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Successes and challenges of measuring and modeling atmospheric mercury at the part per quadrillion level: a critical review

M. Sexauer Gustin[1], H. M. Amos[2], J. Huang[1], M. B. Miller[1], and K. Heidecorn[1]

[1]Department of Natural Resources and Environmental Science, University of Nevada-Reno, Reno, NV, 89557, USA
[2]Department of Environmental Health, Harvard T.H. Chan School of Public Health, Boston, Massachusetts, 02115, USA

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

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Abstract

Measurements of atmospheric mercury (Hg) are being increasingly incorporated into monitoring networks worldwide. These data are expected to support and inform regulatory decision making aimed at protecting human and wildlife health. Here we critically review current efforts to measure Hg concentrations in the atmosphere and interpret these data with Hg models. There are three operationally defined forms of atmospheric Hg: Gaseous Elemental (GEM), Gaseous Oxidized (GOM), and Particulate Bound (PBM). While there is relative confidence in GEM measurements, GOM and PBM 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 can be biased low by a factor of 1.6–12 times depending on the chemical compound. Importantly, efforts to understand the fundamental limitations of atmospheric Hg measurement methods have provided clear evidence that the composition of GOM (e.g., $HgBr_2$, $HgCl_2$, HgBrOH) varies across space and time. This has significant implications for refining existing measurement methods and developing new ones, model/measurement comparisons, model development, and assessing trends. In addition, unclear features of previously published data may now be re-examined and possibly explained, which we present as a case study. Lastly, we outline recommendations for needed research directions as the Hg field moves forward. Priorities include GOM and PBM calibration systems, identification of GOM compounds in ambient air, and identification of redox mechanisms and associated rate coefficients. Determination of a quantitative correction factor for biased GOM and PBM data is also needed to facilitate model-measurement comparisons.

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 speciated atmospheric Hg currently stands and offer suggestions for future research directions that will both advance understanding of Hg cycling in and between the Earth's spheres, and better serve the needs of the Convention.

Although the atmosphere is a relatively minor reservoir of Hg compared to the ocean or soils, it is an important pathway by which Hg is distributed globally over short timescales ($\sim$ 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 suggest 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., 2014b). In contrast, direct observations of atmospheric Hg suggest concentrations have been decreasing over the last $\sim$ 15 years (Slemr et al., 2011; Cole and Steffen, 2010; Soerensen et al., 2012; Cole et al., 2010, 2014), despite trends in global anthropogenic emissions being relatively flat or increasing (AMAP/UNEP, 2013). This unexpected decrease remains unexplained and underscores the need to continue monitoring and studying Hg in the atmosphere.

Measuring speciated Hg in the atmosphere is a difficult and technical undertaking. Speciated atmospheric Hg is operationally defined as gaseous elemental mercury (GEM), gaseous oxidized Hg (GOM), and particulate bound Hg (PBM) (Lindberg et al., 2007; Schroeder and Munthe, 1998; Landis et al., 2002). The difficulty is compounded by the complex fundamental physio-chemical properties of GEM, GOM,

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and PBM; all at low parts per quadrillion by volume (ppqv) concentrations in a multi-phase, ever-changing air matrix. Because of the complexity, recent work has combined GOM and PBM concentrations and defined this as reactive Hg (RM). The Tekran® 2537/1130/1135 system is the most widely adopted method by the international community of scientists and 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.

In this paper, we review current methods for measuring atmospheric Hg in the field, and model studies built around interpreting field observations. These are important topics for addressing the Convention that will need accurate monitoring. 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 these limitations. The number of models that have developed the capacity to simulate speciated atmospheric Hg has multiplied in the last decade. We review major gains in Hg science gleaned from the use of some of these models and observations together, as well as the major questions that are currently unanswered. Lastly, we conclude with a discussion of the outstanding problems facing both the measurement and modeling community, and offer suggestions for moving forward the study of Hg in the atmosphere.

2 Current methods for atmospheric Hg measurements

2.1 Automated systems

2.1.1 Tekran® system

The Tekran® 2537/1130/1135 system, developed by research scientists, has been widely used to measure atmospheric Hg for the past ∼ 15 years (Landis et al., 2002). The first component of the current system developed was the Tekran® 2537 that is

used to measure TGM (TGM = GEM + GOM) or GEM in ng m^{-3}. Next 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 surface used to collect GOM in the 1130 system is a potassium chloride (KCl)-coated denuder; and for PBM a column of quartz chips and a quartz filter are used.

Briefly, this instrument first pulls air through an elutricator that is heated to 50 °C and removes particles > 2.5 µm depending on the flow rate (cf. Lyman et al., 2007). This particle size cut is necessary to keep larger particles from depositing on the denuder. Next, air passes through a KCl-coated annular denuder (1130 unit) that was designed for collecting GOM, then through a quartz filter and chips for collection of PBM. When sampling, the 1130 and 1135 units are maintained at 50 °C. Air then passes through 10 m of heated line with a soda lime trap and Teflon filter at the 2537 inlet, and then finally, into the 2537 where GEM is collected on a gold trap. Mercury is thermally desorbed from the GOM (500 °C) and PBM (800 °C) 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).

This instrument has high temporal resolution that is needed for understanding processes governing the biogeochemical cycling of Hg, low limit of detection (Table 1), and established QA/QC protocols. Best management practices have been carefully developed by the Canadian Mercury Network (CAMNet) and the American Mercury Network (AMNet) (Steffen et al., 2012; Gay et al., 2013, respectively). However, there are no calibration standards for GOM and PBM; discussion regarding whether the 2537 measures TGM or GEM; and collection efficiency for GOM and PBM is uncertain (cf. Gustin and Jaffe, 2010; Huang et al., 2013; Talbot et al., 2010). The magnitude of the GOM bias depends on the form of GOM in air, concentration of ozone, and relative

humidity as demonstrated by laboratory tests (Huang et al., 2013; Lyman et al., 2010a; McClure et al., 2014; Huang and Gustin, 2015a).

