

Chapter 13

The Need for a Coordinated Global Mercury Monitoring Network for Global and Regional Models Validations

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Summary Currently, there is not a coordinated observational network for mercury (Hg) that could be used by the modelling community or for establishing recommendations for protecting human and environmental health on a global scale. Current national networks are inadequate as they lack (1) observations of all forms of Hg in the ambient air and in both wet and dry deposition; (2) long-term measurements of Hg and other air pollutants; (3) comprehensive monitoring sites in the free-troposphere; and (4) measurement sites that permit a careful investigation of inter-hemispheric transport and trends in background concentrations. Programs such as the World Meteorological Organization's Global Atmosphere Watch have made substantial efforts to establish data centers and quality control programs to enhance integration of air quality measurements from different national and regional networks, and to establish observational sites in under-sampled, remote regions around the world. Similarly, the International Global Atmospheric Chemistry project (of the International Geosphere-Biosphere Programme) has strongly endorsed the need for international exchange of calibration standards and has helped coordinate multinational field campaigns to address a variety of important issues related to global air quality. Following the lead of these programs and incorporation of a well-defined Hg monitoring component into the existing network sites would be the most expeditious and efficient approach. Close coordination of the global modelling community with the global measurement community would lead to major advances in the global models and advance our understanding of the Hg science while decreasing the uncertainties in global assessments for Hg.

13.1 Introduction

Mercury in the atmosphere exists in both gaseous phase and particulate phase with three possible oxidation states: zero oxidation state, also called elemental Hg (Hg^0); monovalent state (Hg^I), which is not found in the atmosphere; and divalent state (Hg^{II}) (Schroeder and Munthe, 1998; Lin and Pehkonen, 1999). For operational

reasons, based on methods of quantification, atmospheric Hg is classified as Hg⁰, gaseous Hg^(II) or reactive (divalent) gaseous Hg (RGM), and particulate mercury (PM). Particulate mercury consists of Hg⁰ and Hg^(II) that are associated with atmospheric particulates. Mercury in the atmosphere is dominated (~98%) by Hg⁰ (Schroeder and Munthe, 1998) which is relatively insoluble in water and unreactive, and its atmospheric lifetime (>30 d) allows for global-scale transport. In contrast, RGM in the atmosphere is water-soluble and is efficiently removed through both wet and dry deposition processes. Elevated levels of RGM are typically associated with direct emissions from localized anthropogenic sources, but can also be produced by photochemical conversion from Hg⁰ (e.g. Laurier and Mason, 2007). The importance of the atmosphere in the global redistribution of Hg is well-known. Over the last two decades a significant effort has been made to understand the atmospheric transport, transformation and deposition processes of Hg around the globe.

More recently, developments in measurement and analytical techniques for Hg have led to a much improved understanding of the sources and cycling of Hg in the environment. However, there are many atmospheric chemical and physical processes involving Hg that are still not well understood (see Chapters 14 & 15). For example, Bergan and Rodhe (2001) noted that an important step in our ability to model the global redistribution of Hg involves reducing the uncertainty in our understanding of the removal of gaseous Hg⁰ from the atmosphere via deposition and atmospheric chemical transformation (Schroeder and Munthe, 1998; Selin et al., 2007). Measurements of the key Hg species are critical in our developing a better understanding of these processes, and how they may have changed over time.

It has been suggested that due to intensified anthropogenic release of Hg into the atmosphere, the global pool of Hg has increased in the past 150 years (Mason and Sheu, 2002). Evidence of long-term changes in the atmospheric Hg burden can be derived from a variety of methods including chemical analysis of lake sediments, ice cores and peat deposits (Fitzgerald et al., 2007; Krabbenhoft et al., 2007). Measurements from both hemispheres demonstrate at least a threefold increase of Hg deposition since pre-industrial times (Mason et al., 1994; Lamborg et al., 2002; Fitzgerald et al., 2007). An increase in the global atmospheric pool should also be reflected in the background Hg concentration. However, to date, it has been extremely difficult to derive a multi-decadal global trend estimate based on the existing spatially and temporally uncoordinated air concentration data sets (e.g. Slemr et al., 2003). The estimated large increases in Hg emissions in China (see Chapters 2 & 3) over the last decade are not currently reflected in the long-term measurement of total gaseous Hg at Mace Head, Ireland between 1996 to 2006, nor in the precipitation data of the North American Mercury Deposition Network (MDN), as noted in Chapter 9. Total gaseous Hg (TGM) measurements performed in the Southern Hemisphere also do not suggest that a significant change in TGM levels in the global remote atmosphere over the past two or three decades (Slemr et al., 2003).

Given these observations, and the apparent contradictions, it has become clear that there is a need for global mercury monitoring network incorporating existing long-term atmospheric Hg monitoring stations, such as Mace Head, but with the incorporation of a number of additional sites to obtain a globally representative

picture of atmospheric Hg in the troposphere. While atmospheric Hg models have had some success in predicting the levels and trends in ambient Hg levels, the scarcity of global measurement data available for the comparisons make the exercise and results less significant. Efforts to improve our understanding of atmospheric Hg chemistry and inter-hemispheric transport will require a comprehensive research framework that integrates observations covering a wide range of temporal and spatial scales with modeling and process studies. Hence, there is a critical need for a coordinated global Hg monitoring network designed to support the development of global and regional scale Hg models relied upon in the policy making process. A well-planned international network is required to provide a consistent, standardized set of long-term data on the concentrations and deposition of atmospheric Hg in its various forms, together with trace gases, particles, and physical parameters at strategic sites that are globally distributed.

Such a global Hg network should leverage its efforts by collocating with other existing monitoring programs such as the World Meteorological Organization's Global Atmosphere Watch sites, US and Canadian Monitoring sites, and UN-ECE's European Monitoring and Evaluation Programme (EMEP) sites. In addition, as noted in Chapter 9, there are already aspects of such a monitoring program in Europe, Canada and the USA. In the USA, there has been a recent concerted effort to develop and design a monitoring network that would be able to evaluate the ecosystem response to changing concentrations of Hg in the atmosphere and in deposition, and to examine how this impacts levels of methylmercury (MeHg) in fish (Mason et al., 2005; Harris et al., 2007). While this program focuses on all aspects of Hg biogeochemical cycling, the conclusions of Driscoll et al. (2007) have relevance to the approach to designing a global Hg monitoring network. These authors suggest that a successful network would consist of a relative small number of "intensive" sites, where the full range of measurements are made (e.g. atmospheric Hg speciation and dry deposition estimation, event-based wet deposition and flux, and the measurement of required ancillary parameters and detailed meteorology), and a larger number of "cluster" sites where only weekly wet deposition is collected. The cluster sites would allow for integration between the intensive sites, and examine the effects of local and regional conditions, while the intensive sites would provide the detailed information needed to calibrate and test global and regional Hg models (Driscoll et al., 2007; Saltman et al., 2007). This approach is one model of how such a network would be constructed.

Clearly, the over-arching benefit of a coordinated global Hg monitoring network (CGMMN) would be the universal availability of high-quality measurement data that are desperately needed to develop, refine, and validate models on different spatial and temporal scales. The data from the set of coordinated monitoring sites would support the evaluation and ground truthing of models as research and management tools to evaluate our understanding of the global cycling of Hg and deposition to sensitive ecosystems. This chapter will specifically highlight the need for a global Hg monitoring designed to support the development of global and regional scale Hg models that should be considered as the scientific basis of the policy making process.

To reiterate, the principal goals of a global Hg monitoring network are:

- To study the temporal and spatial variability of atmospheric Hg and atmospheric composition;
- To provide long-term monitoring of changes in the physical and chemical state of Hg in the lower atmosphere; in particular to provide the means to discern and understand the causes of such changes;
- To establish the links between changes in atmospheric Hg, tropospheric chemistry and climate;
- To support intensive field campaigns focusing on specific Hg processes occurring at various latitudes and seasons, and in highly sensitive ecosystems;
- To produce verified data sets for testing and improving global and regional models for atmospheric Hg and those coupled to aquatic and terrestrial ecosystem models.

13.2 Existing Global Monitoring Programs

Currently a global monitoring network for Hg does not exist. There are a number of state and national programs that are collecting atmospheric Hg data but the parameters monitored, the locations of the monitoring sites, and the methods employed may prohibit their utility in assessing global trends and changes. In spite of this, there is a great deal of recent information available on the levels of Hg in the atmosphere around the globe. Chapters 9-12 of this book provide a detailed compilation of the available atmospheric Hg data in the literature. Many of the issues discussed in these chapters, regarding data quality and the need for Hg speciation data at background and source impacted areas, are relevant to the development of a global network as well. It is important to stress that the measurement of Hg by itself is not sufficient for us to improve our understanding of Hg sources and impacts. Measurements of other key atmospheric constituents at the global monitoring sites are necessary for us to develop a better understanding of the global redistribution of Hg and to further refine our model parameterizations of the key processes. The co-location of Hg measurements with ongoing global programs is the most efficient approach to initiating this coordinated monitoring network.

13.2.1 *Ambient Measurements*

Current air monitoring programs for air pollutants such as ozone, sulfur dioxide, and nitrogen compounds include regulatory monitoring networks that report daily air quality changes at sites located primarily in urban or populated areas; global and regional networks designed to measure background atmospheric composition at

selected remote sites or at regionally representative sites; remote-sensing (satellite) instruments that provide global-scale observations of selected atmospheric species; and a variety of radiosonde and aircraft based instrument programs focused on specialized measurement campaigns. These different observational approaches vary widely in their scope and degree of analytical quality. Initial efforts are underway to develop such monitoring capabilities for Hg in the Northern Hemisphere, as detailed in earlier chapters. In the USA, there is currently an effort underway to expand the MDN network to include measurements of Hg speciation in air, and for estimating dry deposition (<http://nadp.sws.uiuc.edu/mdn/>). Coordination of such efforts globally will help advance the development of the CGMMN.

Programs such as the World Meteorological Organization's Global Atmosphere Watch (GAW) have established data centers and quality control programs to push for the integration of air quality measurements from different national and regional networks, and to establish observational sites in data sparse and remote regions of the globe. The International Global Atmospheric Chemistry project (of the International Geosphere-Biosphere Programme) has strongly endorsed the need for international exchange of calibration standards and has helped coordinate multinational field campaigns to address a variety of important issues related to global air quality.

13.2.2 Mercury Measurements at Altitude

Most air quality monitoring networks rely entirely upon ground-based sites that sample within the boundary layer (the lowest portion of atmosphere in contact with the surface). Addressing global air quality problems such as Hg contamination, however, will require observations that are made at higher altitudes above the boundary layer. Studies have shown that transport of pollution including Hg between Asia and the United States occurs primarily through the middle and upper troposphere, and because of the highly episodic nature of this transport, there can be significant inhomogeneity in the air masses reaching the continental United States. Thus, networks that only sample air masses within the boundary layer would not allow a quantitative determination of long-range pollutant fluxes. While sampling with aircraft can provide detailed information about Hg in the upper atmosphere (Banic et al., 2003; Ebinghaus et al., 2000; Friedli et al., 2004; Swartzendruber et al., 2008; Talbot et al., 2007), in terms of long-term monitoring, the use of aircraft has obvious limitations. The preferred approach is to use mountain-top monitoring sites, that are frequently in the free-troposphere, and which located around the globe are essential to understanding the global transport of Hg and other pollutants (Jaffe et al. 2003). Currently, there are a number of such sites in existence, including Mt. Bachelor in the western USA (Jaffe et al., 2003), Mona Loa in Hawaii (Landis et al., 2005), Wank Mt. in Germany (Slemr et al., 2003), and the Lulin station in Taiwan (Sheu et al., 2007).

13.2.3 Episode-based Measurement Intensives

In addition to long-term monitoring efforts, investigations of both ozone and aerosols have included numerous measurement intensives. These have typically featured measurements of a more extensive range of species that are related to photochemistry, including radicals such as OH and HO₂ (e.g. Ren et al., 2006). Intensive field campaigns have occurred in urban, rural and remote locations and have frequently included both surface-based and aircraft measurements (e.g. Daum et al., 2004, Lei et al., 2007). Such intensives have also occurred for Hg (see Chapters 9-12) but in many cases have not included sufficient ancillary information that the details of the formation and removal of various Hg species can be determined in detail (See Chapters 14 & 15).

