Automated Calibration of Atmospheric Oxidized Mercury Measurements

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TOC/Abstract Art

Abstract

The atmosphere is an important reservoir for mercury pollution, and understanding of oxidation processes is essential to elucidating the fate of atmospheric mercury. Several recent studies have shown that a low bias exists in a widely-applied method for atmospheric oxidized mercury measurements. We developed an automated, permeation tube-based calibrator for elemental and oxidized mercury, and we integrated this calibrator with atmospheric mercury instrumentation (Tekran 2537/1130/1135 speciation systems) in Reno, Nevada and at Mauna Loa Observatory, Hawaii, U.S.A. While the calibrator has limitations, it was able to routinely inject stable amounts of $HgCl_2$ and $HgBr_2$ into atmospheric mercury measurement systems over periods of several months. In Reno, recovery of injected mercury compounds as gaseous oxidized mercury (as opposed to elemental mercury) decreased with increasing specific humidity, as has been shown in other studies, although this trend was not observed at Mauna Loa, likely due to differences in atmospheric chemistry at the two locations. Recovery of injected mercury compounds as oxidized mercury was greater in Mauna Loa than in Reno, and greater still for a cation-exchange membrane-based measurement system. These results show that routine calibration of atmospheric oxidized mercury measurements is both feasible and necessary.

1 Introduction

Over the past two decades, atmospheric mercury speciation has been measured routinely at dozens of locations around the world with the Tekran 1130/1135/2537 speciation system (Tekran Instruments Corporation, Toronto, Canada; referred to herein as “Tekran system” or “Tekran speciation system”).[1-5] This system measures atmospheric mercury as three fractions: gaseous elemental mercury (Hg^0, also often referred to as GEM), gaseous oxidized mercury (GOM, also called reactive gaseous mercury, or RGM), and particulate-bound mercury (PBM). It collects Hg^0 on gold traps with periodic thermal desorption into an atomic fluorescence detector. GOM and PBM are collected onto a KCl-coated quartz denuder and quartz fiber filter, respectively, both of which are periodically thermally desorbed at a temperature sufficient to decompose Hg compounds, and the resultant Hg^0 is analyzed by the same gold traps and atomic fluorescence detector.[6]

Unfortunately, a growing body of research is showing that the Tekran speciation system is unable to quantify GOM and PBM consistently. Rutter and Schauer, Talbot et al., and Gustin et al. showed that the system does not accurately distinguish between GOM and PBM.[7-9] Lyman et al. demonstrated that ozone can decompose oxidized mercury compounds from KCl-coated denuders to Hg^0 such that injected oxidized mercury compounds are quantified by the system as Hg^0,[10] and McClure et al. confirmed this finding in the laboratory and in ambient air.[11] McClure et al. also demonstrated that humidity reduces the amount of GOM recovered by KCl-coated denuders in a Tekran system, as has been shown by Huang and Gustin.[12]

Discovery of bias in Tekran system measurements did not occur until after the instruments were in use for at least a decade, at least in part because no system existed for routine verification of atmospheric mercury speciation measurements in ambient air. Such a system has been called for repeatedly.[10, 13-15] High-concentration oxidized mercury calibrators are available for measurements in flue gas (i.e., Thermo Model 81i and Tekran Model 3310/3321), which work by combining Hg^0 with chlorine gas to generate mercuric chloride. However, no commercial calibration system exists that is capable of producing stable, ambient levels of oxidized mercury (zero to hundreds of pg m^{-3}). Some studies have accomplished injections of Hg compounds into mercury measurement systems with manual permeation tube-based calibrators[10-12, 16-17]. Adding standards manually is time-consuming and has not been done routinely, however.

We have developed a permeation tube-based calibrator that is capable of providing automated injections of Hg^0 and Hg compounds at atmospherically relevant concentrations into the inlet of mercury analyzers (patent pending). We integrated this calibrator with Tekran speciation systems in Reno, Nevada and Mauna Loa, Hawaii, resulting in the first routine verification of atmospheric mercury speciation measurements.

2 Experimental

2.1 Sampling Locations

The calibrator was deployed at the College of Agriculture, Biotechnology, and Natural Resources Valley Road Greenhouse Facility at the University of Nevada, Reno campus near downtown Reno, Nevada, and at the Mauna Loa Observatory in Hawaii, U.S.A. For work reported herein, the instrument operated in Reno from 27 February until 7 June 2015 and from 7 May until 3 June 2016, and at Mauna Loa from 7 August until 28 September 2015.

