

# A Synthesis of Progress and Uncertainties in Attributing the Sources of Mercury in Deposition

A panel of international experts was convened in Madison, Wisconsin, in 2005, as part of the 8th International Conference on Mercury as a Global Pollutant. Our charge was to address the state of science pertinent to source attribution, specifically our key question was: "For a given location, can we ascertain with confidence the relative contributions of local, regional, and global sources, and of natural *versus* anthropogenic emissions to mercury deposition?" The panel synthesized new research pertinent to this question published over the past decade, with emphasis on four major research topics: long-term anthropogenic change, current emission and deposition trends, chemical transformations and cycling, and modeling and uncertainty. Within each topic, the panel drew a series of conclusions, which are presented in this paper. These conclusions led us to concur that the answer to our question is a "qualified yes," with the qualification being dependent upon the level of uncertainty one is willing to accept. We agreed that the uncertainty is strongly dependent upon scale and that our question as stated is answerable with greater confidence both very near and very far from major point sources, assuming that the "global pool" is a recognizable "source." Many regions of interest from an ecosystem-exposure standpoint lie in between, where source attribution carries the greatest degree of uncertainty.

## BACKGROUND

The importance of attributing the sources of mercury (Hg) in deposition is now widely recognized, and it is critical for policy development. A panel of international experts was convened in Madison, Wisconsin, in July 2005, to address the state of science pertinent to source attribution. Our key question was this: For a given location, can we ascertain with confidence the relative contributions of local, regional, and global sources, and of natural *versus* anthropogenic emissions to Hg deposition?

Because several of the current participants were panel members at a similar workshop a decade ago (1), we agreed to develop this paper as an update and synthesis of important progress in measurements and modeling since that time. The major conclusions of our synthesis, and the rationale for reaching these conclusions are described in this paper.

## Definitions

Mercury cycling research has matured, and papers now appear in all major Earth science journals. Because the Hg biogeochemical cycle is similar to those of carbon (C), sulphur (S), and nitrogen (N), the panel suggests that some earlier Hg cycling jargon is no longer useful, confusing to outside researchers, and perhaps should be avoided in new studies. The panel also agreed that the widespread use of some common terminology is

confusing the development and implementation of Hg control policy. This is especially true of the phrase "global background Hg." This term may imply that the global pool is entirely "natural," although it is widely accepted that the majority (perhaps two-thirds) consists of Hg that was put into the global cycle by human activity. To facilitate the following discussion, the panel felt it was important to agree on this brief set of definitions (derived and updated from Expert Panel 1994):

- **Anthropogenic emissions:** The direct emissions of Hg from current human activities.
- **Atmospheric half-life:** The time required for the initial concentration of a chemical species to decrease by 50% (for a first-order removal process, half-life  $\approx$  70% of the lifetime).
- **Atmospheric lifetime (or residence time):** Mean time that a chemical species remains in the atmosphere before being removed.
- **Atmospheric mercury depletion events:** Periods during which rapid atmospheric oxidation reactions reduce the concentration of gaseous elemental Hg ( $\text{Hg}^0$ ) (sometimes to concentrations below  $0.1 \text{ ng m}^{-3}$ ), while producing oxidized gaseous and particulate Hg, and leading to elevated deposition.
- **Bidirectional surface fluxes:** The phenomenon by which the flux of gaseous  $\text{Hg}^0$  across the air/surface interface (soil, vegetation, water) occurs in both directions. Regardless of whether the flux is directed up (emission) or down (deposition), it is basically the same phenomenon, though sometimes controlled by different factors.
- **Global sources, global background, and global pool:** The phrase *global background Hg* creates confusion regarding the contribution of anthropogenic emissions to deposition. The global atmospheric pool of Hg is a mixture of Hg emitted from all sources (both natural and anthropogenic) and is dominated by primary and secondary anthropogenic emissions, even at the most remote locations. *Global background concentration* refers to the average sea-level atmospheric concentration of  $\text{Hg}^0$  at remote sites and is currently taken as  $\sim 1.5\text{--}1.7 \text{ ng m}^{-3}$  in the Northern Hemisphere,  $\sim 1.1\text{--}1.3 \text{ ng m}^{-3}$  in the Southern Hemisphere. The term "global sources" should be avoided, because "all sources are local" but have the capacity to contribute to the global pool.
- **Mercury re-emission:** The panel recommends against the continued use of this term. It was defined in the 1994 report as the emission of Hg into the atmosphere by biotic and abiotic processes from land and water surfaces, drawing on a pool of Hg that was previously deposited to Earth's surface after mobilization by anthropogenic or natural activities. *Re-emitted Hg* is *emitted Hg*, and, in most cases, it will be impossible to accurately state the true source of the Hg leaving the surface.
- **Mercury speciation:** A largely operationally defined distinction among various chemical and physical forms of atmospheric Hg. These include gaseous elemental Hg ( $\text{Hg}^0$ ); reactive gaseous Hg (RGM), consisting of various

oxidized gaseous Hg(II) compounds; and particle-bound Hg ( $Hg_p$ ), consisting of various (commonly unknown) Hg compounds.

- **Natural source emissions:** The mobilization into the atmosphere of geologically bound Hg, undisturbed by human activities, by natural biotic and abiotic processes; after ~2000 years of Hg mobilization by human activity, it is doubtful that such emissions can be directly measured without some degree of interference from previously deposited anthropogenic Hg, except perhaps in new volcanic activity.

## THE GLOBAL MERCURY CYCLE AND SOURCE ATTRIBUTION

Attributing the sources of Hg deposited to sensitive receptors requires a clear understanding of the concepts of the global Hg cycle. Global-scale Hg cycling models (2) provide a useful perspective on the behavior and the fate of Hg in the environment. The last decade yielded insights into the dynamics and the chemistry associated with atmospheric Hg cycling. One of the major advances is the experimental observation of the presence and the production of RGM at remote locations, ranging from polar regions to the open ocean (3–6). A sense of the importance of more dynamic cycling of Hg between the Earth's surface and the lower atmosphere can be gained by modification of the Mason Fitzgerald Model (MFM) simulation (7).

The principal features of these global models remain, with the atmosphere and its chemical and physical processes, providing the primary medium for Hg mobilization and exchange in the environment. Uncertainties associated with the fluxes and reservoirs of the Hg cycle are part of the updated perspective. These simulations are usually considered, at best, factors of 2 scaling exercises, which can provide an uncertain but useful framework for generating hypotheses and planning experiments.

Given the caveats, the fluxes derived from the Mason and Sheu model show substantial changes compared with the 1994 MFM version (Table 1). For example, anthropogenic Hg emissions are about 50% smaller than the 20 and 10  $Mmol\ y^{-1}$  used previously, in agreement with new estimates for source strengths and speciation (8, 9).

Uncertainties of  $\pm 30\%$  are given for total anthropogenic Hg emissions. The overall confidence in the portion of the human-related emissions entering the global pool and that depositing locally is around  $\pm 50\%$ . Terrestrial Hg emissions account for an estimated land to air flux of 8  $Mmol\ y^{-1}$ , which is enhanced compared with the value of 5 in the prior MFM simulation. Given the difficulties of scaling results from studies conducted in limited geographic regions to the entire terrestrial realm (10), these categories are highly uncertain (greater than  $\pm 50\%$ ).

The RGM/ $Hg^o$  cycling at the air-sea interface appears to be significant, with 5.7  $Mmol\ y^{-1}$  of the 13  $Mmol\ y^{-1}$  estimated to be evading from the oceans returning to the sea surface in deposition. Comparable RGM/ $Hg^o$  dynamics in the terrestrial realm are contained in the combined wet and dry deposition fluxes. Approximately 3  $Mmol\ y^{-1}$  are attributed to remote dry deposition to land, and this term includes fluxes associated with polar depletion events. Mercury depositional fluxes associated with precipitation might exhibit uncertainties of about  $\pm 30\text{--}50\%$  for both the oceanic and continental reservoirs; dry deposition is more uncertain.

The atmospheric Hg burden shows little change in the updated global Hg model. The average residence time for Hg in the global pool is approximately 0.75 y (compared with 1 y for the MFM model), and the uncertainty in this estimate is about a factor of 2. This global perspective provides an interesting contrast to recent reports of fast Hg oxidation kinetics, leading to estimates of much shorter residence times for Hg in certain situations [e.g., polar regions, marine boundary layer (MBL), upper troposphere], as discussed in the Deposition Mechanisms and Source Attribution section below. This highlights the complexity of the global cycle and suggests the importance of Hg emissions from natural surfaces in maintaining the global pool. It has been suggested that the lifetime of gaseous Hg should be considered a regional, not global, variable (11).

## Historic Anthropogenic Trends in the Global Cycle

The preindustrial simulation from Mason and Sheu (12) is juxtaposed with the modern one in Figure 1. Because such simulations are internally consistent, it is likely that the relative strengths of sources and sinks for Hg may be better constrained than the actual fluxes. Accordingly, the global Hg cycle today has been greatly altered by human-related transfer of Hg from deep geological stores to Earth's surface, especially since the onset of the industrial period (ca. 1850).

