8 December 2018

Dear Dr. Abbatt,

Thank you for the opportunity to revise our manuscript for further consideration by Atmospheric Measurement Techniques. The suggestions made by the reviewers were extremely helpful for reworking our manuscript in a manner that, we hope you will agree, has made it a much stronger contribution to the literature. We seriously considered each comment, and in this document we attempt to address each comment and suggestion. To address these comments we added additional data as well as moved material in the Supplemental Information to the main paper. In addition, we changed the conclusions to a discussion that seems more appropriate and added a brief section describing future work that is needed Below are the original reviewer comments and suggestions in italics and our responses. Accompanying this letter are three documents: 1) manuscript with edits tracked for easier review, 2) manuscript with all edits incorporated and not tracked, and 3) updated supporting information. Again, thank you for the opportunity to submit our revised manuscript to AMT and we look forward to further feedback.

Sincerely,

Sarrah M. Dunham-Cheatham, Postdoctoral Scholar
Mae Sexauer Gustin, Professor
Matthieu B. Miller

Detailed Response to Reviewers:

Reviewer 1:
Evaluation of CEMs for GEM uptake and GOM capture and retention for use in a flow-based technique is an important step towards obtaining realistic measurements of reactive mercury. This study presents data that shows promising results for laboratory air. Of course, further work using an ambient air matrix and other species of GOM is need.

I am concerned there was no mixing volume downstream of the bromide permeation tube. In trying to keep line lengths short to minimize wall losses there may not be adequate mixing to ensure equal concentrations travel through Line 0 and Line 1. This may bias uptake and capture measurements and may have contributed to the mass balance problems. It may be one of the causes of the large amount of noise in the pyrolyzed signal shown in Figure 3. If mixing volume use was not possible then only running with a single Line should have been considered.

We performed a control experiment to ensure that both Lines 0 and 1 were conducting comparable concentrations of mercury under the experimental conditions. We deployed 2-stage filter packs with cation exchange membranes (CEM) in each line at equal distances from the permeation tube. The membranes were deployed for the same amount of time, in triplicate deployments, and analyzed to quantify the amount of mercury sorbed to the membranes. The average % deviation between lines was 2.9%, with a maximum deviation of 5.4%. These results indicate to us that, though there may be some difference in the amount of mercury passing through Lines 0 and 1, the difference is relatively small. These results have been added to the manuscript to help alleviate the concern from readers.

I am also concerned about the poor performance of the pyrolyzer. Inadequate conversion due to residence time and temperature problems is fairly easy to address. It would have been a much better paper if simple tests of increasing the pyrolyzer temperature had been done. Incomplete reduction or varying efficiency may be another cause of the noisey signal in Figure 3.

Additional experiments were conducted to ensure that the temperature of the pyrolyzer was sufficient to convert GOM to GEM. Our results show that, under our experimental conditions, mercury concentrations measured by the downstream Tekran 2537 were not significantly different when the pyrolyzer temperature was 650 C and 800 C. These results have been added to the manuscript supporting information. We agree that the residence time in the pyrolyzer design is short, and that improvements to the pyrolyzer are needed. These are foci of ongoing studies.

Another issue that was not raised in the paper is the effect of back-reactions downstream of the pyrolyzer to reform HgBr2. What is the fate of the bromine?

These are great questions and certainly warrant investigation. However, answering this question is beyond the scope of the current project and assumptions would be unsupported by the presented data; thus, we have decided to leave this discussion out of the manuscript.

Other Comments:

Line 43: Not ppt but parts per quadrillion

Thank you to the reviewer for catching this error. The correction has been made.

Line 145: Locating the AC scrubber downstream of the humidifier could cause problems: the carbon's ability to uptake GEM is reduced at higher humidity. Some AC scrubbers contain iodine which can be released and migrate with humidity, which can then trap Hg downstream.

While we recognize this as a potential issue, the scrubber was located downstream of the humidity source to remove any potential contaminant Hg coming from the DIW used in the humidity source. Our results indicate that at absolute humidity concentrations around 5 g m^{-3}, the water vapor did not have a significant effect on the permeation system performance. However, in the elevated humidity experiment, it was clear that the water vapor resulted in a large pulse of mercury moving through both Lines, and discuss these results in the paper.

