

Comparison of Gaseous Oxidized Hg Measured by KCl-Coated Denuders, and Nylon and Cation Exchange Membranes

Part of the "RAMIX: Reno Atmospheric Intercomparison eXperiment" group

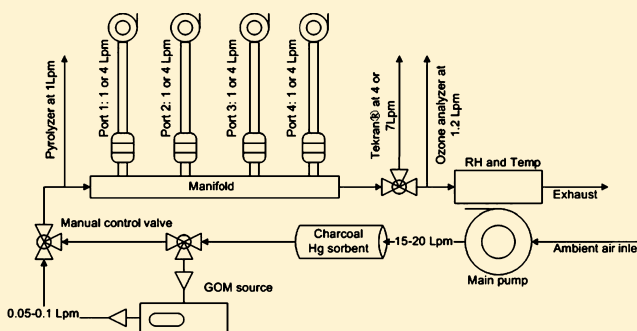
Jiaoyan Huang,[†] Matthieu B. Miller,[†] Peter Weiss-Penzias,[‡] and Mae Sexauer Gustin^{†,*}

[†]Department of Natural Resources and Environmental Sciences, University of Nevada, Reno, 1664, N. Virginia Street, Reno, Nevada 89557, United States

[‡]Department of Microbiology and Environmental Toxicology, University of California, Santa Cruz, California 95060, United States

S Supporting Information

ABSTRACT: The chemical compounds that make up gaseous oxidized mercury (GOM) in the atmosphere, and the reactions responsible for their formation, are not well understood. The limitations and uncertainties associated with the current method applied to measure these compounds, the KCl-coated denuder, are not known due to lack of calibration and testing. This study systematically compared the uptake of specific GOM compounds by KCl-coated denuders with that collected using nylon and cation exchange membranes in the laboratory and field. In addition, a new method for identifying different GOM compounds using thermal desorption is presented. Different GOM compounds (HgCl_2 , HgBr_2 , and HgO) were found to have different affinities for the denuder surface and the denuder underestimated each of these compounds. Membranes measured 1.3 to 3.7 times higher GOM than denuders in laboratory and field experiments. Cation exchange membranes had the highest collection efficiency. Thermodesorption profiles for the release of GOM compounds from the nylon membrane were different for HgO versus HgBr_2 and HgCl_2 . Application of the new field method for collection and identification of GOM compounds demonstrated these vary as a function of location and time of year. Understanding the chemistry of GOM across space and time has important implications for those developing policy regarding this environmental contaminant.



INTRODUCTION

Mercury (Hg) is a unique trace metal that exists in the gas phase as the elemental form and oxidized compounds.^{1–3} Dry and wet deposition are important pathways by which Hg is moved from the atmosphere to terrestrial and marine ecosystems.³ There are three operationally defined “forms” of Hg in the atmosphere, gaseous elemental Hg (GEM), gaseous oxidized Hg (GOM), and particle-bound Hg (PBM).¹ Gaseous oxidized Hg has a short residence time in the atmosphere ranging from hours to weeks.¹ Particle-bound Hg can remain in the atmosphere for days to weeks, and this is dependent upon particle size and interaction with moisture.¹ The chemical compounds of GOM have been suggested to include mercury chloride (HgCl_2), mercury bromide (HgBr_2), mercury oxide (HgO), mercury sulfate (HgSO_4), mercury nitrite ($\text{Hg(NO}_2)_2$), and mercury hydroxide (Hg(OH)_2).^{4–12} Atmospheric measurements in the past have assumed all GOM compounds are captured using a KCl-coated denuder^{13,14} and have not attempted to collect them individually. Since different compounds will have different properties (i.e., water solubility, water-octanol partitioning coefficients, deposition velocities, etc.) they could be collected differently by the denuder, and it is

important to understand their chemistry (cf. Schroeder et al.;¹⁵ Walschlager;¹⁶ and references cited therein).

Methods applied for measurement of GOM have included KCl-coated tubular and annular denuders;^{13,17,18} mist chambers;¹⁹ and cation exchange membranes (CEM).^{20–26} Methods applied for PBM measurements include particulate traps^{9,27} and filter packs.^{28–30} A new method designed for measurement of GOM is the Detector for Oxidized Hg Species (DOHGS).^{31–33} These methods have been compared in field settings with conflicting results.^{13,14,20,34,35} Gustin et al. and Peterson et al.^{34,35} suggested, based on the results of field measurements made in Nevada and Florida, respectively, that discrepancies exist because different compounds of GOM and reactive mercury ($\text{RM} = \text{GOM} + \text{PBM}$) exist across space and time, and different methods measure different chemical forms. If this assertion is correct, then this has significant consequences for policy makers because current knowledge is based on one measurement method that may have systematic errors.

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Ion exchange membranes have been applied for atmospheric gas measurements since the late 19th century, i.e., $\text{SO}_2(\text{g})$, $\text{NH}_3(\text{g})$, and $\text{H}_2\text{O}_2(\text{g})$.³⁶ Polyethersulfone CEMs have been applied for measurement of GOM in the ambient air,^{20,24–26} and were tested by Lyman et al.^{21,22} and Peterson et al.³⁵ The KCl-coated denuder was first investigated by Xiao et al.¹⁷ and modified by Landis et al.;¹³ however, there were few systematic laboratory tests of this method (cf. Gustin et al.,³⁴ Supporting Information (SI)). Nylon membranes were first used for nitric acid (HNO_3) measurements 30 years ago.^{37,38} Because HNO_3 is often used a surrogate for GOM in models,³⁹ we hypothesized that this material might be useful for GOM measurements.

The major hypothesis driving this work was that the chemistry of GOM will vary spatially and temporally, and this will be influenced by the different constituents in the atmosphere. In this study, we investigated the collection efficiency of different chemical compounds of GOM by colocated nylon membranes, CEMs, and KCl-coated denuders using a laboratory manifold system. We used scrubbed (activated carbon column) and filtered ambient air, into which HgO , HgCl_2 , and HgBr_2 were systematically permeated. Data derived using a laboratory framework could provide a foundation for determining if there are systematic biases so that previous data sets could be corrected. Samples were collected using these same surfaces in the field at highway impacted (HI), agriculturally impacted (AI), and marine boundary layer (MBL) sites. The ability of a new method, thermal desorption of nylon membranes, to separate different GOM compounds was also investigated.

