

Reducing the Uncertainty in Measurement and Understanding of Mercury in the Atmosphere

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Elucidating the extent of mercury in the atmosphere requires deployment of robust and sensitive instruments.



Mercury (Hg), a neurotoxicant, is ubiquitous in the environment and a concern for human health primarily as a result of bioaccumulation in aquatic food chains and resulting fish contamination. At the 1990 first International Conference on Mercury as a Global Pollutant, the importance of the atmosphere as source of Hg to ecosystems was identified and later poignantly expressed by Lindqvist et al. (1), “Fish

from low productive lakes, even in remote areas, have been found to have a high Hg content. This pollution problem cannot be connected to single Hg discharges but is due to more widespread air pollution and long-range transport of pollutants.” The currently accepted paradigm is that via the atmospheric pathway, Hg is distributed globally and Hg released from one country has the potential to influence (fish) Hg concentrations in another. Although the atmosphere is a small reservoir of Hg, relative to that contained within the ocean and continents (Figure 1), the continued recycling of Hg between the air and terrestrial surfaces and the potential for air concentrations to increase as the world develops economically, suggests that Hg inputs to pristine ecosystems will persevere into the future. The concern regarding this pollutant is demonstrated by recent initiatives by the United Nations Environmental Program (2), the U.S. National Academy of Sciences (3), and an international consortium focused on long-range transport of air pollution (4).

Over the past 15 years there have been significant advances in our knowledge regarding atmospheric Hg sources and concentrations (2). However, there are still significant gaps in our understanding of the Hg biogeochemical cycle with respect to atmospheric chemistry and distribution, the relative magnitude of specific sources and sinks, and the ultimate fate of Hg once emitted from a specific source. In September 2008 a group of Hg experts met at the University of Washington to assess the current capabilities for measurement of atmospheric Hg concentrations and fluxes, define the uncertainties associated with these methods, and to develop a set of recommendations for future research. This paper summarizes major discussion topics (see Supporting Information (SI) for workshop attendees and presentation topics).

Hg in the Atmosphere. Hg in the air is measured as three operationally defined forms: gaseous elemental Hg (GEM), reactive gaseous or gaseous oxidized Hg (RGM or GOM, e.g., HgO, HgCl₂, HgBr₂, Hg(OH)₂), and particle-bound Hg (PHg), with the sum of GEM and GOM designated as total gaseous Hg (TGM). GEM is ubiquitous in the atmosphere reservoir and derived from a multitude of anthropogenic and natural sources. A component of GEM in the air is legacy Hg, or that emitted from a natural or anthropogenic source in the past remaining in the active Hg pool and cycled between the earth’s surfaces and the atmosphere (Figure 1). This recycling between the air and terrestrial and aquatic ecosystems facilitates global distribution and makes source attribution challenging.

All forms of Hg may be emitted from anthropogenic sources while natural sources are thought to emit primarily GEM. GEM is the dominant form in the air with GOM and PHg typically <2% of the total. All forms may be deposited and GOM is thought to be more readily deposited to ecosystems. While it is known that GOM compounds can exist in the gas phase, to date there has been no identification of specific chemical forms. In addition to release from anthropogenic point sources, GOM may be formed by reactions with atmospheric oxidants in polar regions, the marine and terrestrial boundary layers, and the free tropo-

