

Measurement of Atmospheric Mercury: Current Limitations and Suggestions for Paths Forward

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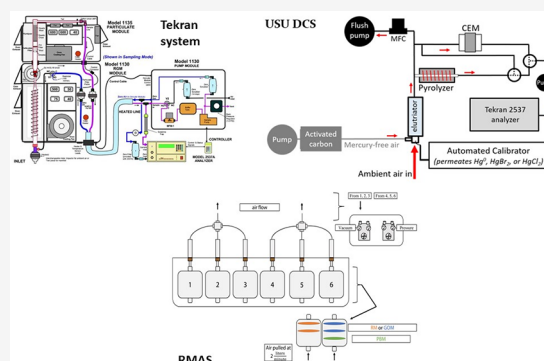
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ABSTRACT: Mercury (Hg) researchers have made progress in understanding atmospheric Hg, especially with respect to oxidized Hg (Hg^{II}) that can represent 2 to 20% of Hg in the atmosphere. Knowledge developed over the past ~10 years has pointed to existing challenges with current methods for measuring atmospheric Hg concentrations and the chemical composition of Hg^{II} compounds. Because of these challenges, atmospheric Hg experts met to discuss limitations of current methods and paths to overcome them considering ongoing research. Major conclusions included that current methods to measure gaseous oxidized and particulate-bound Hg have limitations, and new methods need to be developed to make these measurements more accurate. Developing analytical methods for measurement of Hg^{II} chemistry is challenging. While the ultimate goal is the development of ultrasensitive methods for online detection of Hg^{II} directly from ambient air, in the meantime, new surfaces are needed on which Hg^{II} can be quantitatively collected and from which it can be reversibly desorbed to determine Hg^{II} chemistry. Discussion and identification of current limitations, described here, provide a basis for paths forward. Since the atmosphere is the means by which Hg is globally distributed, accurately calibrated measurements are critical to understanding the Hg biogeochemical cycle.

KEYWORDS: calibration, dual-channel systems, mass spectrometry, monitoring networks, reactive mercury active system



INTRODUCTION

The atmosphere is the primary pathway for the global transport of mercury (Hg).¹ The chemical form of Hg in the atmosphere determines how quickly it is removed through wet or dry deposition.^{2,3} Deposition of atmospheric Hg results in contamination of surface waters and ecosystems,⁴ and can have adverse effects on human and wildlife health.⁵ To monitor and mitigate future effects of global Hg contamination, the Minamata Convention was ratified by 147 countries and entered into force in 2017, with the objective of “protecting human health and the environment from the adverse effects of mercury”.⁶

For scientific understanding and modeling, and to meet the needs of the Convention, it is critical to accurately quantify concentrations of the three main forms of atmospheric Hg: gaseous elemental Hg (GEM, Hg^0); gaseous oxidized Hg (GOM, also denoted Hg^{II} , because it is believed to be almost entirely in the +2 oxidation state);⁷ and particulate-bound Hg (PBM, also believed to be in the +2 oxidation state). Reactive Hg, referred to here as Hg^{II} , is operationally defined as the sum of PBM and GOM.

GEM is taken up by plants through their stomata, assimilated by oxidation, and translocated to the annual growth rings in trees,⁸ resulting in litter and tree fall being a means of GEM deposition to ecosystems.⁹ Isotopic studies showed that some of the Hg^{II} bound on leaves is re-emitted as GEM after photoreduction before leaf fall.¹⁰ GEM is also deposited directly to surfaces, but is readily re-emitted, promoted by sunlight, precipitation, temperature, and interaction of atmospheric ozone with surfaces.^{11–16} GOM and PBM are dry deposited to surfaces, and are removed from the atmosphere in wet deposition. When deposited to foliage, Hg^{II} can also be washed off surfaces to enter ecosystems.¹⁷ When deposited to substrates, Hg^{II} can be methylated in situ,

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Table 1. Methods Used for Measurement of Atmospheric Mercury, Advantages, Limitations, and Improvements Needed

Measurement Method	Advantages	Limitations	Improvements Needed & Comments	Instruments
Gaseous elemental Hg (GEM) Gold trap	Currently, best material for preconcentrating	Expensive Passivates over time	To measure GEM, place a CEM up front To measure TGM, place a thermolyzer up front	Tekran 2537
Cold vapor atomic absorption Sulfur-impregnated carbon	No preconcentration needed Inexpensive Easy to deploy	Only measures GEM Low time resolution (uncertain if adequate precision to monitor subtle trends)	Must be precisely and frequently calibrated Needs to be specially calibrated to measure ambient air More research needed on sampling rates	Lumex MerPAS
Gaseous Hg^{II} KCl denuder		Unequal collection efficiency Biased by humidity, ozone Reduced efficiency over time Requires trained technician Sensitivity dependent on GEM measurement Can be calibrated in the field Rapidly changing concentrations affects measurement	Should be phased out of use	Tekran
Dual-channel system (DCS)	Fast time resolution (10–20 min) Measures Hg ^{II} Inlet system has limitations		Thermolyzer should be regularly calibrated	Currently no standard instrument (USU model under development)
Cation exchange membrane (CEM)	Does not collect GEM Collects RM	Lower recovery than DCS Reactions occur on the membrane surfaces	Tests needed to determine if digestion is complete Surfaces need to be developed that have no potential for reactions and loss and allow for collection at higher flow rates	RMAS
Nylon membrane	Currently the only way to estimate ambient Hg chemistry Allows for thermal desorption Can measure chemistry of Hg ^{II} compounds Can be used to assess GEM release from GOM permeation tubes Potential for fast determination of GOM chemistry Avoids preconcentration	Lower recovery than CEM	Better surfaces need to be developed for Hg chemistry determinations	RMAS
Gas chromatography–mass spectrometry (GC–MS)		Unequal collection efficiency Difficulty getting Hg ^{II} compounds into the instrument Not field deployable Requires preconcentration Not easily field deployed in remote locations	Further research is needed	Currently no standard instrument
Atmospheric pressure chemical ionization–MS (APCI–MS)			Method needs to be developed and tested	Currently no standard instrument
Particulate-bound Hg (PBM)		Currently no method to separate PBM and GOM Cascade impactors Filters	A measurement method is needed	RMAS Filters and collected aerosols collect GOM