METHODS

Sampling Systems. Laboratory Measurements. Laboratory measurements were made using an eight port glass manifold (not coated; URG custom designed). During this study, only four ports were used. Manual denuders were directly connected to the manifold system using Teflon adaptors (see Supporting Information, SI, Figure SI 1). For each port, Teflon joints at the end of each denuder were used to connect to Teflon tubing (OD: 0.635 cm), a mass flow controller, and vacuum pumps (end of manifold flow rate: 2 to 3 Lpm; total manifold flow 15 to 20 Lpm). Manual denuders were maintained at room temperature (20 to 25 °C).

A Tekran 2537/1130 unit was used to measure GEM and GOM concentrations, respectively, collected through tubing connected to the outlet tubing of the manifold. A Tekran 2537 (constant flow of 1 Lpm) with a quartz wool based pyrolyzer maintained at 650 °C at the instrument inlet (see SI for details), used to convert all Hg to GEM, sampled air at the front of the manifold (Figure SI 1: see SI for QA/QC). Air temperature and relative humidity (RH) in the manifold were monitored using a Campbell Scientific CS 500L at the end of the manifold, and data were logged using a CR10X (Figure SI 1). The RH in the manifold was 9 to 20%. The glass manifold and associated Teflon tubing were heated to 100 °C to increase the mobility of GOM in the system. There was no significant difference in the GOM amounts collected using CEM from different ports (ANOVA-ranked); therefore, we assume that the 100 °C for Teflon and quartz surfaces was sufficient to keep the forms of GOM being tested moving through the manifold system. Ozone (O_3) concentrations were also measured periodically at the end of the manifold using a Thermo 49C

(span check at 450 ppb every 3 months, and zero check weekly).

The flow through the Tekran 1130 unit was adjusted to 4 Lpm when the manifold was being used with manual denuders. Manual denuder flow was also 4 Lpm. When sampling using membranes housed in Teflon filter packs in series, the 1130 unit flow was 7 Lpm and flow through the membranes was maintained at 1 Lpm. These differences in flow would not significantly influence the KCl-coated denuder's performance.³⁴ The flows for the inlet, outlet, and four sampling ports were checked before, during, and after all experiments using an external flow meter (Sierra Instrument Inc., CA). On the basis of the flow mass, balance recoveries were >90% indicating that <10% of the Hg permeated was lost from or deposited to the system.

A manual valve was used to control the flow through the GOM permeation system (described below). This was turned on 24 h prior to sampling to obtain stable target concentrations (based on Tekran measurements). After all experiments, the valve was completely closed, and the manifold was flushed with scrubbed air for 24 h to clean out the system. Manifold blanks before permeations were <20 pg m^{-3} .

GOM Collection Methods. Denuders coated with KCl that have been widely applied [cf., ref 13], were used to collect GOM using both automated and manual systems. In addition, nylon membranes (P/N: EW-36229-04, 0.2 μm , Cole Parmer) and polyethersulfone cation exchange membranes (CEM; I.C.E. 450, 0.45 μm , Pall Corporation) were used to collect GOM. Membrane samples were collected over ~8 h and little break through was observed on the second membrane in the series (ratios of Hg amount on the first and second membrane for nylon and CEM range from 0 to 6% and 0 to 16%, respectively). There was no significant GEM capture on nylon membranes at low GEM concentrations (<12.6 ng m^{-3} , collection efficiency <1%), but a small amount at higher GEM concentrations (>200 ng m^{-3} , collection efficiency $7 \pm 2\%$). This check was done using the system in Figure SI 5 of the SI. Total Hg on the CEM membranes was determined using EPA method 1631E (see SI).

As part of this study, other collection materials were tested using the manifold system, including Teflon membranes (P/N EW-36229-24, pore size: 0.2 μm , Cole-Parmer), Tenax traps (P/N Tenax TA 60/80, Supelco), and quartz wool traps (~5 cm in length, P/N 502-177, Leco Corporation). The collection efficiency of these materials for GOM was limited and inconsistent (Hg amount collected on these materials were <1% to 30% of Tekran measurements) and their use was not investigated further (see SI).

Most samples were collected in triplicate; however, for the multiple material comparisons, replicate samples were collected. Since scrubbed (activated charcoal column) or filtered ambient air (glass fiber filter; P/N: GB14047MM, Advantec MFS Inc.) was used in the manifold system, PBM was assumed to be negligible.

GOM Permeation System. Three solid-phase GOM compounds (HgO , HgCl_2 , and HgBr_2 ; Sigma-Aldrich, purity >99.99%), were packed in thin wall polytetrafluoroethylene (PTFE) heat-shrink tubing (O.D. 0.635 cm, P/N: EW-06851-20, Cole Parmer) with solid Teflon plugs in both ends. An active permeation length of 2 mm existed between the plugs. Permeated Hg was carried by scrubbed air into the manifold at ~0.05 to 0.1 Lpm to mix with manifold air and to control the

concentrations in manifold. Permeation tubes were contained in a temperature controlled bath at 0 to 10 °C.