Line 158: Was the dry N2 flow included when calculating the humidity values?

No

Line 165: The volume of pyrolyzer seems small. What is residence time? Were any tests done to ensure that reduction was quantitative?

The residence time in the pyrolyzer tube is approximately 1.5 seconds. Quartz wool was added to the pyrolyzer to increase the amount of surface area available to facilitate reactions and maximize the amount of GOM converted to GEM in the pyrolyzer. We have added this to the text and commented on the fact this is a pretty efficient method for converting GOM to GEM. In addition a comment was added that indicated that having an efficient pyrolyzer allows us to better constrain permeation rates.

Line 327: How did you estimate line losses?
The estimate of line loss was and is described on lines 321-325 of the manuscript.

Line 330: I can believe that the pyrolyzer was not 100% efficient, but did you try to increase the temperature and look for increased conversion?

Yes, we performed an experiment to test if more mercury was converted to GEM, as indicated by an increased measured mercury concentration in the downstream Tekran 2537, with increased pyrolyzer temperatures. There was no significant increase in measured mercury concentrations when the pyrolyzer temperature was increased from 650 C (circa the experimental pyrolyzer temperature) to 800 C. When the pyrolyzer was increased to 1,000 C, significantly more mercury was measured; however, the pyrolyzer design could not be safely sustained at an operational temperature of 1,000 C, and thus due to safety concerns the pyrolyzer operating temperature was set to 600 C. Pyrolyzer improvements in this permeation system are ongoing.

Figure 1: It would be nice to show humidifier in this figure. I am concerned about the lack of mixing volume downstream of the permeation gas TEE. Without adequate mixing there may not be equal concentration of HgBr2 going to Line 0 and Line 1. This may be one of the reasons that there is so much noise of the red trace of Figure 3 and could throw off your mass balance calculations.

The humidifier location was included in the figure caption and we prefer to leave it there rather than add it to this very busy figure.
The mixing volume downstream of the permeation tube is small, by design. We tested for evenness in mercury concentrations reaching each line (as described in more detail above), and found that the average deviation in mercury concentrations between Lines 0 and 1 was 2.9%.

SI Figure 1: The gaps between 2537 calibrations is about a month. Why wasn't it done on a regular basis or at the end of each test?

The system was not operated with an automatic internal calibration cycle to avoid interrupting data collection during experiments. Due to the variable timing and duration of experiments, calibrations were performed between experiments, which in some cases resulted in calibrations that were several weeks apart. However, the calibration data presented in Figure S1 indicates that the system was stable for the duration of the experiment.

Reviewer 2:
Response to Major concerns:
1. In response to the concern that no standard reference material is used during the acid-digestion analysis:
R2 – The reviewers have adequately addressed this concern

2. In response to concerns about pyrolyzer efficiency:

R2 – The authors response is inadequate in regard to the pyrolyzer. The authors attest to the pyrolyzer working at 500 C for GOM by referencing other papers, but their own data shows that there is a rather large discrepancy between the Tekran concentrations and the GOM concentration in this dataset of which the authors acknowledge. This could be (1) inefficient reduction of all GOM to GEM for subsequent Tekran analysis or (2) some other artefact in the experiments. Using the Tekran was a clever way to QA/QC check the concentrations being sorbed to the CEMs. But there was substantial discrepancies in the recoveries. To simply say "the pyrolyzer was inefficient" and then argue in response to my criticism of this by showing references stating that the pyrolyzer should work under at the tested temperatures is inadequate when clearly something was awry in the experiments in terms of these recoveries. The authors could have and should have EASILY re-tested the experiments at the pyrolyzer temperatures they themselves suggest. It is my opinion that this simple, additional experimental treatment needs to be included in the study. This relates to point 5 below.

We performed a test of the pyrolyzer to test the conversion efficiency at increasing temperatures. We have provided more details on this test in the comments above to Reviewer 1. In short, we found that increasing the pyrolyzer temperature to 800 C did not result in a significant increase in conversion of mercury to GEM. We have added the data from this experiment to the manuscript.