2.2 Calibrator Construction and Operation

2.2.1 Permeation Oven

The core of the mercury calibrator was a permeation oven that housed four stainless steel tubes of 5 mm internal diameter coated with deactivated fused silica (Figure 1). Three of these tubes contained permeation tubes, while the fourth was empty, allowing for flushing of mercury-free nitrogen through the system. Upstream of the 5 mm internal diameter tubes were critical orifices designed for a flow of 100 mL min^{-1} (for the Mauna Loa deployment and the 2016 deployment in Reno, a flow of 25 mL min^{-1} was used). No additional flow was provided through the calibrator, so the flow of gas across the permeation tubes was the same as the flow from the calibrator into the measurement system being calibrated. The pressure upstream of the critical orifices was controlled by an Alicat pressure controller. High purity nitrogen from a compressed gas cylinder (Airgas UHP N_2; 99.999% pure, <1 ppm O_2, <1 ppm H_2O, <0.5 ppm

THC, <1 ppm CO + CO_2) provided flow through the tubes. Flow through the tubes was directed either to a vent (with an activated charcoal scrubber) or to the outlet line of the calibrator.

The permeation oven was maintained at 100°C. In previous work with HgX_2 permeation tubes, investigators have kept permeation ovens cooler than this[11, 17], but recent work has shown that HgX_2 passes more efficiently through tubing and decomposes to Hg^0 less when kept at higher temperatures.[18] Also, our own observations and data presented by McClure et al.[11] show permeation rates of permeation tubes maintained at low temperatures may not be stable over time.

The permeation oven housed permeation tubes for Hg^0, $HgBr_2$, and $HgCl_2$ (obtained from Sigma-Aldrich, purity >99.9%). Other mercury compounds besides $HgBr_2$ and $HgCl_2$ may exist in ambient air, and while the compounds that exist in ambient air are not known with certainty, many studies have speculated that halogen-containing mercury compounds exist.[19-21] Furthermore, $HgBr_2$ and $HgCl_2$ are readily available commercially, can survive well in the valve and tubing materials used for the calibrator,[18] and Hg compounds emitted from $HgBr_2$ and $HgCl_2$ permeation tubes have been shown by mass spectrometry to be $HgBr_2$ and $HgCl_2$ (this has not been shown for HgO and $Hg(NO_3)_2$).[18]

All three permeation tubes were constructed from 3 mm internal diameter thin-wall PTFE tubing with 3 mm diameter solid PTFE plugs. The permeable length of the $HgCl_2$ and $HgBr_2$ permeation tubes (i.e., the distance between the plugs where the solid-phase mercury compounds were contained) was 1 mm. For the Hg^0 permeation tube, a 1 mm diameter, 1 mm deep hole was drilled into the solid PTFE plug, the hole was filled with Hg^0, and the plug was then covered with the thin-wall PTFE tubing, sealing the Hg^0 into the tubing. After reaching the set temperature, the permeation tubes required about 24 h to stabilize prior to use.

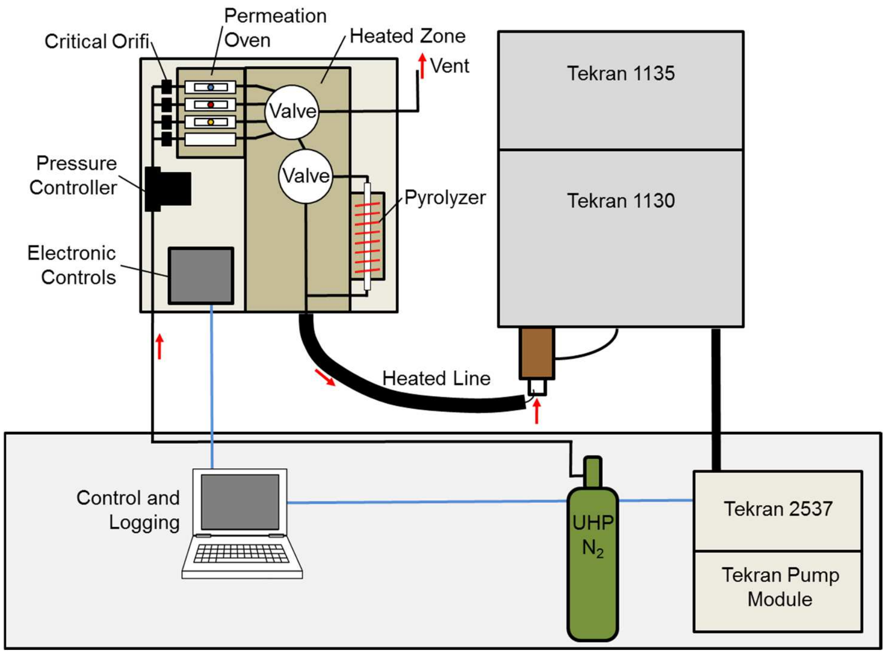

Figure 1. Schematic of the calibrator.