2.1.2 Lumex

Lumex RA-915 and Lumex 915+ (Lumex, St. Petersburg, Russia) units measure GEM and TGM, respectively, with a reported detection limit of $\sim 1\,\mathrm{ng\,m^{-3}}$ for measurements in air. The Lumex uses Zeeman atomic absorption spectrometry. In this instrument a Hg vapor lamp sits in a magnetic field. In the magnetic field, the Hg source generates a 254 nm light wavelength that is split into 3 polarized light fields. A photodetector detects light in one field within the Hg absorption wavelength 254 nm and another lying outside of this wavelength. When Hg is not present the signals from both fields are equal, when Hg is present the Hg component is higher (for details see Sholupov et al., 2004). Based on tests done at the University of Nevada-Reno (UNR), the major drawbacks of this instrument for air measurements are the poor initial run-time stability and lack of ability to calibrate at low air concentrations (additional detail in the Supplement). This instrument takes 1 to 3 h to stabilize and is not designed for automated operation beyond several hours (Table 1).

2.1.3 Gardis

An additional Hg analyzer that has two gold traps, a concentrating and analytical trap, and measures Hg using cold vapor atomic absorption spectrometry (CVAAS) is the Gardis (Institute of Physics, Lithuania). This unit measures GEM; was developed in 1995 by Urba et al. (1995); and in a field comparison concentrations of GEM 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 $0.5\,\mathrm{ng\,m^{-3}}$ (Table 1).

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2.1.4 University of Houston Mercury system (UHMERC)

The University of Houston Mercury system (UHMERC) is a system for measuring GEM and TGM. This instrument uses two Tekran[®] systems that are slightly modified (gold trap heated to 460 °C) (Gustin et al., 2013).

2.1.5 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 to be due to GOM + PBM. The method was first described by Swartzendruber et al. (2009). The measurement of GEM requires that GOM and PBM are selectively removed from the airstream. In early versions, this was accomplished using a KCl-coated denuder. This led to the discovery of a discrepancy between GOM collected on KCl denuders and that measured by the difference method (Swartzendruber et al., 2009). This instrument first used quartz chips maintained at 650 °C using a pyrolyzer to measure TGM, and then pyrolyzed quartz wool (Lyman and Jaffe, 2011; Ambrose et al., 2013).

More recently a cation-exchange membrane filter has been used to as a means to remove GOM compounds. Ambrose et al. (2013), Lyman and Jaffe (2012), and Swartzendruber et al. (2009) made additional modifications to the original instrument. For example provision for more frequent zeroing and calibrations, which are critical for success of the difference method. Extensive testing has been conducted on the DOHGS using calibration sources of Hg^0, $HgBr_2$, and $HgCl_2$.

The method detection limit for RM is $\sim 80\,pg\,m^{-3}$ based on measurements made during the Reno Atmospheric Mercury Intercomparison eXperiment (RAMIX) (Ambrose et al., 2013; Table 1). Despite this, RM concentrations measured by the DOGHS were higher than those measured by the Tekran[®] system and recovered 66 % of the $HgBr_2$ spike during RAMIX.

A limitation of the DOGHS instrument is that it requires well-trained technicians and has been operated primarily by postdoctoral researchers. This is due to the need for

having two Tekran® 2537s accurately and precisely calibrated. Improving the sensitivity of the underlying CVAFS systems would enable more routine operation of the instrument.

2.1.6 Laser systems

Two laser systems have been developed for measurement of GEM (Pierce et al., 2013 Bauer et al., 2002, 2010). 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. The cavity ring down instrument has interferences with ozone (Ashley Pierce, Ph.D. Candidate, UNR, personal communication, 2014). During RAMIX these two instruments were deployed and could only be operated when trained personnel were present. Given the current sensitivity and electrical power use of these instruments (a small city) they are best applied in the lab.

2.2 Integrated samplers

Integrated samplers collect samples over a specific amount of time and then the data collected need to be analyzed using an alternate method. This contrasts with automated samplers, which provide near real-time automated measurements of the sample after or during collection. Integrated samplers may be biotic or abiotic such as mosses, lichens, and plant leaves, or solid surfaces made of metal or some type of filter material, respectively (Table 1). Here we briefly review integrated sampling methods for GEM/TGM, GOM, and PBM. For a critical review of passive integrated samplers see Huang et al. (2014).

2.2.1 Integrated sampling methods for GEM/TGM

Currently the most promising abiotic passive sampler for TGM is sulfate-impregnated carbon contained in an axial sampler (Zhang et al., 2012a). The use of activated carbon as a sampling material for Hg was investigated by Lindberg and Turner (1977),
5 Lindberg et al. (1979), and Lindberg (1980). This material is effective because it retains atmospheric Hg, has a high sorbtion 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). If the carbon sampler was to be applied at remote sites it would need to be deployed for greater than 90 days.
10 However, it is not known whether it measures TGM or GEM. 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).

2.2.2 Integrated sampling methods for GOM

Mist chamber method for GOM

15 Lindberg and Stratton (1998), Lindberg et al. (2000), and Stratton et al. (2001) described development of a mist chamber for measurement of GOM termed reactive gaseous Hg (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 is accumulated in droplets of ~ 3 to $10 \, \mu m$ that are retained on a membrane. This
20 liquid drains into a chamber, is collected, stored in vials, and analyzed using EPA Method 1631 (EPA Method 1631, 2013). Lindberg and Stratton (1998) found average GOM concentrations ranged from 83 to $257 \, pg \, m^{-3}$, at two sites in the central US. The authors acknowledged the potential artifacts with this approach, which was the first method published to measure GOM.
25 Sheu and Mason (2001) compared denuders, mist chambers, and a filter pack method for measurement of GOM (details on their measurement methods and results

are in the Supplement). Results showed GOM concentrations in Maryland could be up to $500\,\mathrm{pg\,m^{-3}}$ and that GOM could be 0.2 to 29.5 % of the TGM. Reported diel concentrations measured by the mist chamber were significantly higher than the denuder during the day ranging from 20 to 700 vs. 20 to $70\,\mathrm{pg\,m^{-3}}$, respectively. These data support evidence (discussed below) that the denuder measurement is biased low.