and directly or indirectly deposited to water bodies where it can be converted to methylmercury, the Hg form that bioaccumulates in food webs.¹⁸ In addition, knowledge of Hg^{II} chemical makeup is crucial, because this controls the competition between (photo)reduction back to Hg(0) and Hg^{II} dry/wet deposition. Thus, it is important to accurately quantify Hg^{II} concentrations and characterize the chemistry of the compounds and processes responsible for forming them.

The commercial Tekran 2537/1130/1135 instrument (graphical abstract) has been used to obtain a large amount of data on the different forms of atmospheric Hg in the past two decades. However, over the past ~10 years it has become apparent that surfaces in this instrument have artifacts (i.e., the KCl-coated denuder used to collect GOM does not capture all Hg^{II}).^{19–26} Recent research, discussed below, by Allen et al.²⁷ demonstrated that the filter used to collect PBM in the 1135 unit also collects GOM, if not removed by the denuder. GOM and PBM measurements have almost always been uncalibrated, and GEM concentrations measured by co-located instruments occasionally exhibit bias as well,^{19,20} perhaps because of inadequate calibration in the ambient range. To address some of the limitations, new methods have been developed to measure GOM and PBM, and each method has its own strengths and weaknesses.

In October 2023, a National Science Foundation-sponsored workshop, “Measurement of atmospheric mercury: Assessment of new measurement and calibration methods, and development of a path forward”, was held at the University of Nevada, Reno, USA. This event brought together atmospheric Hg experts to discuss what is known about current measurement methods, gaps in current technologies, needs for future measurements, and suggestions for improvements. During this workshop, 26 presentations were given on new and evolving atmospheric Hg measurement methods and monitoring network needs; discussion groups were tasked with summarizing limitations associated with different atmospheric mercury measurements, and brainstorming how to improve measurements. This is a summary of the discussions at the workshop and the collective recommendations for a path forward. There have been some recent review papers on atmospheric Hg;^{28–30} however, this manuscript has a different focus in that it is a critical assessment of atmospheric Hg measurement methods.

■ MEASUREMENTS OF GEM AND TGM

Current Methods. Active and passive methods are used to measure GEM and TGM. The most common active method to measure atmospheric Hg is by pulling air through a gold cartridge, then Hg is desorbed from the cartridge into a cold vapor atomic fluorescence spectrometer (CVAFS) or cold vapor atomic absorption spectrophotometer (CVAAS). The Tekran 2537, the leading unit for measurement, relies on two matched gold cartridges that allow for collection and measurement every 2.5 or 5 min. The estimated uncertainty is 16% for the Tekran 2537B series.³¹ There is no published uncertainty for the 2537X unit. The Lumex instrument, utilizing Zeeman background correction in its CVAAS configuration, can continuously measure GEM at ambient levels without preconcentration. However, an uncertainty analysis has not been published for this instrument. To measure ambient concentrations, this instrument requires additional low-level calibration (e.g., ref 32.). These two instruments have been the primary methods for measuring

atmospheric Hg since 2000. Additionally, measurements of GEM or total gaseous Hg (TGM) using gold cartridges in nonautomated active sampling systems have also been used (cf., ref 33.). With this method, ambient air is first pulled through filters, then directly through a gold cartridge using a small vacuum pump.

Development of passive systems for measurements of GEM or TGM has been investigated in a number of studies (cf., refs 34–36.). Currently, the most commonly applied method consists of a radial symmetry diffusive sampler with the one of choice being the Radiello sampler filled with sulfur-impregnated activated carbon.^{35–39} This method, commercialized as the MerPAS (Tekran Instruments Corp.), has demonstrated that concentrations measured in the Northern Hemisphere were greater than in the Southern Hemisphere, and has recorded gradients in Hg concentrations around contaminated areas.³⁹ Field comparisons of three different passive air samplers demonstrated that the MerPAS performed best, with a precision of 5%.³⁷ Comparison of active and passive samplers across a range of concentrations has shown good comparability.³⁷

