



Measuring and modeling mercury in the atmosphere: a critical review

M. S. Gustin¹, H. M. Amos², J. Huang¹, M. B. Miller¹, and K. Heidecorn¹

¹Department of Natural Resources and Environmental Science, University of Nevada-Reno, Reno, NV, 89557, USA

²Department of Environmental Health, Harvard School of Public Health, Boston, MA, 02115, USA

Correspondence to: M. S. Gustin (mgustin@cabnr.unr.edu)

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Abstract. Mercury (Hg) is a global health concern due to its toxicity and ubiquitous presence in the environment. Here we review current methods for measuring the forms of Hg in the atmosphere and models used to interpret these data. There are three operationally defined forms of atmospheric Hg: gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate bound mercury (PBM). There is relative confidence in GEM measurements (collection on a gold surface), but GOM (collection on potassium chloride (KCl)-coated denuder) and PBM (collected using various methods) are less well understood. Field and laboratory investigations suggest the methods to measure GOM and PBM are impacted by analytical interferences that vary with environmental setting (e.g., ozone, relative humidity), and GOM concentrations measured by the KCl-coated denuder can be too low by a factor of 1.6 to 12 depending on the chemical composition of GOM. The composition of GOM (e.g., HgBr₂, HgCl₂, HgBrOH) varies across space and time. This has important implications for refining existing measurement methods and developing new ones, model/measurement comparisons, model development, and assessing trends. Unclear features of previously published data may now be re-examined and possibly explained, which is demonstrated through a case study. Priorities for future research include identification of GOM compounds in ambient air and development of information on their chemical and physical properties and GOM and PBM calibration systems. With this information, identification of redox mechanisms and associated rate coefficients may be developed.

1 Introduction

The Minamata Convention for mercury (Hg) has been signed by more than 120 nations and is now being ratified. The primary objective of the convention is to “protect human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds” (UNEP Minamata Convention, 2014). A key challenge for Hg researchers is developing linkages between Hg in the atmosphere, deposition, and ecosystem contamination (Pirrone et al., 2013). Here we review where the science on measuring and modeling atmospheric Hg currently stands and offer suggestions for future research directions that will both advance understanding of Hg cycling in and between environmental reservoirs and better serve the needs of the convention.

Although the atmosphere is a relatively minor reservoir of Hg compared to oceans or soils, it is an important pathway by which Hg is distributed globally over short timescales (≤ 1 year). Atmospheric deposition represents the major pathway of Hg input to terrestrial and aquatic ecosystems outside areas of direct contamination. A variety of environmental archives, including remote lake sediments, ombrotrophic peat bogs, glacial ice, and tree rings, suggests Hg inputs to the atmosphere have increased several fold in the last 150 years (cf. Engstrom et al., 2014; Schuster et al., 2002; Wright et al., 2014a). Measured concentrations of atmospheric Hg have been declining over the last ~ 15 years (Slemr et al., 2011; Cole and Steffen, 2010; Soerensen et al., 2012; Cole and Steffen, 2010; Cole et al., 2014), despite inventories suggesting global anthropogenic emissions have been relatively flat or increasing (AMAP/UNEP, 2013). This conundrum has challenged our understanding of Hg cycling

and emissions, and underscores the need for continued atmospheric Hg monitoring.

Measuring the forms of Hg in the atmosphere is difficult. Mixing ratios are at low parts per quadrillion by volume (ng m^{-3} and pg m^{-3}). Atmospheric Hg is operationally defined as gaseous elemental Hg (GEM), gaseous oxidized Hg (GOM), and particulate bound Hg (PBM) less than $2.5 \mu\text{m}$ in diameter (Lindberg et al., 2007; Schroeder and Munthe, 1998; Landis et al., 2002). GOM can be present as different forms (Huang et al., 2013, 2015). GOM and PBM have complex fundamental physicochemical properties. Because of the complexity, recent work has combined GOM and PBM concentrations as measured by the Tekran[®] system and defined this as reactive Hg ($\text{RM} = \text{GOM} + \text{PBM}$) (cf. Rutter and Schauer, 2007a, b; Gustin et al., 2013; Weiss-Penzias et al., 2015). Previously it was thought that GEM was 95–99 % of Hg in the atmosphere (cf. Schroeder and Munthe, 1998). Recent work is pointing towards GOM being 25 % of total Hg in the boundary layer (see the discussion below). In the Arctic, up to 100 % conversion of GEM to GOM has been observed (Steffen et al., 2014, 2015). In addition, it has been demonstrated that there are different GOM compounds in the air (Huang et al., 2013, 2015).

Here we review current methods for measuring the forms of Hg in the atmosphere and models used to interpret these data. The advantages and limitations of each measurement method are discussed, and a narrative is provided on how we have arrived at our current understanding of the limitations. The number of models that have developed the capacity to simulate atmospheric Hg has multiplied in the last decade. We review major gains in Hg science gleaned from the use of measurements and models together, as well as key open questions. We conclude with a discussion of outstanding problems facing measurement and modeling communities.

2 Methods for measuring atmospheric Hg

2.1 Atmospheric mercury basics

Mercury is typically detected by atomic absorption (AAS) or atomic fluorescence spectroscopy (AFS). In nearly all cases, Hg forms are pre-concentrated on gold-coated surfaces because the sensitivity of AAS and AFS are, with the exception of laser and Zeeman AAS techniques, not sufficient for direct measurements of Hg at ambient concentrations. GOM and PBM are converted to GEM by thermal desorption from the gold surfaces. Gold is the most frequently used and best-studied pre-concentration material for Hg but can become passivated (Huang et al., 2014; Landis et al., 2002). Currently, the Tekran[®] 2537/1130/1135 system is the most widely adopted method for measurement of atmospheric Hg, and this instrument has been incorporated into monitoring networks, such as the Canadian Mercury Network (CAMNet), Atmospheric Mercury Network (AMNet), and Global

Mercury Observation System (GMOS). Alternate measurement methods have been developed, but are currently operated on a limited scale.

An AAS or AFS instrument combined with a pre-concentration on a gold adsorber with an inline pyrolyzer will provide total gaseous mercury ($\text{TGM} = \text{GEM} + \text{GOM}$) or total atmospheric mercury ($\text{TAM} = \text{GEM} + \text{GOM} + \text{PBM}$). Since GOM is adhesive, sampling lines are often heated and should be kept short in length to prevent wall loss.

GOM and PBM are in temperature-dependent equilibrium (Rutter and Schauer, 2007b; Amos et al., 2012). Specific PBM sampling has to take account of this, in addition to the usual precautions to prevent size-dependent particle losses. Since it is difficult to achieve separation of PBM and GOM without disturbing the equilibrium, RM is a more accurate measurement to use. In addition, due to lack of capture of GOM by the denuder and collection on the PBM unit (Gustin et al., 2013), discussion of RM is more appropriate.