13.2.4 Meteorological Measurements

Meteorological processes operating over a wide range of spatial scales play a central role in the air quality and deposition of all atmospheric pollutants including Hg. The emissions, chemical transformations, deposition, and re-emission of Hg are strongly affected by meteorological parameters such as temperature, cloud cover, humidity, mixing height, and wind speed and direction. In addition, dynamical forces related to vertical temperature profiles control the dispersion of pollution within the urban/local boundary layer and the release of pollutants from the boundary layer into the free troposphere. Finally, the long-range transport of pollutants is influenced by atmospheric high- and low-pressure systems occurring on synoptic scales (100s to 1000s km). Thus, the meteorological context of atmospheric chemical measurements must be established in order to accurately assess impacts of Hg loadings and to develop the models used for studying long-range Hg transport and climate-Hg interactions.

13.2.5 Atmospheric Deposition

The atmosphere provides the main environmental pathway for redistribution of Hg around the globe, and therefore, quantifying the transfer of Hg from the air to the earth's surface via wet and dry deposition is critically important. Like ambient Hg, there is currently not a globally coordinated network of atmospheric Hg deposition sites. However, there are currently a few coordinated networks in certain regions of the world including: North American Mercury Deposition Network (MDN) that was initiated in the early 1990s as part of the National Atmospheric Deposition Program (NADP); EMEP in Europe; and networks in Japan as well as other parts of Asia. Coordination of the national networks in the various regions and formation

of a standard set of measurement objectives and techniques will be important at the onset of the project. While wet deposition networks are currently in-place for Hg, the measurements challenges involved in quantifying Hg dry deposition have thus far prevented these measurements from becoming routine. Dry deposition measurement techniques have been developed using both surrogate surface approaches (Keeler and Dvonch, 2005), and using inferential techniques that measure the various forms of Hg in the atmosphere as well as meteorological parameters to model the dry deposition flux at the measurement site (as discussed in Driscoll et al., 2007). Inferential methods have been used in both US EPA and Environment Canada Networks for acid rain species and may hold the most promise for the global network as well. The key to estimating the dry deposition flux will be the accurate measurement of atmospheric Hg in the gaseous forms and on size-fractionated particulate matter. There is evidence that particulate Hg is bimodal in the atmosphere and undergoes reversible gas-particle partitioning during transport from source to receptor.

13.3 Measurements and Model Development

Models for chemistry and transport of atmospheric species are based on input with a significant range of uncertainty. This is especially true for models for Hg, because essential features of atmospheric cycling and photochemical transformation of Hg involve more uncertainty relative to other atmospheric species. The major role of measurements in model development is to provide a basis for evaluating the model accuracy in simulating ambient conditions. Comparisons between predicted and observed ambient values are the central test for establishing the accuracy of models (e.g. Selin et al., 2007; Strode et al., 2008; Hedgecock et al., 2006). When model predictions show significant differences from measured values, this is frequently regarded as evidence of errors in the models, and prompts investigation and modification of model input assumptions or spatial resolution. As such, ensembles of measured values provide a basis for constraining the assumptions used by models. Chemistry/transport models also use ambient meteorological measurements as direct input. Meteorological input is typically provided by prognostic models with assimilated data in order to generate simulations for specific time periods. The methods of prognostic meteorological modeling and data assimilation have been studied extensively and are used in chemistry/transport models for all atmospheric species. Here we will describe the role of ambient measurements that are used for model evaluation, through comparison with model predicted values, rather than as a source of model input. This type of model evaluation is an essential part of the model development process. Model-measurement comparisons provide a basis for constraining the range of assumptions used by models, especially with regard to emission rates and photochemical reaction sequences. Model-measurement comparisons can also be used to provide evidence on issues that are relevant to policy concerns.

13.3.1 General Evaluation of Model Transport and Photochemistry

Chemistry transport models for ozone and its precursors and for sulfate and nitrate aerosols have been the subject of extensive evaluation over the past 20 years at both the urban/regional and global scales (e.g. TF-HTAP, 2007). Many of the approaches used to evaluate these models are applicable to Hg as well, and thus Hg has been included under the umbrella of HTAP, and many existing models for atmospheric species (e.g. Geos-Chem) have been adapted to include Hg. As with ozone, initial model evaluations must focus on model accuracy and the ability of the model to reproduce peak concentrations and diurnal variations (especially for urban/regional models) and on the vertical distribution throughout the troposphere (for global models) (e.g. Logan, 1999, Oltmans, 2006). As with models for sulfate and nitrate aerosols, many Hg models have focused initially on reproducing the observed wet deposition of the MDN and other networks. As model evaluation continues, there will be an increased emphasis on comparing measurements of a wider variety of species and evaluations that could be used to test the accuracy of specific model components. Efforts for reactive species and Hg have included the following: 1) Correlations with CO as a basis for identifying transport from polluted regions (e.g. Parrish, et al., 1993, Weiss-Penzias et al., 2006; 2007; Jaffe et al., 2005); 2) Correlations between O₃ and NO_x reaction products (HNO₃, various organic nitrates) as a basis for providing constraints on the ratio between the rates of production of O₃ and other species and evaluating chemistry (e.g. Trainer et al., 1993; Sillman et al., 1998; Roberts et al., 2004; Horowitz et al., 2007; Hynes et al., 2008 chapter 14); 3) Direct measurement of OH and HO₂ radicals as a basis for evaluating model chemistry (e.g. Ren et al., 2006, Olson et al., 2006, Lei et al., 2007); 4) A combination of episodic and long-term measurements designed to measure continental outflow and intercontinental transport for O₃ and aerosols (e.g. Prospero et al., 2003, Savoie et al., 2002), and Hg (e.g. Jaffe et al., 2005); and 5) Model evaluations based on a wide range of primary and secondary organic species and reactive nitrogen (e.g. Lei et al., 2007; Bey et al., 2001).

As noted, the evaluation of models for Hg has initially focused on two benchmarks: ambient TGM and the observed wet deposition of total Hg. There have also been limited comparisons with ambient RGM (Selin et al., 2007; Strode et al., 2008). Wet deposition is of interest in particular because it is linked to policy concerns. In addition, the spatial variation of wet deposition within the U.S. provides a basis for evaluating the ability of models to represent the variety of factors (including emissions, transport and chemistry) that affect deposition rates. Comparisons with the observed wet deposition have been a common basis for model evaluation (Figure 13.1) (see Chapter 16). However, although wet deposition will likely remain the most important basis for evaluating model performance, it also has significant drawbacks. Wet deposition alone does not provide sufficient information for evaluating the impact of local versus global emission sources. It also does not provide a basis for identifying photochemical transformations that affect Hg. Significant improvements in model accuracy may be obtained by an expanded range of model-measurement comparisons. Figure 13.2 illustrates the large differences

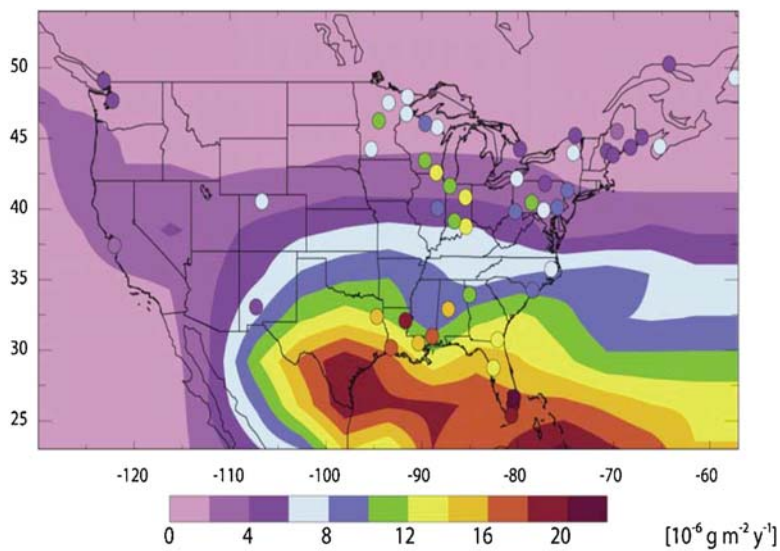


Figure 13.1 Annual mercury wet deposition fluxes over the United States for 2003–2004. Observations from the Mercury Deposition Network (circles) are compared to model results (background). From Selin *et al.* (2007)

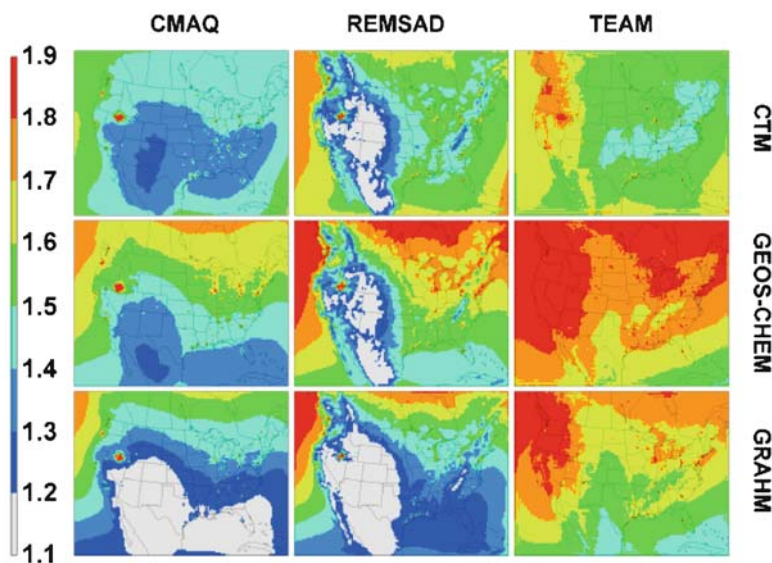


Figure 13.2 Simulated annual surface-level Hg^0 ($ng\ m^{-3}$) from three regional-scale models (CMAQ, REMSAD, TEAM) for North America using results from three different global models (CTM, GEOS-CHEM and GRAHM) as boundary conditions. From Bullock *et al.* (2007)

in ambient Hg^0 and RGM predicted by different regional and global-scale models. The size of these differences identifies the importance of model intercomparisons as a basis for identifying the effects of differing model assumptions. Networks of measurements should provide information for resolving these differences.

13.3.2 Source-receptor Relationships: Long-range Transport Versus Local Sources

The relative impact of local emissions and long-range transport is important because it determines the effectiveness of proposed control strategies for Hg wet deposition. It is especially important to develop methods for testing the accuracy of model predictions in this area and revising models in response to results. Evidence for episodic transport of Hg from Asia to the U.S. has been provided through measurements at sites in the western U.S. (Weiss-Penzias et al., 2006).

As shown in Figure 13.4, measurements showed episodes with elevated ambient TGM, O_3 , particulates and CO coinciding with circulation that suggested possible transport from Asia. Because CO has a lifetime of >2 months it is viewed as a marker for long-range transport and for anthropogenic origin. The observed ratio between CO, and TGM provides a basis for evaluating the accuracy of model representations of emissions and transport. Weiss-Penzias et al. (2007) report values for $\Delta\text{TGM}/\Delta\text{CO}$ plumes of Asian origin as opposed to North American origin and found significant differences ($0.0045\text{--}0.0048 \text{ ng m}^{-3} \text{ ppb}^{-1}$ in Asian plumes vs. $0.0013 \text{ ng m}^{-3} \text{ ppb}^{-1}$ for North American sources). Models should reproduce these ratios. Recent modeling efforts suggest that the agreement is better when non-point source emissions in Asia are accounted for (Strode et al., 2008). Evidence for local emission sources of Hg have largely been based on statistical correlations or relationships between deposited Hg and trace elements or stable isotopic ratios, e.g. Pb 206/204 in rainwater or aerosols (Dvonch et al. 2005; Fitzgerald et al., 2007) (Figure 13.3). This relationship between trace metals and Hg has not been tested yet in comparison with deterministic models. Because the statistical correlation between Hg and trace metals is closely associated with emission sources, this ratio provides a basis for evaluating the accuracy of model representations of local and regional sources.

Model results have suggested that correlations between ambient RGM and Hg^0 , or the lack of such correlations, may also provide evidence for the relative impact of local emissions versus long-range transport. Model results predict that RGM and Hg^0 anticorrelate in situations where RGM has been produced photochemically from the global pool of Hg^0 (e.g. Jaffe et al., 2005) (Figure 13.4), while directly emitted RGM is predicted to positively correlate with Hg^0 (Sillman et al., 2007) (Figure 13.5). More extensive measurements of these species would allow an evaluation of the predicted versus measured correlation, which would provide an indirect evaluation of model representations of local versus global sources.

