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Evaluation of cation exchange membrane performance under exposure to high Hg^0 and $HgBr_2$ concentrations

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Abstract

Reactive mercury (RM) is an important component of the global atmospheric mercury cycle, but measurement currently depends on un-calibrated, operationally defined methods with large uncertainty and demonstrated interferences and artifacts. Cation exchange membranes (CEM) provide a promising alternative methodology for quantification of RM, but method validation and improvement are ongoing. For the CEM material to be reliable, uptake of gaseous elemental mercury (GEM) must be negligible for all conditions, and RM compounds must be captured and retained with high efficiency. In this study the performance of CEM material under exposure to high concentrations of GEM (1.43×10^6 – 1.85×10^6 pg m^{-3}) and reactive gaseous mercury bromide ($HgBr_2$ ~ 5000 pg m^{-3}) was explored, using a custom-built mercury vapor permeation system, with quantification of total permeated Hg accomplished via pyrolysis at 600 °C and detection using a Tekran® 2537A. Permeation tests were conducted for 24 to 72 hours in clean laboratory air, with absolute humidity levels ranging from 0.1 – 10 g m^{-3} water vapor. Gaseous elemental mercury uptake by the CEM material averaged no more than 0.004% of total exposure for all test conditions, which equates to a non-detectable GEM artifact for typical ambient air sample concentrations. Recovery of $HgBr_2$ on CEM filters was >100 % compared to calculated total permeated $HgBr_2$, suggesting incomplete thermal decomposition at the pyrolyzer, as the

CEM material collected $HgBr_2$ with less than 1% downstream breakthrough on average, implying a high collection efficiency.

1 Introduction

Mercury (Hg) is a persistent environmental contaminant with a significant atmospheric life time, and the form and chemistry of Hg is an important determinant of its biogeochemical cycling. Mercury in the atmosphere is found in three forms: gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate bound mercury (PBM). PBM and GOM are often quantified together as reactive mercury (RM = GOM + PBM). Atmospheric GEM, at an average global background concentration of 1 – 2 ng m^{-3}, can be reliably measured with calibrated analytical instruments (Gustin et al., 2015;Slemr et al., 2015). The measurement of GOM and PBM requires detection at the part per trillion (pg m^{-3}) level and depends on un-calibrated operationally defined methods with demonstrated interferences and artifacts, and concomitant large uncertainty. Recent reviews (Gustin et al., 2015;Zhang et al., 2017) detail the shortcomings, difficulties, and needed developments for atmospheric RM measurements.

As an alternative methodology, cation exchange membranes (CEM) have been used to selectively measure GOM concentrations in ambient air (Huang et al., 2013;Huang and Gustin, 2015b;Huang et al., 2017;Sheu and Mason, 2001;Pierce and Gustin, 2017;Marusczak et al., 2017;Ebinghaus et al., 1999;Mason et al., 1997;Bloom et al., 1996). The use of CEM type filters for this purpose was first documented in the literature in a conference presentation (Bloom et al., 1996), although such membranes (then referred to as 'ion exchange membranes') were deployed earlier in a field-based international comparative study of RM measurement techniques in September, 1995 (Ebinghaus et al., 1999). In the comparative study, one participating lab

deployed a series of ion exchange membranes (for GOM) behind a quartz fiber filter (for PBM) at a sample flow rate of 9-10 Lpm, for 24 h measurements (filter pore sizes were not reported). Results for PBM and GOM were in similar ranges of 4.5 – 26 pg m^{-3} and 13-23 pg m^{-3} , respectively (Ebinghaus et al., 1999).

The ion exchange membrane method was also applied in a 1995-96 field campaign for determining the speciation of atmospheric Hg in the Chesapeake Bay area (Mason et al., 1997). This study used a 5-stage Teflon filter pack system that included one up front quartz fiber filter (0.8 µm pore size) to remove particulate, and four downstream Gelman ion exchange membranes (pore size not reported) to 1) capture GOM, 2) capture GOM breakthrough, 3) serve as deployment blanks, and 4) isolate the filter train on the downstream side (Mason et al., 1997). Concentrations of GOM were reported to be 5 – 10 pg m^{-3}, essentially at or below the method detection limit and it was speculated that even this small amount may have been an artifact from fine particulate Hg passing through the 0.8 µm quartz fiber filter (Mason et al., 1997). The 3rd-in-series ion exchange membrane blanks were reported to be not significantly different in Hg concentration from unused membrane material, indicating that breakthrough was not a phenomenon that extended past the second ion exchange filter position.

The particulate Hg artifact problem was subsequently elaborated on in a further comparative study focusing exclusively on RM measurement techniques. Specific concerns included physical particle breakthrough, re-evolution of gas-phase Hg^{2+} from PBM captured on the upstream particulate filters passing downstream to the ion exchange membranes, possible adsorption of GOM compounds to the particulate filters, or a GEM collection artifact on the ion exchange membranes (Sheu and Mason, 2001). None of these concerns were proven or disproven conclusively.