The evidence for the long-term change comes from historic records of Hg deposition preserved principally in lake sediments but also in peat deposits and glacial ice. Although these historic archives are complex recorders of atmospheric deposition, there is a large body of experimental and observational evidence for their reliability (13). A growing number of these core records from remote sites in both the Northern and Southern hemispheres demonstrates about a threefold increase ( $2\times\text{--}4\times$ ) in Hg deposition since preindustrial times (14–17). This convergence of data is significant, because it suggests that anthropogenic emissions have altered Hg fluxes to about the same degree throughout the world, even though contemporary Hg deposition exhibits large temporal and spatial variability.

By accepting the assumptions of these models and that preindustrial Hg deposition was less than current deposition by a factor of three, the global Hg budget in preindustrial times

**Table 1. Model estimates of current global Hg fluxes.**

Emissions	MS* (units $Mmol\ y^{-1}$ )	MFM† (units $Mmol\ y^{-1}$ )	Deposition	MS* (units $Mmol\ y^{-1}$ )	MFM† (units $Mmol\ y^{-1}$ )
Direct anthropogenic Land emissions‡	12	20	Wet deposition to ocean	9.7	10
	8	5	Dry deposition to ocean	5.7	
Ocean emissions (evasion) ‡	13	10	Remote wet deposition to land	10.0	15
			Remote dry deposition to land	2.9	
Total	33	35	Local deposition to land	4.7	10
			Total	33	35

\* From Ref. 7.

† From Ref. 2

‡ Land and ocean emission terms include a substantial portion of Hg ( $\sim 50\%$ ) originally emitted from anthropogenic sources.

es in Hg emissions, possibly related to earlier Hg mining and metallurgy (18–20).

In the final analysis, core records are complex processors of atmospheric Hg and need to be interpreted with caution. Sedimentary processes, such as post-depositional migration and diagenesis, dating uncertainties, and natural variability among (and within) sites, make it unwise to conclude too much from one, or even several, cores. This is especially true for longer (millennial) time scales where factors controlling Hg burial may change.

### Deposition Response to Reduced Emissions on the Global Scale

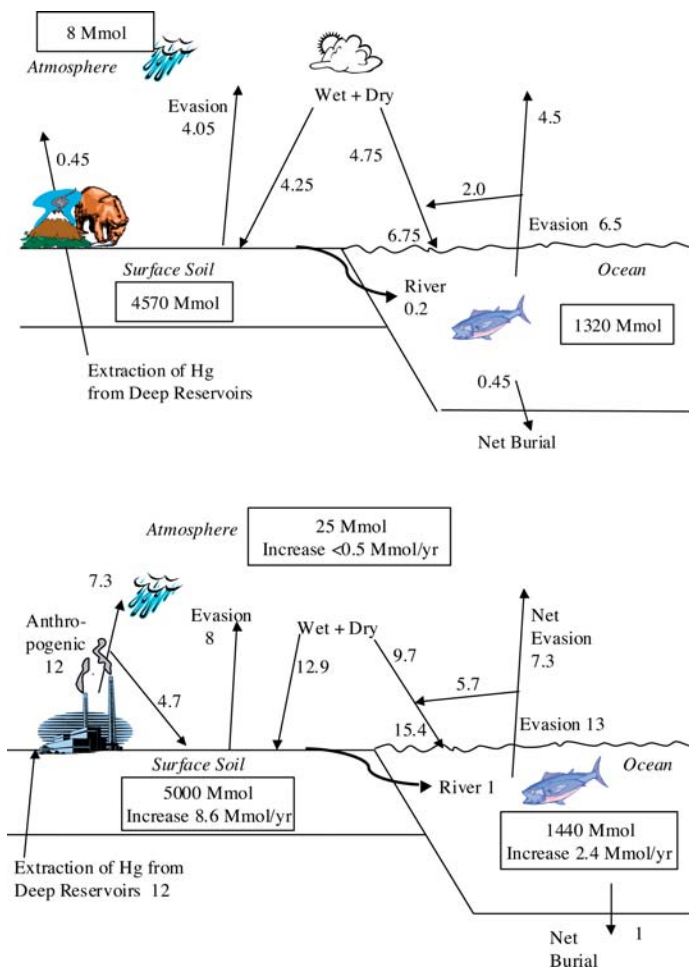
Because of emission of Hg from large stores at the Earth's surface, reductions in anthropogenic inputs will not produce a linear decrease in Hg deposition, especially at remote locations that are dominated by input from the global Hg pool. Deposition declines are expected to lag emission reductions, depending on the response time of the global Hg reservoirs to changing inputs. Because of rapid cycling of Hg in the atmosphere and surface ocean (0–100 m), these pools should achieve a steady state within a few years with respect to reduced loadings. The larger and more slowly cycling Hg reservoir in the ocean thermocline could delay this response by 1 to 2 centuries. However, the net effect of this lag on atmospheric fluxes should be small given the modest (20%) anthropogenic Hg enrichment of the thermocline (17).

The response of the terrestrial soil pool to reduced Hg emissions is less clear. Although the net change in Hg storage in the reservoir of the global soil profile from anthropogenic inputs is probably not large (10% for the entire industrial period), most of the actively cycling Hg likely resides in the top few millimeters to centimeters of soil (21) where anthropogenic enrichment is far greater than for the soil reservoir as a whole (1). If Hg emission rates from this near-surface pool are high, then changes in terrestrial emissions could lag reductions in anthropogenic loading by many years. On the other hand, if terrestrial surface emission is driven largely by Hg<sup>0</sup> production from contemporary deposition—as suggested by recent experiments with Hg isotope additions (22–24)—then the surface soil reservoir may actually represent a long-term sink for Hg inputs, and Hg surface emission can be expected to follow deposition reductions in step.

The response of Hg deposition rates to emission reductions close to anthropogenic sources is expected to be much more rapid than that at remote locations, largely because near-field Hg deposition is probably dominated by local Hg(II) emissions. Indeed, there is good historical evidence from lake-sediment records for rapid and large (30–50%) declines in Hg deposition from urban areas in the United States and Europe (14, 25–26), as well as more widespread declines for the northeastern United States (27). These declines occurred over the last 1 to 3 decades and correspond with known reductions in local and regional Hg emissions for the same areas. However, archives provided by lake sediments are not especially responsive to changes in Hg deposition in remote locations over the recent past (e.g., ~10–20 years). The natural variability, typically low sedimentation rates, and slow Hg transport through catchment soils (27) limit their applicability within this recent time frame.

### Final Perspectives on Global Cycling

It is evident that essential global-scale information for the modern cycling of Hg and its behavior and fate over the past 3 decades is lacking. New and innovative approaches are needed to address potential inconsistencies and to answer the question



**Figure 1. Global mercury fluxes and reservoirs in preindustrial (upper) and modern (lower) times; all fluxes are in Mmol y<sup>-1</sup> (from Mason and Sheu (12); the term “evasion” from land should be “emission”). Reproduced by permission of the American Geophysical Union.**

was dominated by natural evasional fluxes. A comparison of these 2 models (modern and preindustrial) suggests that about one half of the current evasional fluxes from land and ocean is ultimately of anthropogenic origin. This Earth-surface recycling of anthropogenic Hg accounts for about a third of the total present-day atmospheric inputs, whereas new point-source releases and natural emissions (land and ocean) each represent another third.

The models assume no change in atmospheric residence time; however, it is possible that increased concentrations of atmospheric ozone have contributed to higher rates of contemporary Hg deposition, at least regionally (17) and perhaps globally (however, other oxidants such as OH radicals may not have increased similarly). If so, this would imply a slower atmospheric cycling in preindustrial times (relative to today), which, in turn, would require a proportionally larger pool of atmospheric Hg than currently represented in the preindustrial model.

The magnitude of change in Hg deposition to remote terrestrial areas caused by human activity is fairly well constrained by lake-sediment records, with an uncertainty of about 30% (e.g., a  $3 \pm 1 \times$  increase). With far fewer records, trends in the Southern Hemisphere are less secure, and additional sites are needed to solidify current estimates for this part of the world. Moreover, some European peat-core records and a single ice-core profile from the Freemont Glacier (Wyoming, US) suggests an earlier and larger increase in deposition (10×–30×), implying significant preindustrial chang-

as to whether Hg is increasing or decreasing in the biogeochemically active reservoirs at the Earth's surface. For example, Mason and Gill (28) recently reported that Hg in the upper ocean near Bermuda declined between 1979 and 1999–2000. Asian Hg emissions are suggested to be increasing in a dramatic fashion, yet neither the long-term measurements of Hg in rain by the Mercury Deposition Network (MDN) network in North America, nor those of total gaseous mercury (TGM) in the air at Mace Head, Ireland, yet reflect the signal from these new emissions (29, 30). The relative constancy of the modern atmospheric pool at 25 Mmol is an important constraint for global Hg simulations and budgets. This boundary condition places limits on the likely ranges for fluxes and their uncertainties. However, there are documented recent increases in the oxidation potential of the atmosphere, which might account, at least in part, for the discrepancy between TGM trends (steady or decreasing) and Hg emission inventories (increasing). It is reasonable to ask just how uncertain are the inventories.