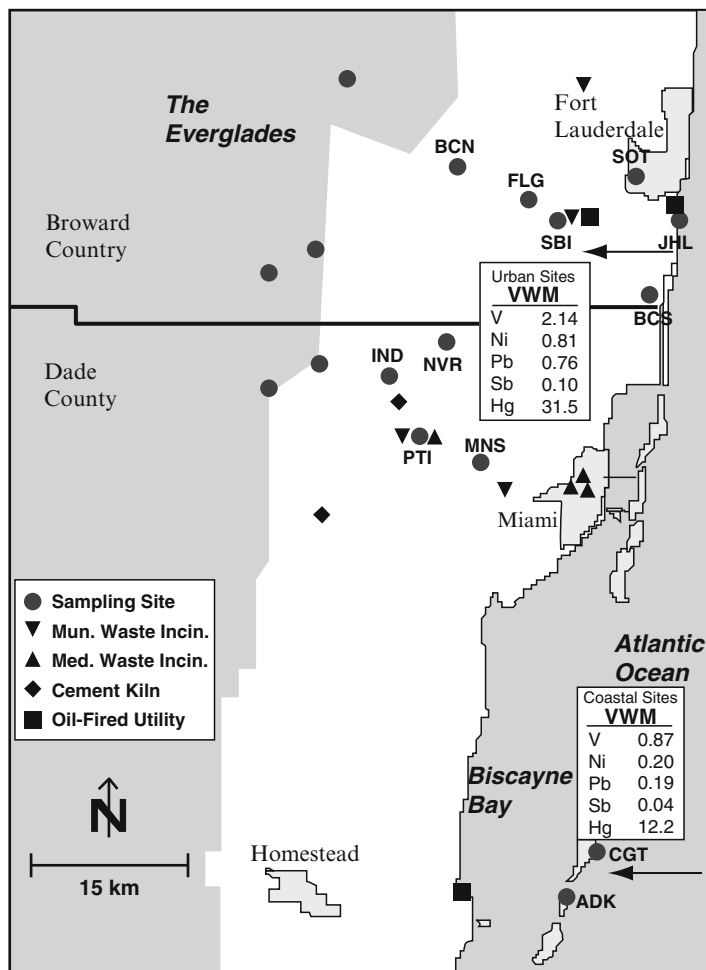


Figure 13.3 Volume-weighted mean concentrations of V, Ni, Pb, and Sb ($\mu\text{g L}^{-1}$) and Hg (ng L^{-1}) in precipitation arriving from the east at SoFAMMS urban (BCN, BCS, FLG, IND, MNS, NVR, PTI, SBI, and SOT) and coastal (ADK, CGT, and JHL) sites. (After Dvonch et al. 2005).

13.3.3 Evaluation of Photochemical Processes

The photochemical transformation between Hg^0 , RGM and PM represents one of the major uncertainties in the current understanding of the cycle of atmospheric Hg. Hg^0 is converted to RGM through gas-phase reaction with OH and O_3 , and through reactions with reactive halogen species, but the rates of those reactions are uncertain (see Chapter 14). RGM may be converted to Hg^0 through aqueous reaction with HO_2 ,

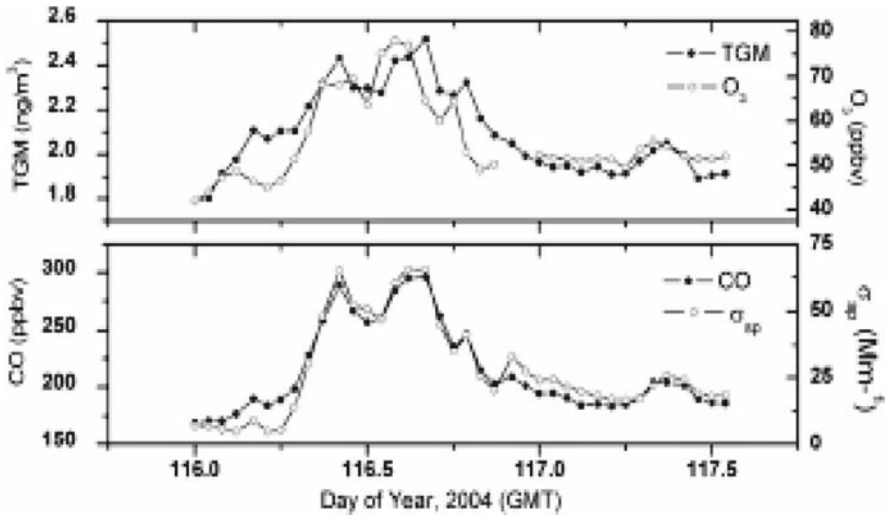


Figure 13.4 Measured O_3 , CO, particulate scattering (σ_{sp}) and total gaseous mercury (TGM) during a pollution transport event at Mt. Bachelor, Oregon. Simultaneous elevated concentrations is interpreted as evidence of transport, most likely from Asia. (From Weiss-Penzias et al., 2006)

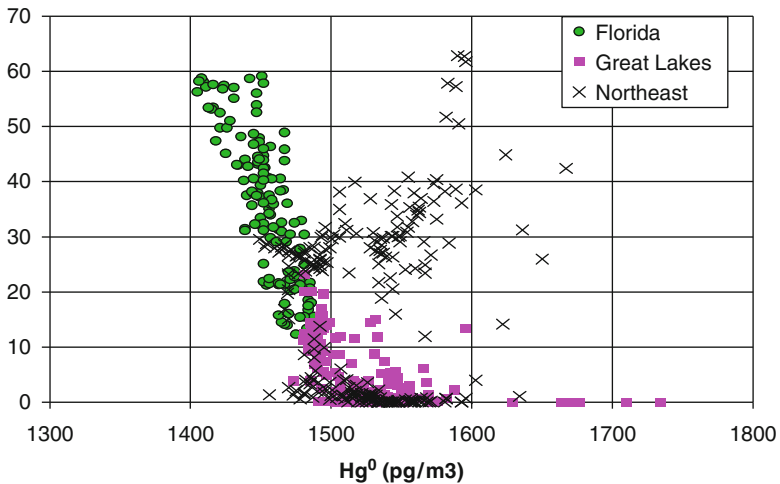


Figure 13.5 Model correlation between Hg^0 and RGM in $pg\ m^{-3}$ for Florida (circles), the northeast corridor (X's) and Great Lakes (squares). Negative correlations identify photochemical production of RGM from global background Hg^0 . Positive correlations identify directly emitted RGM and Hg^0 . (Source: Sillman et al., (2007)

but this reaction is also uncertain (Gartfeldt and Jonnson, 2003). Other mechanisms for the reduction of RGM have also been proposed. Lin et al. (2006; 2007) and Pongprueksa et al. (2007) tested the viability of these proposed reactions and reaction rates in a regional-scale simulation. They used measured wet deposition rates and ambient Hg^0 as constraining factors, proposing in effect that an ensemble of photochemical reaction rates must result in Hg^0 and wet deposition that is consistent with measurements. Pongprueksa et al. (2007) reported that the agreement between model and measured wet deposition is improved somewhat if a reduction reaction between RGM and CO is used in place of aqueous reduction via HO_2 . This type of investigation might be improved if measured ambient RGM were more widely available.

Another approach to evaluating photochemistry is to use correlations between ambient RGM and O_3 . Model results predict a strong correlation between RGM and O_3 , due to enhanced photochemical activity during pollution events with high O_3 (Sillman et al., 2007). Measurements also indicate a correlation between RGM and O_3 (Keeler and Dvonch, 2005). Evaluation of this correlation can also provide an indirect evaluation of model photochemistry. Selin et al. (2007) used the diurnal variation of RGM as a basis for proposing rapid uptake of RGM by sea-salt aerosols.

13.3.4 Evaluation of Gas-particle Partitioning

Studies have shown that PM is primarily from combustion processes and is found mainly in fine fraction particles with aerodynamic diameters below $2.5 \mu\text{m}$ (Keeler et al., 1995; Pirrone et al., 1996). PM associated with coarse particles ($> 2.5 \mu\text{m}$) were also observed in studies conducted in urban/industrial areas (e.g. Keeler et al., 1995). These coarse fractions PM were thought to be formed through near source adsorption of the two gaseous Hg species (Hg^0 and RGM) into the existing aerosols in the air. Since PM has a greater solubility and reactivity, but lower volatility, than Hg^0 , PM produced through adsorption is more likely to be derived from RGM than Hg^0 (Pleijel and Munthe, 1995; EC, 2001). The lifetime of PM in the atmosphere depends on aerosol characteristics such as particle size and the ability of aerosols to be scavenged by precipitation and clouds (Schroeder and Munthe, 1998).

Coarse particles settle more rapidly than fine particles and may play a dominant role in atmospheric dry deposition, especially near the sources; while fine particles can distribute uniformly in the air during their longer atmospheric residence time and contribute substantially to the total atmospheric dry deposition on a larger spatial area (Keeler et al., 1995). In the absence of precipitation, PM has a lower removal rate and longer residence time (days to months) than RGM (hours to days) (Schroeder and Munthe, 1998). Like RGM, high concentrations of PM are often found near emission sources (Keeler et al., 1995). While RGM and PM constitute a small percentage of the total atmospheric Hg, they contribute a significant portion of the deposition of this toxic metal. Studies conducted in the U.S. and in Europe have also shown observing significant spatial gradients in Hg deposition near urban/industrial areas where large anthropogenic Hg sources are located, pointing to the

importance of local anthropogenic influences (Dvonch et al., 1998; Schroeder and Munthe, 1998; Landis and Keeler, 2002; Keeler and Dvonch, 2005). Measurements are needed that can help to validate the model parameterizations used in current Hg models that incorporate gas-particle partitioning which may play an important role in the deposition and transport of PM on global scales. This is particularly important in the upper troposphere where elevated RGM levels would likely result in elevated PM levels at altitude as well.

13.3.5 Evaluation of Emission Inventories

Emission inventories represent a major source of uncertainty in models for Hg, especially on the global scale. Errors and emissions in emission inventories can sometimes be suggested by a careful comparison between model TGM and ensembles of measured values (Selin et al., 2007). Indeed, recent estimates in south Africa suggest that previous inventories are substantially higher than is supported by data and modeling (Chapter 5; Dabrowski et al., 2008; Selin et al., 2008). Evaluations of emission inventories based on ambient measurements have been made based on inverse modeling techniques (Bergamaschi et al., 2000). These approaches have frequently used satellite measurements and have been used to derive emission estimates for CO (e.g. Bergamaschi et al., 2000; Streets et al., 2006), NO_x (Müller and Stavrakou, 2005) and biogenics (Fu et al., 2007). A summary of these studies can be found in TF-HTAP (2007). Although this type of evaluation typically requires satellite measurements that are not available for Hg, it is possible to derive estimates by using ratios of measured TGM to CO (Weiss-Penzias et al., 2006; 2007). Constraints on the emission rates for CO can be used to develop constraints for Hg emissions.

13.3.6 Evaluation of Past/future Changes and Effectiveness of Control Strategies

Evaluation of past changes in pollutant levels based on a historical record of measurements provides a strong basis for evaluating processes related to pollution control. The historical record can identify changes in emission rates and global ambient concentrations that might otherwise be overlooked. A comparison between model and measured ambient concentrations and/or wet deposition for a historical period (e.g. Selin et al., 2008; Sunderland and Mason, 2007) also provides a direct evaluation of changes in response to control strategies, and an evaluation of the model accurately in representing the change.