2.2.2 Pyrolyzer

A pyrolyzer allowed for decomposition of permeated mercury compounds to Hg^0 to determine total mercury permeation rates. The pyrolyzer consisted of a U-shaped 6 mm outer-diameter quartz tube filled with quartz wool, with quartz frits on either end to retain quartz wool in the tube. The pyrolyzer was maintained at 700°C.

2.2.3 Valves and Tubing

VICI GC valves were used to select among the permeation tubes (flow was passed to vent when permeation tubes were not in use), and to select whether the permeated Hg would pass through the pyrolyzer prior to exiting the calibrator. Valves were constructed of deactivated fused silica-coated stainless steel, and valve rotors were composed of Valcon T (a polyimide/PTFE/carbon composite). All connecting tubing consisted of 1.6 mm outer diameter deactivated fused silica-coated stainless steel.

A heated outlet line was also composed of 1.6 mm outer diameter deactivated fused silica-coated stainless steel tubing. The outlet line was insulated except for the final 20 mm, which was bent upwards and placed inside the Tekran speciation system's elutriator inlet. This allowed the Tekran system to sample ambient air without a sampling manifold and allowed all injections from the calibrator to be carried out in ambient air.

Valves and tubing, including the outlet line, were maintained at 200°C. This temperature maximized HgX_2 transmission and minimized decomposition to Hg^0 in tests performed by Jones et al.[18]

2.2.4 Housing

The calibrator was installed outdoors next to the Tekran speciation system to minimize the transport distance of permeated mercury compounds. The calibrator was housed in a weatherproof box with a temperature-controlled fan that ventilated the box if the box temperature increased above 30°C. Communication cables connected the calibrator to an indoor computer with a custom LabVIEW executable file that controlled the calibrator and connected the calibrator to the digital data output from the Tekran 2537.

2.2.5 Software

Through the LabVIEW executable, the calibrator was programmed to inject Hg^0, $HgCl_2$, or $HgBr_2$ for a set number of seconds, and would repeat the programmed injection over a set time interval (1-24 h) on a daily or weekly basis. The Tekran systems in this study sampled ambient air for one hour and then desorbed and analyzed their denuder and pyrolyzer for the next hour. The Hg^0 measurement interval for the Tekran 2537s was 5 min. The calibrator injected a selected calibration gas according to a programmed schedule. Injections only occurred when the Tekran data output received by the calibrator indicated that the instrument had been sampling ambient air for at least 10 min. The calibrator began injections at the beginning of each 5 min measurement period.

Injections of $HgCl_2$ and $HgBr_2$ lasted for 7-100 s, and only occurred once during the hour-long ambient air sampling period. Hg^0 was injected at the start of each 5 min sampling period for the duration of the ambient air sampling hour, and injections lasted for 100-300 s. After $HgCl_2$ and $HgBr_2$ injections were completed, the selection valve switched the flow path to the 5 mm stainless tube that was empty, allowing mercury-free nitrogen to flush through the calibrator and into the measurement system inlet for the remainder of the ambient air sampling hour. The nitrogen flush after Hg^0 injections only lasted for the balance of the 5 min interval. Following the flush, the selection valve switched to a closed position and flow through the outlet line ceased.

In 5 min intervals, the LabVIEW executable recorded the date and time; the temperatures of the permeation oven, valves and tubing, pyrolyzer, outlet line, and housing; the data output from the Tekran 2537; the number of seconds the permeation tube selection valve spent in each possible position; and the time the pyrolyzer selection valve spent in each possible position.

2.3 Tekran Speciation System Measurements

The Tekran system in Mauna Loa is operated as part of the Atmospheric Mercury Network (AMNet) and follows AMNet protocols.[22] The Tekran system in Reno was also operated following AMNet protocols.

2.4 Cation-Exchange Membrane-Based Measurements

In addition to injections into the Tekran system, we used the calibrator to inject $HgCl_2$ and $HgBr_2$ into a cation-exchange membrane-based manual measurement system. The system consisted of an activated polyethersulfone cation exchange membrane (Mustang S, Pall

Corporation), that was housed in a 47 mm PFA filter holder, to collect GOM, followed by a 4 mm inner diameter quartz tube, the center 2-4 cm of which was filled with gold-coated quartz beads, to collect Hg^0. A pump pulled ambient air through the membrane and then the tube at 1 L min^{-1}. The calibrator injected Hg compounds into the PFA filter holder while the pump pulled ambient air through the system. The pump began pulling air through the system 30 seconds before the injection began, and then for 30 seconds after the injection finished.