Passive samplers for GOM

There are two types of passive samplers for GOM currently used. These include surrogate surfaces for measurement of dry deposition, and those that are based on diffusion and measure uptake as a surrogate for concentration. The surrogate surface method currently applied for measurement of GOM deposition (the Aerohead sampler) includes the cation exchange membrane deployed in a down-facing sampler aerodynamic housing (Lyman et al., 2007, 2009). The Aerohead sampler has been deployed in multiple studies (Castro et al., 2012; Sather et al., 2014, 2013; Peterson et al., 2012; Gustin et al., 2012; Wright et al., 2014b; Huang and Gustin, 2015a). The box sampler designed by Lyman et al. (2010b) provides a means of calculating concentrations based on uptake rate. However, recent work suggests the box sampler has significant wall loss (80 %) of GOM (Huang and Gustin, 2015b). All passive samplers are currently limited by the fact they have not been calibrated, and they must be deployed for one to two weeks.

UNR Active System for GOM

The purpose of the UNR active system is quantification of the ambient concentration of GOM, and identification of the chemical forms of GOM in air. The UNR active system consists of a 6-port system each with two in-series Teflon filter packs. Three of the filter packs house nylon membranes and three cation exchange membranes through which air is pulled using a vacuum pressure pump with flow regulated by a mass flow controller at a rate of ∼ 1 Lpm. (Huang et al., 2013).

Cation exchange membranes are analyzed using EPA Method 1631 (EPA Method 1631) for quantifying the concentration of GOM in the air; however this method may not collect all compounds (Wright et al., 2014; Huang et al., 2014; Huang and Gustin, 2015a). Nylon membranes are thermally desorbed to determine compounds present in the air (Huang et al., 2013). Once the system is set up, samples can be easily deployed and collected, and then analyzed. The nylon membrane is influenced by relative humidity (Huang et al., 2013; Huang and Gustin, 2015a). A new material is needed that is not impacted by relative humidity and from which GOM can be easily thermally released. The active system is currently limited to one-to-two week resolution.

2.2.3 Integrated samplers for PBM

Teflon, glass-fiber, and quartz filters have been used in open faced filter packs, cascade impactors, and Micro-Orifice Uniform Deposition Impactors™ (MOUDIs) to measure atmospheric PBM concentrations (Keeler et al., 1995; Wang et al., 2013; Talbot et al., 2011; Engle et al., 2008). See discussion of limitations below.

2.3 Calibration methods

Calibration for GOM and PBM measurements is currently one of the major outstanding issues (Jaffe et al., 2014,). The vast majority of GOM and PBM measurements are not calibrated. Calibration of GOM measurements may be done using manifold and chamber systems. However, these are not automated or widely adopted. This must be done with care because GOM is an adhesive compound. GOM manifold systems must be heated to reduce wall loss, while chamber systems must be well mixed. No calibration methods have been developed for PBM.

Laboratory chambers have been developed for testing of membranes and passive samplers. These are described in Gustin et al. (2011), Lyman et al. (2007, 2010b), and Skov et al. (2007). Laboratory calibration and tests have also been done at UNR using an 8-port glass manifold allowing for collection of GOM on KCl-coated denuders

and different surfaces (cf. Huang et al., 2013). A Tekran® 2537/1130 unit at the end of the manifold is used to measure GEM and GOM concentrations. A pyrolyzer at the inlet was used to determine concentrations being permeated (Huang et al., 2013). This system is designed so specific Hg compounds can be added at different concentrations as well as ozone, water vapor, and other chemical compounds.

For the RAMIX experiment a manifold system similar to that tested in the lab was applied in the field (Finley et al., 2013). This provided a setting for calibrated additions of GEM and $HgBr_2$ into ambient air; transmission efficiencies were 92 and 76 %, respectively. GOM concentrations were verified using a pyrolyzer and a separate Tekran® 2537 (for details see Finley et al., 2013; Gustin et al., 2013)

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

3.1   Are we measuring TGM or GEM?

There has been much discussion among Hg researchers as to whether the Tekran® 2537 measures TGM (GEM + GOM) vs. GEM. Inlet configuration and local atmospheric chemistry will affect this measurement. Limited work in dry air with uncovered lines indicated that the Tekran® 2537 measures TGM (see Supplement). The Tekran® 2537 measures GEM when the inlet lines are covered (Gustin et al., 2013). Brunke et al. (2010) assumed GEM was the only form getting to the 2537 unit deployed due to the long sampling line, high temperature and humidity, and the presence of hydroscopic sea salt. They observed GEM depletion events of 20 % indicating that GOM could make up 20 % of that in the air. This is within the range of that measured by DOGHS collected during RAMIX, and mist chamber data collected in Maryland and other areas (RM 10 to 25 % of TGM). During depletion events in the Arctic, GOM can make up nearly 100 % of the Hg in the air (Steffen et al., 2014).

In addition, passivation of gold surfaces may occur (Barghigiani et al., 1991; Brosset and Iverfeldt, 1989; Gustin et al., 2011; Munthe et al., 1990; Xiao et al., 1991), and this happens for Tekran[®] gold traps over time (personal experience by first author). Landis et al. (2002) mentioned the passivation of the gold traps periodically occurred right after analyses of a denuder, with recovery dropping to 50 %. To measure TGM requires the use of a pyrolyzer.

3.2 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, 2015; Huang and Gustin, 2015a). Laboratory and field experiments indicate that the collection efficiency of the KCl-coated denuder varies depending on environmental conditions (ozone, relative humidity) and Hg(II) compounds present in air. As we are learning about fundamental limitations of current measurements and testing this method, evidence is coalescing to suggest GOM compounds in the air vary seasonally and spatially. Below we discuss the major laboratory experiments and field studies that shape our current understanding of GOM.

3.2.1 Laboratory experiments on O_3 and relative humidity interferences

Laboratory experiments have so far confirmed ozone (O_3) interferences for KCl denuders, and relative humidity interferences for both KCl denuders and nylon membranes. The potential for an O_3 interference for the collection of GOM by KCl-coated denuders was investigated in the laboratory by Lyman et al. (2010a). These experiments utilized denuders loaded with $HgCl_2$, and GOM collected from ambient air in Nevada. When O_3 concentrations were 6 to 100 ppbv, the collection efficiency was reduced by 3 to 37 %. Lyman et al. (2010a) in the Open Discussion suggested reduction was occurring

on the denuder wall and proposed the reaction:

$$HgCl_2 + 2O_3 \rightarrow Hg^0 + 2O_2 + ClO \left(\Delta Gr = -85\,kj\,mole^{-1}\right) \tag{R1}$$
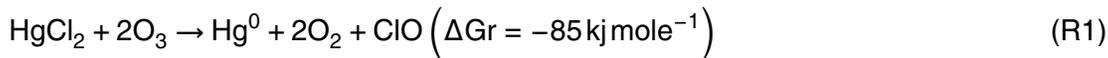
Where ΔGr is the Gibbs free energy of the reaction. Their results also indicated as O_3 exposure time increased, less GOM was recovered (10 to 26 % for 2.5 min, and 29 to 55 % for 30 min at 30 ppbv).