Recent CEM based sampling systems typically deploy a pair of CEM disc filters without a pre-particulate filter, in replicates of 2 to 3 at a flow rate of 1.0 Lpm (Gustin et al., 2016). Each pair of filters constitutes one sample, the first filter serving as the primary RM collection surface, and the second filter capturing breakthrough. Filters are deployed for 1-to-2 weeks and then collected for analysis (CVAFS, EPA Method 1631, modified) (Huang et al., 2017). The CEM material consists of a positively charged polyethersulfone coated matrix (Pall Corporation), and at least one manufacturing evolution has occurred (Huang and Gustin, 2015a). Prior CEM material versions (I.C.E. 450) had a pore size of 0.45 µm, while the current CEM material (Mustang® S) has a manufacturer reported pore size of 0.8 µm.

Previous work with the I.C.E 450 material indicated it does not adsorb significant quantities of GEM in passive exposures, but can selectively uptake gas-phase Hg^{2+} species (Lyman et al., 2007). The CEM material was subsequently adapted for use in active sample flow systems, with the presumption of continued inertness to GEM and selectivity for GOM (Huang et al., 2013;Huang and Gustin, 2015b). These studies and others (Lyman et al., 2016) have shown better GOM recovery on CEM material compared to potassium chloride (KCl) coated denuder methods.

Despite these tests, the transparency of the CEM material to GEM uptake has not been conclusively demonstrated for active sampling flow rates, nor for high GEM concentrations, though limited data using low concentration manual Hg^0 injections through CEM filters suggests little or no GEM uptake (Lyman et al., 2016). However, even small rates of GEM uptake by the CEM material could result in a significant measurement artifact (e.g. a modest 1 – 2% GEM uptake could easily overwhelm detection of typical ambient GOM concentrations). It is therefore of critical importance that such a GEM artifact be ruled out if the CEM material is to be

successfully deployed for ambient RM measurements, first and foremost under controlled laboratory conditions in the absence of confounding variables.

Additionally, previous studies have observed significant amounts of "breakthrough" GOM on the secondary filter. The amount of breakthrough is not consistent, neither as a constant mass, with total Hg ranging from zero to as high as 400 pg (Huang et al., 2017), nor as a percentage of Hg collected on the primary filter, ranging from 0 – 40% (Pierce and Gustin, 2017). Similar variable breakthrough issues were observed in the earliest field-based CEM measurements as well (Mason et al., 1997). In contrast to ambient measurements, previous laboratory experiments have reported only minor (0 – 16%) or no breakthrough (Huang et al., 2013;Huang and Gustin, 2015b). Limited experimental work with flow rates of 1.0 and 16.7 Lpm in ambient air could not provide an explanation for differing breakthrough rates (Pierce and Gustin, 2017).

In this paper we investigate the potential for GEM uptake on CEM material using a custom-built permeation system. In addition, the ability of the CEM material to capture and retain a representative GOM compound (mercury bromide, $HgBr_2$) is discussed with a view to estimate collection efficiency and explain or rule out possible mechanisms of breakthrough for both dry and humid conditions.

2 Methods

A Tekran® 2537A ambient mercury analyzer was integrated with a custom-built permeation system designed to enable controlled exposures of GEM and GOM to CEM filters (Fig. 1). The 2537A analyzer was calibrated at the beginning and periodically throughout the study and checked for accuracy by manual Hg^0 injections (mean recovery 101.1% ± 4.3, n = 10, SI Fig. 1). The entire system was checked for Hg contamination in clean air prior to permeation tests, and

periodically during sampling (SI Fig. 2). All tubing and connections used in the permeation system were polytetrafluoroethylene (PTFE), except for the quartz glass pyrolyzer tube and perfluoroalkoxy (PFA) filter holders. Each of these materials is known to be chemically inert, virtually nonporous, and to have a low coefficient of friction. For these reasons, PTFE/PFA plastic and quartz glass are the standard materials employed in almost all Hg sampling systems, as GEM passes over or through these surfaces without loss (Gustin et al., 2015). Given its reactive nature, some GOM inevitably adsorbs to internal line surfaces, but the capacity of these materials to sorb and retain GOM is not infinite and a steady state of adsorption/desorption is expected after 5-6 hours of exposure to a stable concentration (Xiao et al., 1997;Gustin et al., 2013).

Sample flow through the system was alternated between two PTFE sample lines (designated Line 0 and Line 1) using a Tekran® Automated Dual Switching (TADS) unit. Sample air was constantly pulled through each line at 1.0 Lpm by the internal pump and mass flow controller in the 2537A, or by an external flush pump (KNF Laboport® N86 KNP) and mass flow controller (Sierra Smart-Trak® 2). Laboratory air was pulled through a single inlet at the combined rate of 2.0 Lpm, passing through a 0.2 µm PTFE particulate filter and an activated charcoal scrubber to produce clean sample air. Additionally, for dry air permeations sample air was pulled through a Tekran® 1102 Air Dryer installed upstream of the particulate filter, and for elevated humidity permeations sample air was pulled through the headspace of a distilled water bath (DIW, < 0.2 ng L^{-1} total Hg) that was located upstream from the charcoal scrubber to eliminate the DIW being a potential Hg source to the system. Temperature and relative humidity (RH) were measured in-line (Campbell Scientific CS215) and used for calculation of absolute humidity.