New Information and Recommendations. Two major limitations associated with gold cartridge Hg capture is that gold is expensive and becomes passivated over time (Table 1). Gold cartridges are considered consumables in CVAFS Hg instruments, as indicated by technical documents detailing how to clean and replace passivated cartridges. In addition, gold cartridges must be calibrated frequently and rigorously. The importance of calibration cannot be overstated, for two colocated Tekran 2537 units have been reported in some cases to differ by as much as 30%,^{19,20} though variation between instruments is typically on the order of 5 to 10%. In the Tekran 2537 instruments, gold cartridges are calibrated using a one-point calibration at an unrealistically high concentration for ambient air sampling, and the default peak integration method uses peak area, though there has been evidence that using peak height may be more accurate.^{40,41} It was recommended by the workshop participants that there be multiple calibration points for the instrument, including points at concentrations relevant to ambient air, to better calibrate the low range of the instrument. Experiments using a permeation calibrator investigated these concerns.⁴² Automated calibration systems for GEM that can achieve ambient air concentrations and are field-deployable are being developed (see below). The Tekran 2505 (GEM calibration source) is used for GEM calibration, but requires a stable temperature environment to operate properly.

Recent tests using gold cartridges demonstrated efficient collection of HgBr₂, a proxy for GOM compounds, though only 80% was thermally desorbed.⁴² This has also been shown in the past.⁴³ New measurement methods have demonstrated that GOM concentrations can be 2 to 20% of total ambient air Hg concentrations, up to 100% during Hg depletion events, and high concentrations are in the upper Troposphere-lower Stratosphere.^{19,20,44–47} It is recommended, for now, that to measure GEM a cation exchange membrane (CEM) be placed upstream of the gold cartridge for removal of Hg^{II} from the sampling stream. For TGM measurements, a thermal converter at >700 °C should be placed at the front of the sampling line with a particulate filter in front to convert all gaseous Hg compounds to GEM.⁴² It is important that the GOM reduction efficiency of thermal converter designs be tested prior to deployment.⁴² Given limitations associated with the

particulate filters discussed below, with no particulate filter the thermolyzer-based measurement will provide a total atmospheric Hg concentration that includes both PBM and GOM.

Concentrations measured using CEM and nylon membranes from different manufacturers vary significantly in collection efficiency, and particle loading can result in retention of GOM on particulate filters. For example, Allen et al.²⁷ showed with tests using a permeation tube-based calibrator that polytetrafluoroethylene (PTFE) membranes upstream of GEM measurements collected ~4% GOM, while VWR borosilicate glass filters and Whatman borosilicate glass microfiber membranes retained 92 and 62%, respectively. However, PTFE filters preloaded with ambient particles collected 50% of permeated GOM. Thus, currently CEMs are useful for placement in front of gold traps if GEM quantification is the goal, as CEMs do not take up GEM.⁴⁸ When loading CEM with GOM in the laboratory, all GOM is captured, while in the field, breakthrough is typically on the order of 10% (cf., refs 27, 44, 48). Limited data suggest when there is PBM on the CEM, the CEM does not take up GEM.⁴⁹

Concerns regarding the MerPAS method include the low time resolution (>1 month), thus short-term (<2 to 4 week and diel) variability will not be captured. It is unlikely that the low time resolution can be improved due to the method and the analytical detection limit. That said, the MerPAS is designed for long-term monitoring. Factors that are known to affect the sampling rate include temperature, wind speed, and sampler geometry. One uncertainty is whether the published meteorological correction is suitable for all environments, as it was primarily developed using midlatitude data.⁵⁰ Isotopic characterization has demonstrated only GEM is collected on the carbon in the passive samplers.⁵¹ A consensus was not reached regarding whether the MerPAS has the accuracy needed to measure subtle changes in atmospheric Hg concentrations with emission reductions associated with the Minamata Convention, though it is capable of detecting whether major emission sources are eliminated (i.e., artisanal gold mining; cf. ref 39).

For the Lumex instrument, the detector can only detect GEM, but interferences caused by conversion of GOM and PBM to GEM after deposition to inlet filters and other surfaces upstream of the detector, similar to the Tekran 2537 unit, is a possibility. Recent enhancements in sensitivity and tailored calibration settings underscore its capacity for precise low-level measurements.³²

MEASUREMENTS OF GOM AND PBM

Current Methods. KCl-Coated Denuders. KCl-coated denuders have been the predominant method since the 1990s to measure GOM using glass tubes or an annular denuder that induces laminar flow. Captured GOM is then extracted into a solution and directly analyzed or thermally desorbed into a CVAFS detector, respectively.^{52,53} The Tekran 2537/1130/1135 system (graphical abstract) is designed to sample ambient air and collect GOM (1130 unit) on a KCl-coated denuder, followed by collection of PBM on a particulate filter (1135 unit), while measuring GEM (2537 unit) that passes through both the denuder and filter. Then, during a 30 min period, while the system samples Hg-free air, the denuder and particulate filter are sequentially heated, and released Hg goes through a pyrolyzer, then enters the Tekran 2537 unit where Hg⁰ concentrations are determined. KCl-coated denuders in the Tekran system have

been demonstrated to be biased low by up to 50%, due to reactions with ozone that reduce GOM, collection of different Hg compounds with unequal efficiency, passivation due to water vapor, and decreased efficiency over time.^{24,25,54–57} Repetitive heating decreases the collection efficiency, therefore, denuders should not be used for long periods without recoating.⁵² It is important to consider that the denuder performance will vary according to location. For example, in areas where the air is dry with limited ozone and primarily halogenated Hg^{II} compounds, such as Mauna Loa, USA, and Alert, Canada, measured concentrations will better represent actual concentrations (cf. ref 46, 58.). Since different Hg^{II} chemistry and environmental conditions will be present at different locations, bias and collection efficiencies will vary across measurement sites and temporally at individual locations.