2.2 Active automated systems

2.2.1 Tekran[®] system

The Tekran[®] 2537/1130/1135 system has been widely used to measure atmospheric Hg for the past ~ 15 years (Landis et al., 2002). The Tekran[®] 2537 module measures TGM or GEM in ng m^{-3} and was the first component to be developed. The 1130 and 1135 components were added to this system to measure GOM and PBM in pg m^{-3} (Landis et al., 2002), respectively. The instrument pulls air through an elutriator that is heated to 50°C and removes particles $> 2.5 \mu\text{m}$, depending on the flow rate (Lyman et al., 2007). This particle size cut is necessary to keep larger particles from depositing on the denuder. GOM is collected on a potassium chloride (KCl)-coated denuder, and PBM on a column of quartz chips and a quartz filter. Air passes through 10 m of heated line with a soda lime trap and Teflon filter at the 2537 inlet and then into the 2537 where GEM is collected on a gold trap. It is not known whether the soda lime trap captures and retains GOM. GOM (500°C) and PBM (800°C) are thermally desorbed from their collection surfaces, loaded on the gold traps, and quantified as GEM (gold traps are heated to 350°C) by cold vapor atomic fluorescence spectrometry (CVAFS). Although the particle cut inlet, coated annular denuder, particle filtration device, and heated line are all held at constant temperatures (50°C) when sampling, there are temperature drops within the sampling line and GOM may be lost to the walls (Gustin et al., 2013). Recent work has shown that heating of the inlet to 100°C improves GOM collection (Huang and Gustin, 2015a).

This instrument has high temporal resolution, low limit of detection, and established quality assurance / quality control protocols (Table 1). The CAMNet and AMNet developed best management practices for this instrument (Steffen et al.,

Table 1. Pros and cons of automated and integrative methods used to make Hg measurements.

	Hg form measured/detection limit	Pros	Cons	Suggestion/comments
Automated				
Tekran 2537 gold traps	GEM or TGM; 0.5 ng m ⁻³ ambient air	Low detection limit, 2.5 to 5 min resolution; there is a calibration source, standardized by AMNet and CAMNet (cf. Prestbo and Gay, 2009)	Inlet configuration will impact whether measuring GEM or TGM; requires fairly trained technicians, stable electrical source, regular calibration and checks	Suggest using a pyrolyzer at the inlet if TGM measurement is desired
Tekran 1130 KCl denuder	GOM; 1 pg m ⁻³	Good time resolution (1 to 2 h)	No calibration source; coating denuders needs to be done by one operator; does not measure all the GOM in air	New method needs to be developed that measures all forms in air and is not impacted by relative humidity and ozone; a different denuder coating would be useful
Tekran 1135 quartz filter and chips	PBM; 1 pg m ⁻³	Good time resolution (1 to 2 h)	Positive artifact due to measurement of GOM that passes through the denuder; not all PBM is measured due to select grain size capture	Filter method may be best and suggest using cation exchange membranes
Lumex	GEM or TGM; in liquids, solids, air; 1 ng m ⁻³	Good time resolution (seconds); field portable; allows for measurement of Hg concentrations in environmental media in the field	Not calibrated at low air concentrations	Good for industrial applications
Gardis	GEM or TGM; 0.5 ng m ⁻³	Good time resolution (2.5 min)	Requires trained operators	
DOHGS	GEM and TGM; 80 pg m ⁻³	Good time resolution (2.5 min)	Requires highly trained operators and stable environment	Useful as a research instrument
Laser	GEM	Fast time resolution (seconds)	Requires highly trained operators and a stable environment; cannot quantify GOM	Useful as research instrument
Integrated measurements				
GEM sampler activated carbon	GEM or TGM; 10–80 pg m ⁻³	Easy operation	Long time resolution	Good for areas with high concentration gradients
GOM mist chamber	GOM; Blank: 20–50 pg		Complicated operation; needs acidified solution	Useful as a research instrument; needs to be re-evaluated
GOM passive sampler concentration	GOM; 2.3–5 ng m ⁻³	Easy operation	Long time resolution	Needs a new design
GOM passive sampler deposition	GOM; probably PBM; 0.02–0.24 ng m ⁻² h ⁻¹	Easy operation; real Hg loading to ecosystem	Long time resolution	Good for worldwide network
Direct particulate matter sampler measurement	PBM; probably GOM	Easy operation	Artifacts from GOM partition; choice of filters important to consider and length of sampling line	
UNR active system	GOM; ~ 30 pg m ⁻³	Easy operation; for quantifying GOM and trying to understand the chemical forms in air	Potentially some PBM measured	Good for networks, and it could be used to help calibrate measurements made by the Tekran system

2012; Gay et al., 2013). Co-located GEM measurement can deviate by 20 to 30 % (Aas, 2006; Gustin et al., 2013). Lyman et al. (2007; Supplement) found that TGM could vary by 7.0 ± 5.3 %. There are no calibration standards for GOM, breakthrough can result in collection on the PBM filter, and collection efficiencies for GOM and PBM are uncertain (cf. Gustin and Jaffe, 2010; Huang et al., 2013; Talbot et al., 2011).

2.2.2 Lumex

Lumex RA-915 and Lumex 915+ (Lumex, St. Petersburg, Russia) units measure GEM and TGM, respectively, with a reported detection limit of $\sim 1 \text{ ng m}^{-3}$ for measurements in air. If averaged over the sampling time of the GEM measurement by the Tekran[®] system (5 min), a detection limit of a few tenths of ng m^{-3} can be achieved. The Lumex uses Zeeman atomic absorption spectrometry with Zeeman background correction. In this instrument, a Hg vapor lamp sits in a magnetic field and generates a 254 nm light wavelength split into three polarized light fields. A photodetector detects light in one field within the Hg absorption wavelength 254 nm and another lying outside of this wavelength. The signals from both fields are equal when Hg is not present (for details see Sholupov et al., 2004). The instrument can be periodically calibrated using a permeation source such as used for internal calibration of the Tekran[®] instruments. This is not available commercially (F. Slemr, personal communication, 2015).

2.2.3 Gardis

The Gardis Hg analyzer has two gold traps, a concentrating and analytical trap, and measures Hg using CVAAS (Institute of Physics, Lithuania). Having two gold traps might reduce some interferences, such as passivation. This instrument will measure GEM, TGM, or TAM depending on inlet configuration and was developed in 1995 by Urba et al. (1995). In a field comparison, concentrations were similar to that measured by the Tekran[®] 2537 (Ebinghaus et al., 1999). This unit has had limited use and a reported detection limit of 0.5 ng m^{-3} (Table 1).