3. In response to concerns over removal of first in-series CEM filter during GEM permeations:
R2 - Here I feel the authors have adequately addressed the concern by listing both the proportion of sorbed GEM with and without inclusion of the first filter. It is still my preference that the first filters be included and, as the authors state, this is still a very small amount. This would also reduce the length of the manuscript and discussion on this could easily be moved to the SI without affecting anything, which would help with the suggestion I make in point 5 below. Nonetheless, one concern that is still yet to be addressed is why is the uptake of GEM on the first filter not linear with increasing GEM concentration? It is exponential. I brought up this concern in the previous round of comments and it was ignored.

There are only five data points, so we feel any assertion about this relationship being linear or exponential is not robust. That being said, the relationship is strongly linear ($r2 = 0.98$, $p = 0.001$).

4. In response to the concern over unheated Teflon sample tubing length between Line 1 and Line 0:
R2 - Indeed another factor that may be contributing to the poor recovery results and another part of the experiments that could have easily been adjusted and retested. Possibly not a big issue as the authors suggest, but I imagine it also could have been adjusted easily.

We certainly cannot rule out the possibility that the room temperature lines resulted in line loss and contributed to the decreased recovery. However, we estimate our line loss to be a small contribution to the decreased recovery.

5. "The authors agree that more experimentation is both welcome and necessary, and indeed is now ongoing within the scope of an expanded and fully funded NSF research project. However, our original and primary concern within the more narrow scope of this manuscript was with GEM uptake and HgBr2 breakthrough at high loading rates. These questions were of particular importance to a companion manuscript, also currently

submitted to AMT."
R2 – What the authors are attempting to do here is manuscript quantity over manuscript quality. These experiments show useful data, but as I have suggested they appear rushed and too many questions and concerns have been left unanswered and unaddressed, when they could have easily been rectified by simply re-running experiments making slight adjustments to the existing conditions. This is THE STUDY addressing "GEM uptake and HgBr2 breakthrough at high loading rates" it should not need "companion" studies or "follow-up" studies to comprehensively answer the research question it set out to do. That is the role of this manuscript. It is my suggestion that this study be combined with this "companion study" to make a more complete paper. There is a lot of over-elaboration in the discussion and many points could easily be moved to an SI without loss of information to combine this study with complimentary work. This study definitely has merit, but it needs to be more polished.

We appreciate the comment and have made every attempt to turn this manuscript into a more polished version. We selected not to combine the work in this manuscript with the work of the companion manuscript to avoid an extremely long, cumbersome manuscript that addresses two different, yet complementary, sets of questions. We posit that the two manuscripts are stand-alone studies and respectfully decline to combine them.

6. In response to concerns about high CEM filter blanks:
R2 – This concern was brought up here because it has been inadequately addressed in previous studies. Take the Huang et al (2017) study for example:

"The bi-weekly MDLs (336 h) for active systems with cation-exchange and nylon membranes were 2–68 pg m−3 (mean: 24 pg m−3) and 0.01–14.6 pg m−3 (mean: 2.1 pg m−3), respectively. Biweekly MDL was calculated from 3 times the standard deviation of bi-weekly blanks. The MDL was calculated for each period of sampling, due to the fact this can vary based on treatment of the membranes, the time samples are prepared for deployment, deployment at the field site, and handling once returned to the laboratory. The membranes may also vary by material lot. All samples were corrected by subtracting the blank for the corresponding 2-week period."

(a) A 2 week mean detection limit concentration of 24 pg m-3 is at or below typical GOM concentration even in industrial city sites (examples: Lyman and Gustin 2009; Huang et al. 2012; Choi et al. 2013).

The Huang et al. (2017) reference uses the UNRRMAS system and is not comparable to the system in this study. However, the high blanks (above background) can be attributed to the fact that the CEM material passively collects (and accumulates) ambient GOM. Compared to the actively sampled membranes, the "blank" membrane mercury concentrations are low and are used to represent the amount of Hg sorbed to the material due to variables during preparation, deployment, harvesting, processing, etc.. Thus, "blank correcting" the samples is appropriate in these (actively sampled and/or high concentration) systems. See part (c) below for more details.