Relative humidity interferes with the collection efficiency of multiple GOM methods. In experiments similar to those performed by Lyman et al. (2010a) for O_3, McClure et al. (2014) found that relative humidity had the same effect on $HgBr_2$ loaded on KCl-coated denuders. Huang and Gustin (2015a) permeated $HgBr_2$ and water vapor into a Tekran[®] 2357/1130 system, and found reduction of GOM collection occurred during spikes, and the denuder became passivated over time (Huang and Gustin, 2015a). The nylon membranes that are used for determining the chemical forms of GOM in air, and analyzed by thermal desorption, are influenced by relative humidity (cf. Huang et al., 2013; Huang and Gustin, 2015a).

Figure 1 and Table 2 show the correlation between specific GOM compounds concentrations measured by the nylon and cation exchange membranes vs. the KCl-coated denuder in the Tekran[®] system. These data demonstrate different forms have different collection efficiencies by the denuder. It is important to note that data shown was collected in activated charcoal scrubbed air, which removes O_3 and water vapor. This figure demonstrates that the nylon membrane has equal efficiency for collection of GOM compounds tested, while the cation exchange quantitatively collects the forms of GOM permeated. The collection efficiency of the cation exchange membrane relative to the KCl-coated denuder (in a Tekran[®] 1130) is $HgBr_2$ (1.6) > $HgSO_4$ (2.3) = $HgCl_2$ (2.4) > HgO (3.7) > $Hg(NO_3)_2$ (12.6) (Fig. 1).

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3.2.2 Field studies and GOM intercomparisons

Co-located field comparisons of different methods helps provide a better understanding of what analytical instruments are measuring (Gustin and Lindberg, 2000). Here we use comparison of data collected with the Tekran[®] system with that collected with passive systems to better understand atmospheric Hg concentrations. Data collected as part of a large study in Florida (Peterson et al., 2012; Gustin et al., 2012), provided a start for better understanding of GOM, and was followed by RAMIX (Gustin et al., 2013). Recently comparison of KCl-coated denuder data with the UNR active system (Huang et al., 2013, 2015) has enhanced the understanding of atmospheric Hg concentrations. Laboratory interference testing has helped to support observations in the field studies (Huang et al., 2013; Huang and Gustin, 2015a).

Peterson et al. (2012) compared passive samplers and Tekran[®] data from 3 sites in Florida with the goal of determining whether the samplers could be deployed and successfully resolve spatial trends in a region with high Hg wet deposition, but low measured KCl-coated denuder GOM concentrations (on average 2–8 pg m^{-3}). One site was considered a fairly background site with minor air pollution and a long range transport signature; a second site was primarily impacted by mobile sources and long range transport; and the third site air chemistry was influenced by local point sources, mobile sources, and long range transport (Gustin et al., 2012). Passive samplers and KCl-coated denuder measurements showed different spatial patterns for GOM. Based on passive sampler uptake and calculated deposition velocities, Peterson et al. (2012) suggested there were different compounds containing GOM in the air. Collectively looking at data collected across all seasons using both sampling methods, criteria pollutants and meteorology, Gustin et al. (2012) indicated there were different GOM compounds in air related to primary sources, and to sources producing oxidants that can react with GEM. More recent work using the UNR active system has demonstrated there are different GOM compounds in the air by season (Huang et al., 2015). See additional discussion in the Supplement for new assessment of the Florida data.

The RAMIX experiment further demonstrated that the GOM denuder measurements were biased low through spikes of GOM ($HgBr_2$) into a manifold. The experiment also indicated relative humidity caused the denuders to become passivated over time (Gustin et al., 2013). Spike recoveries of $HgBr_2$ 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 used in the prototype for the UNR active system collected 30 to 50 % more RM than the Tekran[®] system in ambient air. For detailed discussion of comparison of the DOHGS and Tekran[®] data obtained during RAMIX and the potential atmospheric chemistry occurring see the Supplement.

Huang et al. (2013) compared field data collected using the Tekran[®] system, and the UNR active system in the marine boundary layer, at a highway impacted site, and an agriculture impacted site. In general, RM concentrations measured using the cation exchange membranes were greater than those obtained using nylon membranes, which were both greater than Tekran[®] measurements (Huang et al., 2013). Although there was some variation, cation exchange membranes measured concentrations that were 2-to-6 times greater than Tekran[®] RM values. This variability across space and time indicated different forms were present in the atmosphere, and this was supported by thermal desorption profiles from the nylon membranes (Huang et al., 2013). Huang et al. (2015) also report on thermal desorption profiles from the marine boundary layer in Florida. The cation exchange membranes reported higher concentrations than the Tekran[®] RM and the nylon membranes had different desorption profiles that could be attributed to specific sources. Recently Dibble et al. (2012) indicated using Ab initio calculations that OH, Cl, etc. reactions are possible from a thermodynamic perspective. Theoretically this supports the potential for different GOM compounds in air; however, they did not provide associated rate coefficients for the reactions.

3.3 PBM measurements and potential artifacts

PBM measurements have received far less systematic study than those for GOM. 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; Malcom and Keeler, 2007; Kim et al., 2012). The sign and magnitude of the PBM bias is presently unclear. Both high and low biases have been reported for the Tekran[®] PBM measurement, for details see the Supplement (Talbot, 2011; Rutter, 2008; Malcolm, 2007; Gustin et al., 2013).

Known analytical challenges associated with measuring PBM include limited particle size sampling ($< 2.5\,\mu m$), temperature artifacts, interferences with atmospheric constituents such as ozone or water vapor, and GOM breakthrough by the denuder and retention on PBM collection surfaces. The types of filters used in the measurements will affect the observations (Huang et al., 2013). Based on field and laboratory comparisons (Lyman et al., 2009; Huang et al., 2014) the cation exchange membrane has higher collection efficiency and retention for RM than quartz, Teflon[®], or nylon membranes and may serve as a more reliable surface for PBM. However, it may not collect all forms of Hg(II) (cf. Wright et al., 2014) and this needs to be further tested.