2.2.4 University of Houston Mercury system (UHMERC)

UHMERC was designed for measuring GEM and TGM (Talbot et al., 2008). This instrument uses two Tekran[®] systems that are slightly modified (gold trap heated to 460°C). The inlet to the instrument measuring GEM consists of a Teflon filter to remove fine particles ($< 2 \mu\text{m}$) with a molecular sieve trap immediately after to remove GOM (Gustin et al., 2013).

2.2.5 Detector for oxidized Hg species (DOHGS)

The DOHGS instrument measures TGM and GEM using two Tekran[®] 2537 units. The difference between these measurements is interpreted as RM. The original instrument is described in Swartzendruber et al. (2009), and subsequent modifications to the system can be found in Ambrose et al. (2013) and Lyman and Jaffe (2012). The measurement of GEM requires that GOM and PBM be selectively removed from the airstream. In early versions, only GOM was removed using a KCl-coated denuder. This led to the discovery of a discrepancy between GOM collected on KCl-coated denuders and that measured by the difference method (Swartzendruber et al., 2009). The GOM removal method was changed to quartz chips maintained at 650°C as a pyrolyzer to measure TGM and then quartz wool (Lyman and Jaffe, 2012; Ambrose et al., 2013). More recently a cation-exchange membrane filter has been used to remove RM compounds.

The method detection limit for RM is $\sim 80 \text{ pg m}^{-3}$ (Ambrose et al., 2013; Table 1). Extensive testing has been conducted on the DOHGS using calibration sources of Hg^0 , HgBr_2 , and HgCl_2 . Improving the sensitivity of the underlying CVAFS systems would enable more routine operation of this instrument.

2.2.6 Laser systems

Two laser systems have been developed for measurement of GEM (Faïn et al., 2010; Pierce et al., 2013; Bauer et al., 2002, 2010, 2014). One is a cavity ring-down system, and the other operates on the principle of laser-induced fluorescence. Both are calibrated using Tekran[®] data. These do not currently have the ability to measure GOM or PBM. If GOM and/or PBM were to be measured, they must be converted to GEM first. The cavity ring-down instrument has interferences with ozone (O_3) (Faïn et al., 2010; Pierce et al., 2013). Laser systems are best applied in laboratory settings given the current sensitivity, need for a consistent electrical supply, and large electrical power use.

During the Reno Atmospheric Mercury Intercomparison eXperiment, the laser-induced fluorescence system operated by University of Miami successfully sampled on 18 days, typically for between 4 and 6 h a day. The longest period of continuous sampling lasted for 26 h. During RAMIX they sampled directly from the manifold and, in addition, at the end of the campaign sampled ambient air independently, including true in situ sampling on the roof of their mobile lab. They also attempted to measure GOM by pyrolyzing the sample air and measuring the difference between $\text{Hg}(0)$ and TGM (Bauer et al., 2014; A. Hynes, personal communication, 2015).

2.3 Active manual samplers

Here we briefly review manual sampling methods for GEM/TGM, GOM, and PBM. Manual samplers collect over a specific amount of time, and then the samples collected need to be analyzed using an alternate method. In contrast, automated samplers provide short time (seconds to minutes) resolution measurements and do not need measurements by an alternate method.

2.3.1 Mist chamber method for RM

Stratton and Lindberg (1995), Lindberg and Stratton (1998), Lindberg et al. (2000), and Stratton et al. (2001) described development of a mist chamber for measurement of GOM (termed RGM then). The principle of operation includes pulling air at a high flow rate (15 to 20 Lpm) through a fine mist aerosol made of water, NaCl, and HCl. GOM and PBM accumulate in droplets captured on a membrane. This liquid drains into a chamber and is collected, stored in vials, and analyzed using EPA Method 1631 (EPA Method 1631, 2013).

Sheu and Mason (2001) compared denuders, mist chambers, and a filter pack method for GOM (see the Supplement for details). They showed GOM concentrations in Maryland could be up to 500 pg m^{-3} and that GOM could be up to 30 % of the TGM. Reported daytime concentrations measured by the mist chamber were significantly higher (20 to 700 pg m^{-3}) than the KCl-coated denuder (20 to 70 pg m^{-3}).

2.3.2 UNR active system for GOM

The UNR active system measures ambient GOM concentrations and identifies GOM compounds. It consists of a six-port system each with two in-series Teflon filter holders. Three of the filter holders house nylon membranes and three-cation exchange membranes. Air is pulled using a vacuum pressure pump through the membranes with flow regulated by a mass flow controller at a rate of $\sim 1 \text{ Lpm}$. (Huang et al., 2013). This unit is not thought to measure PBM as configured (Huang et al., 2013, 2015).

Cation exchange membranes are analyzed using EPA Method 1631 (EPA Method 1631, 2013) to quantify GOM concentrations. Nylon membranes are thermally desorbed to determine compounds present in the air (Huang et al., 2013, 2015). This method may not collect all GOM compounds (Wright et al., 2014b; Huang et al., 2014; Huang and Gustin, 2015b). The nylon membrane is influenced by relative humidity (RH) (Huang et al., 2013; Huang and Gustin, 2015a). A summary of some advances presented in Huang and Gustin (2015b) associated with this method are described in the Supplement. The active system is currently limited to a resolution of 1 to 2 weeks.

2.3.3 Active manual systems for PBM/RM

Teflon, glass-fiber, and quartz filters have been used in open-faced filter packs, cascade impactors, and Micro-Orifice Uniform Deposition ImpactorsTM (MOUDIs) to measure atmospheric PBM concentrations (Keeler et al., 1995; Wang et al., 2013; Talbot et al., 2011; Engle et al., 2008; Rutter et al., 2008). PBM will vary depending on the chemistry of the aerosol, the atmosphere, and GOM chemistry along with physical conditions of the atmosphere, such as temperature and relative humidity. PBM measurements will collect some GOM and will be impacted by the filter material, flow rate, and inlet configuration.

2.4 Passive samplers

Passive samplers may be biotic (i.e., mosses, lichens, plant leaves) or abiotic surfaces (membranes, water). Huang et al. (2014) recently reviewed passive sampling methods for atmospheric Hg.

2.4.1 Total gaseous mercury

The method developed by W. Zhang et al. (2012) used an abiotic passive sampler with sulfate-impregnated carbon contained in an axial sampler. Activated carbon was investigated as a sampling material for Hg by Lindberg and Turner (1977), Lindberg et al. (1979), and Lindberg (1980). Other materials that have been applied include silver wires, gold-coated plates, and gold plugs (Gustin et al., 2011; Skov et al., 2007; Huang et al., 2014). Sulfate-impregnated carbon is effective because it retains atmospheric Hg, has a high sorption capacity, and will not become passivated over time (cf. Huang et al., 2014). This sampler is best applied for Hg measurements across significant concentration gradients (e.g., urban to rural). The sampler would need to be deployed for more than 90 days at a remote site. It is not known whether it measures TGM or GEM.