(b) These are DETECTION limits. Not QUANTIFICATION limits. Attempting to provide high certainty, quantifiable results at concentrations at or below detection limits is simply erroneous.

We agree that reported concentrations should be above MDLs, and that a quantification limit should be established for each instrument and method in each laboratory. We acknowledge that these are of often 2 different values, with quantification limits typically higher than MDLs. In the current study, we have only reported values above the quantification limits for the respective instruments, and any value below the quantification limit is reported as ND or 0, where appropriate. Additionally direct comparison of the 2 studies is not possible since for one the blank is per unit of digestate, whereas the other one is Hg per volume of air.

(c) The purpose of averaging method detection and/or quantification limits is to prevent exactly what the authors are discussing here by smoothing out inconsistency in variable handling of materials, residual Hg, etc. By subtracting "the blank" (a single blank for a single sampling period; n=1) is again incorrect and biased.

Presumably the reviewer is addressing the sentences in lines 203-206 of the original submission. A total of 50 blank membranes collected over the course of this study were used to represent an average background mercury concentration that could be attributed to the unused CEM material due to manufacturing, shipping/transport, processing (cutting 47 mm rounds from the sheeted material), material storage, sample deployment, sample harvesting, and sample analysis. The blank membranes were handled in the same manner as the sample membranes, and thus represent the cumulative contribution of mercury to the lot of membranes from the numerous potential sources listed above. By subtracting the average blank mercury concentration from the concentration of each sample membrane, we are quantifying the mercury concentration on the sample membrane that resulted from experiment itself. This, of course, is not the ideal method for determining the background concentration of each sample membrane; however, because the analytical procedures are destructive, it is impossible to determine the background mercury concentration on each membrane prior to deployment and therefore we have selected to use the method discussed above and in the manuscript.

(d) This completely contradicts a statement the authors of the current manuscript have introduced in this round of reviews in terms of their attempting to caution the use of the term RM:
"a broad term that favors basic accuracy of measurement over determination of specific compounds"
How can this favor "accuracy of measurement" if attempts at field measurements at typical concentrations encountered in the environment are at or below detection (not quantification) limits. There is no confidence in such results. As such these concerns do still need to be addressed for this sampling method.

The phrase copied above has been removed from the manuscript.

Other comments of this latest version:

Lines 39-40: This "cautionary" description of RM that was suggested by me previously is inadequate as described above. This research group attempts to use this same sorbent material to determine specific compounds of GOM in previous work (Huang et al. 2017). Thus, by making this statement here they are saying the results from this previous work are not accurate measurements.

The second half of this sentence was removed. It added confusion to the discussion.

Line 95: Once again here the authors should include a reference to the Marusczak et al. 2017 that describes how adding the zero flushes from GOM analysis to the actual GOM concentrations increases the derived concentrations to agree more closely with alternative measurement techniques and some modelled values. This was paper was specifically mentioned in the previous round of comments to be added to the literature review to balance impartiality but this comment was ignored.

The reference was in fact added during the last revision We have added an additional citation to this reference in this revision.

Lines 128-131: Can the authors please reference where exactly in the Gustin et al. 2015 paper is the mention of PTFE/PFA producing zero sorption of GEM. Personally, I could not find this specific point within the reference.

This sentence has been removed.

Lines 220-222: Yes, the uptake was linear if the first filter was not included. But when the first filter is included it is exponential. Why? As yet this has not been addressed by the authors anywhere.

We believe that this has been addressed, in response to an above comment and in the manuscript. The first filters clearly do not group with the other samples, despite exposure to essentially identical GEM concentrations We will not assign the behavior of the first filters to GEM uptake because we cannot be sure they are not capturing some small amount of GOM, despite our best efforts. However, we can be very sure that the subsequent downstream CEM filters are being exposed only to GEM, given that the first filter would scrub over 99% of fugitive GOM. Therefore, we feel the downstream filters to be the best representation of GEM uptake behavior on the CEM material.

Line 232: Approximate not approximately.

This correction has been made.