PBM measurements at multiple size fractions are limited. 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; Keeler and Malcom, 2007; Engle et al., 2008). The standard inlet on the Tekran[®] 2537/1130/1135 excludes particles larger than $2.5\,\mu m$ in diameter to prevent large particles from depositing on the KCl-coated denuder (see Sect. 2.1.1). The intake on the UNR active system also is thought to exclude particles and collect primarily GOM (Huang et al., 2013). 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 small aerosol fractions (Lyman et al., 2007).

Temperature and background atmospheric constituents also have the potential to impact measurements. The Tekran® 1135 particulate module is maintained at 50 °C and Hg(II) is semi- volatile. 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 GOM 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). In addition, there is potential for loss from the particle due to the chemistry (Rutter and Schauer, 2007a) and water content of the particles. Malcolm and Keeler (2007) observed less PBM collected on quartz filters for 12 vs. 4 h and suggested a negative sampling artifact that could be due to reduction due to reaction with gases in the air (such as O_3) or relative humidity.

Breakthrough of GOM and/or inadvertent retention of GOM on the PBM collection surface can bias PBM measurements high. Measuring PBM is difficult and requires removal of GOM from the airstream before collection. In principal, the Tekran® 2537/1130/1135 removes GOM on the KCl-coated annual denuder and then PBM is collected downstream. Based on data collected during RAMIX, GOM compounds not collected by the KCl denuder were captured by the rejuvenatable particulate unit (Gustin et al., 2013). Quartz fiber filters used to collect PBM may also collect GOM (Rutter et al., 2007). See Supplement for detailed examples. Lyman et al. (2007) compared calculated dry deposition fluxes from coated (KCl) and uncoated quartz fiber filters against data from cation exchange membrane and quartz filters, both of which yielded significantly lower deposition fluxes. This agrees with the lack of capture and retention by the KCl-coated denuder. Until a new denuder coating is tested and brought into use, it is more robust to interpret RM than PBM.

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

Given the compelling weight of evidence that Tekran® GOM measurements are biased low, we may begin to go back and examine past data that could not be explained. Here we explore Weiss-Penzias et al. (2003), who measured GEM, GOM, and PBM at Cheeka Peak Observatory, Washington, US in the marine boundary layer. They found "air of continental origin containing anthropogenic pollutants contained on average 5.3 % lower GEM levels as compared with the marine boundary", and stated "this result is difficult to reconcile".

Based on the sampling configuration (see Supplement for details) it is likely the difference in the marine boundary and continental air GEM is due to the oxidation and formation of GOM compounds that were not adequately measured by the denuder, and/or lost in the sampling line. This is supported by the fact that decreases in GEM concentrations co-occur with ozone increases. If you assume the marine boundary layer air contains $HgBr_2$ and the continental air contains Hg-O or Hg-S or Hg-N compounds associated with industry or agriculture or mobile sources and GEM is lower when GOM is higher, then you can estimate the amount of GOM based on the loss of GEM. In addition, the capture efficiency of $HgBr_2$ and $HgCl_2$, that would be derived from the marine boundary layer is also better than for O, S, and N compounds. The area to the east is also covered by forests that could generate volatile organic compounds that could contribute to ozone and GOM formation.

GOM and PBM concentrations were very low, $0–20\,pg\,m^{-3}$ and $1–4\,pg\,m^{-3}$, respectively. This is due to lack of collection efficiency of the form of GOM generated, ozone, relative humidity, and loss in the line. However, it is interesting that marine air had significantly higher GEM concentrations than continental air by 2.6 to 6.8 % (Weiss-Penzias et al., 2003 Table 1). This indicates less GEM was being oxidized in marine air. GEM depletion amounts co-occurred with ozone losses. The following equation describes

this relationship:

y (change in GEM concentration relative to marine air)

$= 0.0093 \times$ (change in ozone concentration relative to marine air) $- 0.13$,

$r^2 = 0.6, \quad p = 0.015, \quad n = 8$ \hfill (1)

Data from Table 2 in Weiss-Penzias et al. (2003) that summarizes the change in GEM concentration during local anthropogenic pollution events relative to the mean of monthly marine air (-60 to $-270\,pg\,m^{-3}$) are similar to the disparity in concentrations measured during RAMIX between the DOHGS and Tekran® RM measurement. If you assume the drops in GEM reflect the concentration of GOM and not loss in the sampling line, then you can estimate concentrations. In the winter, the GEM loss was $60\,pg\,m^{-3}$ for continental segregated air, and in the summer, the loss was $120\,pg\,m^{-3}$ (Fig. 3; Weiss-Penzias et al., 2003, Fig. 7).

Weiss-Penzias et al. (2003) observed net loss of GEM from the atmosphere in the fall and winter that primarily occurred at night and they suggested that nighttime oxidants such as NO_3 were forming GOM and removing it from the atmosphere. It is possible this is N_2O_5 and the denuder was not adequately measuring the GOM compounds formed since the uptake of $Hg(NO_3)_2$ is poor (Fig. 2). The study from Weiss-Penzias et al. (2003) provides additional evidence of different oxidants participating in reactions that facilitate formation of GOM from GEM in the atmosphere. Oxidants of probable importance include O_3 (Rutter and Schauer, 2012) and a nitrogen compound (Gustin et al., 2013) such as N_2O_5 or NO_3.

5 Advancing understanding using Hg measurements and models

At the same time our understanding of speciated atmospheric Hg has evolved from the measurement perspective, there has been a parallel evolution from the modeling side. For many years, atmospheric Hg models mostly focused on comparing against and

interpreting TGM or GEM measurements. As the first long-term GOM and PBM records were becoming available, more models began incorporating RM measurements into their framework of study. The number of atmospheric models capable of simulating speciated Hg has multiplied over the last decade (Table 3). Only a short time later, were the measurement interferences and artifacts described in Sect. 3 discovered. Model results must now be interpreted with full knowledge of these artifacts. As demonstrated in Sect. 4 for the Cheeka Peak data, it is true for models too, now that we know more about measurement artifacts we may make more sense of previous model results.