Dual-Channel Systems. Dual-channel systems (DCS) in current operation are designed to measure GEM and GOM by filtering out PBM at the inlet (graphical abstract).²⁰ These instruments measure GOM or GOM + PBM based on the principle of alternate sampling of two channels upstream of an instrument that detects GEM (i.e., one or two Tekran 2537s or a Lumex).^{59,60}

The typical DCS makes a GEM measurement with one channel by passing air through a CEM, effectively removing Hg^{II} from air and allowing only GEM to pass to the detector, and the second channel uses a thermal converter to transform all compounds to GEM, allowing for a TGM measurement. GOM or Hg^{II} concentrations (depending on the inlet configuration) are calculated as the difference between the measurements in the two channels.²⁰ A dual-channel instrument developed at Utah State University has ten-minute time resolution with a 1-h average detection limit of about 10 pg m⁻³,⁶¹ and measurement accuracy has been verified with a permeation calibrator using HgBr₂.^{61–63} Efficiency has not been tested for other compounds. In addition, the effects of relative humidity and reactive gases, like O₃, have not been thoroughly tested and an uncertainty analysis is needed for these measurements. Tang et al.⁴⁹ developed a DCS that consisted of the Tekran 2537/1130/1135 system as one channel, and a CEM that was analyzed and Hg⁰ that was measured by the Tekran 2537 as the second channel. The Tekran Hg^{II} concentrations were 20 ± 22 pg m⁻³, while the CEM concentrations were 454 ± 349 pg m⁻³.

It was noted at the workshop that there did not need to be a standard design for the DCS, for this will promote creativity in application of this method. It is, however, necessary to demonstrate that the DCS makes accurate measurements under given operating conditions that are traceable to standards.

Reactive Mercury Active System. The Reactive Mercury Active System (RMAS) uses membranes to measure Hg^{II}, GOM, and PBM concentrations, depending on the configuration of membranes inside the filter cartridge (graphical abstract). With only CEM or nylon membranes in-line, Hg^{II} is measured. It was thought that by placing a PTFE membrane in front of the nylon or CEM that PBM and GOM could be differentiated. We now know this is not entirely true. CEM are digested and analyzed using a modified EPA method 1631 to determine concentrations, while nylon membranes are thermally desorbed to estimate the chemical composition of Hg^{II} compounds through comparison with desorption profiles developed from pure Hg^{II} compounds.⁶⁴ Recent work has

demonstrated that CEM and nylon membranes can be stored at $-20\text{ }^{\circ}\text{C}$ without degradation or transformation of collected GOM for nine months⁶⁵ and up to a year (data not shown).

The RMAS is cost-effective, can be deployed easily, is more accurate than KCl-coated denuders,²⁰ and is currently the only available method that gives information about possible ambient air Hg compound chemistry. This system has provided a step forward in better understanding actual Hg^{II} concentrations by demonstrating that KCl denuder measurements were biased low. Similar to other measurement methods, an uncertainty analysis is needed.

PBM Measurement Systems. PBM is typically collected on filters, such as quartz fiber and polytetrafluoroethylene (PTFE). PBM measurements have been made with instruments that include equipment such as filter cartridges, cascade impactors, and high-volume samplers (cf., 66–68). The latter two allow for size-distributed measurements.

Limitations and Recommendations (Table 1). *KCl-Coated Denuders.* KCl denuder performance generally depends on the chemical forms of Hg^{II} present, and ambient atmospheric chemistry.^{56,57} The low bias can be up to 50%, but varies with location and environmental conditions.⁵⁸ A correction factor could be used to determine how much measured concentrations should be adjusted at different locations based upon site-specific factors, such as the colocated wet deposition measurement and the degree of scavenging of the atmosphere.⁶⁹ Also, the measurements could be co-located with the RMAS or DCS, which could provide a means of determining the low bias for a specific location.²⁰

It was recommended by the workshop participants that alternative methods should be developed, and the use of the KCl denuder should be phased out for ambient air Hg measurements. Some participants suggested that the observations made by the 1130/1135 units may still be useful for determining temporal trends or to determine emissions from sources. If KCl-coated denuders are to be used, it is important to carefully assess uncertainties, particularly those related to recovery. Including recovery considerations in uncertainty evaluations may lead to disproportionately large uncertainties. This could be detrimental for time and spatial trend analyses, as excessively high uncertainties may compromise the reliability of the data. Therefore, a balanced approach is needed to ensure that uncertainties are appropriately managed, avoiding potential challenges in meaningful time and spatial trend assessments. It is important to understand the factors that cause reduced KCl-coated denuder efficiency when developing alternate methods.