Emission rates of HgBr_2 at 0, 5, and 10 °C were 61 ± 7 , 76 ± 10 , and 107 ± 12 pg min^{-1} (mean \pm standard deviation calculated based on variation in Hg concentrations and the uncertainty of flow rate 0.1 Lpm), respectively, were determined based on air directed through the pyrolyzer to a Tekran 2537. Finley et al.⁴⁰ measured a HgBr_2 permeation rate of 126 ± 4 pg min^{-1} at 50 °C using a similar system. Although these data indicate that the permeation rate increased with temperature exponentially, and are stable after ~ 25 °C, this needs further investigation. Finley et al.⁴⁰ also measured permeation rates using the Tekran 2537 unit after pyrolysis; however, concentrations permeated were >1000 ng m^{-3} . Although the measurement range of the Tekran 2537 unit is from 0.1 to 2000 ng m^{-3} , the linear working range is from 1 to 200 ng m^{-3} . In our study, more dilution zero air was used than that in Finley et al.⁴⁰ and concentrations were <200 ng m^{-3} . Emission rates of a HgBr_2 permeation tube packed in 2007 were compared with a new one generated in 2012 and a $\sim 18\%$ difference was observed (50 ± 11 pg min^{-1} at 0 °C for 2007). This could reflect a decline in permeation over time or a difference in tube packing, since there is no current standard protocol for permeation tube generation.

Permeation rates for HgCl_2 at 0 °C, and HgO at 10 °C (0.1 Lpm), were 25 ± 18 and 38 ± 20 pg min^{-1} , respectively. Although it has been suggested that HgO will partition into a particulate phase,⁵ high GOM concentrations were measured by the Tekran denuder during HgO permeation. Given the purities of the permeation sources provided by the manufacturer, the presence of nontarget compounds would be small. Additionally, since the emitted form passed through thin wall Teflon tubing, it was most likely a gas. We cannot be sure if the chemical compound was HgO or another, such as Hg_2O .⁴¹

Recent work has also reported that little GEM was detected using similar permeation tubes.^{40,42} These results also indicate that gaseous GOM emissions were occurring from the permeation tubes. Thus, it was assumed that no GEM was generated using the GOM permeation tubes under the experimental conditions.

GEM concentrations measured by the Tekran system ranged from <0.5 to ~ 2 ng m^{-3} at the highest GOM concentrations in the manifold. This can be explained by the high GOM concentration in the manifold, the lack of complete capture by the denuder, and some deposition in the ~ 7.5 m line that was heated to 50 °C and located between the 1130 and the Tekran 2537 unit. Additionally, not all of the denuder flow is diverted to the 2537 unit. Deposition to the sampling lines was observed during the Reno Atmospheric Mercury Intercomparison experiment (RAMIX).³⁴

Because of the high emission rates from the permeation tubes, and the need to generate low concentrations (range of 150 to 3000 pg m^{-3}) in the manifold, the flow through the permeation oven was only a few mL min^{-1} . Because of the uncertainty associated with measurement of this low flow rate, we focus on the comparison of the GOM collected by the different methods rather than on the exact concentrations in the manifold.

Field Measurements. Field measurements were made using a 6-port sampling system with three housing nylon membranes and three CEMs (described and shown as a schematic and photograph in the SI). Data were collected from highway and

agriculturally impacted sites (HI and AI, respectively) and in the marine boundary layer (MBL) (see SI for details). During these measurements, a Tekran 2537/1130/1135 unit was used to make simultaneous measurements, except from November 2011 to January 2012, and during April 2012 at the HI site. During this time period at the HI site, the 1135 unit was replaced with quartz fiber filters after the 1130 denuder. The filters were collected weekly as a surrogate for the PBM measurements and analyzed using EPA Method 1631 (see SI Membrane Analyses). The Tekran 1130/1135 units were set to sample over an hour at the AI and HI sites and for two hours at the MBL site.

In the field and laboratory, GOM was measured by the Tekran system using a one hour desorption cycle.⁴³ The 2537 units were calibrated every 24 h using instrument autocalibration and an internal permeation source. The calibration of the Tekran 2537 units applied at the HI and AI sites, and in the laboratory, were checked weekly using manual injections of GEM from an external source, while the system operating at the MBL site was manually calibrated only at the beginning of the experiment. Mercury concentrations at the MBL site were corrected for a sampling bias associated with lower trapping efficiency on one of the two gold traps used to alternately collect GEM based on discrete injections of mercury into ambient air (see SI). Detailed information regarding membrane analyses, data analyses, quality assurance, and quality control are provided in SI.

RESULTS AND DISCUSSION

On the basis of our sampling configurations, laboratory manifold derived samples are considered to contain only GOM; while data collected at field sites may include some PBM, and as such, are considered RM (PBM + GOM).

Laboratory KCl-Denuder 1-h and 8-h Comparison.

Collection of GOM during 1 h measurements made using the Tekran system were compared with those collected over 8 h using denuders connected to the manifold. This was done to check the collection efficiency of the manual denuders over time since the membranes were loaded over 8 h. Concentrations of HgCl_2 , HgBr_2 , and HgO measured by manual denuders (8-h) were 30% to 50% lower than those calculated by integrating the area underneath the curve for the 1 h concentrations made over the same 8-h period by the Tekran automated system (Figure 1; see SI Data Analyses, denuder comparison for calculation). The difference (but not statistically significant, ANCOVA, p -values range from 0.59 to 0.68) varied as a function of GOM compounds being highest for HgO and HgBr_2 , and lower for HgCl_2 . The fact that the KCl-coated denuder collection efficiency was $\text{HgCl}_2 > \text{HgBr}_2 > \text{HgO}$ demonstrates that uptake and retention will be influenced by the compounds of GOM in the air.

The reason for the variability in the 1- and 8-h measurements, shown in Figure 1, could be that measurements were made using filtered ambient air, and collection and retention of the GOM was affected by air chemistry. An O_3 influence on the denuders has been reported.^{34,42} On the basis of measurements made using the laboratory manifold system air containing 5 to 60 ppb of O_3 could have entered the denuders (Figure SI 1 of the SI).