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. 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 by combing models and measurements. Here we will discuss several examples, including marine boundary layer cycling, plume chemistry, source–receptor relationships, gas-particle partitioning, and vertical distribution. Additional discussion on model/measurement comparisons of GOM and PBM can be found in Kos et al. (2013). Limitations and uncertainties of the models themselves have been written about at length in the original research articles and in model intercomparisons (Bullock et al., 2008; Pongprueksa et al., 2008; Lin et al., 2006). The modeling discussion is concluded with priorities and areas of need from the measurement community.

Our understanding of speciated Hg cycling in the marine boundary layer (MBL) is one of the earliest examples 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. 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 de-

position 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).

As operationally defined atmospheric Hg measurements have increased, model-observation comparisons consistently suggest models overestimate GOM surface concentrations, sometimes by as much as an order of magnitude (Amos et al., 2012; Zhang et al., 2012a; Kos et al., 2013; Holloway et al., 2012; Bieser et al., 2014). A high model bias may to some extent be explained by a low sampling bias (see Sect. 3), but this alone is not enough to reconcile the discrepancy. The reduction of GOM to GEM in coal-fired power plant plumes, originally reported by Lohman et al. (2006), has been demonstrated by multiple models to be a potential solution (Amos et al., 2012; Zhang et al., 2012a; Kos et al., 2013; Holloway et al., 2012; Vijayaraghavan et al., 2008). The major limitation of in-plume reduction is that the mechanism remains speculative, which also hinders inference about how in-plume reduction may vary with coal type, control technology, or atmospheric composition. Recent laboratory and field experiments have helped to understand potential mechanisms (Tong et al., 2014; Landis et al., 2014). Landis et al. (2014) suggested reduction of 0 to 55 % depending on the coal used and combustion method. Conversely, Deeds et al. (2013) measured statistically different in-stack and in-plume speciation, but argued it was not conversion of Hg(II) to Hg(0), but rather it could be explained by plume dilution and/or differences in plume and stack measurement methodology. As in-plume reduction is explored, it has become apparent there may be a need to revisit the speciation of anthropogenic emission inventories in order to reconcile the model-measurement RM mismatch (Wang et al., 2014; Bieser et al., 2014). Getting a better handle on in-plume reduction 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 US (Zhang et al., 2012b).

Estimating source–receptor relationships and quantifying domestic contributions to total US deposition is also sensitive to uncertainties in in-plume reduction and emission speciation. On the whole Hg models better simulate wet deposition fluxes than

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surface GOM concentrations (e.g., Amos et al., 2012; Bieser et al., 2014), contributing to the relatively high degree of consensus among a number of source-receptor studies. A model intercomparison on source-receptor analysis found that the models evaluated, agreed within 10 % in terms of the attribution of total Hg deposition to a given continental region (e.g., Europe, Asia) (AMAP/UNEP, 2013; Travnikov et al., 2010). Several source-receptor studies for the US have concluded domestic US emissions contribute ~ 20 % to total Hg deposition over the contiguous US (Selin and Jacob, 2008; Corbitt et al., 2011). However, Zhang et al. (2012a) found that including in-plume reduction, equivalent to decreasing the proportion of total anthropogenic Hg emitted as RM decreased the domestic contribution to wet deposition over the United States from 22 to 10 % (Zhang et al., 2012a).

An additional area of measurement-model study has been gas-particle partitioning of GOM and PBM. Understanding gas-particle partitioning is important for correctly predicting deposition because different physics remove gases and particles from the atmosphere. There is strong 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). The dependence on temperature and aerosols has been observed across highly varied environments (urban, rural, Arctic, coastal, etc.), across all seasons, and using the Tekran® system as well as filter methods (Amos et al., 2012; Rutter et al., 2008; Rutter and Schauer, 2007a; Steffen et al., 2014). Implementing temperature-dependent gas-particle partitioning in a global model increases estimated 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 (UTLS) (Swartzendruber et al., 2009; Lyman and Jaffe, 2012; Murphy et al., 2006). However, all current gas-particle partitioning relationships are derived from surface data and PBM measurements from the summit of Mt Bachelor suggest surface partitioning relationships are not fully capturing PBM dynamics in the free troposphere (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 all potentially contribute to this deficiency.

In addition to gas-particle partitioning, oxidation plays a central but poorly characterized role in Hg cycling at the upper troposphere/lower stratosphere boundary. Comparisons against aircraft vertical profiles of TGM consistently suggest there is too little oxidation in models in the lower stratosphere (Zhang et al., 2012a; Holmes et al., 2010; Hannah M. Horowitz, PhD Candidate, Harvard University, Department of Earth and Planetary Sciences, personal communication, 2014). Observations suggest the vertical profile of total Hg is rapidly depleted in the lower stratosphere (Holmes et al., 2010; Lyman and Jaffe, 2012; Slemr et al., 2014). This is thought to be the result of rapid oxidation of Hg(0) to Hg(II), partitioning of Hg(II) to the sulfate aerosol layer in the lower stratosphere, and subsequent sedimentation of PBM (Lyman and Jaffe, 2012). Aircraft measurements over Washington and Tennessee, US, found GOM in summertime peaks between 2–4 km (Swartzendruber et al., 2009; Brooks et al., 2014). Modeled GOM vertical profiles over the US have a less pronounced peak in summertime and generally place it higher (4–6 km) (Bullock et al., 2008). Correctly modeling the vertical distribution of Hg, particularly of GOM and PBM due to their solubility, is essential for simulating deposition and hence Hg loading to surface ecosystems.

A great amount of coherent science has come from measurement-model comparisons, but analytical uncertainties in GOM and PBM places not unsubstantial limitations on models. Currently, the greatest limitation in using GOM and PBM to support models is that the bias in absolute magnitude of reported concentrations is not entirely known or quantified (Jaffe et al., 2014). Observations serve a vitally important function for models, by anchoring models to reality. The most interesting science often occurs when models and observations disagree, and the reconciliation of the models with observations can spur important advances in our understanding of Hg cycling. This process has become impeded by recent discoveries that speciated Hg observations are affected by biases and interferences that vary in space and time. It is presently not possible to attribute what portion of the GOM and PBM model-measurement mismatch

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is due to instrument error vs. model error (e.g., processes missing in the model). From a modeling perspective, the magnitude of the sampling bias does not matter as long as there is a quantitative and trusted correction factor to apply to affected measurements.