Pure liquid Hg^0 and crystalline $HgBr_2$ (purity > 99.998% Sigma-Aldrich®) were used as Hg vapor sources. The elemental Hg^0 bead was contained in a PTFE vial. Solid $HgBr_2$ crystals were packed in thin-walled PTFE heat-shrink tubing (O.D. 0.635 cm) with solid Teflon plugs in both ends to create a perm tube with an active permeation length of 2 mm (Huang et al., 2013). The $HgBr_2$ permeation tube was also placed in the bottom of a PTFE vial, and the permeation vials were submerged in a temperature-controlled laboratory chiller (0.06 ± 0.13 °C, Cole Parmer Polystat®). A low source temperature was favored both because higher temperatures would have produced unacceptably high concentrations, and because there is evidence that at higher temperatures a small amount of Hg^0 can be evolved from Hg^{2+} compounds (Xiao et al., 1997).

An ultra-high purity nitrogen (N_2) carrier gas was passed through the permeation vials at 0.2 Lpm to carry the target Hg vapor into the main sample line through a PTFE T-junction. The main sample line was split into Line 0 and Line 1 immediately downstream from the permeation flow junction. Line 0 proceeded directly to the 2537A without modification during GEM permeations (Fig. 1A), but housed CEM filters during the $HgBr_2$ permeations (Fig. 1B, 1C). Line 1 held a pyrolyzer unit composed of a quartz glass tube (O.D. 0.625 cm) packed with a 3 cm section of quartz wool heated to 600 °C using a nichrome wire coil (SI Fig. 3 and discussion). The goal of the pyrolyzer was to convert all Hg to GEM for detection on the Tekran® 2537A.

CEM filters were deployed in 2-stage, 47 mm disc PFA filter holders (Savillex©). The primary "A" filter in the 2-stage holder is the first to be exposed to the permeated Hg, with the secondary "B" filter mounted immediately behind the A filter (A to B distance ~ 3mm) to measure potential breakthrough. For GEM permeations, three 2-stage filter holders were placed in-series on Line 1 behind the pyrolyzer unit (Fig. 1A), while total Hg coming through the system was measured on Line 0 with no filters in place. This allowed simultaneous exposure of 6 CEM filters in one GEM

sample exposure. The first CEM filter in-line served to scrub any small residual RM passing through the system and pyrolyzer, and these first in-line filters were removed for the calculations of GEM uptake (SI Fig. 4 and discussion).

For determining the potential for GOM breakthrough, two system configurations were used. In the first configuration (Fig. 1B), the total Hg concentration of air that passed through the pyrolyzer on Line 1 was measured without any filters, while Line 0 held one 2-stage CEM filter pair for $HgBr_2$ loading. This configuration allowed for real time (10 min interval) quantification of the $HgBr_2$ permeation concentration through Line 1 using the 2537A, and comparison with total Hg loading on the CEM filters on Line 0. In the second configuration, replicate filters were concurrently loaded with $HgBr_2$ by placing 2-stage CEM filter holders on both Line 0 and Line 1 (upstream of the pyrolyzer, Fig. 1C). In all $HgBr_2$ exposures, the filter holders were placed as close to the permeation vial as possible, with a total distance from vial to filter surface of approximately 20 cm. Mercury bromide permeation was conducted in dry air and elevated humidity air. The difference between one line being fully open to the $HgBr_2$ permeation flow (configuration Fig. 1B) and then closed by deployment of the CEM filters (configuration Fig. 1C) enabled a rough determination of the amount of $HgBr_2$ line-loss within the system.

After permeation, CEM filters were collected into clean, sterile polypropylene vials and analyzed for total Hg by digestion in an oxidizing acid solution, reduction to Hg^0, gold amalgamation, and final quantification by cold vapor atomic fluorescence spectrometry (CVAFS, EPA Method 1631, Rev. E) using a Tekran® 2600 system. This analysis provided for comparison of total Hg filter loading, and verification of in-line results. A to B filter breakthrough was calculated by comparison of total Hg recoveries on the primary and secondary CEM filters, using Eq. (1):

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$$\%\,Breakthrough = 100 * CEM_{2nd}/(CEM_{1st} + CEM_{2nd}) \quad (1)$$

Blank CEM filters were collected and analyzed in the same manner with every set of sample filters deployed on the permeation system, and the mean filter blank value was subtracted from all total Hg values to calculate the final blank-corrected Hg values used for data analysis. All data were analyzed in Microsoft® Excel (version 16.12) and RStudio® (version 3.2.2).

3 Results

3.1 Elemental Mercury Uptake on CEM Filters

Elemental Hg uptake on CEM material was negligible for permeated Hg^0 vapor concentrations ranging from 1.43×10^6 – 1.85×10^6 pg m^{-3} (Fig. 2). High GEM concentrations were employed in this study under the logic that if no GEM uptake was observed at high concentrations, a similar lack of GEM uptake can be expected for all lower concentrations.