Significant information has been obtained from the historical record for pollutants other than Hg. Measurements in remote locations suggest a significant increase in the global background O₃ in the Pacific (Jaffe et al., 2003; Parrish et al., 2004) (see Figure 13.6), and possibly in the Atlantic (Simmonds et al., 2004; Derwent et al., 2007). The observed increase has amounted to 6 ppb (20%) over a 15-year period (Jaffe

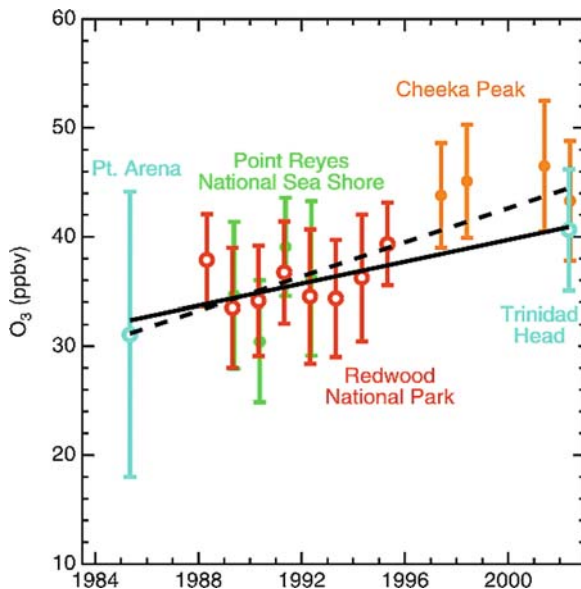


Figure 13.6 Spring mean mixing ratio ± 1 standard deviation for background O_3 at 5 sites representing the marine boundary layer along the U.S. Pacific coast, with linear regression lines. The linear fit to the data from the 4 sea level sites (solid line), yields a slope and year 2000 O_3 mixing ratio (with 95% confidence intervals) of 0.50 ± 0.36 ppbv/year, 39.9 ± 3.3 ppbv, and an r^2 of 0.44. If the higher altitude and latitude Cheeka Peak site is included (dashed line), the calculated slope and year 2000 mixing ratio become 0.78 ± 0.28 ppbv/yr⁻¹, 42.9 ± 2.4 ppbv, and the r^2 is 0.68. (Jaffe et al., 2003)

et al., 2003) and may have a significant impact on air quality in the USA. It is uncertain whether models can identify the reason for the observed increase. Current research also proposes to use measurements and models to evaluate reductions in NO_x emissions in the USA between 2000 and 2004 and their effect on ambient O_3 (Frost et al., 2006). This type of historical evaluation requires sets of measurements that extend over time periods of 10 years or more. Such measurements are rarely available for Hg, especially in terms of its atmospheric chemistry.

13.3.7 Proposed Measurements to Enhance Model Development

A consistent set of measurements made on a global scale would dramatically improve our ability to test and validate global and regional scale atmospheric Hg models. The models would benefit from measurements at surface based sites performed as part of the coordinated network but would also benefit from closely linked intensive aircraft studies. Below is a brief list of some of the most critical measurement needs for model development:

1. A network for monitoring Hg wet deposition at global background sites far from anthropogenic sources as well as sites strategically located in/downwind of various source areas.
2. Surface sites for continuous monitoring of Hg⁰, RGM and PM, along with fundamental gas-phase species: CO, O₃, particulate and possibly reactive nitrogen and sulfate. Sites should include the following:
 - a. Remote locations for tropospheric background condition (e.g. Mt. Bachelor)
 - b. Locations suitable for measuring Asian outflow
 - c. Locations in the USA subject to influence from local sources
 - d. Locations that can examine the reactions in the MBL and the reactions occurring in polar regions, where oxidation of Hg⁰ is enhanced
3. Aircraft-based studies to identify the vertical distribution of Hg and correlations between Hg and other atmospheric species (CO, O₃, aerosols).
4. Aircraft-based studies to evaluate the evolution of Hg⁰, RGM and Hg(p) in plumes downwind of major emission sources, in combination with measurements of gas-phase species (O₃, CO, NO_x, SO_x). Such measurements can be used to resolve the rate of oxidation of Hg⁰ through reaction with O₃ and OH, and evidence for reduction of RGM through reaction with CO or photolysis.
5. Aircraft-based studies to evaluate the effect of cloud processing on ambient Hg, as a basis for assessing the possible reduction of RGM through aqueous reactions.

13.4 Establishment of the Coordinated Global Mercury Monitoring Network (CGMMN)

13.4.1 Key Components of a Coordinated Long-term Network

All global networks must document quality and consistency of routine operations and data treatment through development of protocols for primary and auxiliary measurements, data processing, instrument comparisons, analysis, and data validation. Establishment of a coordinated global Hg monitoring network would benefit greatly from the experience and lessons learned from other global measurement networks, and from the on-going design of regional and national Hg networks (see Chapter 9 and Driscoll et al., 2007). Additionally, climate change research and studies of atmospheric CO₂ and carbon cycling have taught us valuable lessons about what is needed to initiate and maintain effective, reliable networks for observing the chemical state of the atmosphere. As suggested by Driscoll et al. (2007), some of the keys in establishing a successful global network include:

1. Commitment to long-term Hg data collection. Maintaining high-quality, long-term measurement programs for atmospheric Hg requires vision, governmental and international support. There is a need to ensure that the support of observations

is adequate to prevent breaks in the data record. Similarly, mechanisms are needed to provide support for development and validation of new instrumentation and its deployment in the field, which can often take many years.

2. **Calibration.** Inadequate calibration of instruments in a measurement program limits the value of observations for understanding global atmospheric changes. Absolute calibration is critical for calculating the budgets and lifetimes of different chemical species. Relative calibration is essential in applications that require the use of observations from multiple measurement stations or networks. The goal should be to calibrate each species with an absolute accuracy approaching the analytical precision of the measurement technique.
3. **Measurement/Analytical Quality Control/Quality Assurance.** If a quality assurance/quality control structure has not been established or is inadequately funded for a particular measurement program, then the uncertainties associated with the measurements may render them unusable for trend analysis and model evaluation, and thus the collection efforts are wasted. Standardized quality assurance criteria are especially important in efforts to integrate data from multiple observational programs.
4. **Collaboration among researchers with different missions but similar data needs.** Each type of measurement has limitations and is most useful when it can be meaningfully combined with other types of data. Effective coordination among programs with related observational needs can avoid redundant data collection efforts or data gaps that occur when individual programs lack the resources to adequately support continued observational efforts. For example, coordination of ambient Hg measurements with plant uptake or terrestrial cycling can aid both the air quality and biological cycling research communities.
5. **Institutional and Personnel Requirements.** Experience has shown that maintaining and advancing long-term observational science in atmospheric chemistry depends primarily on highly qualified and dedicated individuals. Attracting such individuals requires strong educational programs and promising career opportunities. Having more than one laboratory striving for the same goal is all the most effective way to assure that the highest quality observations will be made (i.e., all key species should be measured by more than one research group). The complexity in making speciated Hg measurements mandates that well-trained operators be identified for this task.

13.4.2 Mercury Measurement Methods

There are a relatively small number of reliable methods that have been developed for the measurement of atmospheric Hg in its various forms. Examples of the sampling and analysis approaches for total gaseous Hg and particulate bound Hg can be found in the literature (e.g. Keeler et al. 1995; Landis et al. 2002). These manual approaches give reliable Hg data but require more operational time and laboratory analysis. More recent advancements have led to the development of field instruments that sample and analyze the concentration of Hg in the gaseous phase and

that fraction associated with fine particulate material. These methods, while not quite at the stage of being routine field instruments, have added greatly to our fundamental knowledge of the behavior of Hg species and its deposition. A brief description of various measurement and analytical methods can be found in Driscoll et al. 2007. Here, a brief description of the type of the ambient Hg instrumentation that would be needed for a global Hg network is described. Continuous instruments that provide equivalent information on the time-scale of minutes to hours are important for a detailed study of Hg transport and chemistry.

Simultaneous measurements of Hg^0 , RGM and PM ($2.5 \mu\text{m}$) can be performed using a Tekran® 2537A/1130/1135 automated Hg measurement system (Tekran Inc., Ontario, Canada). Studies have reported that this system provides reliable data in several intercomparison studies on Hg measurements (Munthe et al., 2001; Landis et al., 2002). The Tekran system measures all three Hg species in a semi-continuous fashion with a total of 12 sample cycles performed within a 24-hour period. Each complete single sample cycle consists of a 1-hour sampling period and a 1-hour desorbing period. The four major parts of the system: Model 2537A analyzer, Model 1130 pump module, Model 1130 denuder module, and Model 1135 particulate module, work in concert through a program installed in the Model 1130 controller.

During sampling, ambient air drawn at a flow rate of 10 liters per minute (L min^{-1}) first passes through a denuder housed in the Model 1130 denuder module. RGM in the air stream is collected by the potassium chloride (KCl) coating of the denuder with a diffusion coefficient $> 0.1 \text{ cm}^2 \text{ s}^{-1}$ (Poissant et al., 2005). The air stream continuously travels to a regenerable particulate filter (RPF) assembly located within the Model 1135. Particulate Hg ($2.5 \mu\text{m}$) in the air stream is captured by a unique quartz filter disk, which resides in the RPF assembly. Any Hg^0 left in the air stream is then directed into the Model 2537A analyzer at a rate of 1 L min^{-1} , while the remaining 9 L min^{-1} is vented out through the Model 1130 pump module.

The Model 2537A is equipped with a pair of gold cartridges which allow alternate sampling and detection of Hg using Cold Vapor Atomic Fluorescence Spectrometry (CVAFS) at a wavelength of 253.7 nm. During the sampling period, Hg^0 is measured and detected every five minutes while RGM and PM are only collected but not measured. A total of twelve readings of Hg^0 concentrations are made in the sampling hour. During the desorbing period, PM was detected in three consecutive 5-minute intervals. The sum of these three 5-minute readings is the total PM collected during the sampling hour. Similarly, the sum of the three 5-minute readings during the denuder heating is the total RGM collected during the sampling hour.

The 10 L min^{-1} flow rate at the inlet corresponding to a standard temperature ($0 \text{ }^\circ\text{C}$) and pressure of 1 atmosphere (STP) was drawn together by the Model 2537A (1 L min^{-1}) and the Model 1130 denuder pump module (9 L min^{-1}). The flow rate and the design of the inlet insure that only particles with aerodynamic diameters $2.5 \mu\text{m}$ continue to the next stage of the sample system, while the coarse fraction ($>2.5 \mu\text{m}$) of the particles are removed by aerodynamic impaction onto a glass impactor plate housed inside the inlet glass-ware (Landis et al., 2002). A heating boot wrapped around the inlet keeps the inlet at $50 \text{ }^\circ\text{C}$ during the sampling

period and at 65 °C during the desorbing period to prevent condensation problems. The RPF-assembly and the denuder are both kept at 50 °C during the sampling period, and are heated to 800 °C and 500 °C during the desorbing period, respectively. Throughout the whole 2-hour sample cycle, the sample air line and the zero air line are kept at 50 °C, while the case of Model 1130 denuder module and Model 1135 module are kept at 35 °C.

The measurement of Hg associated with coarse fraction (>2.5 μm) particles has been performed to date only using manual methods and over longer time intervals than that available using a system such as the Tekran speciation system. In source regions and in coastal regions the measurement of size-segregated particulate Hg is critical to understanding the loading of Hg to terrestrial and coastal ecosystems. Since the deposition velocities of the larger fraction Hg are an order of magnitude greater than the fine fraction Hg, the dry deposition of these large particles is likely to dominate the Hg flux to the surface. More research and development is required before a continuous approach for coarse particle Hg could be deployed in monitoring network. Initially, it is recommended that manual approaches be employed to develop the first order estimate of the importance of the coarse particles in the chemistry and deposition of Hg at different sites around the globe.

13.5 Coordinated Monitoring and Modelling

Integrated measurement programs form the core component of the overall research framework needed for the study of global air quality change. Models also represent a key component of a global research framework, as they are able to play many important roles such as: helping to determine the optimal locations for long-term observational sites and short-term process studies, in order to maximize the usefulness of the data collected; assimilating the observational data acquired from different monitoring systems and helping to place isolated measurements in a larger context; and providing simulations of future Hg trends, fluxes, and coupling with water quality changes. Careful integration of various types of models, modeling tools, and observations will be extremely important in the future. Atmospheric process models can be incorporated into regional-scale models to provide detailed representation of critical chemical and surface processes. Similarly, regional models are embedded in global models to increase the spatial and temporal resolution in areas with sensitive watersheds. Chapter 16 addresses some of these issues in more detail.

Coordinating measurements among various networks, with airborne platforms, and into other special studies, and integrating these measurements with detailed modeling studies presents an immensely complex research challenge. The CGMMN must go beyond model evaluation via comparison with observations/measurements. Model-observation comparisons can elucidate which models might be in error but do not provide information on which model processes are causing the error in large scale simulations. In addition, uncertainties in current Hg measurements can some-

times make results inconclusive. Therefore a comprehensive comparison to multiple types of observations/measurements is needed, and these comparisons should be defined a priori to provide information about the performance of processes in models. This is often difficult as the modeling community often may not understand the technical details of the Hg monitoring and analysis, or what data quality entails and uncertainties actually mean.