Lyman et al.⁴² suggested, in the public discussion, the following potential reaction for HgCl_2 and O_3 on the KCl-coated surface:

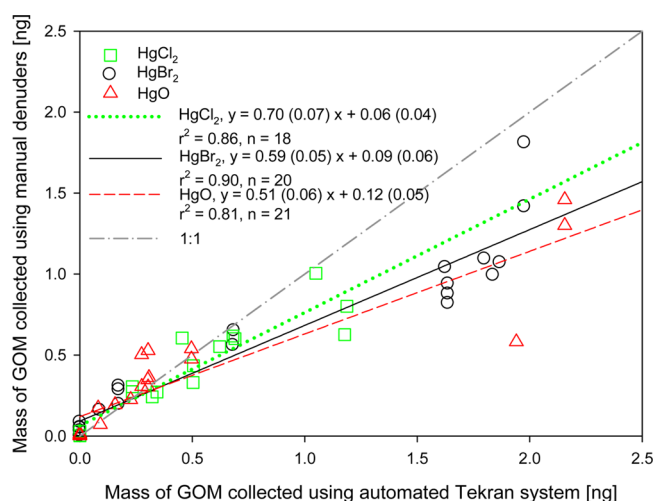
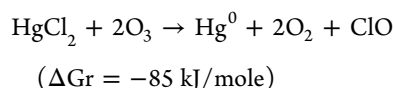


Figure 1. Laboratory comparison of GOM amount (mass ng) as measured by KCl-coated denuders with different exposure times (1 h for every other hour and 8 h) using HgCl₂ (green squares), HgBr₂ (blank circles), and HgO (red triangles) as permeated sources into filtered ambient air. The slopes and intercepts are presented as mean (standard deviation). The x -axis is the extrapolated mass of mercury collected over 8 h based on the sum of 4 individual 1-h measurements taken every other hour. All regression equations are significant at p -value < 0.01; n is the sample number. The fine gray "dotted-dashed" line is the 1:1 comparison. The regression for data when the Hg amount below 1 ng is $y = 0.88x + 0.05$, $r^2 = 0.89$ (all three species together).



They also reported that the longer the O₃ exposure the more GOM lost from the KCl-coated surface. This suggests that GOM could be reduced and lost from the denuder surface due to O₃. Lynam and Keeler³⁰ also showed that O₃ was destroyed by the KCl-coated denuder providing additional evidence for

this hypothesis. Data collected during five Hg and O₃ depletion events at Ny-Ålesund, located on the island of Spitsbergen in the Svalbard Archipelago, administered by Norway, using manual denuders that sampled for 1 to 18 h, and Tekran 1130/2537 systems that sampled for 2 h, found the former to collect 25 to 77% of GOM with respect to the latter.⁴⁴ These observations indicate that the impact of atmospheric chemistry on the denuder measurements needs to be systematically explored.

Laboratory Tekran System and Membrane Comparison. Tekran measured GOM concentrations during permeations ranged from 150 to 3000 pg m⁻³. Because we cannot be sure they are accurate, we discuss the relative amounts collected. Comparison of the data collected using the laboratory manifold showed the highest GOM concentrations in scrubbed air were measured by CEMs, followed by nylon membranes, and then the KCl-coated denuder (Figure 2). The slopes for the comparison of the GOM measured by the denuder versus the nylon membranes were similar for all compounds (1.6 to 1.8, ANCOVA, p -values for HgCl₂ versus HgBr₂, HgCl₂ versus HgO, and HgBr₂ versus HgO were 0.972, 0.121, and 0.211, respectively). Slopes for the comparison of the CEM and KCl-coated denuder varied with HgO > HgCl₂ > HgBr₂. The slopes varied from 1.6 to 3.7 and p -values for HgCl₂ versus HgBr₂, HgCl₂ versus HgO, and HgBr₂ versus HgO were 0.49, <0.01, and 0.04, respectively.

In general, all membranes collected >60% more GOM than denuders. The nylon membrane had 60 to 80% higher capture efficiency than the denuder for all three compounds; while the CEM had uptake capacity that was similar to the nylon membrane for HgBr₂, and much higher uptake for HgCl₂ and HgO relative to the denuder (140 and 270%, respectively). If we use the regression curves in Figure 2, and assume the KCl-coated denuders have the same collection efficiency for individual compounds, then the ratio of the collection efficiencies of HgCl₂, HgBr₂, and HgO on CEM to the nylon membranes (CEM:nylon membrane) are 1.50, 0.95, and 2.06, respectively. A comparison is made of the slopes of HgO versus

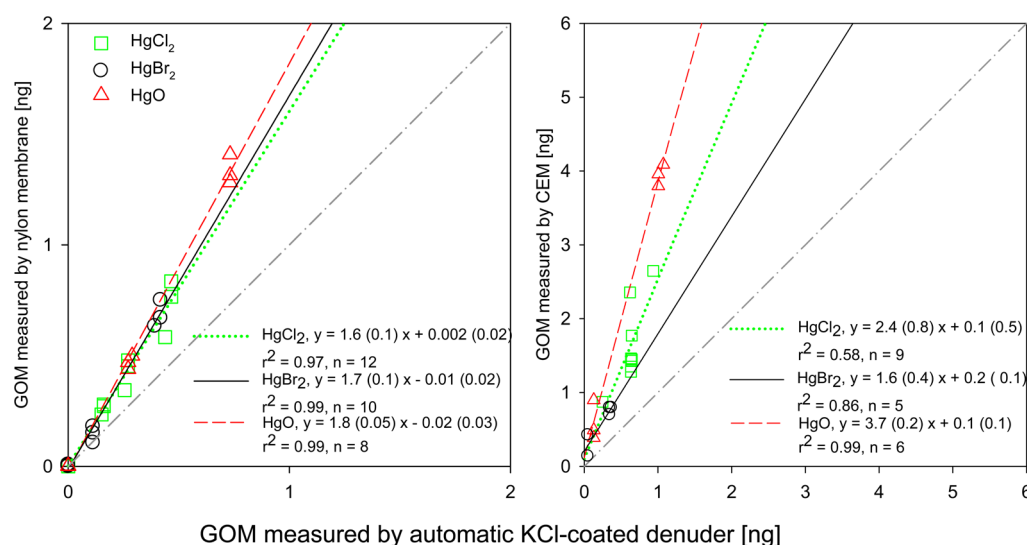


Figure 2. Laboratory comparison GOM measured by Tekran system compared with that measured by the nylon membrane (left) and CEM (right) with HgCl₂ (green squares), HgBr₂ (blank circles), and HgO (red triangles) as permeated sources into charcoal scrubbed air. Note difference in axis scales. The slopes and intercepts are presented as mean (standard deviation), and regression equations are significant at p -value < 0.01; n is the number of samples. The fine gray "dotted-dashed" line is the 1:1 comparison.