2.4.2 Gaseous oxidized Hg

There are currently two types of passive samplers for GOM. These include surrogate surfaces to measure dry deposition, and a measurement of diffusive uptake as a surrogate for concentration. The most widely adopted dry deposition method uses a cation exchange membrane in a down-facing aerodynamic sampler housing (“Aerohead sampler”; Lyman et al., 2007, 2009) and has been deployed in multiple studies (Castro et al., 2012; Sather et al., 2013, 2014; Peterson et al., 2012; Gustin et al., 2012; Wright et al., 2014b; Huang and Gustin, 2015b). Although there are limitations, such as measurement of only unidirectional flux, dry deposition models also apply a similar flux. Huang and Gustin (2015b) found that the surrogate surface better agreed with models when air concentrations measured by the box sampler and calibrated by the Tekran[®] system were adjusted by a factor of 3. The

box sampler designed by Lyman et al. (2010b) provides a means for calculating concentrations based on uptake rate. Recent work suggests the box sampler has significant wall loss (80 %) of GOM (Huang and Gustin, 2015b). Lack of calibration is a limitation for all passive samplers. The temporal resolution is coarse and samplers must be deployed for 1 to 2 weeks.

2.5 Calibration methods

One of the major outstanding issues is that the vast majority of GOM and PBM measurements are not calibrated (Jaffe et al., 2014). Calibration of GOM measurements has been done using manifold and chamber systems. Neither is automated or widely adopted. Coal fly ash is available as a standard for PBM, but calibrations have not been done. Laboratory chambers have been developed for calibrating and testing membranes and passive samplers (Gustin et al., 2011; Lyman et al., 2007, 2010b; Skov et al., 2007).

The UNR manifold calibration system is designed so specific Hg compounds can be added at different concentrations as well as O₃, water vapor, and other chemical compounds. A pyrolyzer at the inlet can be used to determine concentrations of Hg being permeated (Huang et al., 2013). The eight-port glass manifold allows for collection of GOM on KCl-coated denuders and different surfaces (Huang et al., 2013). A Tekran[®] 2537/1130 unit at the end of the manifold is used to measure GEM and GOM concentrations. Manifold calibrations have also been performed by the University of Washington in the laboratory (Finley et al., 2013; McClure et al., 2014) and field (RAMIX; Gustin et al., 2013; Finley et al., 2013). During the RAMIX campaign, transmission efficiencies of GEM and HgBr₂ were 92 and 76 %, respectively.

3 Evolution of our understanding of the limitations of speciated Hg measurements

3.1 Are we measuring TAM, TGM, or GEM?

Inlet configuration and local atmospheric chemistry will affect the measurement of TGM versus GEM. Limited work in dry air with uncovered lines (i.e., exposed to sunlight) indicated that the Tekran[®] 2537 measures TGM (see the Supplement). If GOM is able to pass through the inlet to the Tekran[®] 2537 and the gold traps are not passivated, the instrument will measure TGM (Gustin et al., 2013; Temme et al., 2002). Passivation of gold surfaces can occur (Barghigiani et al., 1991; Brosset and Iverfeldt, 1989; Gustin et al., 2011; Munthe et al., 1990; Xiao et al., 1991), and when this occurs these surfaces are no longer quantitatively collecting atmospheric Hg. Landis et al. (2002) mentioned passivation of gold traps periodically occurred right after analysis of a denuder, with recovery dropping to 50 %. To measure TAM requires the use of a pyrolyzer at the inlet to the sampling line to convert GOM + PBM to GEM. Field data suggest GOM

can constitute up to 25 % of TGM in Nevada, Florida, and Maryland (see Sects. 2.3.1, 3.2.2, 4) and up to 100 % during depletion events in the Arctic (Steffen et al., 2014, 2015).

3.2 PBM measurements and potential artifacts

Relative to GOM and GEM, PBM measurements have received less systematic study. The Tekran[®] system is currently the most widely used configuration for measuring PBM. Other sampling methods tested include filter-based methods (Rutter et al., 2008; Talbot et al., 2011; Malcolm and Keeler, 2007; Kim et al., 2012). The sign and magnitude of the Tekran[®] measured PBM bias is presently unclear. Both high and low biases have been reported (Talbot et al., 2011; Rutter et al., 2008; Malcolm and Keeler, 2007; Gustin et al., 2013).

The particle size distribution of PBM is spatially heterogeneous and can include both fine and coarse fractions (Kim et al., 2012; Keeler et al., 1995; Malcolm and Keeler, 2007; Engle et al., 2008). The standard inlet on the Tekran[®] 2537/1130/1135 excludes particles larger than 2.5 μm (depending on the flow rate; Lyman et al., 2010) in diameter to prevent large particles from depositing on the KCl-coated denuder. Thus in coastal/marine, agricultural, or industrial settings with high concentrations of large particles, reported PBM concentrations represent a lower bound (Malcolm and Keeler, 2007; Kim et al., 2012; Poissant et al., 2005). Surrogate surfaces with cation exchange membranes may collect very small aerosol fractions by diffusion (Lyman et al., 2007; Huang and Gustin, 2015b).

Temperature and atmospheric composition potentially impact PBM measurements. The Tekran[®] 1135 particulate module is maintained at 50 °C to prevent condensation of water vapor. Based on filter experiments compared with Tekran[®] PBM, Rutter et al. (2008) suggested there is evaporative loss of PBM. Thermal desorption profiles using nylon membranes showed that Hg(II) compounds are emitted at temperatures ranging from 50 to 200 °C (Fig. 2), depending on charges on the collection surface and the polarizability of the different Hg compounds (Huang et al., 2013). Lynam and Keeler (2005) observed less PBM collected on quartz filters for 12 versus 4 h, and suggested a negative sampling artifact associated with relative humidity or reaction with gases in the air such as O₃.

Breakthrough of GOM from the upstream denuder can result in inadvertent retention of GOM on the PBM collection surface resulting in biased high PBM measurement. In principal, the Tekran[®] 2537/1130/1135 removes GOM on the KCl-coated annual denuder and then PBM is collected downstream. Field data have shown that GOM compounds not collected by the KCl-coated denuder can be captured by the particulate unit (Gustin et al., 2013). Quartz fiber filters used to collect PBM may also collect GOM (Rutter et al., 2007; see the Supplement for detailed example). Lyman et al. (2007) compared calculated dry deposition fluxes associated with

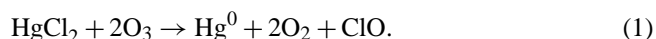
coated (KCl) and uncoated quartz fiber filters against data collected using cation-exchange membranes, both yielded significantly lower deposition fluxes. GOM breakthrough may not occur in all cases. For example, if there are temperature drops within the instrument, then GOM will deposit to the walls (Gustin et al., 2013). Because of these issues, the authors conclude it is presently more robust to interpret RM rather than PBM and GOM data separately.