Currently, there is a lack of a centralized, standardized observational database that includes information on Hg data quality, data uncertainties and other measurement details. Matching the spatial and temporal scales of atmospheric model estimates to the measurements will ensure that meaningful comparisons can be performed. Coordination of the monitoring network with the global and regional modeling community can help to enhance the model-measurement comparisons and help identify key parameters that need to be measured in the network and at what spatial scales.

13.5.1 Importance of Establishing Boundary Conditions

The North American Mercury Model Intercomparison Study (NAMMIS) was conducted to provide guidance to the research community regarding which scientific process uncertainties are contributing most to the observed discrepancies in model simulations of Hg deposition. As a starting point each regional-scale model used the same inputs for initial (IC) and boundary conditions (BC), meteorology and emissions. The three IC/BC data sets were each developed from simulations of one of three global-scale atmospheric Hg models, the Chemical Transport Model (CTM) adapted for Hg (Shia et al., 1999; Seigneur et al., 2001), the GEOS-Chem model adapted for Hg (Yantosca, 2005; Selin et al., 2007), or the Global-Regional Atmospheric Heavy Metal (GRAHM) model (Dastoor and Larocque; 2004; Ariya et al., 2004). In addition, each regional-scale model uses the same horizontal modeling domain.

The study was conducted to, in part, separate the effects of input data and scientific process treatments within each model so they can be better understood. The model intercomparison showed that the models were sensitive to changes in Hg species concentrations at the boundary of the grid, and the lack of observations of Hg species severely limits our ability to evaluate the accuracy of the global model estimates for the boundary conditions, which varied significantly from one model to another. The observed model sensitivity also clearly suggests that global-scale transport is critical in regional-scale assessments. However, the magnitudes on the estimated wet deposition across North America varied significantly using the boundary conditions estimated using the three different models. It was clear from the study (see Figure 13.7) observations of Hg⁰, RGM and Hg(p) are needed at all levels of the troposphere, especially along the western boundary of the North American continent. The model evaluations performed were thought to be largely subjective due to the lack of observation of the Hg species, especially aloft (Bullock, 2007).

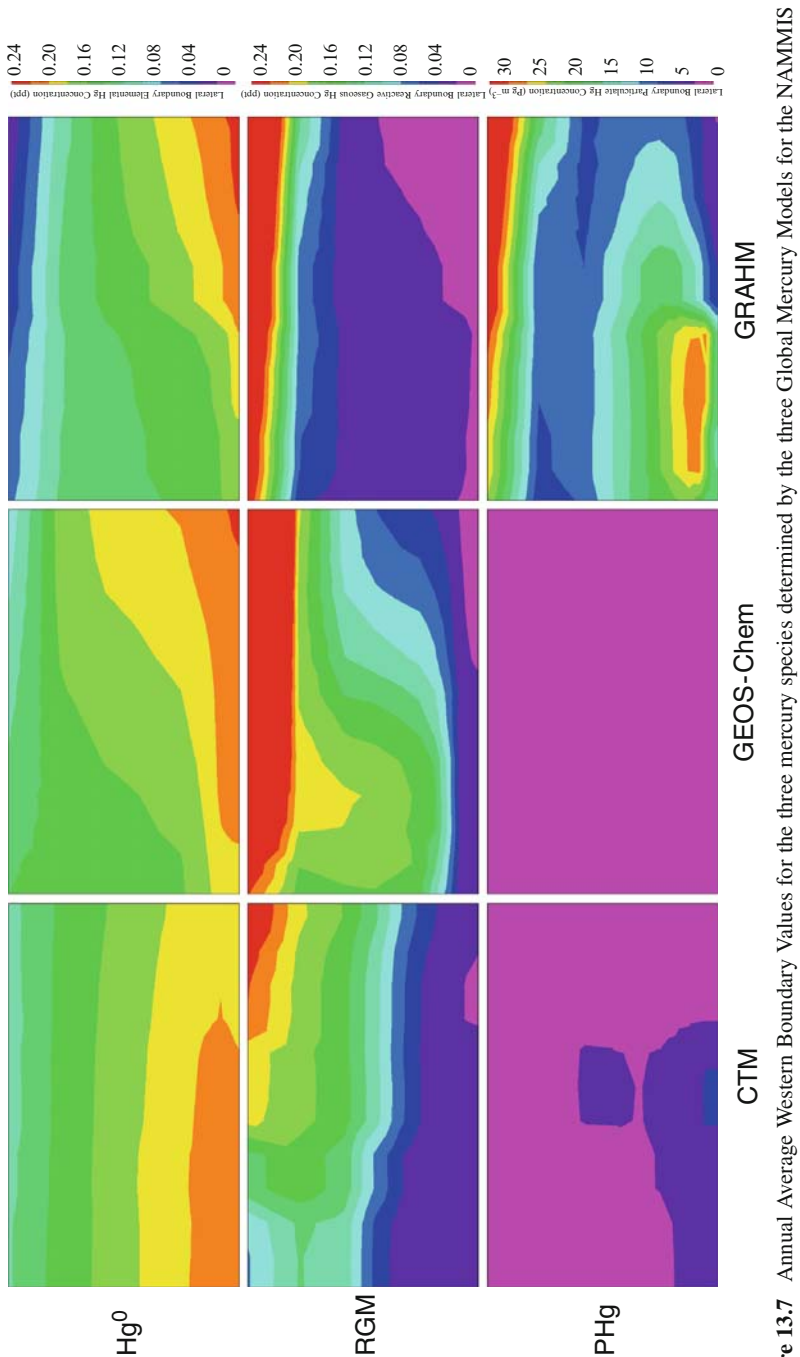


Figure 13.7 Annual Average Western Boundary Values for the three mercury species determined by the three Global Mercury Models for the NAMMIS

13.5.2 Identification of Key Measurements Parameters and Species

Reliably modeling the transport, transformation, and deposition of atmospheric Hg and elucidating the importance of local, regional, and global emission sources is currently limited because of uncertainties in its atmospheric chemistry (Sillman et al. 2007; Chapter 14). While Hg in the atmosphere is dominated by Hg⁰ (Schroeder and Munthe, 1998), it is the RGM which is thought to be most important for wet and dry deposition. Elevated levels of RGM are typically associated with direct emissions from localized anthropogenic sources, but can also be produced by photochemical conversion from Hg⁰ (Liu et al. 2007).

Ambient gaseous Hg species are affected by gas phase and aqueous photochemical reactions that involve a wide range of species (O₃, OH, Cl, Br and sulfates). Modeling the transport and transformation of Hg in the atmosphere is a challenge because it involves processes on widely different spatial and temporal scales. Deposition of Hg is affected by localized convective events, and processing by small-scale convective clouds can also affect photochemistry. Photochemical conversion from Hg⁰ to RGM also results in the formation of TPM, which frequently occurs as part of multi-species conglomerates. Particulate bound Hg in the atmosphere has a bi-modal distribution with a significant fraction of the mass in the >2.5 μm size range (Keeler et al. 1995)

13.5.3 Four-D Data Assimilation

Development must continue on data assimilation methods for weather and climate prediction. They have led to remarkable progress in estimating global water and energy fluxes. Applying the same techniques to biogeochemistry can yield quantitative data for variables that have heretofore been unavailable. Significant progress has been made in validating physical models and in analyzing how calibration can improve their performance. Improvements in modeling have also been directed to problems of water management (e.g., Wood et al., 1993).

Air quality monitoring networks provide extensive ambient measurements of gaseous and particulate pollutant species. Most air quality monitoring sites are sited in populated areas, and are designed to determine whether or not the area is in compliance with national ambient air quality standards. There has been a lack of air monitoring sites across the globe that allow detailed investigation of long-range transport or that provide trends in background concentrations. Trends in pollutants such as ozone in particular are difficult to assess because changes due to anthropogenic forcing are often confounded by natural variations.

Figures 13.8 show comparison between model ambient RGM and measured values from the aircraft flights described in section 2.6. Figure 13.8 shows the variation of RGM with altitude in the model for the 5 d that correspond with measurements

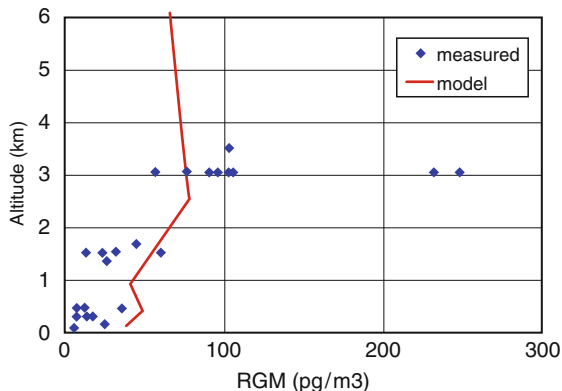


Figure 13.8 Measured RGM (pg/m^3) versus altitude (km) from aircraft measurements over the Atlantic Ocean off the coast of south Florida during June 2000 (points). The line represents model RGM versus altitude, based on an average of model results during the afternoon on the 5 d (9, 12, 14, 25 and 26 June) that coincide with measurements (After Sillman et al. 2007)

(9, 12, 14, 25 and 26 June, always at 1700 LT). Figure 13.8 also shows measured RGM versus altitude for the full ensemble of measurements during June 2000, including days not represented by the model.

The full set of measurements is included here in order to show a complete picture of the observed variation with height. Results show that the model is consistent with measurements in many aspects, although there are also significant discrepancies. RGM increases with altitude from 0 to 3 km in both the model and in the measured ensemble. The rate of increase versus altitude is steeper for the ensemble of measurements than for the model, but the comparison is not extensive enough to show whether this is a consistent trend. Individual vertical profiles of RGM in the model sometimes show a complex layered pattern, reflecting cloud layers at various elevations, but the measurements represent flight path averages and cannot show this type of detail.

13.5.4 Observation-based Apportionment Methods for Emission Inventory Reconciliation

Table 13.1 presents data from the U.S. EPA emissions inventory for point sources within the SoFAMMS study domain developed from a national Hg emissions database (USEPA, 1998). Municipal waste incineration was estimated to be the largest Hg emission source type in south Florida. Municipal waste incineration was found to be the dominant source of Hg wet deposited to Everglades sites during the intensive study. An evaluation of the robustness of the Hg source apportionment was reported

Table 13.1 Mercury emissions inventory for Broward and Dade County, Florida USA

		U.S. EPA estimated Hg emission (<i>kg yr⁻¹</i>)	Revised Hg emission (from this study) (<i>kg yr⁻¹</i>)	Receptor model Hg source apportionment (% of total)
Municipal waste	Dade	1176.35		
	Broward	1125.64		
	total	2301.99	508 ± 101	57 ± 7
Medical waste	Dade	22.62		
	Broward	2.08		
	total	24.70	268 ± 127	30 ± 14 ^a
Utility	Dade	3.25		
	Broward	7.36		
	total	10.61		
Boilers	Dade	67.50		
	Broward	43.70		
	Total	111.20	130 ± 43 ^b	14 ± 5 ^b

^aDetermined from emissions reconciliation

^bIncludes contributions from utility, industrial, and residential oil boilers.

after a detailed reconciliation between the source based emission inventory, the SoFAMMS stack testing data, and the receptor modeling results.

Stack testing was performed at a municipal waste incinerator in Dade County and this incinerator was estimated by the U.S. EPA to account for 50% of total Hg emissions from all municipal waste incinerators in Dade and Broward Counties (USEPA, 1998). Source testing performed during SoFAMMS indicated that emissions of Hg from this facility may have been overestimated in the U.S. EPA emissions inventory by a factor of 4. Although it was estimated in the emission inventory that 1156.1 kg yr⁻¹ Hg were emitted from this municipal waste incinerator, source measurements determined this value to be much lower at 255.0 (50.5 kg yr⁻¹ (Stevens et al. 1996)). As a means of re-assessing emissions from all municipal waste incinerators in Dade and Broward Counties, the factor of four over-estimation was assumed to be consistent for the source category. This factor was applied to all four municipal waste incinerators in Dade and Broward Counties, which lowered the total estimate for municipal waste Hg emissions from 2302 to 508 (101 kg yr⁻¹).

Stack emissions testing was performed at the largest medical waste incinerator in Dade County which accounted for 37% of total Hg emissions from all medical waste incinerators in Dade and Broward Counties. Stack testing indicated that emissions of Hg from this facility was likely underestimated in the U.S. EPA emissions inventory by a factor of 10 for this category in south Florida. Although it was estimated in the emission inventory that 9.2 kg yr⁻¹ Hg were emitted from this medical waste incinerator, source measurements determined this value to be much higher at 100.4 (47.6 kg yr⁻¹) (Stevens et al. 1996). Again, assuming this factor to be consistent for the source category, this underestimation factor was applied to all 12 medical waste incinerators in Dade and Broward Counties. This brought the total estimate for medical waste Hg emissions up from 25 to 268 (127 kg yr⁻¹).