## ATMOSPHERIC EMISSIONS AND SOURCE ATTRIBUTION

### Background

Modeling the transport and deposition of Hg to receptors and understanding its source attribution requires improved data on the spatial and temporal trends in atmospheric emissions. Mercury is emitted into the atmosphere primarily as elemental gaseous Hg<sup>0</sup> and divalent Hg(II) species that can take both gaseous or particulate forms. Emission of gaseous dimethylmercury is also known to occur [e.g., in landfill gas (31) and possibly from the ocean surface (32)]. Although it may explain observations of methylmercury in rain and snow, dimethylmercury represents a very small fraction of emitted Hg. On a global scale, the atmospheric Hg cycle is dominated by elemental Hg vapor. However, the emission speciation of Hg is determined by the source characteristics and consequently shows large regional variability. Atmospheric fate and, especially, Hg deposition are strongly linked to the speciation of Hg released into the atmosphere. The deposition pathway is dominated by the flux of emitted Hg(II) compounds [termed “reactive gaseous mercury” (RGM)], and the oxidation of emitted elemental Hg vapor to Hg(II).

### Anthropogenic Emissions and Regional Trends

Accurate emission inventories of Hg are critical, because they are used to drive atmospheric chemical-transport and source-receptor models for the prediction of Hg deposition rates. These atmospheric Hg models are particularly sensitive to the accuracy of the emissions speciation profile, because the different species can be wet or dry deposited at vastly different rates.

As a result of the global interest in Hg, we are beginning to develop a much clearer picture of trends in emissions. Between 1990 and 2000, the trends were derived for continental anthropogenic Hg emissions as summarized in Table 2.

### Uncertainties

Policy decisions based on source attribution must be developed with a good understanding of the levels of uncertainty that are involved. The uncertainty of emission estimates assigned to individual source categories in this work are listed in Table 3 (8). A conservative assessment of uncertainties in both emission factors and speciation (9) was used to assess overall uncertainties in the continental inventories for the year 2000 (Table 4).

Among Asian countries, China is now regarded as the largest anthropogenic Hg emission source. However, there are very limited data on Hg emission factors from different source categories in China, which are typically adopted from studies conducted in Europe and North America with similar sources. Because the processes and pollution-control techniques used in the industrial activities in China may differ dramatically from those in developed countries, the Hg emission factors in China could significantly differ from the implied assumptions.

Emission inventories are necessarily retrospective and, therefore, current emissions are less certain. However, it can be assumed that current North American and European emissions will remain constant or decrease slightly over time. Emissions from the other continents, especially with highly dynamic economies, may continue to increase.

### Agreement of Emission Inventories with Observational Data

Variations in the global atmospheric Hg pool and its interhemispheric distribution provide essential information regarding the cycling of Hg and its relations to natural and anthropogenic sources, and act as a key constraint for models. Although atmospheric Hg monitoring stations have increased, the database is sparse, especially in remote locations. Slemr et al. (33) attempted to reconstruct the worldwide trend of atmospheric Hg (TGM) concentrations from long-term measurements of known documented quality at 6 sites in the Northern Hemisphere, 2 sites in the Southern Hemisphere, and multiple ship cruises over the Atlantic Ocean made since 1977 (Fig. 2).

**Table 2. Mercury emission trends 1990–2000 (all emissions are approximate).\***

Continent	1990–1995	1995–2000
Africa	Twofold increase	Constant level: 400 t y <sup>-1</sup>
Asia	Twofold increase	Constant level: 1200 t y <sup>-1</sup>
Australia	Twofold increase	Constant level: 100 t y <sup>-1</sup>
Europe	Decline from 550 to 300 t y <sup>-1</sup>	Further reduction to 200 t y <sup>-1</sup>
North America	Slight decline	Fairly constant: 200 t y <sup>-1</sup>
South America	30% increase	Fairly constant: 80 t y <sup>-1</sup>

\* From Ref. 9.

**Table 3. Uncertainty of Hg emission estimates by source category.\***

Industrial source	Uncertainty
Stationary fossil fuel combustion	±25%
Nonferrous metal production	±30%
Iron and steel production	±30%
Cement production	±0%
Waste disposal and incineration	as much as 5×†
Mercury and gold production	? <sup>†</sup>

\* From Ref. 9.

† The information on emissions from Hg production, gold production, waste disposal, and the use of Hg for various purposes is incomplete.

**Table 4. Uncertainty of Hg emission estimates by continent.**

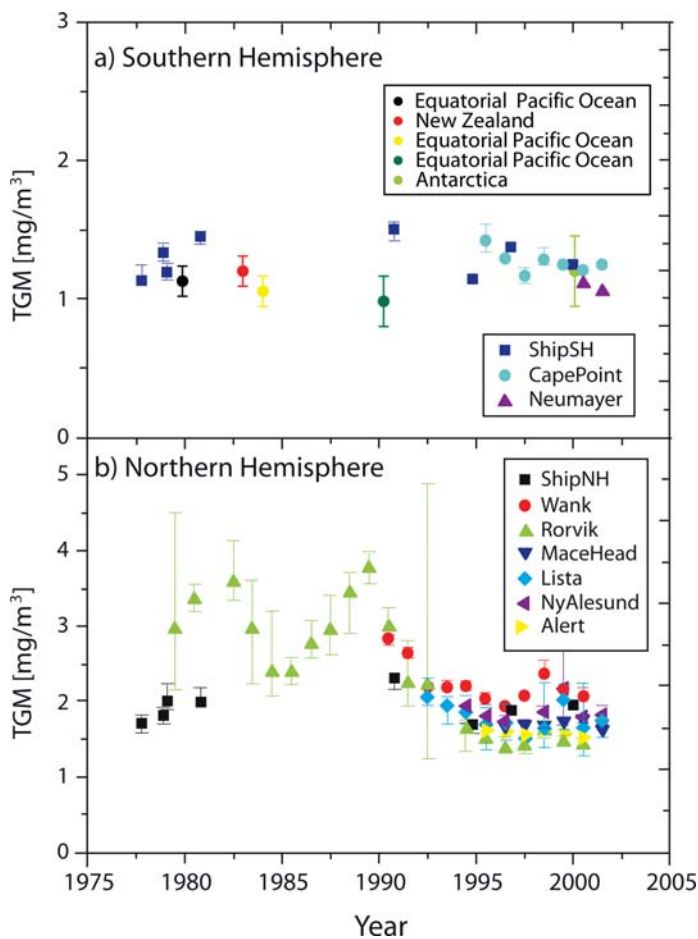
Continent	Uncertainty (±%)
Africa	50
Asia	40
Australia	30
Europe	30
North America	27
South America	50

The authors interpreted this information to suggest that the TGM concentrations in the global atmosphere had been increasing since the first measurements in 1977 to a maximum in the late 1980s, after which Hg concentrations decreased to a minimum in 1996 and then remained constant at a level of about  $1.7 \text{ ng m}^{-3}$ . It was also hypothesized that the observed temporal profile was primarily the result of the trends in global Hg use, supply, and emissions. The temporal trend displays a qualitative relation to changes in the global Hg supply (e.g. see Swain et al., in this issue, p. 46). Although these estimates do not quantitatively reflect the reported emission decrease between 1990 and 1996 (34), this trend may be complicated by trends in the oxidation potential of the atmosphere (33).

This analysis includes several significant assumptions, which make a null hypothesis (i.e., there has been little change in TGM since 1977) equally likely. First, it is assumed that stations on or bordering the Atlantic Ocean provide trend data for TGM that is representative of the worldwide pattern. Second, the principal data for the hypothesized global increase in TGM during the mid-1980s is provided by 1 station, Rörvik, near Gothenburg, Sweden, which is likely to have been affected by regional Hg sources (i.e., eastern Europe before the breakup of the USSR) and perhaps should not be included in a global sense. As noted in Slemr et al. (33), major declines in Hg wet deposition were reported for southwestern Sweden from 1987–1989 to 1997 and are attributed to the large reductions in Hg emissions from eastern Europe (35). If Rörvik were excluded, then the data suggest there has been little change in total gaseous Hg levels in the atmosphere between 1977–1978 and 2002 for most of the stations bordering the Atlantic Ocean.

Additional support for the null hypothesis is provided by TGM measurements for the Southern Hemisphere. The Southern Hemisphere data are seen in the upper portion of Figure 2, along with additional results from several investigations conducted in the south and equatorial Pacific Ocean between 1980 and 1990 (5, 36–38). These combined TGM results for the Southern Hemisphere do not suggest that there has been much change in TGM levels in the global remote atmosphere over the past 25–30 years. Although it may appear that these competing hypotheses on atmospheric TGM levels in recent times would be disconcerting, this situation is not unusual and often aids the development of research strategies. For example, the value of long-term atmospheric Hg monitoring stations and the need for additional sites is obvious, especially in the remote Southern Hemisphere.

Other atmospheric chemistry measurements at the receptor can also provide useful information on source attribution. Mercury isotope mass spectrometry is now capable of detecting differences in the natural isotopic signatures between different sources of Hg (different cinnabars, biota *versus* coal, or sediments of different origin), though the method has yet to be tested in ambient air (39). Similarly, such methods as real-time aerosol mass spectrometers hold promise for rapid measurement of tracers of convenience for use with near real-time measurements of  $\text{Hg}^0$  and  $\text{Hg}_p$  near source areas. Similar methods proved useful in source attribution (40). Another useful comparison involves measurements of the ratio of 2 or more gaseous compounds or substances in the atmosphere to derive quantitative information on emission source strengths. It assumes that the emission ratio of 2 compounds at their source is reflected in their relative ambient concentration at a distance after mixing and dilution. This approach further assumes *i*) no chemical or physical losses (or comparable losses), *ii*) a constant emission source with fixed emission ratio, and *iii*) a constant background concentration. Although the measurements encompass almost exclusively elemental Hg whose anthropogenic emission is only a portion of the entire emission loading, and



**Figure 2.** A comparison of trends in concentrations of airborne  $\text{Hg}^0$  measured at several land-based monitoring stations and on ship cruises in the southern and Northern Hemispheres (also see text for additional data sources); adapted from Slemr et al (33).

emissions estimated from correlations with trace gases also include emissions of geologic and anthropogenic Hg from natural surfaces, these are promising approaches worthy of further investigation. For example, Hg emissions calculated from such ratios are in reasonable agreement with the estimated anthropogenic total Hg emissions for Asia (41).