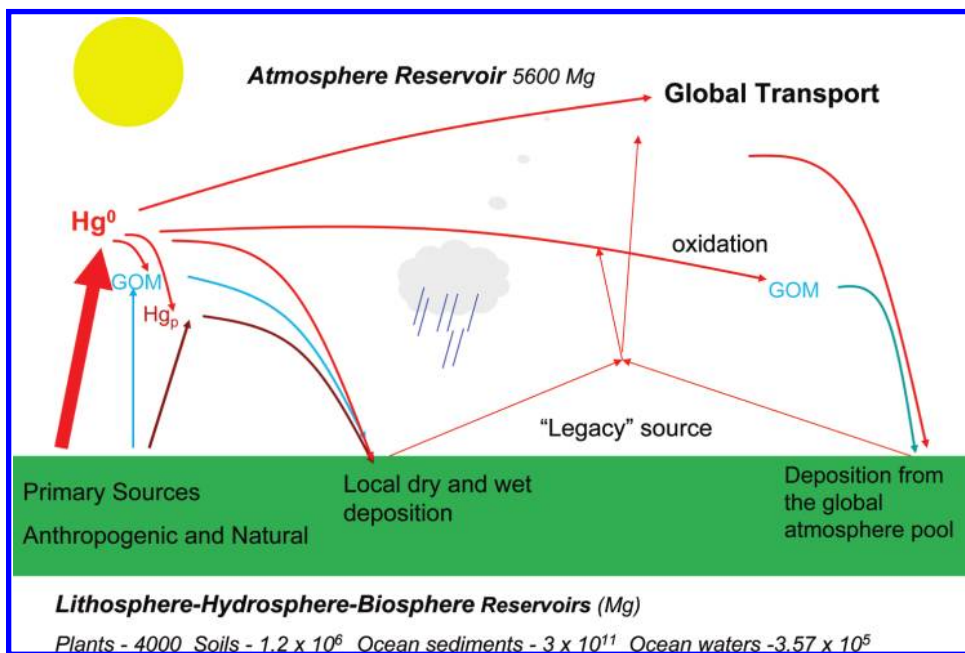


FIGURE 1. Schematic showing the general components and major reservoirs associated with the atmospheric Hg cycle. Note red arrows delineate paths for gaseous elemental Hg (GEM), light blue represents gaseous oxidized Hg (GOM), and purple represents particle-bound Hg (PHg).

sphere (5–9). Modeling and field data have suggested that GOM generated by oxidation of GEM in the free troposphere may be an important input to some ecosystems (8–11). Oxidation of GEM and subsequent deposition is an important means by which Hg derived from any source may impact an area remote from its point of origin.

We have limited understanding of the vertical distribution of the forms of Hg in the atmosphere. TGM has been measured by aircraft in the troposphere with concentrations being variable and the uncertainty in the observations being greater than ground-based detection due to a more challenging calibration environment and a smaller mass of Hg collected (12). Limited data have indicated that PHg concentrations are low ($<5 \text{ pg sm}^{-3}$) (standard m^3) in the free troposphere (9, 13), except when impacted by industrial source regions (e.g., (14)) or fires (15). Only two studies have reported on Hg in the stratosphere: one reporting essentially zero GEM (16), and the other reporting $\sim 50\%$ less than troposphere values (17). The reason for the difference within and between the stratosphere and troposphere concentrations is not clear and may be due to reservoir heterogeneity (8, 9, 11, 18).

Challenges with Current Measurement Methods. Because of the very low concentrations of TGM ($\sim 1.5 \text{ ng sm}^{-3}$) and GOM and PHg ($\sim 10^3$'s of pg sm^{-3}) in the air, measurements are challenging and trace metal clean-handling protocols are required. The standard method applied to measure TGM and operationally defined GEM is collection on a gold (Au) coated substrate followed by thermal desorption and quantification using cold vapor atomic fluorescence spectrometry (CVAFS). Elemental Hg and possibly GOM under certain conditions (see below) are collected using this method. A variety of manufacturers make CVAFS detectors that may be applied toward measurement of atmospheric Hg collected using manual methods: collection on a surface and subsequent separate analysis using CVAFS. For the past >10 years, semicontinuous measurements of atmospheric Hg have been possible using two automated instruments that collect Hg on a Au surface and analyze using CVAFS (Gardis and Tekran 2537A) (19). The Lumex Hg analyzer also continuously measures air concentration but applies differential

Zeeman atomic absorption spectrometry and has a better time resolution than the CVAFS based systems (seconds versus minutes), however it has a higher detection limit (2 versus 0.1 ng m^{-3}) (20). The Tekran and Lumex are commercially available instruments. In methods-comparison studies Hg concentrations (with chemical forms not distinguished) determined with Tekran and Gardis instruments and manual methods compared well (19, 21).