The mean Hg mass on blank CEM filters was 50 ± 20 pg (n = 28). For permeations into dry sample air of 0.5 ± 0.1 g m^{-3} water vapor (WV), total mean Hg^0 permeation exposures of 2.7×10^6 pg (24 h) and 7.3×10^6 pg (72 h) resulted in total (blank-corrected) Hg recoveries on the CEM filters of 100 ± 40 pg (n = 10) and 280 ± 110 pg (n = 5), respectively. These quantities of total recovered Hg equate to a mean GEM uptake rate on the CEM filters of 0.004 ± 0.002%. For GEM permeations into ambient humidity sample air (2 – 4 g m^{-3} WV), at a slightly lower total mean permeated Hg^0 24 h exposure of 2.1×10^6 pg, total (blank-corrected) Hg recoveries on the CEM filters were 55 ± 30 pg (n =10), equating to a GEM uptake rate of 0.003 ± 0.001%. The overall GEM uptake rate was linear (r^2 = 0.97) for the range of concentrations used in this study, indicating a similar low uptake rate can be expected down to lower GEM concentrations.

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3.2 Mercury Bromide Uptake on CEM Filters

Breakthrough of $HgBr_2$ vapor from the primary (A) to secondary (B) CEM filters was low for all conditions tested in this study (Table 1). These conditions included $HgBr_2$ permeated into clean dry laboratory air with < 0.5 g m^{-3} WV, clean air at ambient room humidity (4 – 5 g m^{-3} WV), and clean air at elevated humidity (10 – 11 g m^{-3} WV), at line temperatures between 17 to 19 °C. Overall, the mean A to B filter breakthrough ranged from 0 to 0.5% and averaged 0.2 ± 0.2 % (n = 17), with no statistical difference observed in mean breakthrough rates for the three levels of humidity (ANOVA, p = 0.124).

The first $HgBr_2$ permeation in clean dry (< 0.5 g m^{-3} WV) laboratory air was over a 96 h period, using the system configuration in Figure 1B to establish an approximately permeation rate (Fig. 3). Total Hg reaching the 2537A through the pyrolyzer on Line 1 (red line, Fig. 3) indicates an average $HgBr_2$ exposure concentration of 4540 pg m^{-3}, or about 4.5 pg min^{-1} from the permeation tube. After this permeation, total blank-corrected $HgBr_2$ loading on the primary CEM filter on Line 0 was 49400 pg, but only 50 pg on the secondary CEM filter, indicating a breakthrough rate of approximately 0.1%. Total Hg reaching the 2537A through the CEM filters on Line 0 (black line, Fig. 3) over this time period was 15 pg, mostly at the beginning of the deployment when some ambient Hg entered the opened system. The low concentrations of Hg measured downstream in Line 0 on the 2537A corroborates that breakthrough of $HgBr_2$ was low. These data also demonstrate that the CEM material did not saturate with a $HgBr_2$ loading of ~ 50000 pg, a loading far higher than could be expected in ambient conditions.

Subsequent replicate 24 h $HgBr_2$ permeations in clean dry air resulted in consistent total Hg loading on CEM filters placed on both lines concurrently (8560 ± 320 pg, n = 6, Samples 2-7

Table 1), and mean total Hg on the secondary CEM filters was 20 ± 10 pg (average breakthrough of 0.3%). On Line 0 (black line, Fig.3), which was never open to $HgBr_2$ vapor downstream from the CEM filters at any point in the study, Hg measured at the 2537A was zero for all three 24 h permeations, indicating no breakthrough (Samples 2, 4, & 6, Table 1). However, on Line 1, which had been exposed to the full $HgBr_2$ vapor concentration of 4540 pg m^{-3} over the duration of the 96 h perm test, 1155 pg of Hg were measured downstream in the first 24 h sample (Sample 3, Table 1). The amount of downstream Hg dropped to 10 pg in the second 24 h, and 6 pg in the third 24 h (Samples 5 & 7, Table 1). This downstream Hg in Line 1 (compared to the zero Hg simultaneously observed on Line 0) is attributed to re-volatilization of $HgBr_2$ that had stuck to the line material during the open permeation flow. At the moment CEM filters were deployed on Line 1 (red-to-blue transition, Fig. 3), a rapid asymptotic decline in the Hg signal began. This decay curve supports drawdown and depletion of a Hg reservoir on the interior line surfaces behind the CEM filters, and not a continuous source such as breakthrough from the permeation tube that was still supplying $HgBr_2$ to both sample lines. The total mass of Hg re-volatized from the interior line surfaces (1155 pg) represents 4 – 5% of the total $HgBr_2$ that had passed through Line 1 (~25000 pg based on 2537A measurement). Eventually, Hg reaching the 2537A through Line 1 decreased to zero during the same 24 h filter deployment, indicating a majority of $HgBr_2$ line contamination can be expected to flush out within ~12 h.

Additional $HgBr_2$ permeations were made at two levels of in-line humidity. At ambient room humidity (4 – 5 g m^{-3} WV), mean total Hg measured on the CEM filters was 7910 ± 520 pg (n = 4; Samples H2-5, Table 1), with an average breakthrough to the secondary filters of 0.3%. When normalized for sample volume, the mean $HgBr_2$ loading on CEM filters during ambient humidity (5968 ± 125 pg) and dry air (5995 ± 188 pg) permeations was not statistically significantly

different (t-test $p = 0.790$). $HgBr_2$ breakthrough rates were also the same (0.3%) as during the dry air permeations, indicating that the permeation system was operating similarly at the two humidity levels, and suggesting that absolute humidity concentrations around 4 – 5 g m^{-3} WV have insignificant effects on collection of $HgBr_2$ in clean laboratory air by the CEM material.