Dual-Channel Systems. If an atmospheric Hg analyzer is available, sample introduction at the front end of the DCS system can be configured to provide individual Hg fractions (i.e., GEM and TGM). However, this requires comparability and traceability of calibration. Sampling lines should be short and heated. The thermal converter should be standardized and the efficiency of GOM to GEM reduction, together with the temperature used in the thermolyzer, should be verified and monitored regularly. This system must be frequently calibrated.²⁰

Several challenges need to be overcome to facilitate wider adoption of DCS. First, the sensitivity of these systems depends on the sensitivity of the GEM instrument. Different Tekran 2537 units used with the same DCS can have different detection limits.⁶² Careful maintenance of GEM instrumentation and selection of stable instruments are both important.

Also, for systems that measure the two channels sequentially, rapid changes in GEM can confound determination of GOM or GOM+PBM, decreasing sensitivity and sometimes resulting in negative calculated concentrations.²⁰ Use of a Lumex analyzer with rapid channel switching and extensive averaging, rather than a gold cartridge/CVAFS may overcome both of these challenges. Alternatively, new data processing schemes could be developed that detect and correct for the effects of rapid GEM changes. Ultimately, the expanded uncertainty of each DCS needs to be thoroughly evaluated. Again, the GEM measurement will affect the calculated Hg^{II} concentrations.

Elutriators. Elutriators at the inlets of sampling systems are often used to remove coarse particles. For example, the Tekran 2537/1130/1135 system uses an elutriator with a cutoff of $2.5\text{ }\mu\text{m}$, as does the Utah State University DCS. Work in the marine boundary layer and Arctic has shown that coarse particles can be an important component of atmospheric Hg measurements,^{70,71} thus removal of coarse particles may affect assessment of Hg concentrations. Measuring Hg in coarse particles is important, because they are removed readily during wet deposition,⁷² and are dry deposited quickly surrounding emission sources and in regions where they are produced, such as in polar regions or the open ocean.^{64–73} Because Hg^{II} compounds are only semivolatile and chemically labile, design of an inlet that quantitatively separates PBM of a given size fraction from GOM is another challenge for DCS and other Hg^{II} measurement methods (cf., ref 60 for further discussion).

Reactive Mercury Active System. CEM and Nylon Membranes. The RMAS has limitations. First, the sampling resolution of one- to two-weeks does not allow for understanding atmospheric processes, such as diel variations in GOM formation rates. It has been demonstrated that increasing the sampling flow rate from $1\text{ to }2\text{ L min}^{-1}$ results in loss of ambient air Hg^{II} from CEM membranes,²⁷ thus reducing sampling duration may not be possible for this system. Sampling duration is determined by the ambient Hg^{II} concentration and the volume of air needed to be sampled to ensure sufficient mass of Hg on the membrane for downstream quantification. In addition, no tests have been done to determine whether losses occur at 1 L min^{-1} . Plasma-generated HgO has been demonstrated to be lost from the CEM in clean air.^{54,74} It has been shown in lab studies that the CEM collects all Hg^{II} when permeated. However, in field studies, breakthrough occurs.

Nylon membrane Hg^{II} concentrations are typically lower than those obtained with the CEM, and they do not collect all compounds with equal efficiency.⁴⁴ There is no quantifiable Hg left on the nylon membrane after desorption. Interferences due to atmospheric conditions and ambient air chemistry, such as relative humidity, temperature, and atmospheric oxidants have not been adequately tested.

Comparison between the Pall CEM and those available from Cole-Parmer and Sartorius showed the former was the best material for collecting Hg^{II} .²⁷ The effectiveness of the CEM to retain GOM needs to be definitively established, for it has been demonstrated that use of this membrane in direct sampling systems collects less GOM than that measured with DCS.²⁰ One consideration is that the current CEM digestion method may not be adequate.⁵⁰

To improve this method, new surfaces are needed that capture all GOM compounds efficiently and can be thermally desorbed to release compounds into an instrument capable of measuring the chemical composition of the compounds.

Ideally, these surfaces do not capture GEM, have no Hg^{II} -altering chemistry, quantitatively retain the compounds, allow for collection at higher flow rates to reduce sampling duration, and release all Hg^{II} compounds to enable material/surface reusability. New materials must be calibrated in both laboratory and field settings. Because the RMAS is simple to deploy (consisting of measuring flows, deploying and collecting membranes, then shipping to an analytical laboratory) compared to automated instruments, it might be useful for measurement networks.

PBM Measurements. In the RMAS, it was thought that by adding a PTFE membrane upstream of the other membranes, GOM and PBM could be differentiated; however, when particles are loaded on the PTFE membrane, GOM (as HgBr_2) has been found to be captured on active surface area provided by the particles,²⁷ biasing both the PBM and GOM measurements. HgX_2 compounds are Lewis acids that readily bind to electron-rich surfaces/materials. Thus, we currently have no membrane-based method for separation of GOM and PBM. There was a consensus among workshop participants that a method is needed to collect and accurately quantify PBM without collecting GOM and/or GEM on particles.