3.3 GOM: biases, interferences, and shedding light on the spatiotemporal variability of GOM compounds in air

Based on laboratory and field studies, concentrations of GOM collected on the nylon and cation exchange membranes are higher than those collected by the Tekran[®] system by 60–1000 % (Huang et al., 2014; Huang and Gustin, 2015a, b). Laboratory and field experiments have demonstrated the collection efficiency of KCl-coated denuders varies with environmental conditions (O₃, RH) and Hg(II) compounds present in air. Below we discuss recent laboratory experiments and field studies that have shaped our understanding of the limitations of GOM measurement methods.

3.3.1 Ozone and relative humidity interferences

Laboratory experiments have confirmed O₃ interferences for KCl-coated denuders and relative humidity interferences for both denuders and nylon membranes (Lyman et al., 2010a; McClure et al., 2014; Huang and Gustin, 2015b). Lyman et al. (2010a) found the collection efficiency of HgCl₂ loaded on a KCl denuder was reduced by 3 to 37 % when O₃ concentrations were 6 to 100 ppbv. Lyman et al. (2010a) proposed reduction was occurring on the denuder wall:



Their results also indicated less GOM was recovered as O₃ exposure time increased (10 to 26 % removed from loaded denuders for 2.5 min and 29 to 55 % for 30 min at 30 ppbv).

In experiments similar to those performed for O₃, McClure et al. (2014) found RH had a similar effect on HgBr₂ loaded on KCl-coated denuders. Huang and Gustin (2015a) permeated HgBr₂ and water vapor into a Tekran[®] 2357/1130 system in ambient air and found collection efficiencies dropped during the spikes of RH, and the denuder became passivated over time.

They found the following at RH of 21 to 62 %:

$$\text{RH} = 0.63 \text{ GOM loss \%} + 18.1, \quad r^2 = 0.49, \quad p \text{ value} < 0.01. \quad (2)$$

Huang and Gustin (2015a) found a greater impact of relative humidity than O₃.

3.3.2 Variability of RM composition and concentrations

Here we use comparisons of data collected with a variety of sampling methods to better understand atmospheric Hg concentrations and how measurement discrepancies vary with environmental setting (e.g., RH and O₃) and Hg(II) compounds present in the ambient atmosphere. This includes data collected as part of a large study in Florida (Peterson et al., 2012; Gustin et al., 2012), the RAMIX field campaign (Gustin et al., 2013), recent comparison of KCl-coated denuder data with the UNR active system (Huang et al., 2013, 2015), and laboratory testing (Huang et al., 2013; Huang and Gustin, 2015a, b). For a historical review of additional literature see the Supplement in Gustin et al. (2013), Huang et al. (2014), and this paper.

Peterson et al. (2012) compared passive samplers and Tekran[®] data from three sites in Florida. The region has high Hg wet deposition but low GOM concentrations (on average 2–8 pg m⁻³ as measured by the Tekran[®] system). In general, the Aerohead or dry deposition sampling system (described above), showed higher deposition for GOM than that calculated using KCl-coated denuder concentrations and a dry deposition model. Based on passive sampler uptake and calculated deposition velocities, Peterson et al. (2012) suggested the difference could be explained by the presence of different GOM compounds in the air (see the Supplement for additional detail). Examining the data across all seasons, using three Hg measurement methods, criteria pollutants, and meteorology, Gustin et al. (2012) concluded there were different GOM compounds in air that were derived from different primary sources, sources producing different oxidants, and variation across season.

Data from the RAMIX experiment also indicated the KCl-coated denuder measurements were biased low through spikes of GOM (HgBr₂) into a manifold. Ambient air RM concentrations measured by the DOGHS were higher than those measured by the Tekran[®] system and this instrument recovered 66 % of the HgBr₂ spike during RAMIX (Gustin et al., 2013). The experiment also indicated RH caused the denuders to become passivated over time (Gustin et al., 2013). Spike recoveries of HgBr₂ by KCl-coated denuders were 2 to 5 times lower than that measured by the DOGHS, with mean values for spikes ranging from 17 to 23 % recovery. Replicate nylon membranes collected 30 to 50 % more RM than the Tekran[®] system in ambient air. For a concise summary of the results of the RAMIX DOGHS versus Tekran[®] data and an explanation for a component of the atmospheric chemistry occurring see the Supplement.

Figure 1 and Table 2 show correlations between specific GOM compounds concentrations measured by the nylon and cation exchange membranes versus the KCl-coated denuder in the Tekran[®] system (see Huang et al. (2013) for detail on the experimental setup). These data demonstrate different compounds have different collection efficiencies by the

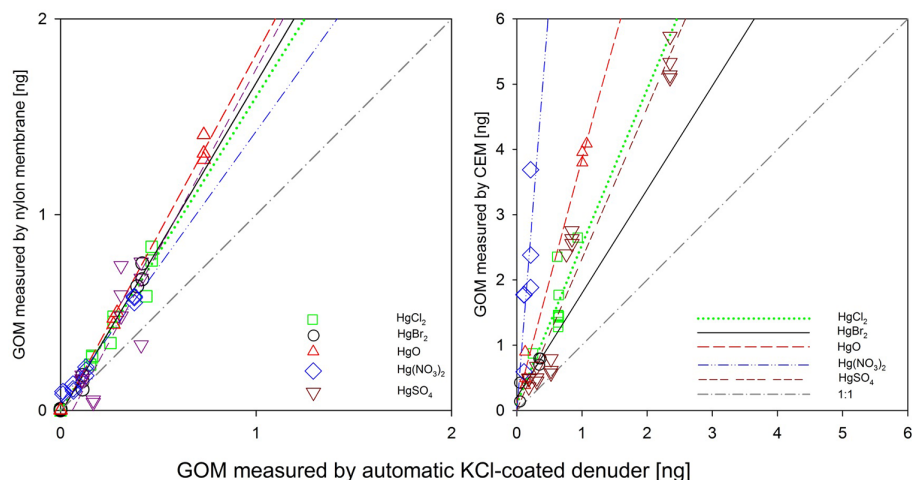


Figure 1. Correlation between GOM concentrations measured by KCl-coated denuder and the nylon and cation exchange membranes in activated charcoal-scrubbed air. Modified from Huang et al. (2013).