We observed that an increase in humidity resulted in an initial large increase in Hg measured at the 2537A downstream of the CEM filters on Line 0 (Sample H1, Table 1), concurrently with an open $HgBr_2$ permeation flow through Line 1 while both lines were subjected to increased RH. This downstream Hg on Line 0 dropped substantially to zero in ~10 h in the first 24 h deployment (Sample H2, Table 1), and was zero for the duration of the second 24 h deployment (Sample H4, Table 1). As this downstream Hg rapidly declined to zero, we believe this was also an off-gassing effect, likely induced by the increased humidity, which perhaps facilitated a heterogeneous surface reduction of $HgBr_2$ to GEM in the short section of line between the perm source and CEM filters, with the GEM then passing through to the 2537A. As the breakthrough rate and the mean $HgBr_2$ loading on the CEM filters did not change between the dry air and ambient humidity permeations, the downstream Hg observed at the 2537A during the ambient humidity permeations cannot be attributed to a loss of Hg from the CEM filters and is more likely due to a process in the sample lines.

As a further test of possible humidity effects, two replicate 24 h CEM filter deployments were conducted in elevated humidity conditions (10 – 11 g m^{-3} WV) created by an in-line water bath. Mean total Hg loading on the primary CEM filters was higher compared to the previous permeations (11700 ± 720 pg, n = 4, Samples H9-12, Table 1), indicating an increase in the effective $HgBr_2$ permeation rate, possibly due to the perturbation caused by a poor filter seal and small leak in the preceding deployment (Sample H7-8, Table 1). However, mean total Hg on the

secondary CEM filters was 20 ± 20 pg, indicating an average breakthrough of 0.1%, less than the breakthrough observed for the lower humidity permeations.

4 Conclusions

GEM uptake on the CEM material was negligible under the laboratory conditions and high GEM loading rates (2 orders of magnitude above ambient) tested in this study, with an overall linear uptake rate of 0.004% for permeated GEM concentrations between 1.43×10^6 – 1.85×10^6 pg m^{-3}. This uptake rate would be insignificant at typical ambient atmospheric Hg concentrations (1 – 2 ng m^{-3}). As a hypothetical example, a CEM filter sampling ambient air at an average GEM concentration of 2 ng m^{-3} for a typical 2-week sample period would have a total Hg^0 exposure of ~40000 pg. At the calculated uptake rate of 0.004%, a maximum 1.6 pg of Hg observed on the sample filter could be attributed to GEM artifact and given that blank filters have a mean total Hg mass of 50 ± 20 pg, this amount would be below detection. This corroborates the lack of GEM uptake seen by Lyman et al. (2016) for manual Hg^0 injections on CEM filters at lower total mass loadings of 300 – 6000 pg.

Mean $HgBr_2$ breakthrough from primary to secondary CEM filters averaged 0.2 ± 0.2% over all test conditions, using $HgBr_2$ as a test GOM compound. A to B filter breakthrough was derived from a comparison between the large amount of $HgBr_2$ permeated onto the primary CEM filters, to the small amount of $HgBr_2$ that collected on the secondary CEM filters, 3 mm immediately downstream. The measurement of 1000s of pg of Hg on the primary filter, and only 10s of pg on the secondary filter, leads to the conclusion that the primary filter removed the majority of $HgBr_2$ from the sample air stream. In addition, low breakthrough was corroborated by downstream measurement of the air stream passing through the CEM filters, using the Tekran® 2537A. The

average breakthrough to the 2537A was 0 pg for 24 h permeations in dry air and 0 – 40 pg in humid air, for those filter deployments than can be considered steady-state (> 24 h without large perturbations).

While the permeation system was not specifically optimized for a quantitative mass balance between permeated $HgBr_2$ and $HgBr_2$ recovered on the CEM filters, a rough estimation of the CEM collection efficiency is possible. Using the $HgBr_2$ permeations conducted in clean dry air (mean loading 8560 pg) and comparing this to the mean Hg concentration measured at the 2537A analyzer during the last 24 h of the 96 h permeation measurement (4680 pg m^{-3}, or 6739 pg per 24 h), the $HgBr_2$ recovery on the CEM filters averaged 127%. Adjusting the expected permeated $HgBr_2$ mass for our estimated line-loss (~4-5%) improves the recoveries to ~123%. Still, $HgBr_2$ loading on the CEM filters was therefore ~23% higher than expected based on the pyrolized total measurement on the 2537A.

The technique of gold amalgamation in general, and specifically including the Tekran® 2537 analyzer, is widely considered to provide a quantitative *total gaseous Hg* measurement, at or very near 100% collection efficiency for Hg^0 and Hg compounds (Dumarey et al., 1985;Schroeder and Jackson, 1985;Landis et al., 2002;Temme et al., 2003;Schroeder et al., 1995). However, to our knowledge collection and desorption efficiencies on gold traps have not been demonstrated for $HgBr_2$. The stated desorption temperature of the Tekran® 2537A gold traps is 500 °C, but temperatures as low as 375 °C have been reported (Gustin et al., 2013), which would likely cause reduced thermal decomposition efficiency for all captured GOM compounds, including $HgBr_2$. We speculate that a combination of incomplete thermal decomposition to Hg^0, at both the 600 °C pyrolyzer and during the best-case 500 °C desorption

of the 2537 gold traps, resulted in ~20% non-detection of total permeated $HgBr_2$ as it passed through the CVAFS optical path without generating the necessary fluorescence signal.

