breezes. On days when air masses coming off the land return onshore in the form of ocean breezes or come directly off the ocean into the RGM-rich nearshore environment, some of the RGM and (or)  $Hg^0$  appears to be scavenged and incorporated onto large aerosol particles, which contain sea salt from the ocean air. Combining mercury and air contaminant sources on land with onshore ocean breezes that are warm and humid and contain sea salt provides an environment that may allow for enhanced deposition of mercury along the Gulf Coast compared to inland areas or sites over the open ocean (fig. 5).

### Other Research Sites

Additional studies with the mobile mercury lab are planned to test the effect of ocean temperature and sampling-site location on the model developed for the Gulf Coast by deploying the lab at more northerly coastal sites in the Mid-Atlantic region and possibly New England. Our overall hypothesis is that the marine boundary layer (the intrinsic characteristics of the atmosphere overlying the ocean) interacts with atmospheric mercury in

near-coastal settings to enhance mercury deposition, and the strength of this interaction depends on factors such as ocean temperatures and wind patterns. Thus, the marine boundary layer is hypothesized to have a smaller effect on mercury deposition in cooler oceanic settings such as the Mid-Atlantic or New England states than at the warmer Gulf Coast and southeast Atlantic sites.

At existing air-quality-monitoring sites, the capabilities of the mobile mercury lab can be nearly duplicated by adding an analyzer that measures forms of atmospheric mercury to the instruments that are already in place. This approach was taken in 2006 at Shenandoah National Park-Big Meadows in Virginia and in 2007 in western Pennsylvania and is planned for other study areas. Studies at these inland sites are intended to illustrate what is happening in the atmosphere nearer to mercury sources such as coal-fired utility power stations, in order to understand the factors that control the reactivity of atmospheric mercury and the mechanisms by which mercury begins to separate from other atmospheric constituents derived from coal combustion.

### Summary

Mercury deposited from the atmosphere is added to aquatic ecosystems, where it can be converted to toxic organic forms such as methylmercury and taken up in the food web, ultimately resulting in unsafe levels for human consumption of fish. Our work in coastal Alabama shows that, in some cases, air masses containing mercury derived from the land mix with marine air masses, generating high concentrations of reactive gaseous mercury that can be deposited directly or possibly adhere to sea-salt particles that are deposited or dissolved in precipitation. This reactive gaseous mercury and particulate mercury is available to be deposited in mercury-sensitive coastal ecosystems, which may explain in part why mercury deposition is greater along the Gulf Coast than in the Ohio Valley, even though coal use for power generation is much more prevalent in the Ohio Valley than along the Gulf Coast.

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