### Natural Emissions

Mercury is emitted to the atmosphere from numerous sources, and current anthropogenic and natural sources are thought to contribute about equally to the global tropospheric pool. Gustin and Lindberg (10) suggest that early estimates of natural source strengths, such as background soil and geologic sources, are low. Other new studies also suggest that volcanic emissions may also have been underestimated (42). The assessment of truly natural Hg sources and their relative importance compared with direct anthropogenic emissions and emissions from natural surfaces is a fundamental problem in studying the global cycling of Hg. Natural emissions cannot readily be reduced or controlled, and, when deposited, Hg, whether from a natural or anthropogenic source, enters an environmental compartment, it is subject to the same transport and transformation processes as Hg from other sources.

### Emissions from Natural Surfaces

Approaches for measuring  $\text{Hg}^0$  flux include controlled laboratory exposure chambers, field soil and foliage chambers, and

micrometeorological methods (43). These methods operate across various spatial scales and have the ability to quantify bidirectional fluxes over land and water, but they can be subject to artifacts (44). Recent developments in analytical and flux technology (4, 45, 46) generated significant new data that influence the conventional wisdom regarding the global Hg cycle. For example, oxidized Hg (which exhibits a shorter lifetime), is readily reduced to Hg<sup>0</sup> after deposition to various surfaces (4, 47), giving it the ability to be rapidly emitted back to the atmosphere as a gas. New estimates of short-term surface emission rates measured with Hg isotopes suggest that on the order of 5–40% of deposition can be emitted soon after deposition, depending on the surface (22, 23). This rapid “redox recycling” gives Hg the appearance of exhibiting a longer lifetime in the atmosphere than it actually has, because all “sinks” are not permanent.

Wildfires have the potential to volatilize previously deposited Hg in terrestrial organic pools into the atmosphere, and several new studies are developing data from which global emission estimates are possible (48). Even when using the more conservative estimates (range, ~400-1300 T y<sup>-1</sup>), this must be considered an important global source, perhaps the major source in the Southern Hemisphere. When considering the huge pools of anthropogenic Hg currently “stored” in surface soils (>500 000 T by some early estimates), land use and climate changes, as well as fire also have the known ability to mobilize some portion of these pools, both to air and water (49). For example, the “reservoir effect” increases Hg mobilization into biota after flooding of forests (50).

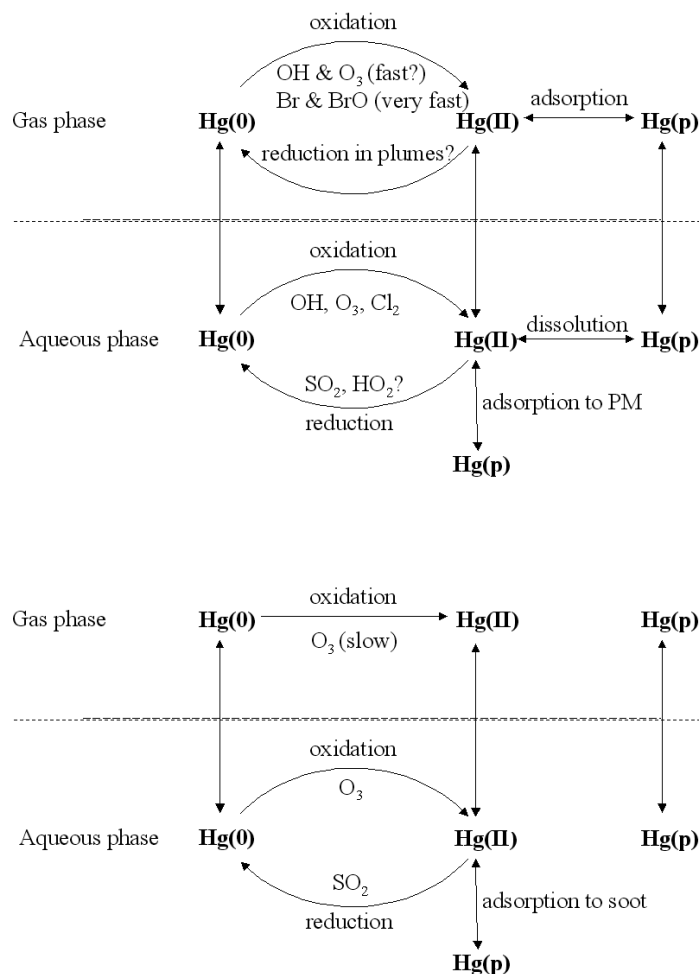
A similar situation exists for the oceans, where evasion is sensitive to altered climate and circulation patterns. Mercury evasion over water can be measured by using chambers, but it is more commonly estimated by using a thin-film model with measurements of dissolved gaseous Hg. However, our understanding of the evasion process limits the accuracy of the evasion models, especially under moderate or greater wind/wave conditions. New approaches should be developed to accurately extrapolate from measured small-scale fluxes in both oceanic and terrestrial systems. The experience of research communities studying the global cycles C, N, and S suggests that scaling is best done with models based on the mechanisms that control exchange over water, soil, and vegetation. More thorough studies of these mechanisms for Hg remain a major research need.

## THE ROLE OF CHEMICAL TRANSFORMATION MECHANISMS IN SOURCE ATTRIBUTION

### Background

Because of its very low solubility, Hg<sup>0</sup> is removed slowly from the atmosphere via wet and dry deposition, whereas Hg(II) species (i.e., RGM) are removed rapidly because of their high solubility and reactivity with surfaces. Thus, chemical transformations between these 2 oxidation states directly affect the atmospheric lifetime of Hg: oxidation of Hg<sup>0</sup> to Hg(II) increases atmospheric deposition, whereas reduction of Hg(II) to Hg<sup>0</sup> decreases atmospheric deposition. It, therefore, is essential to understand the reduction/oxidation (redox) processes that govern the speciation of Hg in the atmosphere and the sorption of gaseous Hg species to particulate matter (PM), because gas/particle conversion also affects Hg deposition.

Our overall knowledge of the chemistry of atmospheric Hg today (51, 52) compared with a decade ago is depicted in Figure 3 (1, 53). Our knowledge has improved significantly, but major uncertainties remain, which affect our ability to predict source-receptor relations.



**Figure 3. Evolution of knowledge of atmospheric Hg chemistry over the past decade: top, current (see text for details); bottom, former (1).**

### Oxidation of Hg<sup>0</sup>

In 1994, the only major Hg<sup>0</sup> oxidation reactions that were identified were the gas-phase (54) and aqueous-phase (55) reactions with ozone (O<sub>3</sub>). The kinetics of those reactions led to a global chemical half-life of Hg<sup>0</sup> of about 1 y. Since then, several gas- and aqueous-phase reactions were identified that exhibit much faster oxidation kinetics, depending on the environmental conditions. New laboratory data on the gas-phase O<sub>3</sub> reaction suggested a faster kinetics (56), although it is possible that this fast kinetics results from heterogeneous reactions on the reactor vessel walls (57). Such heterogeneous reactions may also occur in the atmosphere (e.g., on particles and surfaces), but their effect on O<sub>3</sub> reaction kinetics is unknown. Major new gas-phase reactions have also been identified, including reactions with OH, Br, and BrO. The fast kinetics of the OH reaction reported by 2 laboratories would lead to a chemical half-life of Hg<sup>0</sup> of about 2 to 4 months (58, 59); however, theoretical calculations raise questions regarding the laboratory conditions, and this reaction may be significantly slower in the ambient atmosphere (57).

The oxidation of Hg<sup>0</sup> by halogens was investigated to explain the Hg depletion events observed in the Arctic (see below). The oxidation of Hg<sup>0</sup> by chlorine compounds was found to be slow, but the oxidation reactions with Br and BrO (and possibly other bromine species) suggested by several Arctic research teams were confirmed to be fast (60). Such reactions lead to a chemical half-life <1 d and can significantly affect the atmospheric residence time of Hg at the poles, possibly also in the MBL (6)

and in the upper troposphere, where those radicals are present in sufficient concentrations (61). Two new  $\text{Hg}^{\circ}$  oxidation reactions in the aqueous phase have also been identified, including those with OH radicals (62, 63) and dissolved chlorine ( $\text{Cl}_2$ ) (64). The latter reaction could significantly affect  $\text{Hg}^{\circ}$  oxidation in the MBL because of its fast kinetics.

### Reduction of Hg(II)

In 1994, only 1 major pathway (aqueous-phase reaction of  $\text{Hg}^{2+}$  with dissolved  $\text{SO}_2$ ) was identified for the reduction  $\text{Hg(II)}$  to  $\text{Hg}^{\circ}$  in the atmosphere (65). The kinetics of this reaction were revised (66, 67), and its importance is limited by the fact that the formation of other complexes, e.g.,  $\text{HgCl}_2$ , occurs preferentially. The aqueous-phase reaction of  $\text{Hg(II)}$  with  $\text{HO}_2$  was proposed as a significant  $\text{Hg(II)}$  reduction pathway (68); however, the validity of this experimental result was proved incorrect (69). Evidence of measurable  $\text{Hg(II)}$  reduction in power plant plumes was obtained from  $\text{Hg}$  speciation measurements at ground-level sites downwind of power plants, from aircraft in power plant plumes, and from dilution chambers approximating plume dispersion at several power plants (70, 71). The exact mechanism leading to gaseous  $\text{Hg(II)}$  reduction is unknown and requires further investigation.