While our results validated some basic performance metrics for the CEM material, they did not provide data that could fully explain the higher levels of breakthrough observed for CEM filters deployed in ambient air over the 1 to 2 week sample periods in previous studies. Increasing humidity by itself did not affect observed $HgBr_2$ breakthrough. A $HgBr_2$ loading of ~50000 pg also did not lead to increased breakthrough, indicating there is no saturation effect on CEM filter capacity at a GOM loading far greater than expected from ambient concentrations. It remains unclear, though, whether breakthrough results from different collection efficiencies for GOM compounds other than $HgBr_2$, or whether breakthrough results from a degradation of GOM retention capacity in the CEM material when exposed to ambient air chemistries not simulated in this study. Also, our experiments were conducted in particulate-free air, which leaves open the possibility that breakthrough is related to capture (or lack thereof) of PBM by the CEM material.

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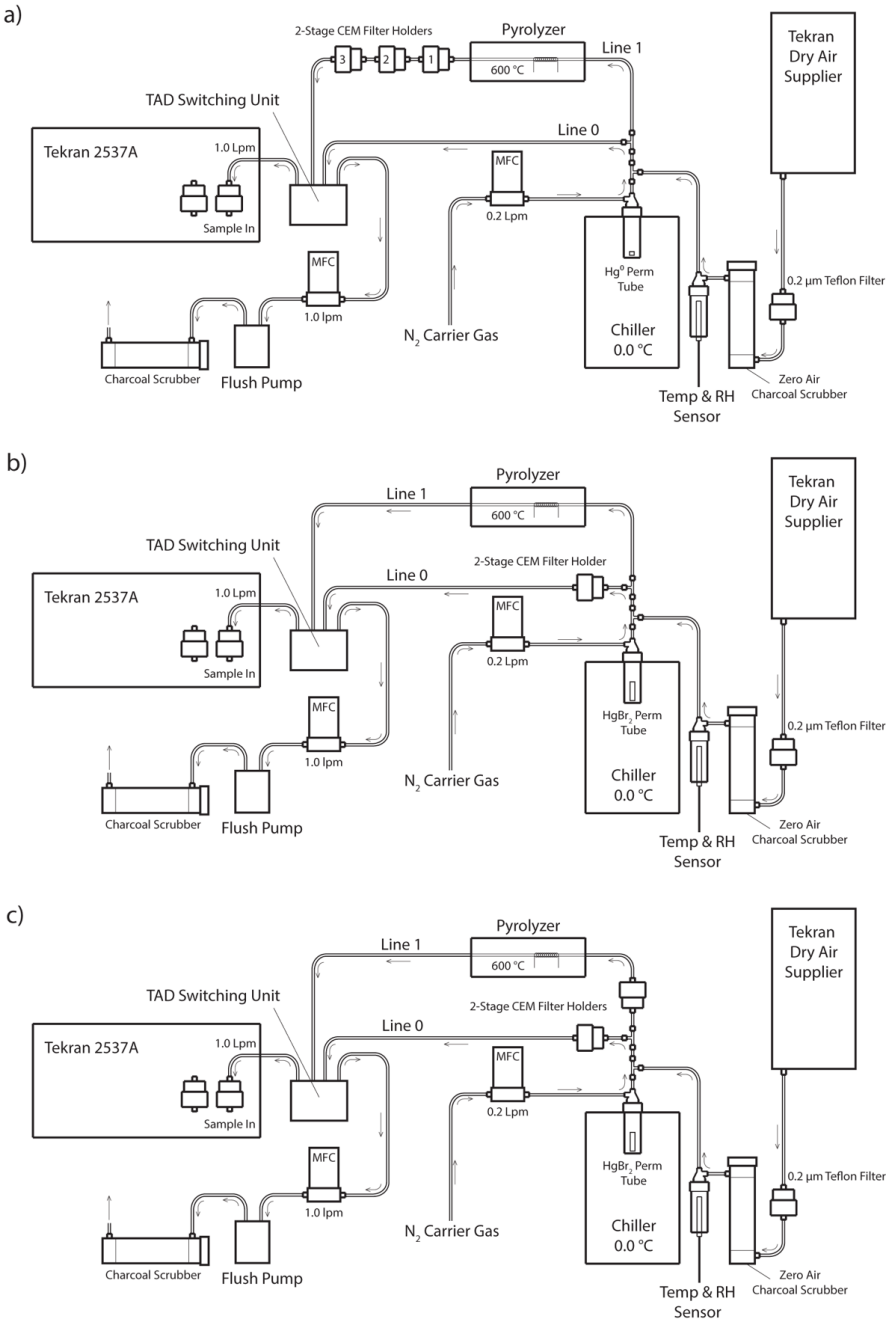

Figure 1. Schematic of the Hg vapor permeation system configurations for: a) GEM permeations b) $HgBr_2$ permeations c) Simultaneous $HgBr_2$ loading on two sample lines. Note dry air supplier disconnected for ambient and elevated humidity $HgBr_2$ permeations, with sample path starting at 0.2 µm Teflon particulate filter and water bath inserted immediately in front of the charcoal scrubber. All tubing is chemically inert PTFE, except for the quartz glass pyrolyzer tube, and PFA filter holders.