Manual methods for the measurement of GOM and PHg apply denuders and filters, respectively (cf. 21–23). For the former, tubular and annular denuders have been applied as has a mist chamber, with the latter found to have sampling artifacts (23). For particulate Hg a variety of filter systems have been applied (21, 22, 24, 25). Tekran has developed a system (2537A, 1130 and 1135 units) that includes an annular denuder to first collect GOM, followed by a quartz fiber filter to collect PHg. Coarse particles ($>2.5 \mu\text{m}$) are typically removed with an impactor prior to entering the measurement system. Since GOM and PHg concentrations are present at much lower concentrations than GEM (pg sm^{-3}) longer collection times (one to several hours) are required. Environment Canada (S. Steffan, personal communication) and the Mercury Deposition Network (26) have developed Standard Operating Procedures for this instrument.

Measurement Limitations. Currently, there is some disagreement as to whether collection of gaseous Hg using a Au trap quantifies TGM or GEM. Tests suggest that under certain conditions (dry air) and with specific inlet configurations TGM may be collected (17, 27). Whether environmental conditions also play a role in influencing the form of Hg collected has not been systematically investigated.

An annular denuder coated with KCl is currently the primary method applied for collection of GOM; however collection efficiency has only been checked using permeated HgCl_2 compounds (23) and potential interferences due to environmental conditions have not been systematically investigated. An additional method that may be useful in the future involves the use of two Tekran 2537A units with one measuring GEM concentrations and the other quantifying Hg in air passed through a pyrolysis unit thought to convert all GOM to GEM (S. Brooks personal communication). PHg collected on filters may be quantified after digestion or by

thermodesorption using CVAFS. Recent work suggests there are sampling artifacts associated with PHg data collection due to the duration of sampling, temperature, and atmospheric chemistry (25, 28, 29). Interferences and potential sampling artifacts have not been systematically investigated for the Tekran PHg sampling system.

Calibration and Uncertainty. Calibration of CVAFS instruments for GEM is done by injection of air from a saturated Hg vapor source maintained at constant temperature. A vapor pressure versus temperature relationship is then used to determine the injected amount. For the past >20 years, most Hg researchers have applied the equation developed by Dumarey et al. (30, 31). Recently a new vapor pressure curve was published by the National Institute of Science and Technology (NIST) based on data collected in a vacuum (32). This curve differs from the Dumarey equation by approximately 7% at relevant temperatures. Brown et al. (33) reported that the Dumarey equation better predicts the concentration of saturated elemental Hg (Hg^0) vapor in air at ~1 atm. Because of this discrepancy, scientists at NIST (S. Long, personal communication) collected additional data that are consistent with the Dumarey relationship and are finalizing their recommendation.

For most CVAFS systems a linear calibration curve is applied; following this norm, the Tekran 2537A calibration is conducted with two points: 0 and ~100–150 pg. Under typical atmospheric concentrations trap loadings of ~7–10 pg during sampling are common and in situations such as in aircraft sampling these may be even lower. A recent study showed that the calibration begins to show nonlinearity at ~5 pg and that changing system integration parameters or data processing may be necessary to adjust for this (12).

Comparison of Hg concentrations measured by collocated automated instruments and manual collection systems in the field as well as estimates from propagation of errors have shown the uncertainty of GEM or TGM measurements is 10–20% (2 σ) (19, 21, 34–36). The uncertainty in GOM measurements is much greater than that for GEM, with differences of 30–40% reported for collocated GOM measurements using essentially the same method (21, 34, 35).

Future Directions. Alternate methods to measure Hg in the air would be useful, as would clarification of limitations of current measurement methods. Laser methods have been and continue to be investigated for measurement of GEM, however current detection limits are high (37–39). Additionally, the development of passive samplers that could be utilized without electricity, thus in remote areas, would allow us to better understand spatial and temporal distributions of atmospheric Hg. Recently a passive sampler has been developed for GOM (40) and several methods have been applied or are under investigation for GEM or TGM (41, 42). New aircraft methods to measure GEM and GOM with higher time resolution are also being developed (43).