Membranes were handled and analyzed by EPA Method 1631, as described by Huang and Gustin.[12] Gold traps were analyzed by atomic fluorescence spectrometry, as in Gustin et al.[23]

2.5 Data Processing and Reporting

The amount of Hg recovered from calibrator injections is reported in this work as total pg or pg s^{-1} (the observed permeation rate). For Hg^0 injections, the total pg recovered was calculated by correcting for measured ambient Hg^0 concentrations (measured during the first 10 min of each 1 h ambient air sampling cycle, units of ng m^{-3}), then multiplying by (1) the m^3 of air sampled by the Tekran speciation system during each 5 min measurement period and (2) 1000 pg ng^{-1}.

For $HgCl_2$ and $HgBr_2$ injection periods, total GOM recovered from desorption of the KCl denuder and PBM recovered from desorption of the particulate filter (units of pg m^{-3}) were added together, ambient air concentrations of GOM and PBM from previous and subsequent sampling periods were subtracted, and the resultant value was multiplied by the m^3 of air sampled during the 1 h ambient air sampling period. Hg^0 recovered during $HgCl_2$ and $HgBr_2$ injection periods was calculated in the same way as during Hg^0 injection periods, except that Hg^0 enhancements above ambient levels were calculated and summed for each 5 min measurement period subsequent to injection.

The permeation rates of the permeation tubes used in the calibrator were not verified independently of the measurement systems being calibrated, so percent recoveries are not reported for automated calibrator results. Instead, recovered pg or observed permeation rates are reported. Coefficient of determination (r^2) values shown in this work were determined by ordinary least squares regression, and p values shown for comparison of two datasets were calculated using student's t-tests. Statistical significance was determined at $\alpha = 0.05$.

3 Results and Discussion

3.1 Repeatability and Variability

Figure 2 shows the recovery of Hg^0, $HgBr_2$ and $HgCl_2$ injected by the calibrator into the Tekran system while it was deployed in Reno, as well as the recovery of Hg^0 injected manually from a temperature-controlled Hg vapor source. None of the injected compounds exhibited a statistically significant change in recovery over the measurement period. A slight (but statistically insignificant) decreasing trend was observed for recovery of GOM + PBM from $HgCl_2$ and $HgBr_2$ injections in Figure 2. A weak but statistically significant increase in dew point occurred over the same period ($r^2 = 0.09$; $p < 0.01$), possibly accounting for the decreasing trend (see discussion about dew point below). Recovery from $HgBr_2$ injections at Mauna Loa did not exhibit a temporal trend. $HgCl_2$ and Hg^0 injections were only performed at the beginning of the Mauna Loa deployment, so temporal trends could not be established.

GOM and PBM results from the Tekran system were summed for Figure 2 and elsewhere in this work because GOM and PBM both increased when $HgCl_2$ or $HgBr_2$ was injected into the Tekran, and because the ability of the Tekran to distinguish quantitatively between GOM and PBM is in question[7-9]. 20 ± 4% (mean ± 95% confidence interval) of GOM + PBM recovered from $HgBr_2$ injections was PBM, and an average of 18 ± 3% of GOM + PBM recovered from $HgCl_2$ injections was PBM.

Recovery of Hg^0 from manual injections in Reno was 101.9 ± 5.9% for gold trap A and 104.3 ± 8.3% for gold trap B. Hg^0 injections from the calibrator exhibited similar variability, with 96.2 ± 6.5% recovery for trap A and 103.8 ± 7.4% recovery for trap B (percent recovery calculated as the recovered amount divided by the average recovery for both traps over the operation period). The amount of the variability in recovery that was due to the calibrator versus the Tekran system cannot be ascertained from this dataset.