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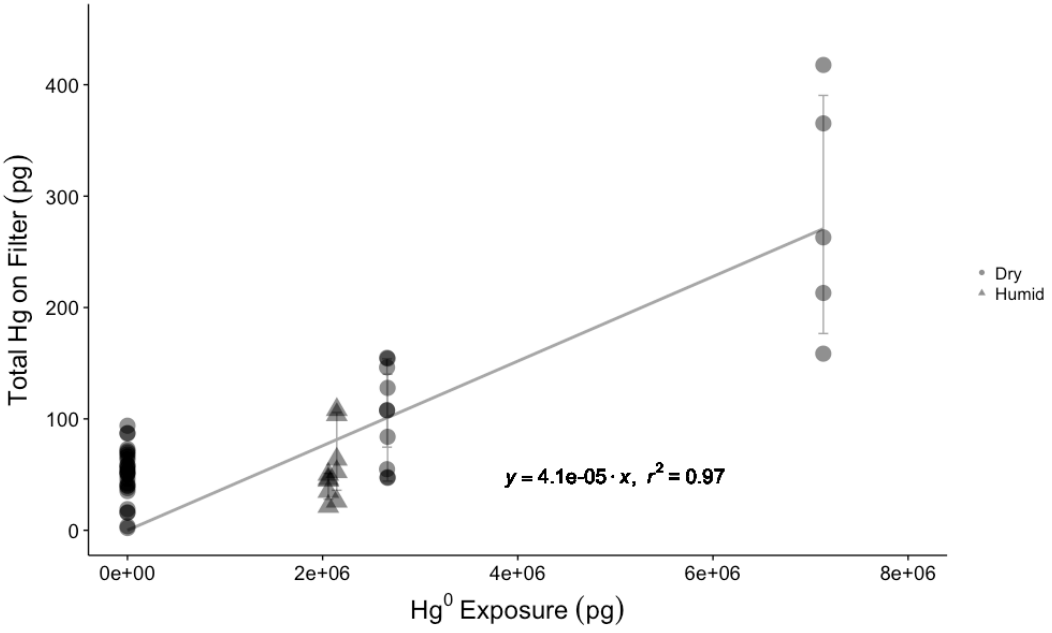

Figure 2. Total Hg recovered on CEM material for blank filters (Hg exposure = 0 pg) and different Hg^0 vapor permeations in dry (0.5 ± 0.1 g m^{-3} WV) and humid air (2-4 g m^{-3} WV). Circles represent dry air permeations, triangles represent humid air exposures, and all permeation exposures were blank-corrected. The regression line shows the relationship between total Hg^0 exposure and blank-correct mean total Hg recovered on CEM filters (error bars ± one standard deviation), with a slope of 4.1×10^{-5} indicating a linear uptake rate of 0.004%.

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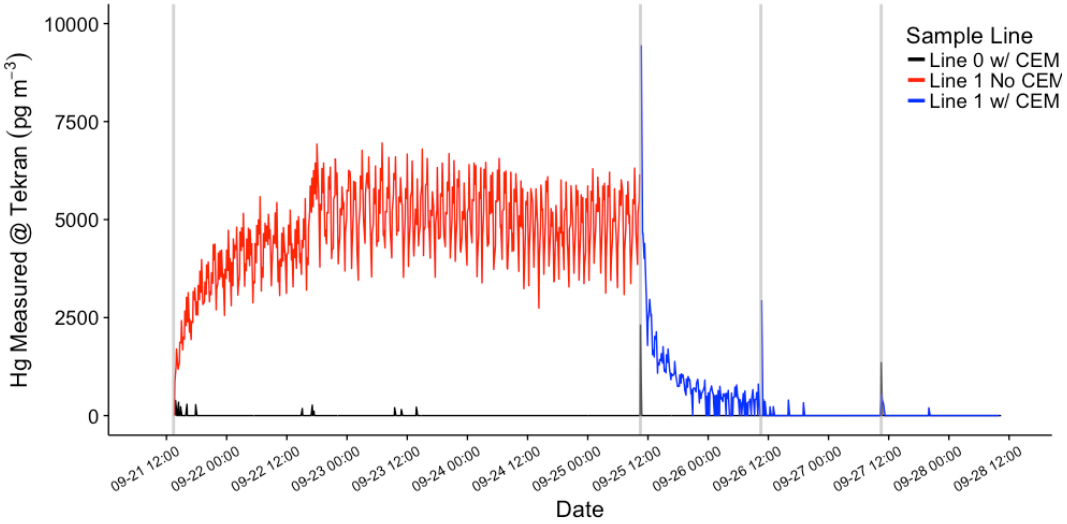

Figure 3. $HgBr_2$ permeations in clean dry lab air using the configuration in Figure 1B (red line) and Figure 1C (blue line). The red line indicates total Hg released from permeation tube and passing through pyrolyzer on Line 1 before being measured by Tekran 2537A, black line indicates Hg reaching 2537A through CEM filters on Line 0. Vertical grey lines indicate open system during filter deployments.