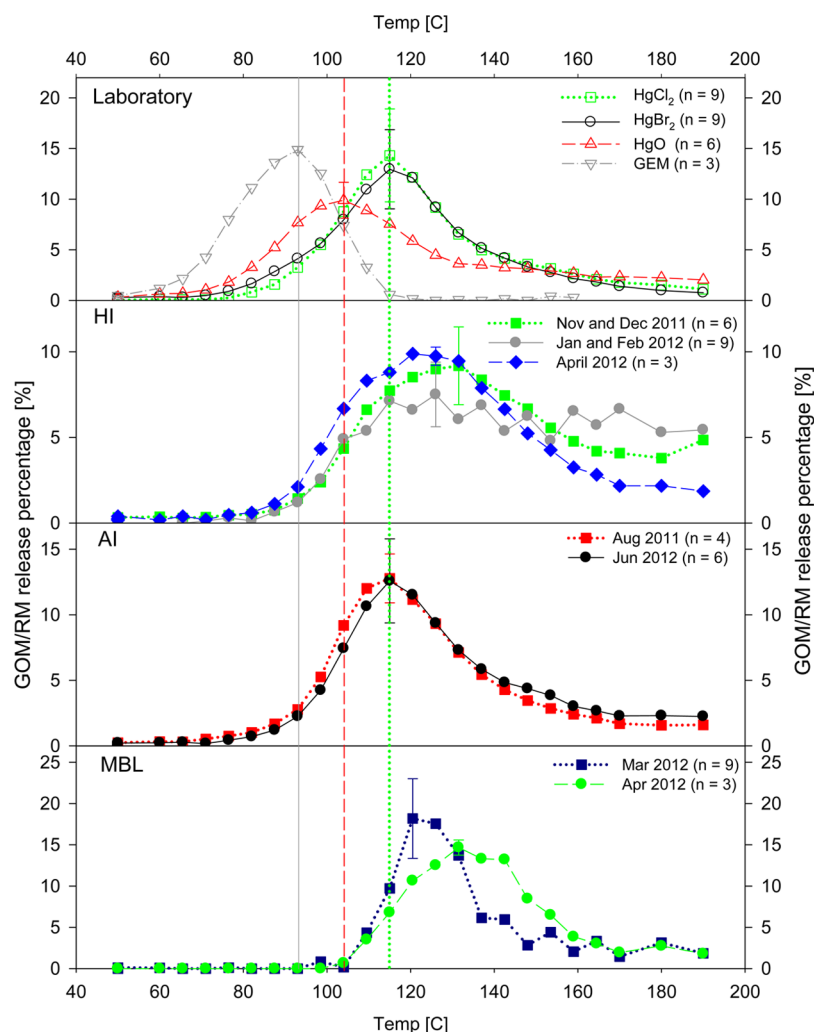


Figure 3. Percent GOM and RM desorption profiles for nylon membranes. Percent released is the amount released at a specific temperature as a function of the total amount released by the membrane. The standard deviation (as $n > 3$) is presented as the error bar in peak of the curve. The error bar for GEM is too small to see (laboratory panel). The open and solid symbols represent the measurements in laboratory and field, respectively. The lower three panels represent desorption profiles for the samples collected at highway impacted (HI), agricultural impacted (AI), and marine boundary layer (MBL) sites. The vertical lines indicate peak desorption temperatures for GEM (gray solid), HgO (red dashed), and HgCl₂/HgBr₂ (green dotted). The desorption profile of GEM is based on a high GEM concentration exposure ($>200 \text{ ng m}^{-3}$).

HgCl₂, and HgO versus HgBr₂, for the CEM data shown in Figure 2 (0.65 and 0.41, respectively), and assuming that the CEMs have the same capture efficiency for all three GOM compounds, as shown by Lyman et al.²² (See Data Analyses, efficiency calculation in the SI); this indicates KCl-coated denuder has highest collection efficiency for HgBr₂, followed by HgCl₂, and then HgO:

$$\begin{aligned} y(\text{Hg amount, ng, on CEM membrane}) \\ &= 1.5(\text{ng, HgBr}_2 \text{ on denuder}) \\ &= 2.4(\text{ng, HgCl}_2 \text{ on denuder}) \\ &= 3.7(\text{ng, HgO on denuder}) \end{aligned}$$

This order of capture efficiency (Br > Cl > O) tracks that of the static average electric dipole polarizabilities for ground state atoms of Br, Cl, and O which are 3.05×10^{-24} , 2.18×10^{-24} , and $0.802 \times 10^{-24} \text{ cm}^3$, respectively.⁴⁵ This would influence the GOM uptake on the KCl coating. Polarizability is a “measure of the extent to which the electron cloud of an atom or molecule

can be distorted by an external electrical charge.”⁴⁶ The polarizability also corresponds with an element’s Van Der Waals radius. The more easily distorted the electron cloud, the more readily this element would be taken up by the KCl denuder. This would explain the observed order of uptake of the Hg compounds tested.