Overall Needs. The methods discussed above have vastly different time resolutions. For example, the Tekran system resolution for GEM is 5 min and for Hg^{II} is 1 to 2 h, the DCS has a 10 min resolution, while for the RMAS it is one- to two-week resolution, the Lumex measurements are averaged over 1 to 10 min,⁷⁵ and the MerPAS is greater than a month. Varied sampling durations complicates comparisons of the different methods. In addition, high time resolution analyzers will provide information on processes and short-term variability, while longer duration measurements may be more useful for general monitoring and long-term trends. Despite the long time resolution for the RMAS, this method allows for a qualitative estimate of the Hg^{II} chemistry. This method also requires laboratory analyses, as does the MerPAS. The Lumex only allows for measurement of GEM, and the DCS, depending on the configuration, measures GOM + some PBM. Specific methods will be needed to address research objectives.

For surfaces used to collect and analyze GOM and/or PBM, it is critical that they are laboratory- and field-tested, compared against other traceable methods, and calibrated. GOM sorption occurs (1) at sampler inlets, and on impactors and tubing, (2) on particle collection filters, and (3) on particles on filters. GOM sorption to filters will bias PBM samples high, while PBM captured appropriately on filters may volatilize into GOM or be reduced to GEM during sampling, biasing PBM concentrations low. Because PBM and GOM behave differently in the environment, more work is needed to develop a method that quantitatively separates PBM and GOM with improved time resolution.

■ GOM CALIBRATION METHODS

Current Methods. An ideal calibration system should be traceable to metrological standards, have stable, continuous flow, be field deployable, and be able to add GOM spikes to analyzers during ambient air sampling. Several methods are being developed for calibration at ambient concentrations of GOM, including a temperature-controlled box holding permeation tubes,⁵⁸ a method to oxidize GEM into GOM with custom ligands (i.e., Br^- , Cl^- , O^{2-}) in nonthermal plasma,^{26,76,77} and a gas-phase generator developed by LGC

Group, United Kingdom. The Tekran system is calibrated using GEM injections from an internal permeation tube; internal calibrations of this system can be checked using manual injections. For the Tekran system, if there is a bias in the GEM measurement, it will be reflected in the other measurements, thus making accurate GEM measurements is critical for the accuracy of concentrations for all Hg forms.

New Information and Recommendations. The development of a field-deployable National Institute of Standards and Technology (NIST)-traceable GOM calibrator will be critical for the atmospheric Hg measurement community. NIST-traceable calibration of GOM is now possible,⁷⁸ as demonstrated by nonthermal plasma generation of GOM (traceable to NIST 3133).⁷⁶ However, the field application of plasma calibration strategy comes with certain challenges, as it is currently developed as a discrete method that requires periodic calibrations during continuous GOM measurements (Table 1). The permeation tube-based calibrator is the only system that has been used routinely in real field conditions. GOM-emitting permeation tubes (e.g., HgBr_2 and HgCl_2) used in available calibration systems emit some GEM (<10% of total Hg). The permeation tube emission speciation has been characterized by gas chromatography–mass spectrometry (GC-MS), but this method is not currently NIST-traceable.^{78,79} Permeation tubes were recently compared to NIST-traceable GOM created using cold plasma, while the calibrator was at the Jožef Stefan Institute.⁷⁸

A laboratory-based GOM standard is needed for calibration. Calibrated permeation tubes should be used in GOM calibrators. A chemical ionization mass spectrometry-based method that has recently been developed,⁸⁰ even if it is not capable of directly detecting ambient GOM, can serve as a primary calibration method that can be deployed both in the lab and in the field if sufficient power and infrastructure are available. Furthermore, the sensitivity of this method can be improved similar to what is done for gaseous sulfuric acid (e.g., refs 81–83.), to achieve direct detection of GOM in ambient air.

Commercialization of a calibration system would allow for more routine calibration of GOM measurements, particularly for networks. The methods in development are promising, but they still suffer from significant challenges. For example, the permeation tube-based system is not yet fully NIST-traceable, while the nonthermal plasma-based system currently only allows for loading GOM onto collection surfaces and cannot be used to calibrate a continuous sampling instrument, such as a DCS. GOM compounds are only slightly volatile, readily sorb to surfaces, and easily decompose to GEM; thus, development of systems that can quantitatively transport GOM through valves or tubing, and into an analyzer is a unique challenge.⁶⁰

■ DETERMINING THE CHEMICAL COMPOSITION OF Hg^{II} COMPOUNDS

Current Methods. Currently, the only method applied for understanding the ambient chemistry of Hg^{II} compounds is the collection of Hg^{II} or GOM on nylon membranes in the field followed by thermal desorption and the comparison of ambient air profiles with those developed using relatively pure commercial Hg^{II} compounds. Some workshop participants were skeptical of this method. This method is not ideal, as the membranes do not collect all compounds with equal efficiency and concentrations are lower than those measured with simultaneously deployed CEM (Table 1). In addition, the

standard thermal desorption profiles are developed from pure compounds that may not adequately represent Hg chemistry in air. Thermal desorption profiles could be deconvoluted in different ways (e.g., with peak temperature fixed or unfixed). The uncertainties in the profile deconvolution process need to be evaluated.

Despite these limitations, data developed with this method showed consistent trends.^{44,58} For example, a summary of data collected from 13 locations found, in general, that N, S, and organic Hg^{II} compounds were associated with city and forest locations, halogenated compounds were derived from the marine boundary layer, and O compounds were associated with long-range transport.⁵⁸ Despite the limitations, this method has allowed for demonstrating there are multiple forms of atmospheric Hg^{II}, an important finding that could eventually inform understanding of atmospheric Hg chemical mechanisms for global models.