Lines 236-237: "but it should be noted that the performance of the CEM filters at low concentrations could be slightly different"
This should be changed to:
"but it should be noted that these concentrations are 50-1000x above typical background concentrations and the performance of the CEM filters at low concentrations could be slightly different"as was previously suggested.

We apologize for the oversight. This statement has been adjusted in the manuscript to reflect the reviewer's suggestion.

Lines 263-266: Caution needed here. You would never use such a system that has been used in contaminated environments for background work. Even a small memory of the Hg would overwhelm the background signal. Lines would need to be discarded or thoroughly acid cleaned *for background work. Please make a cautionary note on this here. A comment was made about this in the previous revisions, but ignored.*

This comment was not ignored. We have very clearly indicated that this is a laboratory system used exclusively for high concentration permeation work and is never used for background measurements. However, we have added additional elaboration on this point to the manuscript.

Lines 284-285: Again I ask is "photochemistry driven by room fluorescent lighting" a process reported in the literature? If so please reference, if not this is just pure speculation.

This statement has been adjusted to remove speculation.

Lines 340-343: Again, why speculate when this could have easily been determined by repeating the experiments at higher pyrolyzer temperatures?

As mentioned above, the pyrolyzer temperature did not significantly affect the amount of mercury transformed by the pyrolyzer to GEM when the temperature was increased to 800 C. Though higher pyrolyzer temperatures (1,000 C) transformed significantly more mercury, the temperature was unsustainable and unsafe for the pyrolyzer design. Therefore, the lower (safer) pyrolyzer temperature was used with the tradeoff being that not all GOM was converted to GEM and detected.

Revised Manuscript, Tracked Changes:

Evaluation of cation exchange membrane performance under exposure to high Hg^0 and HgBr$_2$ concentrations

Matthieu B. Miller[1], Sarrah M. Dunham-Cheatham[2], Mae Sexauer Gustin[2], Grant C. Edwards[1, †]

[1]Faculty of Science and Engineering, Department of Environmental Sciences, Macquarie University, Sydney, NSW, 2109, Australia

[2]Department of Natural Resources and Environmental Science, University of Nevada, Reno NV, 89557, United States

[†]Deceased 10 September 2018

Correspondence to: Matthieu B. Miller matthieu.b.miller@gmail.com and Mae Sexauer Gustin mgustin@cabnr.unr.edu

Abstract

Reactive mercury (RM), the sum of both gaseous oxidized Hg and particulate bound Hg, 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 improvements are ongoing. For the CEM material to be reliable, uptake of gaseous elemental mercury (GEM) must be negligible under 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 to 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. Quantification of total permeated Hg was measured 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 to 10 g m^{-3} water vapor. GEM uptake by the CEM material averaged no more than 0.004% of total exposure for all test conditions that equates to a non-detectable GEM artifact for typical ambient air sample concentrations. Recovery of HgBr$_2$

Deleted: Mae S. Gustin[2],

Deleted: (

Deleted:)

Deleted: ,

Deleted:

Deleted: for

Deleted: , with

Deleted: q

Deleted: accomplished

Deleted: Gaseous elemental mercury

Deleted: , which

on CEM filters was >100 % compared to calculated total permeated $HgBr_2$ based on the downstream Tekran® 2537A data. These results suggest incomplete thermal decomposition due to the pyrolyzer or the gold trap in the Tekran 2537, as the CEM demonstrated a high collection efficiency for $HgBr_2$, as indicated by less than 1% downstream breakthrough on average.

Deleted: ,
Deleted: ing
Deleted: at the
Deleted: material collected $HgBr_2$ with
Deleted: , implying a high collection efficiency of the target analyte…

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 to 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 quadrillion (pg m^{-3}) concentrations, and depends currently on un-calibrated operationally defined methods with demonstrated interferences and artifacts, and concomitant large uncertainty (Marusczak et al., 2017; Jaffe et al. 2014; McClure et al. 2014; Gustin et al. 2013; Lyman et al. 2010). Recent reviews (Zhang et al., 2017; Gustin et al., 2015) detail the shortcomings, difficulties, developments, and ongoing improvements for atmospheric RM measurements.