Sheu and Mason¹⁴ reported GOM concentrations measured by KCl-coated denuders were 51% of those measured by filter packs [that consisted of three CEMs preceded by two Teflon filters (five membranes in-series)]. Although the Teflon filters could have influenced the downstream GOM measurements,¹³ laboratory tests of this material showed little affinity for GOM. Notably, we show that KCl-coated denuders collected only 27% to 60% of GOM measured by CEMs, and these numbers are within the range of values obtained for comparison of the Tekran denuder versus a reactive mist chamber (27 to 37%;^{13,14}). Recent data collected during RAMIX showed that the Tekran system measured 45 to 54% of spiked HgBr₂ compared to that measured by DOHGS, respectively.³⁴

Although the CEM showed the highest GOM capture efficiency, it can only be analyzed using wet digestion. These

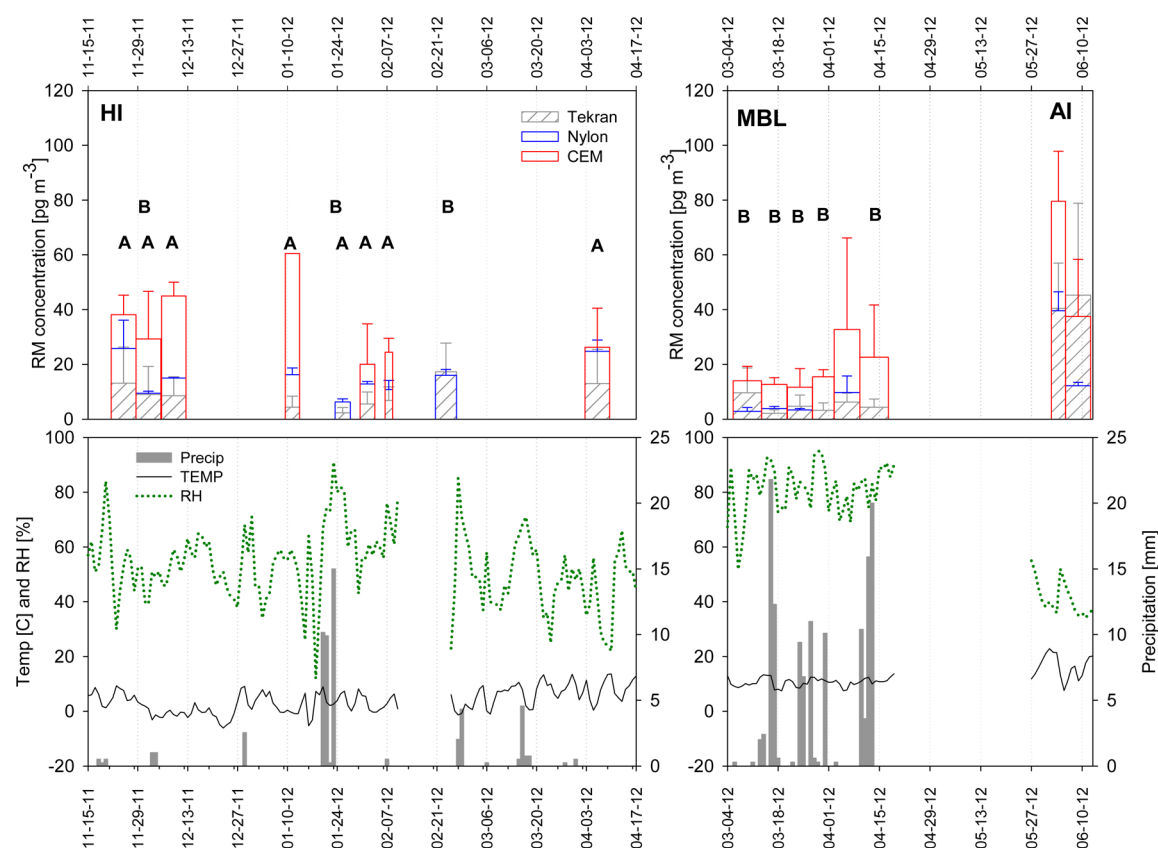


Figure 4. Bar graph showing RM concentrations measured by a Tekran (gray shadow) system, nylon membranes (blue), and CEMs (red) at the three field sites. The whisker indicates standard deviation (or relative percent difference) for triplicate membranes (or replicate membranes) and for 1 to 2 h Tekran measurements over the sampling period. Note the one bar without standard deviation was only a single sample. The width of the bar indicates the length of the sampling period from two to eight days. The 1135 component of the Tekran system was not available during the events marked as A. The events marked as B were time of precipitation. The bottom panels are the meteorological data with precipitation (vertical bar, y-axis on the right), temperature (solid line, y-axis on left), and relative humidity (dotted line, y-axis on left). Tekran data collected at the MBL site during 3/13/2012 and 3/27/2012 were incomplete and subjected to a correction factor.

results indicate that when used in tandem, the CEM can be used to quantify the amount of GOM in air, while nylon membranes can be used to qualitatively identify the chemical compound, since it collected the three compounds with equal capture efficiency.

We tested the hypothesis that if all compounds of GOM are collected on the nylon membrane, then these could be separated as a function of temperature (Figure 3). Tests of GEM release from the nylon membranes, after exposure to high concentrations ($>200 \text{ ng m}^{-3}$), showed a sharp desorption curve starting at 60°C , a peak at $\sim 95^\circ\text{C}$, and all was removed by 120°C (Figure 3). Tests at lower exposure concentrations $<13 \text{ ng m}^{-3}$, and a loading amount of 260 pg, showed that little GEM was collected ($<10 \text{ pg}$). The GEM desorption profile was cleaner than that of the GOM desorption profiles with no residual tail. This suggests that GEM bonding on the nylon surface might be due to van der Waals forces, which would be disrupted at lower temperatures. In contrast, GOM release from the nylon membrane started at 75°C , and peaked at 105°C for HgO , and 115°C for HgCl_2 and HgBr_2 , respectively (Figure 3). Desorption profiles for these compounds extended to the highest desorption temperature of $\sim 190^\circ\text{C}$. Subsequent analyses of these membranes, by wet digestion and cold vapor atomic fluorescence (EPA method 1631 E), showed little residual Hg, $0.13 \pm 0.05 \text{ ng}$, an amount not significantly different from that of the membrane blanks ($0.07 \pm 0.06 \text{ ng}$ $n =$

4 Mann–Whitney test, $p\text{-value} = 0.054$). Nylon material has a long molecular chain that is dominated by hydrogen bonding, and binding with this surface is driven by electrostatic interactions. We suggest that based on the polarizability of Hg, that is 5.1 to $5.7 \times 10^{-24} \text{ cm}^3$,⁴⁵ this element was dominant in influencing the binding of GOM compounds.