New Information and Recommendations. Direct methods for measurement of GOM and PBM concentrations, and for the chemistry of Hg^{II} compounds, are needed. Atmospheric pressure chemical ionization mass spectrometry (APCI-MS) may be able to achieve the extremely low detection limits needed for ambient detection, improving on the existing APCI-MS.⁸⁰ GC-MS identification is a possibility, although the method requires preconcentration, and methods for volatilization of captured GOM compounds currently lead to unacceptably high decomposition to Hg^{II} compounds.⁷⁹ If the issue of sample introduction to the instrument could be solved, GC-MS presents a viable option for Hg^{II} measurements. However, neither GC-MS nor APCI-MS are techniques that can be easily adaptable to remote field locations nor can be readily utilized by many research groups. Collection of GOM on a surface that releases the compounds quantitatively into a GC-MS or APCI-MS would be ideal, similar to approaches used for chemical analyses of particles (cf., refs 81–85.). Information regarding Hg^{II} bonding to membranes and particles would be useful for determining viable surfaces and particles that are important for retaining Hg^{II}. One way to identify potential surfaces is to investigate whether compounds are bound by physio- or chemi-sorption. Experiments such as those done by Mao et al.⁸⁶ and Khalizov et al.⁸⁷ are a start for investigation of Hg^{II} binding to materials.

A global, field-based, chemically resolved, direct measurement of ambient Hg^{II} compounds is the goal. Before a method can be developed that is capable of these measurement, further comprehensive laboratory experiments need to be performed to better understand atmospheric Hg chemical reactions so methods can be tuned and optimized for Hg compounds that exist in the atmosphere. Such experiments could be performed in a large smog chamber or in an urban tunnel, helping to decipher the GOM-PBM connections. Hg stable isotope measurements can also be used in concert with the measurements described here to understand atmospheric processes and chemistry.⁸⁸ Such experiments will help improve description of gas-particle and in-particle interaction mechanisms in Hg models in conjunction with recent model developments that account for solid-vs-liquid-vs-viscous particles.⁸⁸ However, an instrumental method(s) for quantitative separation of GOM and PBM is also needed.

Direct detection of Hg compounds does not completely address the issue of understanding the chemistry involved in atmospheric Hg reactions. Gas particle partitioning used in models is based on KCl-coated denuder measurements, using

information from Hg depletion events. Recently, laboratory experiments have reported on kinetics of gas-particle partitioning of HgCl₂ with surfaces composed of environmentally atmospherically relevant inorganic⁸⁶ and organic⁸⁷ chemicals. Further measurements are needed in different well-characterized environments to build models that more accurately represent atmospheric Hg reactions and behavior to support the objectives of the Minamata Convention.

■ NETWORK CONSIDERATIONS

Each network has its priorities, such as testing whether air Hg concentrations are declining to meet the goals of the Minamata Convention, or measuring/estimating atmospheric Hg deposition (e.g., National Atmospheric Deposition Program objective). Thus, one measurement solution may not be the best approach for all; rather, the methods used should meet the network-specific objective(s). For sampling methods to be applicable for network applications, they need to be simple to deploy and cost-effective. It is also important to point out here that the Mercury Deposition Network precipitation measurements do not suffer from the biases and limitations discussed here.

Currently, PBM and GOM measurement methods using membranes are not adequate for networks, but CEM measurements alone may be useful. As new methods are being developed to differentiate between PBM and GOM, the use of a PTFE in front of a CEM provides a qualitative estimate. The CEM and nylon membranes in the RMAS have provided new information on concentrations and potential chemical composition of Hg^{II} compounds. This method serves as a stopgap until new methods/surfaces are developed.

Alternate methods will need to be applied, and thus standard operating procedures for networks will need to undergo a revision. Changes should consider the ongoing discourse concerning GEM and TGM measurements. Attention must be devoted to development of methods employed for the measurement of GOM and PBM, as all methodologies exhibit biases that contribute to uncertainties in measurements. Moreover, for a valid and reliable comparison of atmospheric Hg measurements, it is important to report not only the measured values, but also the measurement uncertainties following metrological standards. This ensures a clear understanding of the accuracy and reliability of the data, enabling proper comparisons between different measurement results.

There are different ways that Hg is deposited to ecosystems, such as foliar uptake of GEM, wet deposition, and dry deposition. Foliar uptake and wet deposition are measured in National Atmospheric Deposition Program networks, but dry deposition of Hg^{II} is not adequately measured. Since wet and dry deposition are important inputs of Hg^{II} into ecosystems, methods are needed that accurately measure concentrations of Hg^{II} under field conditions to estimate deposition or direct methods need to be applied. Selected methods need to be cost-effective, easily deployable, and to provide accurate measurements of concentrations for calculating deposition. High-time resolution methods provide a framework for understanding processes. Calibrated, traceable GEM and GOM measurements are essential for all network locations, and high quality GOM and PBM measurements are needed in representative locations.