The use of observations by Dvonch et al. 1999 revealed that 57% of the Hg wet deposited at the Everglades sites was accounted for by municipal waste incineration. Since nearly all of the Hg emitted from waste incineration sources was measured during the study in a highly soluble RGM form, these emissions should be directly proportional to the measured wet deposition. Therefore, the 57% Hg contribution from municipal waste incineration emissions would correspond to the 508 kg yr⁻¹ Hg estimated to be emitted from municipal waste incinerators within the SoFAMMS study domain. Using this approach, the 268 kg yr⁻¹ Hg estimated to be emitted from medical waste emissions would correspond to a 30 (14%) contribution of Hg wet deposited at the Everglades sites (with the uncertainty estimate derived from the variability in the SoFAMMS medical waste incinerator stack data). It was previously determined that 29% of the Hg measured at the Everglades sites was left unaccounted for by the PCA/MLR receptor modeling approach. Therefore, from the previous analysis, it was estimated that Hg emissions from medical waste incineration sources within the SoFAMMS study domain may account for the 29% of Hg wet deposition at the Everglades sites that was previously left unexplained.

As evidenced by the large degree of uncertainty associated with the apportionment of Hg to medical waste incineration, it was acknowledged that additional sources within the study domain as well as regional sources associated with long-range transport may have contributed to the Hg deposited and could be responsible for a portion of the deposition unaccounted for by the PCA/MLR model. Although the multivariate model did not identify any additional significant source(s) of the remaining (29%) Hg, a number of smaller sources that did not significantly add to the variance in the data set may have contributed to the measured deposition. However, like the medical waste incinerators, they were not traceable using the methods employed in this study.

Mercury stack testing was not performed at oil combustion sources during SoFAMMS. However, the emission/deposition relationship established above was also used to predict Hg emissions from utility, industrial, and residential boilers within the SoFAMMS domain. The 14% of Hg in precipitation at Everglades sites determined from PCA/MLR analysis to be contributed from oil combustion sources would equate to an emission of 130 (43 kg yr⁻¹) Hg from oil boilers. This estimated value of Hg emitted is in agreement with the 122 kg yr⁻¹ Hg that was calculated by the U.S. EPA to be emitted from oil combustion associated with utility, industrial, and residential boilers within the SoFAMMS study domain. However, since previous source tests of fossil fuel combustion sources within the United States have indicated the ratio of Hg^(II)/Hg^(total) in emissions to be much less than 0.5, these source reconciliation results suggest that either the oil combustion sources in south Florida are emitting a much greater amount of total Hg or that they are simply emitting a much higher percentage of Hg^(II) than previous estimates suggested. Lastly, it was estimated that 1.8 kg day⁻¹ Hg, on average, is wet deposited to the Florida Everglades during the spring and summer seasons. The revised Hg emissions inventory, calculated using the actual emissions measured at sources in south Florida during SoFAMMS, indicated that 2.5 (0.5 kg day⁻¹) Hg was emitted from municipal waste, medical waste, and oil combustion sources in Dade and Broward Counties alone.

Therefore, enough Hg was emitted in these two counties alone, which was measured during the study in a soluble Hg^(II) form that is easily incorporated into cloud droplets, to account for the Hg wet deposited to the entire Florida Everglades.

13.5.5 Case Study of Coordinated Measurement/Modeling in the Mediterranean

Both box model and regional model studies have been carried out for the Mediterranean region to study the Hg cycle between the sea surface and the atmosphere. The models were used to elucidate the chemical mechanisms which oxidise Hg in the marine boundary layer (MBL) and to estimate both Hg deposition and re-emission. These modeling studies made use of data obtained during measurement campaigns performed as part of three EU funded projects (MAMCS, MOE and MERCYMS). The measurement campaigns of two and four weeks were performed in each project (one each season). This relatively sparse database of measurements was supplemented by both atmospheric and aquatic measurements performed aboard the Italian CNR *R.V. Urania*. More recently two monitoring stations, one in the Calabria mountains, and the other on the Tyrrhenian coast of Calabria, have come on-line and provide continuous measurement data for Hg and ancillary pollutants. Using the MECAWEx model (Hedgecock, et al. 2006) the twelve-month period during which the four MAMCS measurement campaigns (one each season) were performed was simulated. The simulation results were in reasonable to good agreement

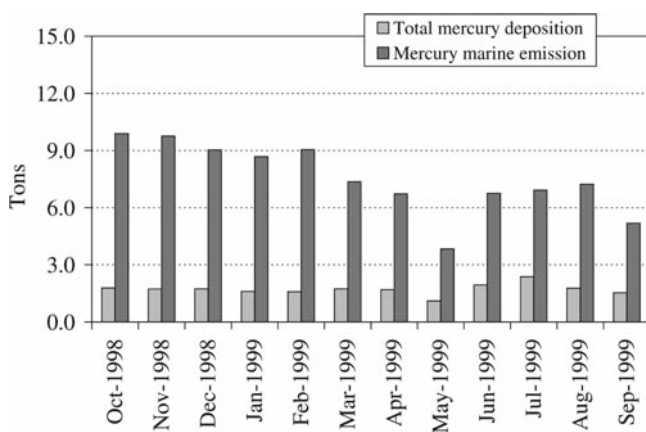


Figure 13.9 Calculated monthly total deposition and evasion of mercury (1 ton=1Mg) to and from the surface of the Mediterranean Sea during the MAMCS campaign (Hedgecock et al. 2006)

with the total Hg observed at the five measurement sites, and allowed estimates to be made of the annual deposition to and emission from the surface of the Mediterranean Sea (Figures 13.9 and 13.10).

Further studies were performed comparing MECAWEx output with the results obtained from research cruises aboard the R.V. *Urania*, (the Med-Oceanor campaigns) which added another dimension to the quality of the comparison between model and measurements because $\text{Hg}_{(g)}^0$, RGM and TPM were measured. The other benefit that ship board measurements have is that the measurements are performed in what in the model is the first layer of the atmosphere and that which is directly influenced by the parametrisation employed to calculate the evasive flux from the sea surface, Figure 13.11.

The only measured data available for Hg deposition within the modelling domain at present is from some of the EMEP stations in northern Europe. These data, which are mostly available as monthly totals, were used to validate the model results, Figure 13.12. It would be extremely useful however for modellers to have Hg in precipitation data available on an event basis as this really would illustrate the model's skill in reproducing Hg deposition fields.

The results from the oceanographic cruises were also studied using a photochemical box model, which uses a much more complex chemical scheme than MECAWEx, including as it does both sea salt and non-sea-salt sulphate aerosol phases in order to simulate the release of reactive halogen containing compounds from aerosol particles, (Hedgecock, et al. 2005). The studies suggested that the cycling of Hg emitted from the sea surface could be quite rapid given the appropriate meteorological conditions.

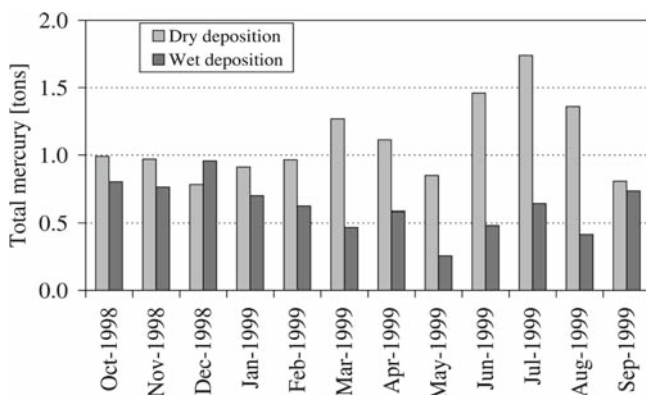


Figure 13.10 Calculated monthly dry and wet deposition (1 ton=1Mg) to the surface of the Mediterranean Sea during the MAMCS campaign (Hedgecock et al. 2006)

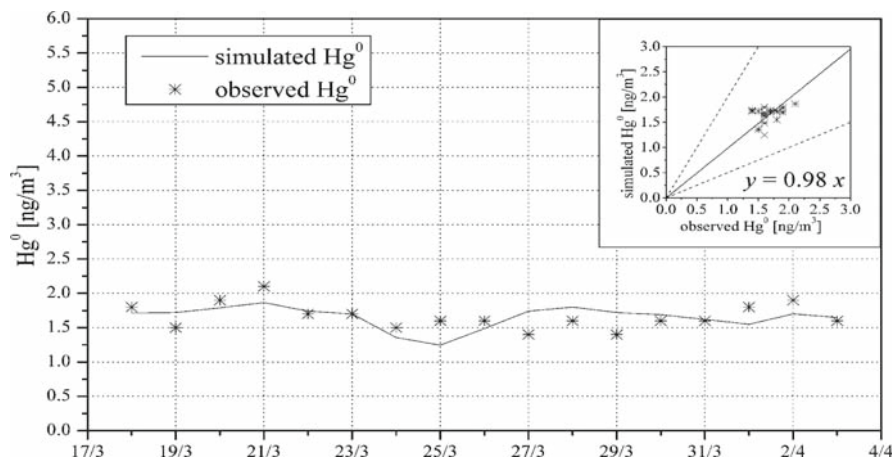


Figure 13.11 The measured and calculated $Hg^0_{(g)}$ concentration during the Med-Oceanor 2004 oceanographic campaign (Hedgecock et al. 2006)

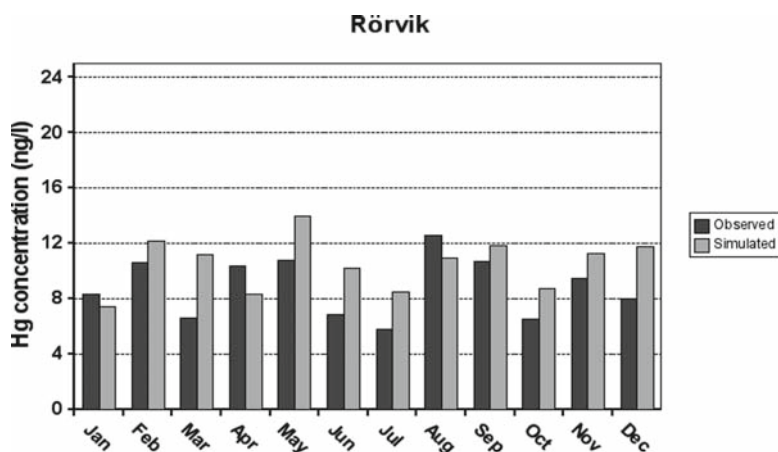


Figure 13.12 Comparison of monthly average Hg concentration in rain for the EMEP site at Rörvik during 2000 (Pirrone et al., 2008)

However, notwithstanding the progress made in the understanding of Hg cycling in the MBL and the ability to reproduce reasonably TGM values over a region as large as the Mediterranean, there remain some uncertainties which cannot be addressed using a measurement campaign approach. The hourly, daily and monthly variation in TGM does not actually cover a very wide range of values; this makes it difficult not only to be certain that the model is reproducing atmospheric transport and transformation phenomena accurately, but it also makes statistical analyses of

the simulated vs. observed results less easy to interpret. As regional Hg models have improved over the years it has become clear that global models are required to provide time-dependent boundary conditions, as discussed earlier in this chapter. The results obtained with MECAWEx showed that, even over a domain which covers Europe, the whole of the Mediterranean Sea and a substantial part of N. Africa, the simulated concentration fields at the centre of the domain can still be sensitive to the boundary conditions when transport into the model domain is relatively rapid, for example when there are strong westerlies. During typical Mediterranean anticyclonic summer conditions the boundary conditions play a less significant role due to restricted transport.

Estimating annual deposition and emission fluxes in the case of the Mediterranean is also fraught with uncertainty for two fundamental reasons. Firstly, the model validation over the long term was based on the results from four two week measurement campaigns which measured TGM and not speciated Hg concentrations. Admittedly this situation was improved by the results obtained from the cruises, but the second point of uncertainty is that there are no measurements of deposition fluxes for the Mediterranean region, neither wet nor dry. Dry deposition of Hg is extremely difficult to quantify but Hg in precipitation is regularly measured in some parts of the world.