### Adsorption of Hg Species to Particulate Matter

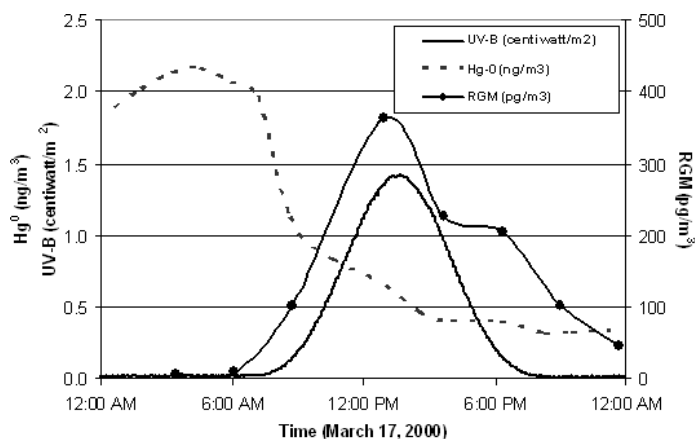
The original concept of  $\text{Hg(II)}$  adsorbing to soot in cloud droplets was extended to adsorption of  $\text{Hg(II)}$  to PM in both the gas phase and the aqueous phase (72). In addition,  $\text{Hg}^{\circ}$  may adsorb to PM, and both  $\text{Hg}^{\circ}$  and  $\text{Hg(II)}$  may undergo heterogeneous reactions at the surface of particles (73). Large uncertainties remain regarding *i*) the partitioning of  $\text{Hg}$  species between the bulk gas/aqueous phase and PM, and *ii*) the kinetics of heterogeneous reactions.

### Polar Hg Depletion Events

Field measurements in the Arctic and the Antarctic during polar spring showed that airborne  $\text{Hg}^{\circ}$  can be rapidly converted to  $\text{Hg(II)}$  (Fig. 4). These events coincide with  $\text{O}_3$  depletion and the presence of halogen species, and new experimental evidence suggests that Br and BrO, which participate in  $\text{O}_3$  depletion, lead to this oxidation of  $\text{Hg}^{\circ}$ . The oxidation products involve  $\text{Hg(II)}$  and possibly unstable  $\text{Hg(I)}$  intermediates (74, 75), and these species rapidly deposit to snow. Some deposited  $\text{Hg}$  is reduced to  $\text{Hg}^{\circ}$  and emitted back to the atmosphere; however, there is clear evidence of  $\text{Hg}$  deposition, and model calculations suggest that depletions could account for  $\sim 100\text{--}150 \text{ Mg y}^{-1}$  of Arctic deposition (4, 52, 76). Empirical reconstruction of atmospheric  $\text{Hg}$  fluxes with dated lake sediments from the North Slope of Alaska (Toolik Lake Field Station environs,  $68^{\circ}38' \text{ N}$ ,  $149^{\circ}38' \text{ W}$ ), suggests that these phenomena increased current deposition at Toolik by about 75% (77).

### Marine Boundary Layer

The chemistry of  $\text{Hg}$  may be affected in the MBL by the presence of sea salt halogens and deliquescent particles. In the presence of sunlight and low temperature, rapid oxidation of  $\text{Hg}^{\circ}$  by halogen species may occur in the open ocean MBL leading to  $\text{Hg(II)}$  formation and deposition to the water surface (6, 11). Mercury can later be emitted again as  $\text{Hg}^{\circ}$ , thereby leading to a dynamic exchange of  $\text{Hg}$  between the MBL and marine waters. In warm coastal waters such as off the coast of Florida,  $\text{Hg(II)}$  formation may not be as significant (78), possibly because the kinetics of  $\text{Hg(II)}$  formation via halogen chemistry is favored at lower temperatures. Therefore,  $\text{Hg}$



**Figure 4.** Time series of gaseous  $\text{Hg}$  species measured at Barrow, Alaska, during a mercury depletion event, illustrating how  $\text{Hg}^{\circ}$  is rapidly converted to  $\text{Hg(II)}$  (RGM) during full sunlight (4).

chemistry within the MBL is likely to vary spatially and temporally, depending on meteorological and sea conditions.

### Upper Atmosphere

The chemical speciation of  $\text{Hg}$  differs in the free troposphere and lower stratosphere from that in the boundary layer, because of lower temperature, the lack of  $\text{Hg(II)}$  removal by dry deposition, and different concentrations of oxidants (e.g., halogen atoms and ozone in the stratosphere) in the upper atmosphere. For example, high concentrations of  $\text{Hg(II)}$  were observed in the free troposphere (79) and particulate-bound  $\text{Hg(II)}$  has been observed to dominate  $\text{Hg}$  speciation near the tropopause (61). Because the intermediate  $\text{HgBr}$  species tends to decompose back to  $\text{Hg(0)}$  as the temperature increases (75), the oxidation of  $\text{Hg(0)}$  to  $\text{Hg(II)}$  by Br is favored at the low temperature of the upper atmosphere; this could explain, in part, the high  $\text{Hg(II)}$  concentrations observed near the tropopause. Gas-to-particle conversion of  $\text{Hg(II)}$  may also be favored by low temperature, which would explain the observation of particulate-bound  $\text{Hg(II)}$  in the upper troposphere and lower stratosphere (61). Such  $\text{Hg(II)}$  present in the upper atmosphere could be removed via wet deposition during deep convective storms.

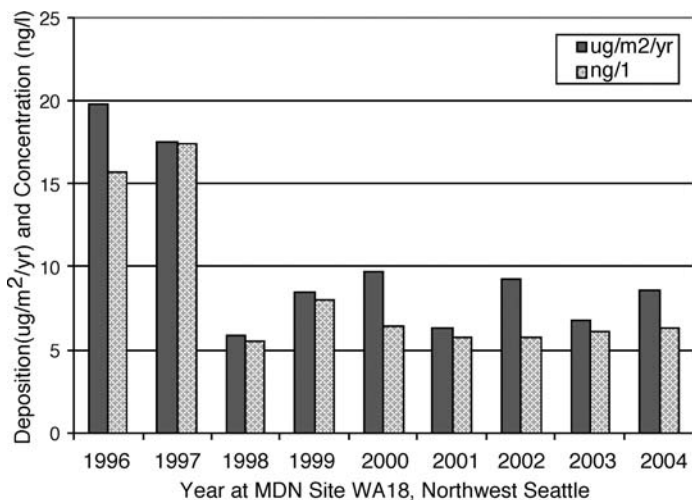
### Atmospheric Hg and Climate Change

Temporal variations in deposition and in the cycling of  $\text{Hg}$  between the atmosphere and ecosystems can result from changes in emissions of  $\text{Hg}$ , as well as of other atmospheric contaminants (e.g.,  $\text{NO}_x$ ,  $\text{SO}_2$ ), and from climate change. Primary effects include increases in air and sea temperatures, wind speeds and variation in precipitation patterns, and secondary effects that are related to increases in  $\text{O}_3$  concentration and aerosol loading, a decrease of sea ice cover in the Arctic, and changes in plant growth regimes. All these effects will influence the atmospheric residence time of  $\text{Hg}$ ; its deposition; and, ultimately, its dynamics on local, regional, and global scales. This will lead to increases in the overall uncertainty in the assessment of ambient concentrations and deposition rates of  $\text{Hg}$  compounds (11).

## DEPOSITION MECHANISMS AND SOURCE ATTRIBUTION

### Background

One of the most critical measurements needed to understand the  $\text{Hg}$  biogeochemical cycle and to verify source attribution models is its rate of atmospheric deposition. The measurement



**Figure 5. The closure of several medical waste incinerators in Northeast Seattle in 1998 was captured by the MDN WA18 site, where average deposition dropped from  $18.7 \pm 1.6 \mu\text{g m}^{-2} \text{y}^{-1}$  in 1996–1997 to  $7.9 \pm 1.5 \mu\text{g m}^{-2} \text{y}^{-1}$ . The trend analysis indicates that it is significant ( $p < .001$ ) (107).**

of Hg wet deposition is now straightforward, and accepted standardized methods are used by national (e.g., the US Mercury Deposition Network, in operation since about 1995) (29, 80) and regional networks (35, 81, 82). In contrast, the accurate measurement (and modeling) of Hg dry deposition is difficult and remains the most challenging gap in our understanding of fluxes.

### Wet Deposition

The global pool of atmospheric Hg is continually being depleted by wet deposition. Except for the polar regions, and possibly the MBL, the primary mechanisms for wet deposition are in-cloud oxidation of  $\text{Hg}^0$  by  $\text{O}_3$ , and the gas-phase oxidation of  $\text{Hg}^0$  by OH and  $\text{O}_3$  followed by cloud-droplet uptake. Particle-bound Hg also contributes to wet deposition through cloud-droplet activation and precipitation scavenging. Wet deposition rates can be enhanced close to major Hg sources by the direct cloud-droplet uptake of emitted  $\text{Hg(II)}$  and  $\text{Hg}_p$  (35, 83). The dominant form of Hg in wet deposition is dissolved and particulate  $\text{Hg(II)}$ . Methylmercury is commonly found in rain and snow at concentrations  $\sim 0.5$ – $2.5\%$  of total Hg, with excursions of  $>10\%$  for single events (32), and some investigators have argued that wet deposition could be an important source of methylmercury to certain ecosystems (84).