Desorption profiles of GEM and HgCl_2 occurred at temperatures from 60°C to 120°C , and 75°C to 190°C , respectively, and overlapped the range reported in Feng et al.⁹ (the references therein) for these compounds added directly to coal fly ash. Feng et al.⁹ added elemental Hg as a gas phase but other compounds were added as solid phases by “dry dilution”. Feng et al.⁹ reported an HgO single peak at $\sim 500^\circ\text{C}$. The discrepancy between our HgO profile and that of Feng et al.⁹ could be due to the different addition methods, and the fact that fly ash contains activated carbon and other impurities (Al_2O_3 , K_2O , MgO , SO_3 , P_2O_5 , etc.) that would provide different chemical bonding between different compounds of GOM and the collection surfaces. Nylon is a uniform material with a specific physical bonding force that will also influence its ability to collect certain compounds of GOM. If we assume that no particulate phase HgO was present, for this form could be deposited to the manifold,^{5,34} then the lower released temperature of “ HgO ” or another compound (i.e., Hg_2O) from nylon is due to a lower electrostatic charge on this compound relative to HgBr_2 and HgCl_2 .

Field Measurements. Field results were similar to those observed in the laboratory with the RM (designated as RM due to uncertainty as to whether aerosols were collected) concentrations measured by CEM being higher than those measured by the Tekran denuder and nylon membranes, except for a measurement made in June 2012 at the AI site (considered an outlier-discussed below) (Figure 4). Statistical comparison of the data showed that the CEM collected a significantly higher amount of GOM relative to the nylon membranes (ANCOVA, p -value < 0.01). Since the time resolution of the Tekran measurement (1 h, on average) is different from that of the membrane (1 week), they cannot be statistically compared; however, given that the mean of the Tekran data represents the average of multiple measurements, this strengthens the argument for the lower concentration as measured by this instrument.

Reactive Hg concentrations as measured by nylon membrane were not consistently higher than those measured by the Tekran system at the MBL site, unlike the results observed in the laboratory with scrubbed air. During times of precipitation (marked as B in Figure 4), the ratio of Hg amount measured by nylon membrane to the RM measured by the Tekran system was < 1.05 (0.75 ± 0.33). However, during these time periods, the CEM consistently recorded higher concentrations. The CEM is designed for proton exchange. Cation exchange membranes used were hydrophilic and had a neutral surface.⁴⁷ This material also wets out (or is impregnated by water) quickly.⁴⁸ This suggests that due to the nature of this material it collected RM during humid conditions (cf. Peterson et al.³⁵).

Although correlation coefficients comparing the Tekran system derived RM and membrane measurements across all sites are significant (Figure SI 6 of the SI, $r^2 = 0.53$ to 0.71 , p -value < 0.01), r^2 values and slopes, were lower than those observed in the laboratory ($r^2 = 0.58$ to 0.99 , p -value < 0.01 , Figure 2). This may be due to other atmospheric constituents that have stronger polarizability out competing Hg for binding sites on the nylon membrane such as water vapor. Similarly, relative humidity has been suggested to influence the KCl-coated denuder performance,^{13,18,24} as moisture could hydrolyze the KCl-coated surface. Water might create another layer for compounds to be transported from air to the collection surface for some materials; however, as mentioned above, RH likely inhibited capture by the nylon membranes but could provide a means by which GOM is captured by the CEM since this material “wets out” quickly. If the data collected using the nylon membranes during precipitation are removed, the following equation is obtained:

$$\text{GOM concentrations on the nylon membrane (ng)} = 1.6$$

$$\text{GOM Tekran denuder(ng)} + 4.8, r^2 = 0.88,$$

$$p\text{-value} < 0.01, n = 10 \text{ sets}$$

The slope for this equation is the same as that obtained for the nylon membrane-denuder laboratory comparisons (Figure 2).

Since different RM/GOM compounds have different basic chemistry, this will influence their affinity for and retention by the collection surface. Unlike laboratory experiments, in the field, the membranes could collect particulate matter as well as the gaseous compounds. Linear regression analyses comparing membrane field data with RM as measured by the Tekran system showed the CEM measured more RM than the denuder

($y = 1.5x + 17$, $r^2 = 0.53$, p -value < 0.01); however, this was not the case for the nylon membrane ($y = 0.89x + 5.1$, $r^2 = 0.71$, p -value < 0.01) (Figure SI 6 of the SI). These data analyses included one outlier. Since there were no significant differences in meteorological conditions during the week outlier data were collected at the AI, and the Tekran system data were variable, this data point was removed. Removal of this outlier resulted in the equation $y = 2.0x + 17.5$, $r^2 = 0.45$, p -value < 0.01 , for the Hg measured on the CEM (assumed to be GOM in Figure SI 7 of the SI) versus the GOM measured by the Tekran 1130; and for the nylon membrane of $y = 1.3x + 4.2$, $r^2 = 0.67$, p -value < 0.01 . The resulting relationships were similar to those measured using the laboratory manifold. This suggests that the membranes as deployed were measuring primarily GOM.

Particle-bound Hg as measured by the Tekran system was higher at the MBL site (56 to 86% PBM/RM) and AI sites (47 and 63%) relative to that measured at the HI site (35% Tekran based; 0 to 15% quartz filter based; Table SI 1 of the SI). Given the chemical composition of aerosol in the MBL site, the form of GOM could be quite different from that at the HI and AI. This is suggested by the desorption profiles discussed below.