■ PARTING COMMENTS

During the workshop, several main themes and concerns emerged. First, eliminating the preconcentration step in ambient Hg sampling is preferred, since this step can result in changes in the chemistry of the compounds on the collection surface, and collection efficiency can be influenced by Hg compounds and ambient air chemistry. However, without preconcentration, it is currently not possible to determine the chemical composition of Hg^{II} compounds. Second, all methods must be calibrated and traceable to a metrological standard, which is not currently the case. Third, wall losses are important; therefore, sample introduction lines should be as short as possible and heated to above ambient temperatures so that the chemical makeup does not change due to gas-surface partitioning. Higher flow rates and inert coatings may help to reduce wall losses of Hg^{II} compounds. When measuring Hg^{II}, lines need to be “seasoned”, or saturated, prior to quantitative measurements, and it must be recognized that if conditions change, Hg can be released from surfaces. For example, if relative humidity changes, this could result in GEM production and release from the sampling lines.²⁰ Fourth, new collection surface materials for GOM measurements are needed. These should have high specific area, be selective for GOM only, and ideally not collect GEM nor allow for alteration of the chemistry of the sorbed Hg^{II} compounds.

In addition, method development is limited by the chemical compounds that are available for making permeation tubes and developing thermal desorption profiles. Currently, HgBr₂ and HgCl₂ are being used in permeation systems, and HgO, HgBr₂, and HgCl₂ are synthesized *in situ* in nonthermal plasma calibrations. It is unclear if these are the most representative chemical compounds for calibration to test methods, as the actual composition of Hg^{II} compounds in the atmosphere is largely unknown and based primarily on quantum calculations.^{7,89–91} Regardless, whatever methods are developed, each must be thoroughly validated under a range of conditions and calibrated with multiple compounds that are traceable to international standards.

A reference method that is officially recognized or declared as a standard must be developed. Methods developed need to be traceable to standard units established by the International System of Units. Accuracy, precision, and traceability must be ensured.

Given the list of analytical needs detailed and summarized above, accurate measurements of Hg^{II} are challenging due to the low concentrations and the inherent “sticky” nature of the compounds. As with the development of any new method and knowledge on the cutting edge, this takes time. All currently available methods have limitations. That said, new methods, such as DCS and RMA, have provided important information regarding atmospheric Hg concentrations and the chemical composition of Hg^{II} compounds, moving the Hg scientific community forward. Work is ongoing regarding the development of materials that could capture GOM compounds and release them with equal efficiency and without interferences. Development of these would allow for a system that could accurately measure GOM and PBM. Modifying the Tekran 2537/1130/1135 system to do this could be cost-effective and allow for ease of deployment, since monitoring sites are already in place. DCS allow for measurement of concentrations of GOM or GOM and a fraction of PBM, depending on the inlet

configuration. Calibration systems being developed and fine-tuned will provide a means of verifying the accuracy of the measurements. Automated systems require more attention than filter- or cartridge-based systems. However, the former have short time resolutions allowing for better understanding processes. The filter-based system can provide preconcentration, allowing for estimations of Hg^{II} compound chemistry. Better methods to do this are being developed. In addition, use of Hg isotopes can aid in source determination and to better understand atmospheric processes, and may play an important role moving forward and should not be overlooked, but was not a focus of this workshop discussion. These are all positive steps toward more accurate atmospheric Hg measurements.

An important goal is to develop a global, field-based, chemically resolved, direct measurement of ambient Hg^{II} compounds in ambient air. In an effort to get there, given our current understanding of Hg^{II}, priority future research paths for quantifying and characterizing Hg^{II} include: development of surfaces that allow for the collection and release of Hg^{II} compounds without alterations to the initial Hg^{II} compound(s); identification and improvement of analytical methods for characterizing the chemistry of Hg^{II} compounds; optimization of methods for calibration of field measurement systems; development of systems that can measure chemistry in real time; development of a method that allows for differentiating between PBM and GOM; and performing thorough uncertainty analyses for all methods.

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Biography



Professor Mae Sexauer Gustin has been at the University of Nevada, Reno, USA, for ~30 years with her research primarily focused on understanding the fate and transport of mercury (Hg) in the environment. Much of her work has been centered on development of methods for measuring Hg fluxes, atmospheric Hg deposition, atmospheric Hg concentrations and chemistry, and the use of tree rings as archives for atmospheric Hg concentrations; and application of these methods for understanding Hg behavior in the environment. She has worked on environmental issues associated with Hg contamination in Nevada, meeting the University's Land Grant mission, and better understanding the role of vegetation in the Hg biogeochemical cycle. She has measured atmospheric ozone across Nevada, and written manuscripts regarding the behavior of and the sources of this oxidant in the western United States. Her formal educational trainings (B.S., M.S., and Ph.D.) were in Geosciences. She was raised in eastern North Carolina, USA, by a weaver and a printmaker.

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ABBREVIATIONS

APCI-MS	Atmospheric Pressure Chemical Ionization Mass Spectrometry
CEM	Cation Exchange Membrane
CVAFS	Cold Vapor Atomic Fluorescent Spectrometry
DCS	Dual-Channel System
GEM	Gaseous Elemental Mercury
GOM	Gaseous Oxidized Mercury
MerPAS	Mercury PASSive sampler
PBM	Particulate-Bound Mercury
PTFE	PolyTetraFluoroEthylene
RMAS	Reactive Mercury Active System

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