Table 2. Regression equations comparing nylon membrane and cation exchange membrane measured GOM concentrations to those measured by the denuder using the UNR laboratory manifold system and charcoal-scrubbed air.

	HgCl ₂	HgBr ₂	HgO	Hg(NO ₃) ₂	HgSO ₄
Nylon membrane (y) KCl denuder (x)	$y = 1.6x + 0.002$ $r^2 = 0.97, n = 12$	$y = 1.7x + 0.01$ $r^2 = 0.99, n = 10$	$y = 1.8x + 0.02$ $r^2 = 0.99, n = 8$	$y = 1.4x + 0.04$ $r^2 = 0.90, n = 12$	$y = 1.9x - 0.1$ $r^2 = 0.6, n = 12$
Cation-exchange membrane (y) KCl denuder (x)	$y = 2.4x + 0.1$ $r^2 = 0.58, n = 9$	$y = 1.6x + 0.2$ $r^2 = 0.86, n = 5$	$y = 3.7x + 0.1$ $r^2 = 0.99, n = 6$	$y = 12.6x - 0.02$ $r^2 = 0.50, n = 6$	$y = 2.3x + 0.01$ $r^2 = 0.095, n = 18$

denuder. Figure 1 shows the nylon membrane has equal efficiency for all Hg(II) compounds tested, and the cation exchange membrane quantitatively collects the Hg(II) compounds permeated. The collection efficiency of the cation exchange membrane relative to the KCl-coated denuder in a Tekran[®] 1130 is HgBr₂ (1.6) > HgSO₄ (2.3) = HgCl₂ (2.4) > HgO (3.7) > Hg(NO₃)₂ (12.6).

Huang et al. (2013) compared field data collected using the Tekran[®] system and the UNR active system. Cation-exchange membranes measured concentrations were 1.1 to 3.7 times greater than the nylon membranes and 2 to 6 times greater than Tekran[®] RM values. Substantial spatial and temporal variability in the difference between the cation-exchange membrane and Tekran[®] RM values were observed. Thermal desorption profiles from the nylon membranes indicate this is explained by variability in the Hg(II) compounds present in air (Huang et al., 2013, 2015).

Data collected using the UNR Active System can be compared to KCl-coated denuder measurements in different areas and used for understanding the GOM concentrations and chemistry for different areas.

4 Case study demonstrating how we can use past measurements to move forward

In light of the new information about interferences affecting GEM measurements, we may begin to go back and re-examine features of past data that previously could not be explained. Here we explore Weiss-Penzias et al. (2003) as a case study. They measured GEM, GOM, and PBM at Cheeka Peak Observatory (Fig. 3), Washington, USA, in the marine boundary layer and found “air of continental origin containing anthropogenic pollutants contained on average 5.3 % lower GEM levels as compared with the marine boundary”. GOM and PBM concentrations in continental air were very low, 0–20 and 1–4 pg m⁻³, respectively. At the time, the results were “difficult to reconcile”. Now we see that the change in GEM concentrations during local anthropogenic pollution events relative to the mean of monthly marine air (−60 to −270 pg m⁻³) in Weiss-Penzias et al. (2003) are similar to the disparity in concentrations measured during RAMIX between the DOHGS and Tekran[®] RM measurement.

Retrospectively, we suggest the observed differences between the two air masses reported can be explained by dif-

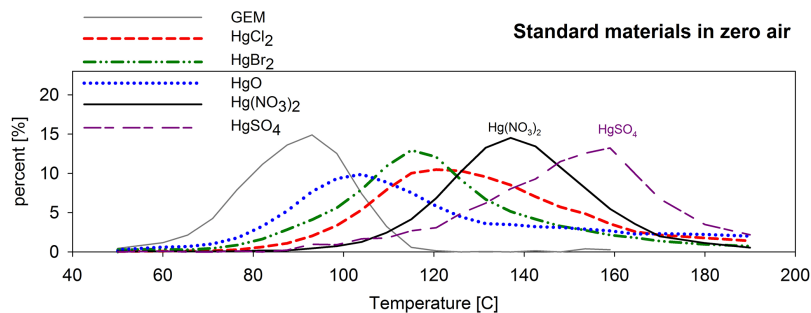


Figure 2. Thermal desorption profiles generated by permeating different Hg compounds. Modified from Huang et al. (2013). Percent indicates the amount released relative to the total. Profiles were developed in activated charcoal-scrubbed air. Compounds being permeated may not be the exact compound in the permeation tube, and this needs to be verified.

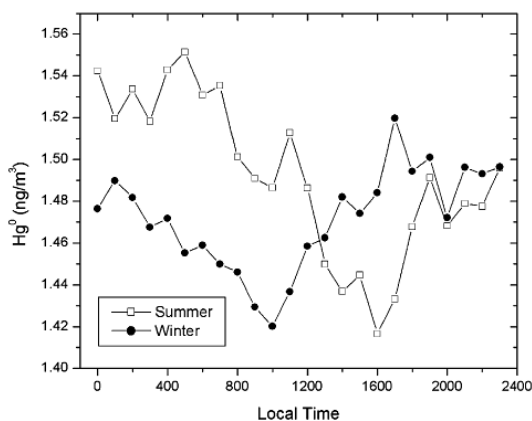


Figure 3. Figure 7 from Weiss-Penzias et al. (2003). Reprinted with permission from Weiss-Penzias et al. (2003), copyright: 1 September 2003 American Chemical Society.

ferences in the mix of oxidants and the resultant Hg(II) compounds formed. GOM and PBM were likely low due to lack of collection efficiency, interferences with O_3 , and loss in the sampling line (see the Supplement for details of sampling set up). Significantly lower GEM concentrations in the continental air are indicative of greater oxidation, which is supported by decreases in GEM concentrations coincident with O_3 increases. Eastern Washington is covered by forests, which generate volatile organic compounds that could contribute to O_3 and GOM formation. The marine air masses likely contained $HgBr_2$ or $HgCl_2$, and the continental air $Hg-O$, $Hg-S$, and $Hg-N$ compounds associated with industry, agriculture, and mobile sources. The capture efficiency of $HgBr_2$ and $HgCl_2$ is greater than for O, S, and N compounds (Fig. 1; Table 2). The case study exemplifies how we can use the loss of GEM as a means of understanding the amount of GOM present or produced in air.

5 Advancing understanding using Hg measurements and models

Here we discuss several key scientific advancements that have come from comparing models with speciated measurements, as well as the major questions left open by these studies. The number of atmospheric models capable of simulating speciated Hg has multiplied over the last decade (Table 3). Detailed discussion on model/measurement comparisons of RM can be found in Kos et al. (2013). Limitations and uncertainties of the models themselves have been written about at length in original research articles on model inter-comparisons (Bullock et al., 2008; Pongprueksa et al., 2008; Lin et al., 2006). Fully acknowledging current limitations, there have still been huge strides made in our scientific understanding of the processes controlling GEM, GOM, and PBM cycling in the atmosphere including: marine boundary layer cycling, plume chemistry, source–receptor relationships, gas–particle partitioning, and vertical distribution.