The chemical forms and compounds measured by the Tekran GOM and PBM measurements are uncertain. Gustin et al.³⁴ and Lynam et al.³⁰ suggested that GOM can pass through the KCl-coated denuder, be collected on downstream particle filter, and analyzed as PBM. Thus, under certain conditions, the Tekran system might underestimate GOM and overestimate PBM concentrations. It is possible that the denuder, as prepared, results in an alignment of charges across the surface that is more electropositive or negative. This could result in preferential collection of specific forms of GOM. Additionally, as mentioned, KCl is hygroscopic.¹³ This means that it attracts and holds on to water molecules. Materials with this property when exposed to water change by increasing in volume, and as such, the denuder coating would lose the ability to capture GOM because the water molecules become suspended between the KCl molecules. This process could limit the ability of the denuder to collect GOM and result in compounds being collected on the downstream particulate measurement. This also suggests the denuder could be passivated quickly, given it is heated to high temperatures during desorption. This would explain the higher PBM measurements made at the MBL site (Table SI 1). In contrast, because of the configuration of the Tekran system (50 °C for entire sampling system), GOM may be deposited within the system.³⁴ The complexities of the Tekran system make the observations uncertain; and the influence of water on the denuder needs to be systematically investigated.

Other evidence to support that GOM was the primary form collected using nylon membranes, as opposed to PBM, is that the slope of the relationship when using all data at the field sites without PBM was 1.3 ± 0.2 , similar to that obtained for the laboratory experiments, with a higher r^2 value (Figure SI 7 of the SI) than for the RM comparison. In addition, the GOM or RM concentrations measured by Tekran system in the field were only ~20% of those measured by CEM, and this number is consistent with the ambient GOM recovery measured during RAMIX.^{31,34} Particle-bound Hg concentrations measured weekly on quartz filters were significantly lower than those measured using the Tekran 1135 system. This also suggests that using quartz filters after KCl-coated denuders for PBM measurements does not collect PBM.

Different desorption profiles were obtained for membranes collected from the three field sites (Figure 3). At the HI site, the RM release started at 75 °C similar to profiles obtained in the laboratory; however, these curves peaked at ~130 °C, which is 15 °C and 25 °C higher than HgCl₂/HgBr₂ and HgO (or Hg₂O) collected in laboratory, respectively. Furthermore, there was high residual RM after 150 °C, especially for the samples collected in the coldest time periods (January and February). From late fall to early spring, wood fired stoves are frequently used in Reno, NV, and an inversion layer often occurs due to topography. Huang et al.⁴⁹ reported, when using a Tekran system, that PBM was the dominant form of RM measured and suggested that wood combustion for space heating in winter was important. Since PBM is thought to be decomposed at higher temperatures than GOM,¹³ and little residual GOM (digested membranes after desorption 0.26 ± 0.13, *n* = 9; blanks 0.29 ± 0.23 ng, *n* = 7; total 4 sets of data, 2 for HI and 2 for the MBL site) was measured on the membranes, this suggests that a different form of GOM than permeated in the laboratory was present in the air.

The GOM or RM desorption profile in summer time at the AI site was identical to that of HgCl₂ and HgBr₂ collected in scrubbed air using the laboratory manifold system. This site could be influenced by NO₃⁻ and NH_x related chemistry due to nearby livestock, agricultural activities, and/or wastewater treatment and usage. Limited work using Hg(NO₃)₂ showed a peak desorption temperature of 110 °C (data is not shown due to limited tests *n* = 2). This site has also been demonstrated to be impacted by free troposphere air that has been suggested to include HgBr₂ (cf. Gustin et al.).³⁴

Interestingly, the desorption profile of RM collected at the MBL site showed a significant temperature lag (starting from 105 °C) and peaked from 120 to 135 °C. This pattern is not similar to the GOM compounds permeated, and we suggest that a different form of GOM was present. Engle et al.⁵⁰ showed, based on Tekran measurements, that unpolluted air from the MBL site was not a source of GOM and based on limited data PBM was associated primarily with particulate matter >2.5 μm. On the basis of their comparison of Hg concentrations measured as a function of particle size, and the inlet for our sampling system, we would not be sampling this coarse fraction. If one assumes that our field system is only measuring GOM, based on data presented in Figure SI 6 and 7 of the SI, then a similar capture efficiency is shown for GOM compounds by the nylon membrane, and the CEM data are a better indicator of actual concentration. The field data demonstrate that the denuder method underestimates GOM by 2-fold and that GOM compounds other than those tested were being collected; and GOM varies spatially and temporally.

Implications. The use of a KCl-coated annular denuder underestimates the concentrations of HgCl₂, HgBr₂, and HgO in air. Given the different forms suggested to be present in the atmosphere,^{4–6,9–12} and that we do not know all of the compounds present, it is possible that some may not be collected by the denuder as suggested by Gustin et al.³⁴ On the basis of systematic laboratory experiments, the relative collection efficiency for GOM by the denuders in ambient air is HgBr₂ > HgCl₂ > HgO. Comparison of denuder-measured concentrations with those measured using the CEM represents the start of a quantitative framework for calibrating past measurements. This framework is supported by understanding the basic chemistry of the anions bound to the Hg. In order to understand and calibrate GOM measurements, permeation

rates of GOM compounds, including HgBr₂, HgCl₂, HgO, and HgSO₄, and Hg(NO₃)₂ must be developed for a standard system with standard sources. Field and laboratory research are pointing toward KCl denuder interferences with water vapor and O₃. More work is needed to develop calibration factors that will allow us to correct past field measurements using the denuder method for spatial and temporal variations in atmospheric chemistry and GOM compounds.

In scrubbed air experiments, HgCl₂ and HgO amounts measured using CEMs were higher than those measured using nylon membranes; however, there was no difference using these two methods during HgBr₂ permeation. This indicates that bonding of HgCl₂ and HgBr₂ is different for these different surfaces, and that the CEM is a more robust collection surface for quantifying total GOM. Furthermore, different desorption profiles were observed for GEM, HgO, and HgCl₂/HgBr₂; this is due to the overall different affinities between GOM compounds and the nylon surface. Limited field data indicated that PBM was not measured using our field sampling system.

On the basis of thermodesorption profiles, the atmospheric chemistry of GOM varies over space and time. Since GOM has a high deposition velocity and is readily bioavailable, accurate measurements are needed to assess the environmental impacts of this global contaminant.

■ ASSOCIATED CONTENT

Supporting Information

Additional text, Table, 7 Figures, and additional references. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 1-775-784-4203; e-mail: mgustin@cabnr.unr.edu.

Notes

The authors declare no competing financial interest.

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