A minor limitation is the ambiguity in comparing modeled Hg(II) compounds to the operationally defined quantities, GOM and PBM. Models either have a lumped Hg(II) tracer or explicitly resolve individual Hg(II) compounds, such as HgO or $HgCl_2$ (Table 3). Field and laboratory work suggests different Hg(II) compounds have different collection efficiencies (see Fig. 1), further confounding how modelers should best construct a GOM-like quantity to compare against observations. An active dialogue between researchers and modelers is encouraged as the community moves forward, with the development of either new analytical techniques or correction factors for existing techniques, so modelers may implement Hg tracers that emulate the Hg compounds/species measured.

Chemistry has been and remains the greatest uncertainty in Hg models. Evidence is mounting that different chemical regimes may dominate in different parts of the atmosphere (see Sects. 3 and 4). Improving the reliability of GOM and PBM measurements can help determine the mechanism(s) at play. 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. However, there is still a general lack of rate coefficients and corresponding step-by-step reaction mechanisms available for modeling the chemistry.

6 Outstanding issues and overcoming technical challenges

Our understanding of Hg cycling in the atmosphere has made huge strides in the last 15 years. Mercury is present in the atmosphere at ultra-trace parts per quadrillion concentrations and successful measurement is in itself a substantial technical accomplish-

ment. The atmosphere is the best observed, and therefore best constrained, global reservoir of Hg when compared to the ocean and soils. The body of atmospheric Hg knowledge served as a core piece of the science behind the 2013 Minamata Convention. High quality, ongoing measurements of atmospheric Hg will be key in evaluating the environmental benefit of regulatory interventions to curb anthropogenic Hg emissions.

Here we have provided a review of the current state of the science for measuring and modeling atmospheric Hg concentrations. Recent laboratory and field investigations have shown that current methods for measuring atmospheric Hg can be affected by numerous analytical artifacts that vary with environmental setting. Some environments such as those with low humidity and low ozone may be less susceptible to sampling interferences than others.

An important and unexpected outcome of investigating the limitations of measurement methods is that there is now clear evidence of the spatiotemporal variability of GOM compounds present in air. Better characterizing the limitations of measurements methods also allows us to revisit and better explain certain features of previous data sets and measurement-model comparisons. Moving forward, data will need to be interpreted within this new paradigm.

Fundamental research is needed on measurement methods and the atmospheric chemistry of Hg. This will help support model development and better address the needs of the Convention. The following are recommendations for specific areas of research needed to move the science of atmospheric Hg forward. Keeping an active dialogue going between researchers and modelers as we work through these problems will benefit the whole community.

- A standard, field-deployable calibration system is needed. Lack of calibration is currently a major shortcoming for most Hg measurement systems and is urgently needed.

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

- Identifying the chemical compounds of GOM in the atmosphere is essential. Knowing the dominant compounds would help with the design of measurement methods and determination of deposition velocities. Thermal desoprtion shows promise and the concept has already been proven for field measurements taken in Nevada and Florida. Mass spectrometry may be a way to verify compounds.

- Improvements to the Tekran® 2537/1130/1135 system are needed. The Tekran® system is the most widely adopted measurement method and has high time resolution and low detection limits. Systematic investigations are needed for the inlet configuration and alternative annual denuder coatings. A pyrolyzer should be used if TGM, not GEM, is desired.

- 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. The depletion of GEM measured in air can be used as a surrogate for estimating RM concentrations in past measurements. We present a case study which demonstrates this can be done successfully for marine boundary layer and continental air. Alternatively, a measurement system that collects GOM on a denuder using an elutricator, and separate measurement on a filter using a cation exchange membrane could be used for measurement of GOM and RM. Then the PBM could be determined by difference. Due to negative artifacts during long sampling times measurements should be done for ≤ 24 h.

- Quantitative correction factors are needed for GOM and PBM collected with the existing Tekran® 2537/1130/1135 configuration in order to use measurements for

model evaluation and development. One potential way to correct measurements is to develop a calibration system for multiple Hg(II) compounds that allows for permeation of these compounds into ambient air and on-site calibration.

– 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 1 week), 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.

– Narrowing uncertainty in the emission speciation of coal-fired utilities, and better understanding of the mechanism and prevalence of in-plume GEM reduction to GOM would be useful. One way to help address both is a fixed measurement platform downwind of a plant or passive samplers deployed surrounding a facility (cf. Huang et al., 2014).

– Identifying the major reduction and oxidation pathways of Hg in the planetary boundary layer, free troposphere, and upper troposphere/lower stratosphere region may be done once we know the chemical forms present. This includes identifying step-by-step oxidation and reduction reactions and associated rate coefficients. Gas-phase, aqueous, and heterogeneous reactions should all be explored.

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

	Hg form measured/ detection limit	Pros	Cons	Suggestion/comments
Automated				
Tekran 2537-gold traps	GEM or TGM $0.5\,\mathrm{ng\,m^{-3}}$ ambient air	Low detection limit, 2.5 to 5 min resolution, there is a calibration source, standardized by AM-Net 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 $1\,\mathrm{pg\,m^{-3}}$	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 $1\,\mathrm{pg\,m^{-3}}$	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. Not certain for air. $1\,\mathrm{ng\,m^{-3}}$ for other media	Good time resolution (seconds) Field portable Allows for measurement of Hg concentrations in environmental media in the field	Not calibrated at low air concentrations, low run time due to low stability, long warmup time	Good for industrial applications
Gardias	GEM or TGM	Good time resolution (2.5 min)	Requires trained operators	
DOHGS	GEM and TGM $80\,\mathrm{pg\,m^{-3}}$	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 Passive Sampler	GEM or TGM $10–80\,\mathrm{pg\,m^{-3}}$	Easy operation	Long time resolution	Good for worldwide network
GOM Mist Chamber	GOM Blank: $20–50\,\mathrm{pg}$		Complicated operation Need acidified solution	Useful as a research instrument, needs to be re-evaluated
GOM Passive sampler-concentration	GOM $2.3–5\,\mathrm{pg\,m^{-3}}$	Easy operation	Long time resolution	Needs a new design
GOM Passive sampler-deposition	GOM Probably PBM $0.02–0.24\,\mathrm{pg\,m^{-2}\,h^{-1}}$	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 $\sim 30\,\mathrm{pg\,m^{-3}}$	Easy operation, 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.