To better understand the sources of GOM, development of a method to identify specific forms of this compound in the air would be useful. Identification of the chemical forms of GOM may be possible based on temperature desorption profiles from KCl or uncoated denuders and/or mass spectrometry, e.g., API-MS/MS/MS; ESI/MS/MS/MS.

More data on the vertical distribution of Hg in the atmosphere and the forms of Hg present are needed. Within the aircraft setting, the inlet system, calibration of the instrument, system flows, and detector sensitivity need to be assessed. Comparison of high-elevation observations made simultaneously with aircraft measurements could be used to help evaluate concentrations.

Hg Fluxes. Accurate measurement of airborne Hg concentrations and speciation are critical for determining air–surface exchange. Dynamic field chambers and micrometeorological methods (Figure 2) provide a measure-

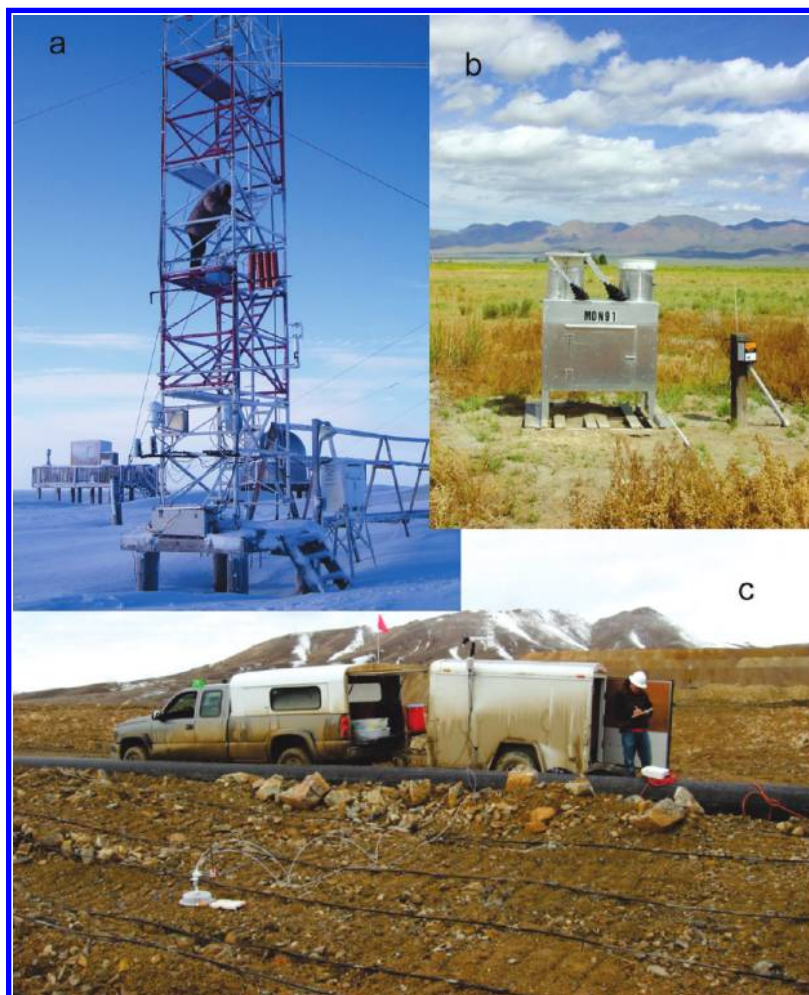
ment of the net gas exchange of Hg between surfaces and the atmosphere. Stable isotope applications have proven to be a useful tool for estimating ecosystem retention and loss of Hg after input by wet deposition (44, 45). Reported gas fluxes associated with most terrestrial and aquatic surfaces are small (0–10 ng m⁻² h⁻¹) but significant when applied to these landscapes that cover large regional and global scales.