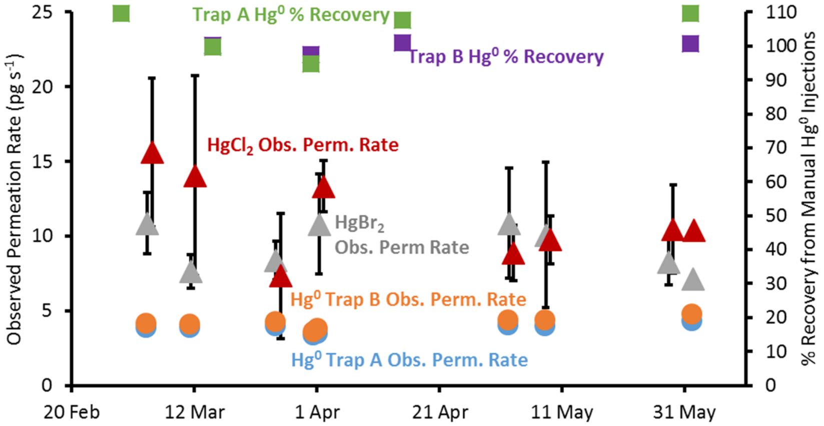

Figure 2. GOM+PBM recovered by the Tekran speciation system from injections of $HgBr_2$ and $HgCl_2$ by the calibrator while operated in Reno, Nevada. Recovery of Hg^0 from injections of Hg^0 by the calibrator and % recovery from manual injections of Hg^0 from a temperature-controlled Hg vapor source are also shown. Whiskers represent 95% confidence intervals. n = 2-5 for each point shown.

The majority of $HgCl_2$ and $HgBr_2$ injected into the Tekran System in Reno was recovered as Hg^0, and the amount recovered as Hg^0 was consistent for the 2015 and 2016 deployments (Figure 3). The percentage of injected Hg that was recovered as Hg^0 was greater for $HgBr_2$ than for $HgCl_2$, though the difference was not statistically significant ($p = 0.11$). Hg-Br bonds require less energy to break than Hg-Cl bonds,[24] so reactions that decompose Hg compounds could affect $HgBr_2$ more strongly than $HgCl_2$. In contrast with Reno, the majority of Hg recovered from $HgBr_2$ injections in Mauna Loa was GOM + PBM, perhaps because of differences in air chemistry at the two locations (see discussion below). Calibrations in Reno occurred during spring, while calibrations in Mauna Loa occurred during late summer and early fall. More study is needed to determine whether oxidized Hg recovery by the Tekran system exhibits seasonality.

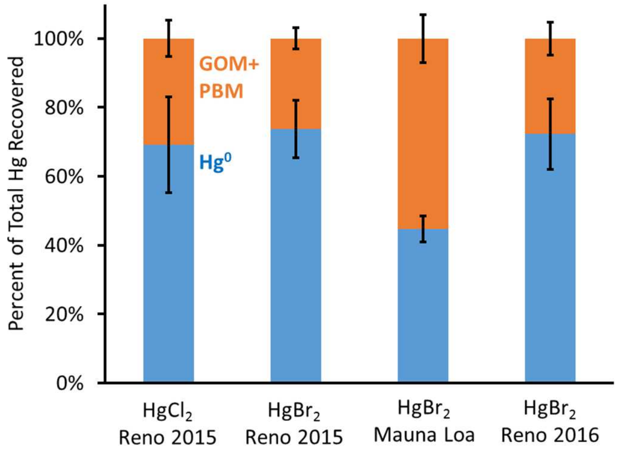

Figure 3. Average percent of total Hg recovered as Hg^0 and GOM+PBM by the Tekran system for injections of $HgBr_2$ and $HgCl_2$ in Reno during 2015, injections of $HgBr_2$ in Reno during 2016, and injections of $HgBr_2$ in Mauna Loa during 2015. Whiskers show 95% confidence intervals. n = 28 for $HgCl_2$, 25 for $HgBr_2$ in Reno 2015, 82 for Mauna Loa, and 44 for $HgBr_2$ in Reno 2016.

3.2 Recovery Under Different Conditions

In Reno and Mauna Loa, no statistically significant relationships were observed between ozone and GOM+PBM recovery from Hg compound injections or for the percent of recovered Hg that was Hg^0 (p values for correlations were all greater than 0.24). Laboratory studies have established that ozone leads to reduction of Hg halides on KCl denuders to Hg^0,[10-11] and McClure and Jaffe[11] noted a negative correlation between ambient ozone and recovery of injected $HgBr_2$ by a Tekran system, but, using data from their Table S2, that correlation was also not statistically significant ($r^2 = 0.23$; $p = 0.08$).

McClure et al. report a significant correlation between ambient specific humidity and recovery of $HgBr_2$ by a Tekran system in the Southeast United States ($r^2 = 0.70$; $p < 0.01$).[11] Huang and Gustin also showed that water vapor negatively impacts the retention of Hg compounds by KCl denuders.[12] In this study, recovery of GOM+PBM from $HgBr_2$ injections in Reno decreased and the percent of total recovered Hg that was Hg^0 increased with increasing specific humidity (Figure 4). The intercept for this relationship (i.e., zero water vapor in ambient air) was 61% Hg^0 in total Hg recovered, higher than the % Hg^0 in Hg recovered from $HgBr_2$ injections at Mauna Loa. This indicates that something other than water vapor likely also decreased the recovery of $HgBr_2$ as GOM + PBM in Reno.