Our understanding of speciated Hg cycling in the marine boundary layer (MBL) is one example of Hg science advancing as a result of using measurements and models in combination. GOM in the MBL has a diurnal pattern characterized by a midday peak and is depleted through deposition at night (Laurier and Mason, 2007; Laurier et al., 2003; Sprovieri et al., 2003). The use of observations and models together determined that the MBL has bromine photochemistry and was not affected by the hydroxyl (OH) radical. This drives the midday photochemical peak in GOM concentrations in the MBL and that scavenging by sea salt was driving rapid deposition at night (Holmes et al., 2009; Selin et al., 2007; Obrist et al., 2010; Hedgecock and Pirrone, 2001, 2004; Hedgecock et al., 2003; Jaffe et al., 2005; Laurier and Masson, 2007; Laurier et al., 2003; Sprovieri et al., 2003).

Model–observation comparisons consistently suggest models overestimate GOM surface concentrations, sometimes by as much as an order of magnitude (Amos et al., 2012; W. Zhang et al., 2012; Kos et al., 2013; Holloway et al., 2012; Bieser et al., 2014). The measurement–model mis-

Table 3. Atmospheric models with speciated mercury.

Model name	Domain	Type	Explicit or lumped Hg(II)	References
GRAHM	Global	3-D, Eulerian	Explicit (HgCl ₂ , HgO)	Dastoor and Larocque (2004); Ryaboshapko et al. (2007a, b); Dastoor et al. (2008); Durnford et al. (2010); Kos et al. (2013); Dastoor et al. (2014)
GEOS-Chem	Global*	3-D, Eulerian	Bulk Hg(II)	Selin et al. (2008); Selin and Jacob (2008); Holmes et al. (2010); Corbitt et al. (2011); Amos et al. (2012); Y. Zhang et al. (2012); Chen et al. (2014); Kikuchi et al. (2013)
CMAQ-Hg	Continental USA	3-D, Eulerian	Explicit (HgCl ₂ , HgO)	Bullock and Brehme (2002); Vijayaraghavan et al. (2008); Holloway et al. (2012); Bash et al. (2014)
GLEMOS	Variable, global to regional	3-D, Eulerian	Lumped	Travnikov and Ryaboshapko (2002, EMEP report); Travnikov (2010)
ECHMERIT	Global	3-D, Eulerian	HgO _(g) , HgCl _{2(g)} , lumped Hg(II) _(aq)	De Simone et al. (2014); Jung et al. (2009)
WRF-Chem	Regional	3-D, Eulerian	Lumped	Gencarellia et al. (2014)
MSCE-Hg-Hem	Northern Hemisphere	3-D, Eulerian	HgO _(g) , HgCl _{2(g)} , lumped Hg(II) _(aq)	Travnikov and Ryaboshapko (2002); Travnikov (2005); Travnikov and Ilyin (2009)
ADOM	North America, Europe	3-D, Eulerian	HgO _(g) , HgCl _{2(g)} , lumped Hg(II) _(aq)	Petersen et al. (2001)
DEHM	Northern Hemisphere	3-D, Eulerian	HgO _(g) , HgCl _{2(g)} , lumped Hg(II) _(aq)	Christensen et al. (2004); Skov et al. (2004, EST)
WoRM3	Global	2-D, multi-media	Lumped	Qureshi et al. (2011)
PHANTAS	Arctic	box model	Detailed, explicit Hg(II) compounds	Toyota et al. (2014)
HYSPLIT	Global	3-D, Lagrangian	HgO _(g) , HgCl _{2(g)} , lumped Hg(II) _(aq)	Cohen et al. (2004)
TEAM	North America	3-D, Eulerian	HgO _(g) , HgCl _{2(g)} , lumped Hg(II) _(aq)	Bullock et al. (2008, 2009)
CTM-Hg	Global	3-D, Eulerian	HgO _(g) , HgCl _{2(g)} , lumped Hg(II) _(aq)	Shia et al. (1999); Seigneur et al. (2001, 2003, 2004, 2006); Lohman et al. (2008)
REMSAD	North America	3-D, Eulerian	Explicit (HgCl ₂ , HgO)	Bullock et al. (2008, 2009)
EMAP	Europe	3-D, Eulerian	Lumped	Syrakov et al. (1995)

* The standard GEOS-Chem has a global domain with the option to have a nested high-resolution simulation over North America (Zhang et al., 2012).

match is now understood as being partly explained by a low sampling bias (see Sect. 3), but this alone cannot reconcile the discrepancy. Reduction of GOM to GEM in coal-fired power plant plumes (Edgerton et al., 2006; Lohman et al., 2006) has been invoked as a possible explanation (Amos et al., 2012; W. Zhang et al., 2012; Kos et al., 2013; Holloway et al., 2012; Vijayaraghavan et al., 2008). The mechanism for in-plume reduction (IPR) remains speculative, hindering inference about how in-plume reduction may vary with coal type, control technology, or atmospheric composition. Results from recent field and laboratory data have been mixed, providing evidence for and against IPR (Tong et al., 2014; Landis et al., 2015) (Deeds et al., 2013). The speciation of anthropogenic emission inventories is also being revisited in order to reconcile model–measurement RM mismatches (Wang et al., 2014; Bieser et al., 2014). Improving our understanding of IPR and emission speciation has important implications for the efficacy of domestic regulation such as the US EPA Mercury Air Toxics Standard and for potentially attributing trends in Hg wet deposition over the USA (Y. Zhang et al., 2012).

Derived source–receptor relationships will also be sensitive to uncertainties in IPR and emission speciation. On the whole, Hg models simulate wet deposition fluxes better

than surface GOM concentrations, contributing to the relatively high degree of consensus among source–receptor studies. A comparison of source–receptor studies found models agreed within 10 % in terms of the attribution of total wet Hg deposition to a given continental region (e.g., Europe, Asia) (AMAP/UNEP, 2013; Travnikov et al., 2010). Several source–receptor studies have concluded domestic US emissions contribute ~ 20 % to total Hg deposition over the contiguous USA (Selin and Jacob, 2008; Corbitt et al., 2011). W. Zhang et al. (2012) found that including IPR in a model decreased the domestic contribution to wet deposition over the USA from 22 to 10 %.