### Dry Deposition

Dry deposition by definition occurs continually except during periods of rainfall (typically,  $\sim 2$ – $5\%$  of the time for the mid-latitudes). Thus, Hg dry deposition is occurring up to 98% of the time and can be a significant input to aquatic, marine, and terrestrial ecosystems. Dry deposition of Hg occurs via two processes. One is the direct deposition of the gas-phase compounds  $\text{Hg}^0$  and RGM and, to a lesser extent, deposition of atmospheric particles containing Hg. Vegetation covers a significant portion of the Earth's surface and is known to enhance dry deposition. The rate-limiting step for gas-phase  $\text{Hg}^0$  dry deposition to plants is stomatal uptake (85). However, for RGM, which has a high sticking coefficient, the rate-limiting step is the turbulent transport of gases to the leaf surface (this would also hold for gaseous dimethylmercury). For  $\text{Hg}_p$ , impaction and sedimentation are the controlling mechanisms. All of these processes are challenging, both to measure and

model, and they depend on meteorological phenomena, such as temperature, surface wetness, and wind speed, as well as surface geomorphology. Considerable work remains to be done to accurately quantify Hg fluxes over plant canopies, especially because they can also emit  $\text{Hg}^0$  (86).

### Unique Environments

New data suggest that local atmospheric conditions lead to enhanced deposition in several unique ecosystems. Enhanced polar springtime deposition to snow is driven by the reactive halogen cycle (87, 88). Some of the deposited Hg is emitted again during snowbelt, and some remains in runoff (4, 32, 89). In the MBL, observations and new models indicate fast *in situ* photochemical production of RGM (6, 11), which may lead to enhanced deposition in coastal and estuarine areas (12). In urban areas, where there are abundant Hg-containing particles generated by mobile and industrial sources, both wet and dry Hg deposition rates can be dominated by  $\text{Hg}_p$  removal (90, 91). Finally, based on a few direct measurements, but significant research on other atmospheric constituents, montane ecosystems receiving direct cloud-water deposition will likely exhibit enhanced Hg loading relative to nearby lower elevation sites (18, 92, 93). These observations suggest that gradients in total Hg deposition may be greater than perhaps previously understood.

### Measurement Methods and Uncertainty

**Wet Deposition.** Four key components are required for accurate Hg wet-deposition measurements: *i*) a trace-clean sample train with an HCl preservative in the collection bottle, *ii*) a temperature-controlled collector with an automated rain sensor, *iii*) a rain gauge to verify the rainfall depth collected, and *iv*) a cold-vapor atomic fluorescence spectrometer system to measure the Hg concentration (80, 82, 94). Manual event-based Hg wet-deposition sampling is also possible for intensive studies (83). When comparing results of the analysis of the same sample by qualified independent laboratories, the uncertainty is typically less than 10% (e.g., co-located sites in the National Atmospheric Deposition Program (NADP) MDN showed median absolute differences in Hg wet-deposition rates of 6–14% (95). Measured wet-deposition rates are not likely a major factor in the uncertainty in source attribution analyses.

**Dry Deposition.** Unlike wet deposition, where the flux occurs over a short period at relatively high and easily detectable rates, dry deposition occurs over much longer periods at relatively low rates. Further complicating the development of measurement methods is the fact that there are at least 3 distinct atmospheric species of Hg that contribute to dry deposition, particulate-bound ( $\text{Hg}_p$ ), RGM, and  $\text{Hg}^0$ . Not only do these 3 species have different chemical and physical properties that affect their dry deposition rates, they are also present at  $<1$  ppt ( $\text{Hg}^0 \sim 5 \times 10^6 \text{ molec cm}^{-3}$ , and  $\text{Hg}_p$  or RGM  $\sim 5 \times 10^4 \text{ molec cm}^{-3}$ ). Finally, once dry deposited, Hg may be emitted again in the same or a different chemical form (22, 96, 97), which further increases the measurement challenge when considering the sample integration time and frequency.

There are 3 methodologies for the estimation of Hg dry-deposition rates. Each carries unique advantages, yet also exhibits critical limitations that are important to understand but are too numerous to list [see the review by Hicks et al. (98)]. The first methodology is termed “direct” and includes surrogate surfaces, dew fall, litterfall (LF), throughfall (TF), and subtracting wet-only deposition from bulk deposition (78, 99–101). The second methodology is “inferential” and uses Hg species air concentration and meteorological measurements to model dry-



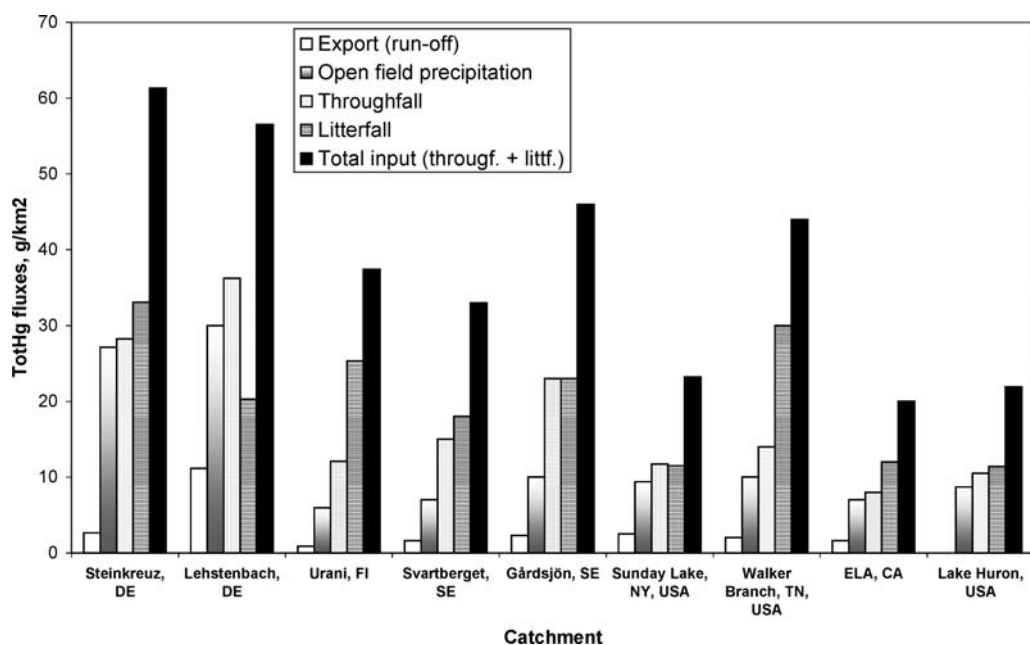


Figure 6. Annual input and output of total mercury in 9 forested catchments. The black bar is the total input estimated from the sum of LF + TF. Dry deposition can be estimated as the difference between the estimated total input (black bars) minus the measured open field precipitation (gray bars). Compiled by Munthe et al. (118) from published studies in Sweden, Germany, Finland, the United States, and Canada.

deposition rates (85, 102). The third approach is “micrometeorological” and includes gradient, modified Bowen ratio and relaxed eddy accumulation methods (46, 96, 103, 104). These methods must still be considered as experimental when applied to Hg, and flux validation is a major research need.

### Observations and Trends

**Wet Deposition.** The atmospheric Hg record in Sweden is of sufficient quality and length to provide the clearest example on a regional scale of the link between anthropogenic emission reduction and decreasing air concentration and deposition. The rapid Hg emission reduction in northern Europe, because of the economic and political changes occurring in the early 1990s, resulted in ~40% decrease in Hg wet deposition for southern Sweden, as reflected by decreasing air concentrations, wet-deposition rates, and sediment core trends (35).

Over the last decade, North America has the most extensive measurements of Hg in wet deposition, primarily from the MDN, Canadian Atmospheric Mercury Measurement Network, and smaller research networks (29, 81, 82, 105, 106). Two sites with about a decade of precipitation data showed the following: no trend at Underhill, Vermont (1993–2003) (81) but significant decreases in wet deposition of Hg in Seattle (1996–2004) (107), coincident with decreasing emissions from local waste incineration sources (Fig. 5). As of 2006, the MDN has 93 sites in operation, with 48 operating for  $\geq 5$  y. With the advent of new Hg air-emission regulations in Canada and the United States, the MDN represents a means to measure the efficacy of future regulatory changes. This will be especially true with the recent addition of MDN sites in predicted source-influenced locations, including several with event-based sampling.

**Dry Deposition.** There are few measurements of Hg dry deposition in the literature (101, 108, 109), and the only large-scale estimates of Hg dry deposition come from regional and atmospheric models (110–113). Direct measurements of Hg<sup>0</sup> dry deposition generally come from studies of Hg<sup>0</sup> emission from terrestrial landscapes (96, 114), most often at very low rates at night or under conditions of elevated Hg<sup>0</sup> concentrations in laboratory studies (86). The limited field studies and modeling of the stomatal uptake suggest that foliar uptake of Hg<sup>0</sup> is characterized by deposition velocities ( $V_d$ ) on the order of 0.01–0.05 cm s<sup>-1</sup> (85, 103). Although these values suggest a slow uptake, the concentration of Hg<sup>0</sup> is large enough relative to

other Hg species (generally representing >95% of total airborne Hg) that dry deposition of Hg<sup>0</sup> can be significant.