The r^2 value for the relationship of specific humidity with GOM+PBM recovery was not significant for $HgCl_2$, but a significant relationship was observed between specific humidity and percent Hg^0 in total Hg recovered from $HgCl_2$ injections ($r^2 = 0.19$, $p = 0.02$).

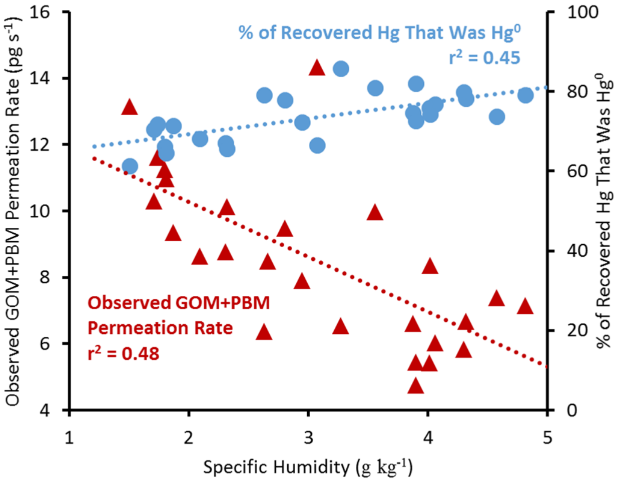

Figure 4. GOM+PBM recovery from $HgBr_2$ injections in Reno and percent of recovered Hg that was Hg^0 versus ambient specific humidity.

Surprisingly, the percent Hg^0 in total Hg recovered from $HgBr_2$ injections in Mauna Loa was weakly negatively correlated with specific humidity (Figure 5; $p < 0.01$). Percent Hg^0 in total Hg recovered was positively correlated with carbon monoxide in Mauna Loa (Figure 5; p <

0.01), and specific humidity and carbon monoxide were inversely correlated with each other ($r^2 = 0.24$; $p < 0.01$). It is possible that some anthropogenic pollutant for which carbon monoxide is a tracer led to the conversion of injected $HgBr_2$ to Hg^0 at Mauna Loa, obscuring the impact of water vapor. It may be that the relatively pristine atmosphere at Mauna Loa led to the improved recovery of injected $HgBr_2$ as GOM + PBM relative to Reno (Figure 3). No meaningful correlations between carbon monoxide concentrations and $HgBr_2$ recovery were observed in Reno ($r^2 < 0.001$; carbon monoxide range of 137 to 1034 ppb).

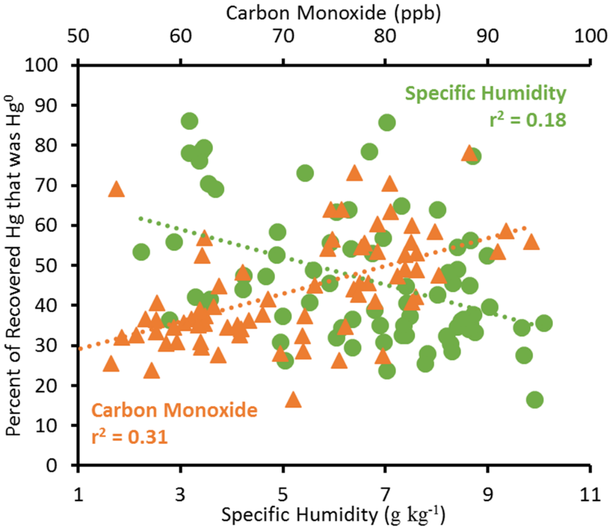

Figure 5. Percent of recovered Hg that was Hg^0 versus ambient specific humidity and ambient carbon monoxide at Mauna Loa Observatory.

Recovery of GOM+PBM was inversely correlated with the percent of total recovered Hg that was Hg^0 ($r^2 = 0.52$ for $HgBr_2$ injections in Reno), and the total Hg recovered did not vary with specific humidity ($p = 0.31$), indicating that, while some of the injected Hg compounds were likely converted to Hg^0 under ambient conditions, the total amount of Hg recovered by the Tekran system was conserved.