A majority of the problems discussed above could be resolved by the establishment of a monitoring network, with some monitoring stations measuring speciated Hg compounds and Hg in precipitation. If this were to be done, then with the computing power which is currently available it would be possible to use models much more extensively. Combining models and monitoring data it would provide a more solid base than currently exists for assessing the reliability of emission inventories, assessing atmospheric chemistry parameterisations, quantifying the influence of regional and global sources and therefore also for evaluating the effectiveness of pollution control initiatives and strategies on both local and global scales in combating the impact on ecosystems of Hg deposition.

References

- Ariya P, Dastoor A, Amyot M, Schroeder W, Barrie L, Anlauf K, Raofie F, Ryzhkov A, Davignon D, Lalonde J, Steffen A. 2004. Arctic: A sink for mercury. *Tellus*, 56B: 397–403.
- Banic, S.T. Beauchamp, R.J. Tordon, W.H. Schroeder, A. Steffen, K.A. Anlauf and H.K.T. Wong, Vertical distribution of gaseous elemental mercury in Canada. *J. Geophys. Res.* 108 D9 (2003), p. 4264.
- Bergan et al. (1999). L. Gallardo and H. Rodhe, Mercury in the global troposphere: a three-dimensional model study. *Atmos. Environ.* 33 (1999), pp. 1575–1585.
- Bergan T. and H. Rodhe, Oxidation of elemental mercury in the atmosphere; constraints imposed by global scale modeling, *Journal of Atmospheric Chemistry* 40 (2001), pp. 191–212.
- Bergamaschi, P., R. Hein, M. Heimann, and P.J. Crutzen (2000), Inverse modeling of the global CO cycle 1. Inversion of CO mixing ratios, *J. Geophys. Res.*, 105(D2), 1909–1927.
- Bey, I., D. Jacob, R. Yantosca, J. Logan, B. Field, A. Fiore, Q. Li, H. Liu, L. Mickley, and M. Schultz (2001), Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation, *J. Geophys. Res.*, 106(D19), 23,073–23,096.

- Bullock and Brehme (2002). Atmospheric mercury simulation using the CMAQ model: formulation, description and analysis of wet deposition results. *Atmos. Environ.* 36 (2002), pp. 2135–2146.
- Bullock, R. Jr., Benjey W.G. and Keating, M.H. (1997) The modeling of regional scale atmospheric mercury transport and deposition using RELMAP. In: J.E. Baker, Editor, *Atmospheric Deposition of Contaminants to the Great Lakes and Coastal Waters*, SETAC, Pensacola, FL (1997), pp. 323–347.
- Bullock O.R., Brehme KA. 2002. Atmospheric mercury simulation using the CMAQ model: formulation, description, and analysis of wet deposition results. *Atmospheric Environment*; 36: 2135–2146.
- Bullock O. R., (2007) Braverman T., Chapter 2.2 Application of the CMAQ mercury model for U.S. EPA regulatory support *Developments in Environmental Sciences*, Vol.6 pp. 85–95
- A.P. Dastoor, Cloudiness parameterization and verification in a large-scale atmospheric model. *Tellus* 46A (1994), pp. 615–634.
- Dastoor AP, Larocque Y. 2004. Global circulation of atmospheric mercury: A modeling study. *Atmos. Environ.* 38, 147–161.
- Daum, P. H., L. I. Kleinman, S. R. Springston, L. J. Nunnermacker, Y.-N. Lee, J. Weinstein-Lloyd, J. Zheng, and C. M. Berkowitz (2004), Origin and properties of plumes of high ozone observed during the Texas 2000 Air Quality Study (TexAQ5 2000), *J. Geophys. Res.*, 109, D17306, doi:10.1029/2003JD004311.
- Derwent, R. G., P.G. Simmonds, A.J. Manning and T.G. Spain, Trends over a 20-year period from 1987 to 2007 in surface ozone at the atmospheric research station, Mace Head, Ireland, *Atmos. Environ.*, 41, 9091–9098, 2007.
- Driscoll, C.T., Han, Y.J., Chen, C.Y., Evers, D.C., Lambert, K.F., Holsen, T.M., Kamman, N. Dvonch, J.T., Graney, J.R., Marsik, F.J., Keeler, G.J., Stevens R.K. (1998) An investigation of source–receptor relationships for mercury in south Florida using event precipitation data. *The Science of The Total Environment*, Vol. 213, Issues 1-3, Pages 95–108.
- Dvonch, J.T., Graney, J.R., Keeler, G.J., and Stevens, R.K. Utilization of Elemental Tracers to Source Apportion Mercury in South Florida Precipitation. *Environmental Science and Technology* 33, 4522–4527. 1999.
- Dvonch, J.T., Marsik, F.J. and Keeler, G.J. The Use of WSR-88D Radar Data for Source-Apportionment of Wet-Deposition Measurements from the 1995 SoFAMMS. *Journal of Climate and Applied Meteorology*. 1421–1435, 2005.
- Ebinghaus R, Slemr F. 2000. Aircraft measurements of atmospheric mercury over southern and eastern Germany. *Atmos. Environ.*, 34(6): 895–903.
- Ebinghaus, R, R.M. Tripathi, D. Wallshlager and S.E. Lindberg, Natural and anthropogenic mercury sources and their impact on the air-surface exchange of mercury on regional and global scale. In: R. Ebinghaus et al. *Mercury Contaminated Sites*, Springer, New York (1999), pp. 1–50.
- Fitzgerald, W.F., Lamborg, C.H. and Hammerschmidt, C.R., 2007. Marine biogeochemical cycling of mercury. *Chemical Reviews*, 107(2): 641–662.
- Friedli, H.R. et al., 2004. Mercury in the atmosphere around Japan, Korea, and China as observed during the 2001 ACE-Asia field campaign: Measurements, distributions, sources, and implications. *J. Geophys. Res.-Atmospheres*, 109(D19).
- Frost G. J., et al. (2006), Effects of changing power plant NO x emissions on ozone in the eastern United States: Proof of concept, *J. Geophys. Res.*, 111, D12306, doi:10.1029/2005JD006354.
- Fu, T.-M., D. J. Jacob, P. I. Palmer, K. Chance, Y. X. Wang, B. Barletta, D. R. Blake, J. C. Stanton, and M. J. Pilling (2007), Space-based formaldehyde measurements as constraints on volatile organic compound emissions in east and south Asia and implications for ozone, *J. Geophys. Res.*, 112, D06312, doi:10.1029/2006JD007853.
- Gardfeldt, K., and M. Jonsson, Is Bimolecular Reduction of Hg(II) Complexes Possible in Aqueous Systems of Environmental Importance, *J. Phys. Chem. A.* 107 (22); 4478–4482, 2003.
- Gildemeister, A.E., Keeler, G.J. and Graney, J.R. Source proximity reflected in spatial and temporal variability in particle and vapor phase Hg concentrations in Detroit, MI. *Atmos. Environ.* 38, 5227–5236. 2005.

- Hedgecock, I. M., Trunfio, A., Pirrone, N., Sprovieri, F. (2005) Mercury Chemistry in the MBL: Mediterranean Case and Sensitivity Studies Using the AMCOTS (Atmospheric Mercury Chemistry Over the Sea) Model. *Atmospheric Environment*, 39, 7217–7230.
- Hedgecock, I.M., Pirrone, N., Trunfio, G., Sprovieri, F. (2006) Integrated mercury cycling, transport, and air-water exchange (MECAWEx) model. *Journal of Geophysical Research*, 111 (D20302), doi: 10.1029/2006JD007117.
- Horowitz, L. W., A. M. Fiore, G. P. Milly, R. C. Cohen, A. Perring, P. J. Wooldridge, P. G. Hess, L. K. Emmons, and J.-F. Lamarque (2007), Observational constraints on the chemistry of isoprene nitrates over the eastern United States, *J. Geophys. Res.*, 112, D12S08, doi:10.1029/2006JD007747.
- Hoyer M, Burke J, Keeler G. 1995. Atmospheric sources, transport and deposition of mercury in Michigan: two years of event precipitation. *Water Air Soil Poll.*, 80: 199–208.
- Jaffe, D., H. Price, D. Parrish, A. Goldstein, and J. Harris (2003), Increasing background ozone during spring on the west coast of North America, *Geophys. Res. Lett.*, 30(12), 1613, doi:10.1029/2003GL017024.
- Keeler, G.J., Glinsorn, G., Pirrone, N., 1995 Particulate mercury in the atmosphere: Its significance, transport, transformations and sources. *Water Air Soil Poll.* 80, 159–168.
- Keeler, G.J., Hoyer, M. 1997. Recent measurements of atmospheric mercury in the Great Lakes region. In: *Atmospheric Deposition of Contaminants to the Great Lakes and Coastal Waters*. (Baker JE, editor), SETAC Press, Pensacola, FL, USA, 477pp.
- Keeler, G.J. and Dvonch, J.T. Atmospheric Mercury: A Decade of Observations in the Great Lakes. In: *Dynamics of Mercury Pollution on Regional and Global Scales: Atmospheric Processes and Human Exposures around the World*. N. Pirrone and K. Mahaffey Eds. Kluwer Ltd. 2005.
- Keeler, G.J., Gratz, L. and Al-Wali, K. Influences on the Long-term Atmospheric Mercury Wet Deposition at Underhill, Vermont. *Ecotoxicology*, 14, 71–83. 2005.
- Kellerhals, M., S. Beauchamp, W. Belzer, P. Blanchard, F. Froude, B. Harvey, K. McDonald, M. Pilote, L. Poissant, K. Puckett, B. Schroeder, A. Steffen and R. Tordon, Temporal and spatial variability of total gaseous mercury in Canada: results from the Canadian Atmospheric Mercury Measurement Network (CAMNet). *Atmos. Environ.* 37 7 (2003), pp. 1003–1011.
- Lamborg, C.H. et al., 2002. Modern and historic atmospheric mercury fluxes in both hemispheres: Global and regional mercury cycling implications. *Global Biogeochemical Cycles*, 16(4): art. no.-1104.
- Landis MS, Keeler, GJ. 1997. A critical evaluation of an automatic wet-only precipitation collector for mercury and trace element determinations. *Environ. Sci. Technol.* 31: 2610–2615.
- Landis, M.S., Stevens, R.K., Schaedlich, F., Prestbo, E.M., 2002. Development and characterization of an annular denuder methodology for the measurement of divalent inorganic reactive gaseous mercury in ambient air. *Environ. Sci. Technol.* 36, 3000–30009.
- Lei, W., B. de Foy, M. Zavala, R. Volkamer, and L. T. Molina Characterizing ozone production in the Mexico City Metropolitan Area: a case study using a chemical transport model, *Atmos. Chem. Phys.*, 7, 1347–1366, 2007.
- Li, Q., D.J. Jacob, I. Bey, P.I. Palmer, B.N. Duncan, B.D. Field, R.V. Martin, A.M. Fiore, R.M. Yantosca, D.D. Parrish, P.G. Simmonds, and S.J. Oltmans, Transatlantic transport of pollution and its effects on surface ozone in Europe and North America, *J. Geophys. Res.*, 107, doi: 10.1029/2001JD001422, 2002.
- Lin, C., Pehkonen, S.O., 1999. The chemistry of atmospheric mercury: a review. *Atmos. Environ.* 33, 2067–2079.
- Lin, C.-J., P. Pongprueksa, S. E. Lindberg, S. O. Pehkonen, D. Byun, C. Jang, Scientific uncertainties in atmospheric mercury models I: Model science evaluation, *Atmos. Environ.* 40 (2006) 2911–2928.
- Lin, C.-J., P. Pongprueksa, O.R. Bullock, S.E. Lindberg, S.O. Pehkonen, C. Jang, T. Braverman and T.C. Ho, Scientific uncertainties in atmospheric mercury models II: sensitivity analysis in the CONUS Domain, *Atmos. Environ.* 41 (2007), pp. 6544–6560.
- Liu, B., Keeler, G. J., Dvonch, J. T., Bares, J. A., Lynam, M. M., Marsik, F. J., and Morgan, J.T.: Temporal variability of mercury speciation in urban air, *Atmos. Environ.*, 41, 1911–1923, 2007.