Deleted: , a broad term that favors basic accuracy of measurement over determination of specific compounds
Deleted: trillion
Deleted: level

One alternative methodology that may provide improved measurement of ambient RM involves use of cation exchange membranes (CEM). CEM materials have been used to selectively measure GOM concentrations in ambient air in previous studies (Huang et al., 2017; Marusczak et al., 2017; Pierce and Gustin, 2017; Huang and Gustin, 2015a; Huang et al., 2013; Sheu and Mason, 2001; Ebinghaus et al., 1999; Mason et al., 1997; Bloom et al., 1996). Use of CEM type

Deleted: might
Deleted: The u

filters for this purpose was first documented in the literature in a conference presentation (Bloom et al., 1996). These werereferred to as ”ion exchange membranes”. These 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 to 10 Lpm, for 24 h measurements (filter pore sizes were not reported). Results for PBM and GOM were in similar ranges of 4.5 to 26 pg m^{-3} and 13 to 23 pg m^{-3} , respectively (Ebinghaus et al., 1999).

Deleted: , although such membranes (then

Deleted: ‘

Deleted: membranes’

Deleted:)

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 particules, 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). These low concentrations are likely due to GOM being degraded on the quartz fiber filter or inefficient uptake by the Gelman filter (see Supplemental Information Gustin et al. 2013). 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.

Deleted: particulates

The particulate Hg artifact problem was subsequently elaborated on in a further comparative study focusing exclusively on RM measurement techniques (Sheu and Mason, 2001). 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. None of these concerns were proven or disproven conclusively.

Deleted: (Sheu and Mason, 2001)

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 (Huang et al., 2017). The CEM material consists of a negatively charged polyethersulfone coated matrix (Pall Corporation), and at least one manufacturing evolution has occurred (Huang and Gustin, 2015b). 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 selectively uptakes 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 and Gustin, 2015a; Huang et al., 2013). These studies and others (Lyman et al., 2016) have shown better GOM recovery on CEM material compared to potassium chloride (KCl) coated denuder methods.

Deleted: can

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 lLimited 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 to 2% GEM uptake could easily overwhelm detection of typical ambient GOM concentrations). It is therefore important that a GEM artifact be ruled out if the CEM material is to be successfully deployed for ambient RM measurements.

Deleted: of critical importance

Deleted: such

Deleted: , first and foremost under controlled laboratory conditions in the absence of confounding variables

Additionally, previous studies 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 to 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 to 16%) or no breakthrough Huang and Gustin, 2015a; Huang et al., 2013). 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).

Deleted: have

In this research we investigated the potential for GEM uptake on CEM material using a custom-built permeation system. Tests were done to investigate the ability of a pyrolyzer to convert GEM to GOM. In addition, the ability of the CEM material to capture and retain a representative GOM compound (mercury(II) bromide, $HgBr_2$) and to estimate collection efficiency of this compound and explain or rule out possible mechanisms of breakthrough for both dry and humid conditions.

Deleted: paper

Deleted: is discussed with a view

Deleted: analyte

2 Methods

2.1 System for sampling configuration

Formatted: Font: Bold

Formatted: Indent: First line: 0.25"

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. 1). See SI for additional information on Tekran quality control. All tubing and connections used in the permeation system were polytetrafluoroethylene (PTFE), except for the quartz glass pyrolyzer tube and perfluoroalkoxy (PFA) filter holders. 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).

Deleted: 2

Deleted: Each of these materials is known to be chemically inert, virtually nonporous, and to have a low coefficient of friction and 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). …

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 (MFC) in the 2537A, or by an external flush pump (KNF Laboport® N86 KNP) and MFC (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 (granular activated carbon 6-12 mesh, FisherChemical®) 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 because higher temperatures would have produced unacceptably high concentrations, and there is evidence that at higher temperatures a small amount of Hg^0 can be evolved from Hg^{2+} compounds (Xiao et al., 1997).

Deleted: both

Deleted: because

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, with flow on each line controlled by MFC. 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 contained an in-line pyrolyzer unit The goal of the pyrolyzer was to convert all Hg to GEM for detection on the Tekran® 2537A.

Deleted: held a

Deleted: 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).