Figure 6 shows the average concentration of Hg^0 measured by the Tekran system during sampling periods when $HgCl_2$ was injected. Hg^0 increased above the ambient level for the 5 min period during which the injections occurred, and while it decreased again following the injection period, it stayed statistically significantly above ambient Hg^0 for the remainder of the 1 h ambient air sampling period ($p = 0.01$). Under normal operation, after the calibrator injected $HgCl_2$ ($HgCl_2$ injections lasted 20 s for the results shown in Figure 6), it flushed the outlet line with nitrogen for the remainder of the sampling period. While Figure 4 provides evidence that conversion of some injected $HgCl_2$ to Hg^0 within the Tekran system did occur, continued release of Hg^0 from the calibrator during flushing could also explain the excess Hg^0 after the initial injection period shown in Figure 6. We tested this by manually ending the calibrator flush 5 min after some injections (Figure 6). The increase in Hg^0 after injections was not statistically significantly different for the two flush times ($p = 0.87$), showing the increase was likely due to $HgCl_2$ breakdown within the Tekran system, rather than from Hg^0 introduced by the calibrator during flushing. The amount of excess Hg^0 collected in the 45 min following injection was ~120 pg, which is ~18% of the total Hg recovered from $HgCl_2$ injections.

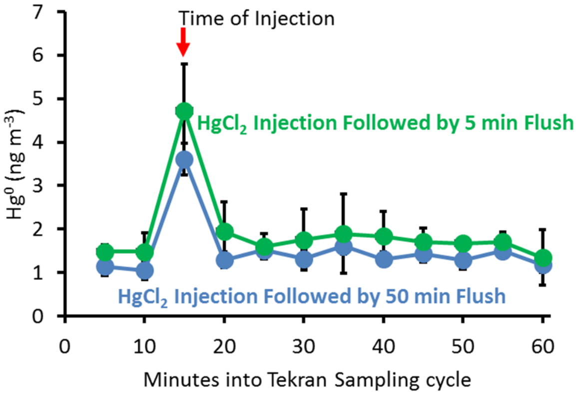

Figure 6. Average 5-min Hg^0 measurements collected by the Tekran system for hours during which $HgCl_2$ was sampled. $HgCl_2$ injections followed by a 5 min flush and a 50 min flush are shown. Whiskers show 95% confidence intervals. n = 4-5 for each point shown.

3.3 Comparison With a Cation-Exchange Membrane System

The Tekran system captured 34% less of injected $HgBr_2$ and $HgCl_2$ as GOM+PBM relative to the cation exchange membrane and gold trap-based system (Figure 7). Ambient air flowed through the membrane system for just a few minutes during each injection, rather than for the 1 h Tekran ambient air sampling period. Thus, only the Hg^0 recovered from the Tekran system in the 5 min during which injections occurred were used in Figure 7.

Injections of Hg^0 from a temperature-controlled Hg vapor source through a membrane and into a Tekran 2537 mercury analyzer showed the same amount of Hg^0 whether a cation-exchange membrane or Teflon membrane was installed ($p = 0.74$; 120.36 ± 0.77 ng m^{-3} recovered), indicating that the cation-exchange membranes did not adsorb a detectable amount of Hg^0. In tests with two cation-exchange membranes in series, Huang and Gustin did not observe any measurable breakthrough of permeated Hg compounds in activated carbon-scrubbed air,[12] while tests with ambient Hg in ambient air resulted in a median breakthrough of 25%.[25] If breakthrough of $HgBr_2$ or $HgCl_2$ did occur, the percent of recovered Hg that was Hg^0 could be overestimated for the membrane and gold trap system. Some evidence exists that recovery of Hg compounds by cation-exchange membranes may depend on ambient conditions,[12] and the membrane system is not definitive. In fact, no method for collection of Hg compounds has been shown to be unbiased by ambient conditions. This comparison shows, however, that the membrane system was better able to recover injected Hg compounds as GOM than the Tekran system.

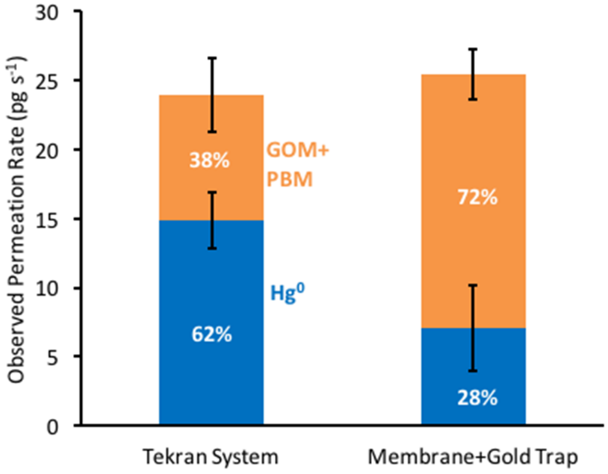

Figure 7. Average recovery of injected $HgCl_2$ and $HgBr_2$ as Hg^0 and GOM+PBM by the Tekran system (subset of data from 9-10 May 2015) versus a cation exchange membrane (CEM) followed by a trap filled with gold-coated quartz beads (injections performed on 7 May 2015). Whiskers show 95% confidence intervals. n = 6 for the Tekran system, 4 for the membrane + gold trap system.