For dynamic field chamber measurements, the operating conditions, dimensions, and material have been shown to influence calculated fluxes ((46) and references therein). Field chambers operating conditions also alter surface turbulence and concentration gradients. Since chambers collect data from a limited surface area, the representativeness of the area sampled should be ascertained (Figure 2). Micrometeorological measurements do not disturb the surface–air boundary layer and allow for data collection over a larger surface area; however this method is limited to very specific site criteria (horizontally uniform surface with a homogeneous mass; 47, 48). In application of gradient based micrometeorological methods, determination of flux may be hindered by small concentration differentials and the analytical precision of the air Hg measurements. Application of eddy covariance and relaxed eddy accumulation methods allow for maximizing concentration differentials (Figure 2; (49)). Application of micrometeorological methods requires that a variety of other parameters also be accurately measured. Because long-term (>1 week) data collection is needed to obtain robust results, sampling is often relegated to one stationary location. In contrast, chamber methods are more portable, less labor intensive, less expensive, and require less setup time and monitoring. Comparison of fluxes determined with multiple methods simultaneously is suggested given the limitations.

The above methods are used to measure gaseous fluxes. To do a complete ecosystem mass balance, Hg wet deposition also needs to be quantified. In North America this is done using a standard set of procedures applied by the Mercury Deposition Network (MDN (26); Figure 2). Since recent work has shown that a significant component of the Hg input by wet deposition is re-emitted over a year (44, 45), this sink should not be considered the end point for atmospheric Hg.

In contrast to wet deposition there is no standard method for measurement of dry deposition. All forms of Hg may be dry deposited and this process is influenced by meteorological variables, surface characteristics, and the chemical speciation (50). Research applying surrogate surfaces to quantify dry deposition has been done by several groups ((51) and references therein). These methods may be useful for broad regional networks like MDN; however, results need to be compared to physical measurements. Since these methods apply a uniform surface for deposition, the variability associated with natural surfaces may not be adequately simulated (52). Lastly, since the oceans cover a large fraction of the surface of the earth, understanding air–ocean exchange is important. There are a small number of direct flux observations for marine systems; most often air and dissolved gaseous Hg concentrations along with air and ocean temperatures and wind speed are applied (2).

Future Research Needs. As world energy and resource use increases, Hg emissions will likely see global increase. Because Hg released from one country has the potential to be a component of deposition in another, it is critical that we understand the amount released from natural and anthropogenic sources as well as the potential for transport, deposition, and recycling. To further our knowledge the limitations of the current methods to measure atmospheric Hg need to be systematically addressed. The development and application of alternate methods to validate current results and less expensive, more user-friendly measurement tools that may be applied across broad spatial and temporal



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FIGURE 2. (a) Application of a relaxed eddy accumulation method for the measurement of GOM flux in the Arctic. Photograph from H. Skov (49). (b) Mercury wet deposition sampler located in Paradise Valley, NV at Mercury Deposition Network site MDN NV 02 (noted in (26)). (c) Dynamic flux chamber being applied to measure Hg flux from cyanide heap leach pile Twin Creeks Gold Mine, Nevada (as noted in (46); photograph by Matthieu Miller).

scales would promote better understanding of the Hg releases. The atmospheric chemistry of Hg, the oxidation and reduction pathways, and gas-particle partitioning remain poorly understood: these knowledge gaps impede our ability to understand global cycling. Since Hg is emitted and transported with other atmospheric species, simultaneous collection of ancillary air quality data is necessary. Regular collection of observational data on multiple scales (e.g., surface, aircraft, and satellite) and comparison of observations among research/analysis groups are needed to provide data for validation of model processes and predictions, understand the source-receptor relationships, and understand potential long-term changes in the global Hg cycle. Such knowledge will help inform regulatory actions for reducing the health and environmental impacts of Hg.

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Acknowledgments

The workshop that was the basis for this work was supported by the National Science Foundation Grant 085054 and EPRI. Any opinions, findings, conclusions, or recommendations expressed reflect those of the authors and do not necessarily reflect the views of the National Science Foundation. The authors extend special thanks to Eric Hintsa NSF project manager and to all the workshop participants, listed in the SI, whose participation and discussion helped formulate this review. Lastly, we thank three critical reviewers who pointed out important omissions of information in the original manuscript.

Supporting Information Available

List of the workshop participants and the presentations given. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ES902736K