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Table 2. Regression equations comparing nylon membrane and cation exchange membrane measured GOM concentrations vs. those measured by the denuder using the University of Nevada, Reno (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)	$y = 2.4x + 0.1$ $r^2 = 0.58$, $n = 9$	$y = 1.6x + 0.2$ $r^2 = 0.86$, $n = 5$	$y = 3.7x + 0.1$ $r^2 = 0.99$, $n = 6$	$y = 12.6x - 0.02$ $r^2 = 0.50$, $n = 6$	$y = 2.3x + 0.01$ $r^2 = 095$, $n = 18$

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); Ryaboshopka et al. (2007a, b); Dastoor et al. (2008, 2014); Durnford et al. (2010); Kos et al. (2013)
GEOS-Chem	Global[a]	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); Zhang et al., (2012); Chen et al. (2014); Kikuchi et al. (2013)
CMAQ-Hg	Continental US	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, 2004, 2003, 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)

[a] 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).

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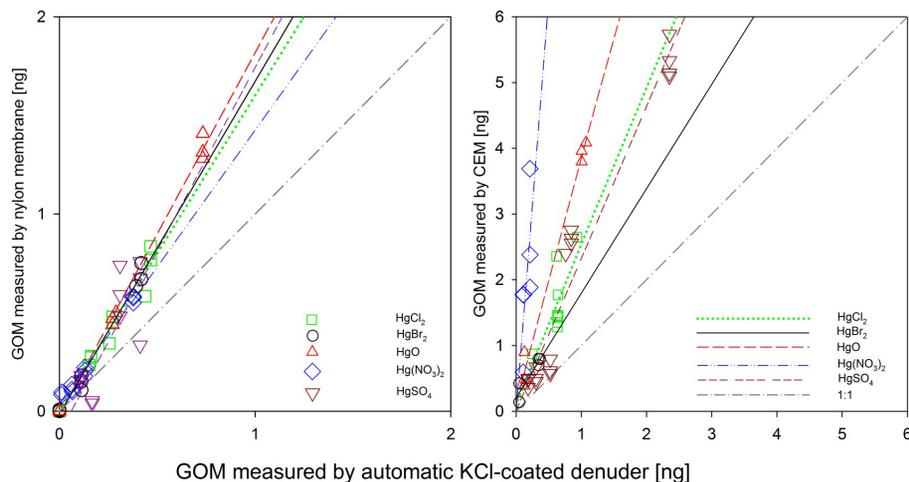
Figure 1. Correlation between GOM concentrations measured by KCl-coated denuder vs. the nylon and cation exchange membranes in activated charcoal scrubbed air. Modified from Huang et al. (2013).
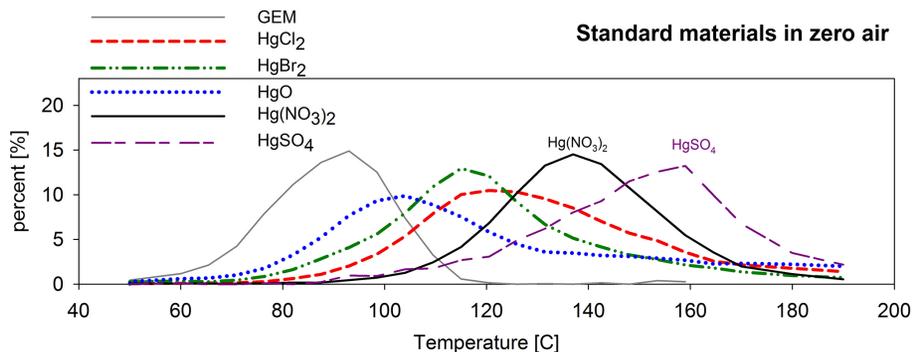
Figure 2. Thermal desorption profiles generated by permeating different Hg compounds. Modified from Huang et al. (2013). Percent indicates the amount released relative to the total. Profiles were developed in activated charcoal scrubbed air. Compounds being permeated may not be the exact compound in the permeation tube and this needs to be verified.
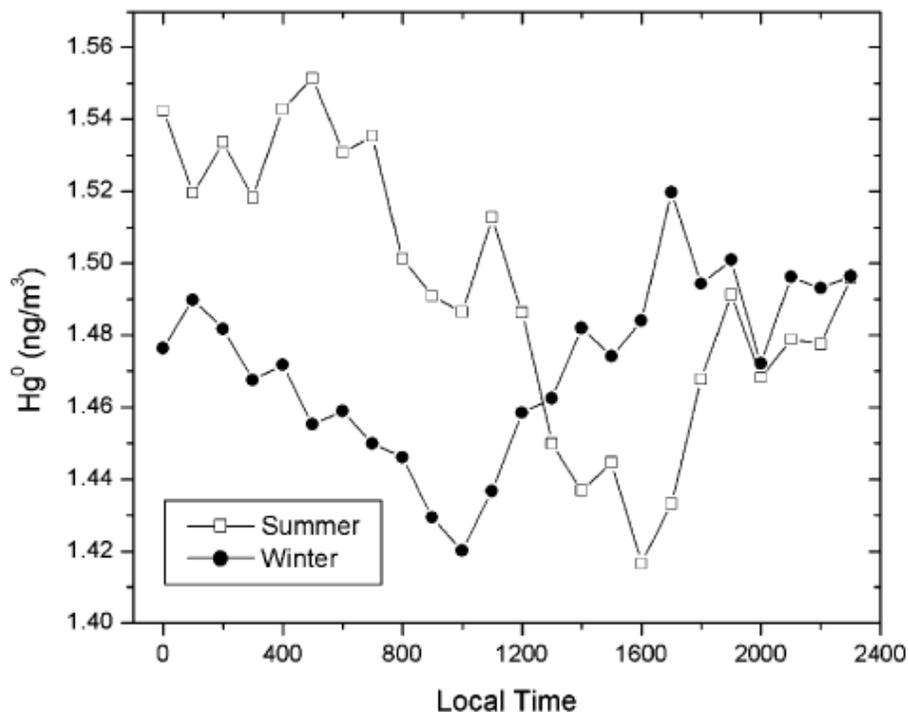
Figure 3. Figure 7. from Weiss-Penzias et al. (2003). Reprinted with permission from Weiss-Penzias et al. (2003), Copyright 1 September 2003 American Chemical Society.

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