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Table 1.

Sample	Start	End	Sample Time (min)	Sample Flow (lpm)	Sample Volume (m^3)	Total Hg on CEM (pg)	Blank Correct (pg)	Total Hg @ Tekran (pg)	A to B Filter Brkthru (%)
Mean CEM Filter Blank							54		
Clean Dry Air (0.3 ± 0.05 g m^{-3} wv)									
HgBr 1P	*9/21/17 13:25*	*9/25/17 10:25*	*5580*	*1.00*	*5.580*	*na*	*na*	*25181*	*na*
HgBr 1A	9/21/17 13:25	9/25/17 10:25	5580	1.00	5.580	49478	49424	15	0.10
HgBr 1B						101	47		
HgBr 2A	9/25/17 10:30	9/26/17 10:30	1440	1.00	1.440	8901	8847	0	0.20
HgBr 2B						71	17		
HgBr 3A	*9/25/17 10:30*	*9/26/17 10:30*	*1440*	*1.00*	*1.440*	*9125*	*9072*	*1155*	*0.36*
HgBr 3B						*86*	*33*		
HgBr 4A	9/26/17 10:40	9/27/17 10:25	1425	1.00	1.425	8494	8440	0	0.28
HgBr 4B						77	24		
HgBr 5A	*9/26/17 10:40*	*9/27/17 10:25*	*1425*	*1.00*	*1.425*	*8306*	*8253*	*10*	*0.36*
HgBr 5B						*83*	*29*		
HgBr 6A	9/27/17 10:35	9/28/17 10:25	1430	1.00	1.430	8496	8442	0	0.22
HgBr 6B						72	19		
HgBr 7A	*9/27/17 10:35*	*9/28/17 10:05*	*1410*	*1.00*	*1.410*	*8386*	*8333*	*6*	*0.15*
HgBr 7B						*66*	*13*		
Clean Humid Air (4.4 ± .2 g m^{-3} wv)									
HgBr H1P	*10/2/17 16:10*	*10/3/17 15:20*	*1390*	*1.00*	*1.390*	*na*	*na*	*5888*	*na*
HgBr H1A	10/2/17 16:10	10/3/17 15:20	1390	1.00	1.390	10498	10444	1700	0.25
HgBr H1B						80	27		
HgBr H2A	10/3/17 15:30	10/4/17 14:40	1390	1.00	1.390	8589	8535	164	0.13
HgBr H2B						65	11		
HgBr H3A	*10/3/17 15:30*	*10/4/17 14:40*	*1390*	*1.00*	*1.390*	*8182*	*8129*	*420*	*0.54*
HgBr H3B						*98*	*44*		
HgBr H4A	10/4/17 14:50	10/5/17 11:50	1260	1.00	1.260	7504	7451	0	0.31
HgBr H4B						76	23		
HgBr H5A	*10/4/17 14:50*	*10/5/17 11:50*	*1260*	*1.00*	*1.260*	*7576*	*7522*	*25*	*0.25*
HgBr H5B						*73*	*19*		
HgBr H6P	*10/5/17 12:05*	*10/9/17 10:25*	*5660*	*1.00*	*5.660*	*na*	*na*	*11889*	*na*
HgBr H7A	10/9/17 10:40	10/10/17 10:45	1445	1.00	1.445	9024	8970	105	na
HgBr H7B						2672*	2618*		
HgBr H8A	*10/9/17 10:40*	*10/10/17 10:45*	*1445*	*1.00*	*1.445*	*12359*	*12305*	*397*	*na*
HgBr H8B						*75*	*21*		
Clean High Humidity Air (10.9 ± 1.7 g m^{-3} wv)									
HgBr H9A	10/10/17 10:50	10/11/17 9:30	1360	1.00	1.360	10920	10866	181	0.22
HgBr H9B						78	24		
HgBr H10A	*10/10/17 10:50*	*10/11/17 9:30*	*1360*	*1.00*	*1.360*	*11413*	*11359*	*308*	*0.00*
HgBr H10B						*53*	*0*		
HgBr H11A	10/11/17 9:35	10/12/17 9:35	1440	1.00	1.440	12001	11947	5	0.00
HgBr H11B						52	0		
HgBr H12A	*10/11/17 9:35*	*10/12/17 9:35*	*1440*	*1.00*	*1.440*	*12579*	*12525*	*40*	*0.29*
HgBr H12B						*90*	*36*		
HgBr H13P	*10/12/17 9:40*	*10/13/17 9:40*	*1440*	*1.00*	*1.440*	*na*	*na*	*1430*	*na*
HgBr H13A	10/12/17 9:40	10/13/17 9:40	1440	1.00	1.440	13152	13099	4	0.12
HgBr H13B						69	16		

Table 1. Summary of CEM filter loading and breakthrough during $HgBr_2$ permeations. Samples denoted P indicate approximate permeation rate check through Line 1 via pyrolyzer and Tekran 2537A, italics indicate filter deployments on Line 1, and * indicates high values due to leak around first filter seal.