An additional area of measurement–model study has been gas–particle partitioning of GOM and PBM. Understanding gas–particle partitioning is important because gases and particles are removed from the atmosphere by different physical processes. There is observational and laboratory evidence that gas–particle partitioning between GOM and PBM is driven by air temperature and aerosol concentrations (Rutter and Schauer, 2007a, b; Steffen et al., 2014; Rutter et al., 2008; Amos et al., 2012; Chen et al., 2014). Implementing temperature-dependent gas–particle partitioning in a global model increased simulated annual Hg deposition at higher latitudes (Amos et al., 2012). Aircraft observations suggest

gas–particle partitioning also plays a major role in influencing the vertical profile of Hg, especially in the upper troposphere/lower stratosphere (Swartzendruber et al., 2009; Lyman and Jaffe, 2012; Murphy et al., 2006). Current gas–particle partitioning relationships are derived from surface data. PBM measurements from the summit of Mt. Bachelor suggest these relationships do not capture PBM dynamics aloft (Timonen et al., 2013). Effects of aerosol composition (Rutter and Schauer, 2007b), relative humidity, or even repartitioning of RM within the Tekran[®] (see Sect. 3.3) could potentially contribute to this deficiency.

Oxidation also plays a central role in Hg cycling at the upper troposphere/lower stratosphere boundary. Comparisons against vertical aircraft profiles of TGM consistently suggest there is too little oxidation in models in the lower stratosphere (W. Zhang et al., 2012; Holmes et al., 2010). Observations show that total Hg is depleted in the lower stratosphere (Holmes et al., 2010; Lyman and Jaffe, 2012; Slemr et al., 2014), which is thought to be the result of rapid oxidation of Hg(0) to Hg(II), partitioning of Hg(II) to sulfate aerosol, and subsequent sedimentation of PBM (Lyman and Jaffe, 2012). Aircraft measurements over Washington and Tennessee, USA, found summertime GOM peaks between 2 and 4 km (Swartzendruber et al., 2009; Brooks et al., 2014). Modeled GOM vertical profiles over the USA have a less pronounced peak and generally place it higher (4–6 km) (Bullock et al., 2008). Correctly modeling the vertical distribution of Hg, particularly GOM and PBM, is essential for simulating deposition and hence Hg loading to surface ecosystems.

Chemistry remains one of the greatest uncertainties in Hg models. Improving measurements to determine the chemistry can help determine the mechanism(s) at play. There is still a general lack of rate coefficients and corresponding step-by-step reaction mechanisms available. The estimated tropospheric lifetime of RM against deposition and reduction is 40 days (Holmes et al., 2010), but the reduction pathway is highly uncertain (Subir et al., 2011; Pongprueska et al., 2008), and the burden of RM in the free troposphere is uncertain by at least a factor of 2 (Selin et al., 2008; De Simone et al., 2014). Improving our knowledge of the reduction and oxidation rates in the atmosphere will allow models to better capture the vertical distribution of Hg and in turn better simulate Hg deposition. The recent AMAP/UNEP (2013) assessment identified this as the highest priority for Hg models due to the importance in the Hg exposure pathway.

A persistent issue is the ambiguity in comparing modeled Hg(II) compounds to GOM and PBM, which are operationally defined. Models either have a lumped Hg(II) tracer or explicitly resolve individual Hg(II) compounds (Table 3). Since different Hg(II) compounds have different collection efficiencies by the KCl coated denuder (Fig. 1), this further confounds how to best construct a GOM-like model quantity to compare against observations. An active dialogue between experimentalists and modelers is encouraged as the commu-

nity moves forward, so modelers may implement Hg tracers that emulate the Hg compounds measured.

Recent papers have used a three-fold correction factor to adjust the GOM concentrations measured by the Tekran[®] system to calculate dry deposition using models in the western USA and Florida (cf. Huang and Gustin, 2015a; Huang et al., 2015). Use of this correction factor is based on the discrepancy between denuder measurements in the field and cation exchange membranes dry deposition measurements and concentrations collected using the UNR active system. Weiss-Penzias et al. (2015) found the GEOS-Chem model overestimated RM/GEM by a factor of 2.8 compared to Tekran[®] RM/GEM, which is roughly in line with this correction factor. These field observations were collected in dry and humid conditions and at O₃ concentrations typically observed in the atmosphere. Additional consideration could be based on the RH and O₃ concentrations and the potential GOM compounds in the air.

6 Outstanding issues

Mercury is present in the atmosphere at pg m^{-3} to ng m^{-3} , and the capability to measure it is a substantial analytical accomplishment. Ongoing measurements of atmospheric Hg will be key in evaluating the environmental benefit of regulation on behalf of the Minamata Convention.

Here we reviewed the current state of the science for measuring and modeling atmospheric Hg concentrations. Recent laboratory and field investigations have shown numerous artifacts and environmental interferences can affect measurement methods. Some environments such as those with low humidity and O₃ may be less susceptible to sampling interferences than others. In light of new information about the limitations of sampling methods, we may revisit and better explain certain features of previous data sets and measurement–model comparison.

Fundamental research is needed on measurement methods and the atmospheric chemistry of Hg. We need to obtain agreement between several methods for understanding the chemical forms and compounds in the air. Only through comparison of multiple calibrated measurements can results be determined to be accurate.

Identifying the chemical compounds of RM in the atmosphere is a top priority. Understanding the final oxidation products are key for resolving questions regarding Hg chemistry. Knowing the dominant compounds would help with the design of measurement methods and determination of deposition velocities. Thermal desorption shows promise and mass spectrometry may be a way to verify compounds.

Development of a standard, field-deployable calibration system is needed. This system should provide spikes into ambient air and allow for studying sampling efficiencies and artifacts associated with ambient air. Lack of calibration is currently a major shortcoming.

A pyrolyzer should be used at the inlet of the 2537 if the goal is to measure TAM. The way the Tekran® 1130/1135 system is configured to capture GOM first and then PBM is the best method to measure these two compounds. However, given the difficulty of separating GOM from PBM, we recommend interpreting the sum of RM instead of PBM alone until separation is improved.

A measurement system that collects GOM on a denuder material demonstrated to work for all compounds of GOM, and a separate measurement on a filter using a cation-exchange membrane could be used for measurement of GOM and RM. Then PBM could be determined by difference. Due to negative artifacts during long sampling times measurements should be done for < 24 h.

A new passive sampler design is needed that quantitatively determines concentrations and is calibrated. Use of a computational fluid dynamics model to help design the sampler could be one successful way forward. Passive samplers and surrogate surfaces have longer time resolution (1 day to weeks), but are relatively inexpensive and easy to operate and could provide an alternative measure of GOM concentrations and dry deposition fluxes in large-scale sampling networks once the above issues are resolved.

The Supplement related to this article is available online at doi:10.5194/acp-15-5697-2015-supplement.

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