Complicating matters is the fact that the exchange of Hg<sup>0</sup> in vegetation is bidirectional, with Hg<sup>0</sup> exhibiting a compensation point, similar to the behavior of ammonia in green plants (86), and some have argued that there is no net accumulation of Hg with this process. However, laboratory studies clearly indicate that exposure of vegetation to elevated levels of Hg<sup>0</sup> results in a net accumulation of Hg in plant tissue (115).

Using measured values of  $V_d$ , estimates of dry deposition suggest that foliar uptake of Hg<sup>0</sup> (if retained and not emitted again) would rival or surpass wet deposition even at near-background concentrations (101). Though rarely measured in direct deposition studies, RGM and Hg<sub>p</sub> are readily dry deposited, further adding to the dry flux. Reactive gaseous Hg is especially important, because of its solubility, and the few direct measurements published suggest a high dry-deposition velocity, similar to nitric acid vapor ( $>1.0$  cm s<sup>-1</sup>) (104, 116), whereas the  $V_d$  for Hg<sub>p</sub> is only marginally larger than that of Hg<sup>0</sup>, suggesting generally low dry-deposition fluxes.

There are no long-term measurements of both wet and dry deposition for direct comparison. However, if one accepts the premise that LF and net TF (NTF; the flux in TF minus that in rain) reflect the net dry deposition of Hg (25, 94, 100, 117), then some crude comparisons can be made. Munthe et al. (118) compiled measurements of ecosystem fluxes of Hg at watersheds in Europe and the United States that operated for  $\geq 1$  y. In every case, the estimates of dry deposition from LF + NTF were  $\geq$  fluxes of total Hg in wet deposition (Fig. 6). Clearly, there is a significant need to develop accepted methods to measure dry deposition and to carry out long-term intercomparison studies with all methods at sites with ongoing wet-deposition measurements. These would be especially valuable at locations with a history of wet-deposition data, such as at the US NADP MDN sites. Without these data and a better understanding of dry-deposition mechanisms, we are missing a major component of the source attribution puzzle.

### MODELING ATMOSPHERIC TRANSPORT AND ATMOSPHERIC MERCURY SOURCE-RECEPTOR RELATIONS

Atmospheric Hg simulation and source attribution models that operate on a wide range of spatial scales were developed by

various research organizations (110, 112, 113, 119–124). Local-scale air-quality models (e.g., ISC-3) do not generally treat slower chemical reactions, such as those known to affect Hg but instead focus on the physical dispersion characteristics of exhaust plumes (125). For applications involving Hg, they usually simulate transport and deposition based on the chemical and physical forms of the Hg as emitted from the sources being studied (126). However, some local-scale models were developed that include chemical transformation of Hg (e.g., ROME, TRUE) (127, 128). Models capable of simulating Hg on regional and global scales (e.g., CMAQ, TEAM, GRAHM, HYSPLIT, ADOM) treat chemical and physical transformations, in addition to transport and deposition (52). As noted previously, advances in computing equipment and technology allowed the development of models treating chemical and physical processes with much greater detail. Multiscale air-quality models are now capable of simulating atmospheric flows throughout the troposphere (0–15 km height), with horizontal resolutions as fine as only a few kilometers for continental-sized domains, or resolutions of tens to hundreds of kilometers over global domains. These models are also capable of simulating time periods of 1 y or more with hourly resolution.

Regional-scale models are dependent on accurate representations of the air concentrations of the various forms of Hg at their lateral boundaries, along with similar estimates of the concentration of important Hg reactants, like ozone and hydroxyl radical. Most models assume no transfer of air or pollutants across the top boundary, if that boundary is near the top of the troposphere. These lateral boundary conditions are sometimes defined to be variable in time and are derived from global-scale model simulations (124, 129). Otherwise, estimates of the average concentrations over time are used (e.g., monthly, seasonal). In the past, these boundary conditions for Hg concentrations were often held constant in the vertical dimension but that is changing now that important vertical gradients in the various species of Hg were observed (79). Other critical inputs of such models include emissions and meteorology. Uncertainties in those inputs are reflected in the model simulation results and it, therefore, is essential to minimize those input uncertainties.

Receptor modeling techniques also were applied to Hg (40, 130). Those techniques use ambient concentration data for several chemical species (i.e., Hg and other gases) to identify the relative contributions of various source categories (some techniques assume typical chemical profiles for selected source categories, whereas others identify those chemical profiles from the raw data). Receptor modeling techniques are sometimes combined with meteorological information to construct back-trajectories and to complement the source category information with geographical information (131). Thus, better identification of possible source contributions can be obtained. Receptor modeling techniques are based on the principle of mass conservation and do not account for chemical transformation. They are most useful to ensure that all possible sources were included in the emission inventory and to corroborate the results of the regional-scale models described above. The combination of various modeling techniques can bring some valuable “weight of evidence” for source (or source region) attribution.

## **POLICY RELEVANCE AND THE ISSUE OF UNCERTAINTY IN SOURCE ATTRIBUTION**

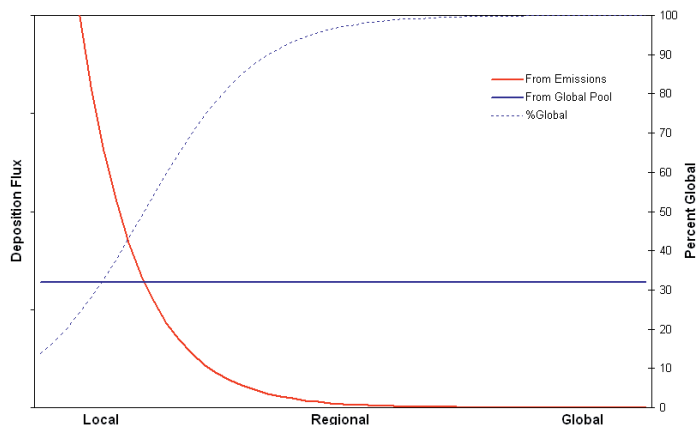
The question of source attribution is central to the development of control policy for environmental Hg by any authority. Without an understanding of the sources responsible for an observed Hg deposition, it is impossible to develop a cost-

effective emission control policy to reduce that flux. A critical element of our question is the term “with confidence.” Our scientific understanding of any environmental process is never absolute and is rarely complete. Environmental protection policy is almost always developed with some level of inherent uncertainty and political controversy. Environmental Hg control policy is no exception.

When considering the key question in a positive light, there are indeed some locations where we can say “with confidence” that atmospheric Hg deposition is predominately from local sources or predominately from the global pool. It is well known that some forms of atmospheric Hg are rapidly deposited by both wet and dry processes, and emissions of these forms of Hg, especially near ground level, are responsible for a large portion of the observed Hg deposition in the surrounding area. These more reactive forms of Hg (e.g., RGM and some Hg<sub>p</sub>) are usually deposited from the atmosphere before they can travel long distances. However, there are special atmospheric conditions under which they can travel longer distances. Therefore, the existence of reactive Hg in a particular air sample does not necessarily indicate the existence of a local emission source. Significant air concentrations and deposition of reactive Hg can also be the result of atmospheric chemical reactions involving less reactive forms of Hg transported from distant sources (e.g., elemental Hg). In remote locations far removed from emission sources of reactive Hg, we can conclude with confidence that this latter process is primarily responsible for the observed deposition. In this case, any significant reduction of Hg deposition would have to come from global-scale Hg emission reductions and/or a reduction in the oxidation potential of the atmosphere at that remote location.

When regarding the differentiation between natural and anthropogenic sources, it is generally accepted that reactive Hg emissions arise primarily from anthropogenic sources. Natural additions to the Hg cycle and emissions of previously deposited Hg that facilitate the cycle are primarily in the less-reactive elemental form (some important exceptions may exist). Therefore, undisturbed natural sources of atmospheric Hg seldom have a localized impact, and their effects occur mostly on the global scale in concert with the atmospheric chemical reactions mentioned above. The same is true for the large-scale surface emission of Hg, which has both a natural and an anthropogenic component. A differentiation between these 2 components of Hg recycling is necessary to accurately assess the overall importance of natural *versus* anthropogenic sources, but this differentiation is generally difficult.