3.4 Limitations

The automated calibrator was stable over time, was useful for determination of the influence of ambient conditions on Hg recovery, and provided for comparisons among Hg measurement methods. The calibrator's ability to inject directly into the Tekran system's inlet allowed for the addition of Hg compounds into ambient air without the use of a manifold, since manifolds have been shown to retain Hg compounds.[17] However, this inlet design did not allow for injection into zero air (e.g., air scrubbed with activated carbon), which rendered us unable to compare recoveries in ambient vs. zero air. A system is needed that will allow for injections in zero and ambient air, and yet still perform injection of Hg compounds without a manifold. The calibrator injected Hg compounds at the tip of the Tekran inlet, allowing for a realistic determination of passage of Hg compounds through the entire inlet system. The Tekran system can provide zero air to the inlet, but it adds zero air downstream of the inlet's elutriator and particle impactor, where previous research has shown that more than 30% of injected $HgCl_2$ is lost.[26] Thus, injection by the calibrator downstream of the Tekran system's zero air port would likely lead to unrealistic calibration results.

Since Tekran systems can quantitatively recover injected $HgBr_2$ and $HgCl_2$ in zero air,[6, 11] comparisons of calibration results in zero and ambient air will allow for a more quantitative determination of the Tekran instrument's bias in ambient conditions, and for determination of the amount of Hg emitted from permeation tubes that is Hg^0. However, National Institute of Standards and Technology (NIST)-traceable standards that are independent of measurement systems being calibrated are still needed to provide definitive calibration of Hg measurement instrumentation. Our $HgCl_2$ and $HgBr_2$ permeation tubes emitted about 30 pg s^{-1} of Hg (Figure 3), equivalent to 18 µg $week^{-1}$. This is adequate to verify permeation rates gravimetrically with a µg-sensitivity scale, as has been done by others.[27] Gravimetric verification of permeation rates could make permeation tubes for Hg compounds traceable to NIST gravimetric standards if the speciation of Hg emitted from the tubes can be reliably and independently determined. Unfortunately, the amount of Hg^0 emitted from permeation tubes used in this study is unclear, since the amount of injected Hg recovered as Hg^0 varied with ambient conditions. A standardized, independent method (independent of permeation tubes *and* the measurement systems to be calibrated by permeation tubes) is needed to determine the speciation of Hg emitted from $HgCl_2$ and $HgBr_2$ from permeation tubes.

In order to provide an independent, NIST-traceable, reliable source of Hg compounds in the gas phase, permeation tubes need to be (1) stable over time, (2) emit enough Hg to be gravimetrically verifiable, and (3) emit very little Hg^0 (or at least the amount of Hg^0 emission needs to be independently verifiable). Our calibrator achieves the first two benchmarks, but work is needed on the third. Some low-temperature Hg compound permeation tubes have achieved the third, but not the first two.[10, 17, 26]

The calibrator's pyrolyzer was designed to provide simple, real-time verification of total Hg permeation rates by converting permeated Hg compounds to Hg^0,[16] followed by detection with the Tekran system's 2537 analyzer. Passing permeated Hg^0, $HgCl_2$, and $HgBr_2$ through the pyrolyzer resulted in total Hg recoveries that were not significantly different from un-pyrolyzed Hg ($p = 0.11$ to 0.56), though some of the pyrolyzed Hg was still recovered as GOM + PBM (average of 7% for $HgBr_2$ and $HgCl_2$ injections). It is not clear whether pyrolyzed Hg that was recovered as GOM + PBM was due to inefficient pyrolysis or contamination of the pyrolysis system with $HgBr_2$ or $HgCl_2$.

3.5 Implications

Similar to other studies, automated calibrations in this study showed that Hg compounds are converted to Hg^0 within the Tekran system, resulting in GOM + PBM measurements that are biased low. This study also showed, however, that Tekran systems deployed in different locations can have different levels of bias, perhaps because of differences in atmospheric chemistry. Relationships between Tekran recovery and atmospheric conditions were not consistent across the two study locations, indicating that more research is needed to understand the mechanisms that lead to bias in Tekran systems.

These results show that the bias in Tekran speciation system-based measurements is not consistent spatially or temporally. This suggests that the spatial and temporal trends in Hg speciation observed in previous studies could be due, at least in part, to instrument bias, rather than real changes in atmospheric Hg chemistry. It also implies that correction of Tekran system data that were collected without routine calibration may only be able to be accomplished if adequate ancillary data are available. While improvements to the automated calibrator presented here are needed, it is clear that routine calibration of atmospheric Hg measurement instrumentation will increase the validity and utility of collected data.

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