- Logan L.A., et al., (1999), Trends in the vertical distribution of ozone: A comparison of two analyses of ozonesonde data, *J. Geophys. Res.*, 104, D21, 26373–26399.
- Lynam, M.M. and Keeler, G.J. Automated speciated mercury measurements in Michigan, *Environ. Sci. Technol.* 39, 3289–3299, 2005.
- Mason, R.P., Fitzgerald, W.F. and Morel, F.M.M., 1994. The aquatic biogeochemistry of elemental mercury. *Geochim. Cosmochim. Acta*, 58: 3191–3198.
- Mason, R.P. and Sheu, G.R., 2002. Role of the ocean in the global mercury cycle. *Global Biogeochemical Cycles*, 16(4): art. no.-1093.
- Mason, R.R. et al., 2005. Monitoring the response to changing mercury deposition. *Environ. Sci. Technol.*, 39(1): 14A–22A.
- Miller, E.K., Van Arsdale, A., Keeler, G. J., Chalmers, A. Poissant, L. and Kammen, N. Estimation and Mapping of Wet and Dry Mercury Deposition Across Northeastern North America. *Ecotoxicology*, 14, 53–70. 2005.
- Müller, J.F. and T Stavrakou (2005), Inversion of CO and NO_x emissions, *Atmos. Chem. Phys.*, 5, 1157–1186.
- Munthe, J., Wangberg, I., Pirrone, N., Iverfeld, A., Ferrara, R., Ebinghaus, R., Feng., R., Gerdfeldt, K., Keeler, G.J., Lanzillotta, E., Lindberg, S.E., Lu, J. (2001). Intercomparison of Methods for Sampling and Analysis of Atmospheric Mercury Species. *Atmospheric Environment*. Vol. 35, 3007–3017.
- Munson, C., R.K., 2007. Mercury contamination in remote forest and freshwater ecosystems in the northeastern U.S.: sources, transformations and management options. *BioScience* 57 (1)
- Olson, J. R., J. H. Crawford, G. Chen, W. H. Brune, I. C. Faloona, D. Tan, H. Harder, and M. Martinez (2006). A reevaluation of airborne HO_x observations from NASA field campaigns, *J. Geophys. Res.*, 111, D10301, doi:10.1029/2005JD006617.
- Oltmans, S.J., et al., (2006), Long-term changes in tropospheric ozone, *Atmos. Environ.*, 40, 3156–3173.
- Parrish, D. D., et al. (2004), Changes in the photochemical environment of the temperate North Pacific troposphere in response to increased Asian emissions, *J. Geophys. Res.*, 109, D23S18, doi:10.1029/2004JD004978.
- Pai, P. P. Karamchandani and C. Seigneur, Simulation of the regional atmospheric transport and fate of mercury using a comprehensive Eulerian model. *Atmos. Environ.* 31 (1997), pp. 2717–2732.
- Parrish, D. D., J. S. Holloway, M. Trainer, P. C. Murphy, G. L. Forbes, and F. C. Fehsenfeld. Export of North American ozone pollution to the North Atlantic Ocean. *Science*, 259, 1436–1439, 1993.
- Pirrone, N., G. J. Keeler, I. Allegrini (1996). Particle size distributions of atmospheric mercury in urban and rural areas. *Journal of Aerosol Science*, Vol. 27, Suppl. 1, 1996, pp.S13–S14.
- Pleijel K. and J. Munthe, Modelling the atmospheric mercury cycle-chemistry in fog droplet, *Atmospheric Environment* 29 (1995), pp. 1441–1457.
- Pongprueksa, P., C-J. Lin, S.E. Lindberg, C. Jang, T. Braverman, O.R. Bullock, T.C. Ho and H-W. Chu, Scientific uncertainties in atmospheric mercury models III: Boundary and initial conditions, model grid resolution, and Hg^(II) reduction mechanism, *Atmos. Environ.*, 2007, in press, doi:10.1016/j.atmosenv.2007.11.020.
- Poissant L., Pilote, M., Beauvais, C., Constant, P., Zhang, H.H., 2005. A year of continuous measurements of three atmospheric mercury species (GEM, RGM, and Hgp) in southern Quebec, Canada. *Atmos. Environ.* 39, 1275–1287.
- Prospero, J. M., D. L. Savoie, and R. Arimoto, (2003), Long-term record of nss-sulfate and nitrate in aerosols on Midway Island, 1981–2000: Evidence of increased (now decreasing?) anthropogenic emissions from Asia, *Journal Geophysical Research* 108(D1),4019, doi:10.1029/ 2001JD001524.
- Rea, A.W., S.E. Lindberg and G.J. Keeler, Dry deposition and foliar leaching of mercury and selected trace elements in deciduous forest throughfall. *Atmos. Environ.* 35 (2001), pp. 3453–3462.

- Ren, X., et al. (2006), OH, HO₂, and OH reactivity during the PMTACS–NY Whiteface Mountain 2002 campaign: Observations and model comparison, *J. Geophys. Res.*, 111, D10S03, doi:10.1029/2005JD006126.
- Roberts, J. M. et al., (2004), Measurement of peroxy-carboxylic nitric anhydrides (PANs) during the ITCT 2K2 aircraft intensive experiment, *J. Geophys. Res.*, 109(D23S21), doi: 10.1029/2004JD004960.
- Savoie, D.L., R. Arimoto, W.C. Keene, J.M. Prospero, R.A. Duce and J.N. Galloway, (2002), Marine biogenic and anthropogenic contributions to non-sea-salt-sulfate in the marine boundary layer over the North Atlantic, *J. Geophys. Res.*, 107, 4356, doi:1029/2001JD000970.
- Schroeder, W.H., Munthe, J., 1998. Atmospheric mercury --- an overview. *Atmos. Environ.* 32, 809–822.
- Schroeder, W.H. K.G. Anlauf, L.A. Barrie, J.Y. Lu, A. Steffen, D.R. Schneeberger and T. Berg, (1998) Arctic springtime depletion of mercury. *Nature* 394 (1998), pp. 331–332.
- Seigneur C, Karamchandani P, Lohman K, Vijayaraghavan K, Shia R.-L. 2001. Multiscale modeling of the atmospheric fate and transport of mercury. *J. Geophys. Res.* 106(D21), 27,795–27,809.
- Selin, NE, Jacob DJ, Park RJ, Yantosca RM, Strode S, Jaegle L, Jaffe D. 2007. Chemical cycling and deposition of atmospheric mercury: Global constraints from observations. *J. Geophys. Res.* 112: D02308, doi:10.1029/2006JD007450.
- Selin, N.E. et al., 2008. Global 3-D land-ocean-atmosphere model for mercury: present-day vs. preindustrial cycles and anthropogenic enhancement factors for deposition. *Global Biogeochem. Cycles*, Accepted.
- Shia RL, Seigneur C, Pai P, Ko M, Sze ND. 1999. Global simulation of atmospheric mercury concentrations and deposition fluxes. *J. Geophys. Res.* 104(D19), 23,747–23,760.
- Sheu G, Lee C, Lin N. 2007. Measurements of atmospheric mercury at a high elevation site (Lulin Atmospheric Background Station, LABS). Abstract A53C-1350, AGU Fall meeting, San Francisco, 2005.
- Sillman, S., D. He, M. Pippin, P. Daum, L. Kleinman, J. H. Lee and J. Weinstein-Lloyd. Model correlations for ozone, reactive nitrogen and peroxides for Nashville in comparison with measurements: implications for VOC-NO_x sensitivity. *J. Geophys. Res.* 103, 22629–22644, 1998.
- Sillman, S., F. J. Marsik, K. I. Al-Wali, G. J. Keeler, and M. S. Landis (2007), Reactive mercury in the troposphere: Model formation and results for Florida, the northeastern United States, and the Atlantic Ocean, *J. Geophys. Res.*, 112, D23305, doi:10.1029/2006JD008227.
- Simmonds P., R. Derwent, A. Manning, and G. Spain, (2004), Significant growth in surface ozone at Mace Head, Ireland, 1987–2003, *Atmos. Environ.*, 38(28), 4769–4778.
- Slemr, F. et al., 2003. Worldwide trend of atmospheric mercury since 1977. *Geophys. Res. Lett.*, 30(10).
- Slemr (1992). F. Slemr and E. Langer, Increase in global atmospheric concentrations of mercury inferred from measurements over the Atlantic Ocean. *Nature* 355 (1992), pp. 434–437.
- Slemr et al (1995). F. Slemr, W. Junkermann, R.W.H. Schmidt and R. Sladkovic, Indication of change in global and regional trends of atmospheric mercury concentrations. *Geophysical Research Letters* 22 (1995), pp. 2143–2146.
- Stevens, R. K.; Zweidinger, R.; Edgerton, E.; Mayhew, W.; Kellog, R.; Keeler, G. Source Characterization in Support of Modeling the Transport of Mercury Emissions in South Florida. Presented at Measurement of Toxic and Related Air Pollutants Symposium, May 7-9, Research Triangle Park, NC, 1996. (25) Dzubay, T.; Stevens, R.; Lewis, C.; Hern, D.; Courtney, W.; Tesch,
- Streets, D.G., Q. Zhang, L. Wang, K. He, J. Hao, Y. Wu, Y. Tang, and G.R. Carmichael (2006), Revisiting China's CO emissions after the Transport and Chemical Evolution over the Pacific (TRACE-P) mission: Synthesis of inventories, atmospheric modeling, and observations, *J. Geophys. Res.*, 111, D14306.
- Strode, S.A. et al., 2008. Trans-Pacific transport of mercury. *J. Geophys. Res.-Atmospheres*, 113 (D15).

- Sunderland, E.M. and Mason, R.P., 2007. Human impacts on open ocean mercury concentrations. *Global Biogeochem. Cycles*, 21: GB4022, doi:10.1029/2006GB002876.
- Swartzendruber, P.C. et al., 2008. Vertical distribution of mercury, CO, ozone, and aerosol scattering coefficient in the Pacific Northwest during the spring 2006 INTEX-B campaign. *J. Geophys. Res.-Atmospheres*, 113 (D10).
- Talbot, R., Mao, H., Scheuer, E., Dibb, J. and Avery, M., 2007. Total depletion of Hg degrees in the upper troposphere-lower stratosphere. *Geophys. Res. Lett.*, 34 (23).
- Task Force on Hemispheric Transport of Air Pollution (TF-HTAP), Hemispheric Transport of Air Pollution 2007, United Nations Economic Commission for Europe, Air Pollution Studies No. 16, Report number ECE/EB.AIR/94, 2007. Available at [www.htap.org/activities/2007_interim_report/HTAP 2007 EB version.pdf](http://www.htap.org/activities/2007_interim_report/HTAP_2007_EB_version.pdf)
- Trainer, M., D. D. Parrish, M. P. Buhr, R. B. Norton, F. C. Fehsenfeld, K. G. Anlauf, J. W. Bottenheim, Y.Z. Tang, H.A. Wiebe, J.M. Roberts, R.L. Tanner, L. Newman Correlation of ozone with NO_y in photochemically aged air. *J. Geophys. Res.*, 98, 2917–2926, 1993.
- U.S. Environmental Protection Agency. Mercury Study Report to Congress; EPA-452/R-97-003; Office of Air Quality Planning and Standards, Office of Research and Development, U.S. Government Printing Office: Washington, DC, 1998.
- VanArsdale, A., Weiss, J., Keeler, G.J. and Miller, E. Patterns of mercury deposition in northeastern North America (1996-2002). *Ecotoxicology*, 14, 84–101. 2005.
- Weiss-Penzias, P., D. A. Jaffe, P. Swartzendruber, J. B. Dennison, D. Chand, W. Hafner, and E. Prestbo, Observations of Asian air pollution in the free troposphere at Mt. Bachelor Observatory in the spring of 2004, *J. Geophys. Res.*, 110, D10304, doi:10.1029/2005JD006522, 2006.
- Weiss-Penzias, P., D. A. Jaffe, P. Swartzendruber, W. Hafner, D. Chand, and E. Prestbo, Quantifying Asian biomass burning sources of mercury using the Hg/CO ratio in pollution plumes observed at the Mount Bachelor Observatory. Article In-Press, *Atmos. Environ.*, February 2007.
- Woods JS, Martin MD, Naleway CA, Echeverria D. Urinary porphyrin profiles as a biomarker of mercury exposure: studies in dentists with occupational exposure to mercury vapor. *J Toxicol Environ Health*. 1993;40:235–246.
- Yantosca B. 2005. GEOS-Chem v7-03-06 User's Guide, Atmospheric Chemistry Modeling Group, Harvard University, Cambridge, MA, posted 8 November 2005 at www.as.harvard.edu/chemistry/trop/geos/doc/man/index.html.