We can say with confidence that elemental Hg is more inert and can be transported globally and that oxidized Hg compounds are more reactive and travel much shorter distances before depositing. However, there remains considerable uncertainty regarding the chemistry and reaction rates that govern the oxidation state of atmospheric Hg. There is also some uncertainty about the rate at which emissions of reactive Hg deposit and the distance at which they contribute to the total deposition flux. These uncertainties in rates reduce the confidence with which we can assess the contribution of anthropogenic sources on the intermediate, regional scale. For example, more rapid oxidation of elemental Hg, either in air or in atmospheric waters, increases the relative importance of natural and anthropogenic emissions of elemental Hg on the global scale to the Hg deposition at any given location. More rapid deposition of emitted reactive Hg decreases the distance over which these emissions travel and influence total deposition flux. The assumption of rapid Hg oxidation and rapid deposition of reactive Hg emissions is illustrated in Figure 7 (Hypothetical Case 1). If the opposite were true, slower Hg oxidation and slower deposition of reactive Hg emissions, this



**Figure 7. Illustration of Hypothetical Case 1: Rapid atmospheric oxidation of mercury and rapid deposition of reactive mercury emissions. Note that the percentage of deposition from global influences is high at the regional scale of transport from anthropogenic sources. Transport scale = X axis.**

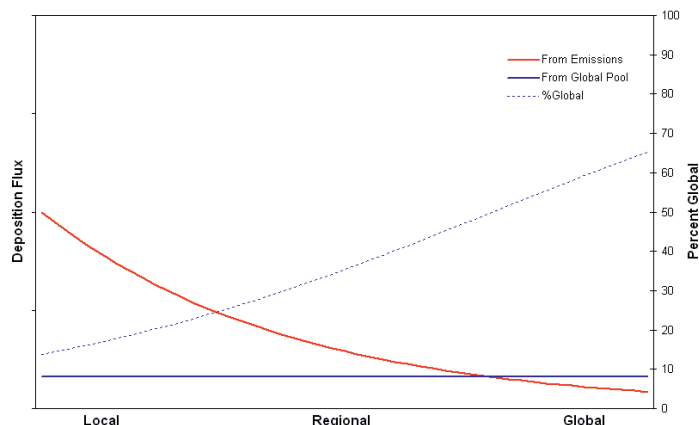
would result in a quite different result, as shown in Figure 8 (Hypothetical Case 2). In this hypothetical case, more of the reactive Hg that dominates the deposition flux must come directly from emission sources rather than from atmospheric oxidation of Hg<sup>0</sup>. Without a confident understanding of atmospheric Hg chemical kinetics and Hg deposition processes, assessment of the relative importance of the intermediate, regional-scale sources is very difficult.

Another issue that must be considered by environmental policy makers is the expected time scale for decreases in atmospheric Hg deposition brought about by proposed regulatory action. Here again, uncertainty about atmospheric Hg chemical kinetics makes a confident assessment difficult. We know that the global emission flux of Hg to the atmosphere must roughly balance with the global deposition flux, because the global-average Hg burden in air is observed to be quite stable, at least on the generally accepted time scales of atmospheric Hg cycling. More rapid oxidation of atmospheric Hg implies a generally higher total deposition flux that must be balanced by the sum of all anthropogenic emissions and emissions from natural surfaces.

Although we have a relatively good understanding of primary anthropogenic emissions, this is not the case for natural and recycled (Hg emitted after being deposited) Hg emissions. Assuming vigorous atmospheric oxidation of Hg implies that vigorous emissions from natural surfaces must be compensating. In this case, reducing or even eliminating anthropogenic emissions of Hg would have a smaller than expected effect on the total emission flux. Significant reductions in deposition would not occur until a commensurate fraction of the Hg now involved in the global-scale cycle is somehow sequestered (e.g., in geologic formations, much as it was before human industrialization). However, if atmospheric oxidation of Hg is slow, then more of the observed deposition flux must be coming from anthropogenic emissions of reactive Hg. In this case, reductions in anthropogenic emissions of Hg would lead to a more rapid decrease in the total Hg deposition flux. The importance of resolving these issues for policy development is clear. Their associated uncertainties critically impact our ability to predict the outcome of any proposed emission-control strategies.

## SUMMARY AND CONCLUSIONS

During our synthesis of progress in the last decade, the panel altered its opinion on the question of source attribution. Initially, the panel was divided among “yes,” “no” (we cannot



**Figure 8. Illustration of Hypothetical Case 2: Slow atmospheric oxidation of mercury and slow deposition of reactive mercury emissions. Note that the percentage of deposition from global influences is low at the regional scale of transport from anthropogenic sources. Transport scale = X axis.**

yet attribute sources at any location) and “maybe.” By the end of our synthesis, the panel agreed that the answer is a “qualified yes.” The qualification is strongly dependent upon what level of uncertainty we can ultimately accept in our answer. We agreed that the uncertainty is strongly dependent upon scale and that our question as stated is answerable with greater confidence both very near and very far (remote) from major point sources (if we accept the “global pool” as a recognizable “source”). Unfortunately, many regions of interest (from an ecosystem-exposure standpoint) lie in between, where source attribution carries the greatest degree of uncertainty. This situation will improve with a better understanding of atmospheric Hg chemical kinetics and deposition processes. The panel also agreed that all aspects of predicted climate changes have the potential to affect the Hg cycle in ways that will increase the uncertainty of source attribution.

The panel felt that answers are forthcoming from the two primary approaches: direct measurements and models, both of which are subject to uncertainty. Application of measurement approaches by using isotopic signatures and tracers of convenience (e.g., trace metals, carbon monoxide) require intensive high-resolution sampling efforts but hold promise as analytical technology improves. Although these approaches are typically applied to atmospheric concentrations, they may be adapted to provide data on source attribution for both wet and dry deposition, and they are most likely to succeed close to well-characterized sources.

The modeling “frameworks” for simulating pollutant transport, transformation, and deposition are quite mature and ready to apply for Hg, if we knew the values of the required modeling parameters (e.g., chemical kinetics rates). The models are there, but their accuracy is limited. The ability to determine the accuracy of current models is severely limited by the lack of dry deposition measurements; uncertainties in the altitudinal distributions of Hg species; and uncertainties in atmospheric, especially heterogeneous, reaction rates, emission Hg speciation, Hg emission rates in developing nations, and model parameterizations for dry deposition and meteorology.

## Significant Advances

The panel noted several important advances in our understanding of atmospheric Hg over the past decade that have important implications for the question of source attribution. These include:

- An understanding of the broad uniformity of Hg deposition changes in remote areas ( $3 \pm 1 \times$  increase);

- improved laboratory data on reaction kinetics and new field measurements, indicating that fast oxidation of Hg<sup>0</sup> is occurring in certain environments (e.g., seasonally at the Poles, in the MBL, and in the upper troposphere);
- improved knowledge of the lifetime of Hg<sup>0</sup>, which is not a fixed value but may vary significantly with season, latitude, and ambient concentration of atmospheric oxidants;
- widespread availability of automated instrumentation for measuring atmospheric concentrations, speciation, and surface fluxes;
- improved modeling at local, regional, and global scales;
- establishment of large-scale national Hg wet-deposition networks; and
- development of methods for accurately quantifying the isotopic signature of Hg.

## Research Needs

The panel also noted the importance of further research on several fronts:

- The effects of all aspects of climate change, including wildfire, on the atmospheric Hg cycle must be understood, because this phenomenon could be the primary factor influencing the future distribution of Hg on global and regional scales;
- improved understanding of the role of halogen and OH radical chemistry involving atmospheric Hg<sup>0</sup>;
- improved measurement and modeling of the 2 largest global fluxes: Hg dry deposition and evasion across the air-water interface (especially in marine systems);
- a global Hg monitoring network is needed to assess long-term changes in atmospheric Hg concentrations and wet + dry deposition;
- an assessment of the magnitude of change in the oceanic Hg reservoir since pre-industrial times, especially in the surface ocean (0–100 m);
- an accurate determination of whether Hg is currently increasing or decreasing in the biogeochemically active reservoirs at the Earth's surface;
- a better understanding of anthropogenic Hg emissions from developing nations is needed to improve the accuracy of global Hg cycling models, and
- accurate scaling-up of air/surface exchange of Hg is not possible from small-scale field measurements alone but must also rely on large-scale modeling, which requires an improved understanding of the physical and biological mechanisms that influence these processes.

## Conclusions

Finally, the major conclusions of our synthesis include the following:

### Long-term Anthropogenic Changes

- Deposition, even at the most remote locations, contains a significant fraction of anthropogenic Hg.
- We are confident of the overall global increase in Hg deposition since the Industrial Revolution (by a factor of  $3 \pm 1$ ).
- It is possible that the global cycling of Hg has been impacted not only by anthropogenic emissions but also by increases in the atmospheric ozone concentration since the Industrial Revolution.

### Current Emission and Deposition Trends

- There has been no discernible net change in the size of the atmospheric pool of Hg in the Northern Hemisphere since the mid-1970s.

- North American and European emissions are decreasing, whereas those in Asia and Africa are increasing, but the latter changes are less well constrained.
- Decreases in local emissions have resulted in decreases in near-field deposition.

### Chemical Transformations and Cycling

- There have been important developments in analytical and sampling methodology, which provide a much clearer picture of atmospheric Hg species behavior.
- Hg fluxes by dry deposition, terrestrial surface emission, and ocean evasion are globally significant but represent important gaps in measurements, data, and understanding.
- New understanding of Hg cycling in the MBL, and much more rapid cycling in the atmosphere (fast chemistry leading to a more heterogeneous atmosphere than previously imagined), is making modeling results more uncertain.
- The relative importance of Hg redox chemistry varies dramatically in space and time, and uncertainties in those redox reactions and physical transformations significantly impact the ability to develop source/receptor relations.

### Modeling and Uncertainty

- There is a large discrepancy between progress made in measurement technology and the development of accurate global-emission inventories.
- Higher-resolution emission estimates would facilitate improved model verification.
- Hg isotope signatures and tracers of convenience hold promise for source attribution, particularly at the local scale.
- The uncertainty associated with current models must be relayed to and understood by policy makers.

### The Bottom Line

The answer to “can we attribute sources to Hg deposition?” is a qualified “yes.”

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