2.2 Pyrolyzer

Formatted: Font: Bold

Formatted: Indent: First line: 0.5"

The pyrolyzer used in the study (SI Fig. 3) consisted of a 25.4 cm long quartz glass tube of 0.625 cm diameter (custom, URG Corporation). A loosely packed 3 cm section of quartz wool was lodged in the mid-section of the tube, and this 3 cm section was wrapped with 22 gauge Nichrome wire (18 loops). The quartz tube was closely contained within 2.5 cm thick quartz fiber insulation within a 1.6 mm aluminum casing, except for an enclosed air space around the heated Nichrome coil section. The coil wire was connected to 16 AWG stranded copper wire with all metal disconnects that were buried within the quartz fiber insulation to reduce thermal fatigue on the connections. The copper wire insulation was stripped and replaced with higher temperature heat-shrink insulation where the wiring passed through the pyrolyzer case to the external power supply. The tip of a 150 mm long K-type thermocouple (Auber WRNK-191) was inserted through the insulation into the heated air space next to the coil to provide a temperature feedback for a PID controller (Auber SYL-1512A). Power to the Nichrome coil was supplied by a 12 VDC transformer through a solid-state relay (Auber MGR-1D4825) switched by the PID controller.

It was found that the position of the feedback thermocouple in the airspace outside of the heating coil caused a large discrepancy between nominal temperature setpoint and actual temperature inside the heated section of pyrolyzer tube. In general, much higher temperatures are achieved inside the coil than outside. To compensate for this, actual temperature at the heated coil section was verified to 600°C by external IR sensor and internal thermocouple probe.

Formatted: None

To test if higher pyrolyzer temperatures converted more GOM to GEM for detection by the Tekran 2537, the pyrolyzer temperature was increased to 650, 800, and 1,000^{o}C (SI Fig. 4). Pyrolyzer temperatures were measured by placing a thermocouple inside the pyrolyzer. GOM concentrations measured as GEM by the Tekran 2537 increased at 600 and 800^{o}C relative to 375^{o}C. There was no significant difference between the amount of mercury concentrations in the downstream Tekran 2537 when the pyrolyzer was at 600 and 800^{o}C C (*t-test*, $p = 0.08$), indicating that the increased pyrolyzer temperature did not convert more GOM to GEM. However, when the pyrolyzer temperature was increased to 1000 ^{o}C, significantly more mercury was measured by the downstream Tekran 2537 relative to when the pyrolyzer was at 650^{o}C (*t-*

test, $p = 0.00$), indicating that the higher temperature was more efficient at converting GOM to GEM; however, the pyrolyzer design could not sustain the 1000 ^{o}C temperature and was deemed unsafe to use in the experimental permeation system. Thus, all experiments were performed with a pyrolyzer temperature of 600^{o}C.

The residence time in the pyrolyzer tube was approximately 1.5 seconds. Quartz wool was added to increase the amount of surface area available to facilitate reactions and maximize the amount of GOM converted to GEM in the pyrolyzer. Because of the conversion rate (discussed below), this is a pretty efficient method for converting GOM to GEM. Having an efficient pyrolyzer provides us with a means of constraining perm tube permeation rates.

Formatted: Space After: 0 pt

2.3 Sample deployment

Formatted: Font: Bold

Formatted: Indent: First line: 0.5", Space After: 0 pt

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 mean GEM uptake rate, (SI 5 and discussion).

Deleted: Fig

Deleted: 4

For determining the potential for GOM breakthrough, two system configurations were used. In the first configuration (Fig. 1B), total Hg concentrations 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 10 min interval quantification of the HgBr$_2$

Deleted: the

Deleted: real time (

Deleted:)

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.

2.4 Analyses of cation exchange membranes

Formatted: Font: Bold

Formatted: Font: Bold

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. The system background Hg signal was determined for every analytical run by analyzing pure reagent solution in the same vials and at the same volume as used for actual filter samples. Total Hg standards (5 to 100 ppb) were analyzed before and after each batch of 10 filter samples to check precision and recovery, and the mean recovery for all Hg standards was 97.2 ± 5.0 % (n = 37). Analysis for total Hg on the CEM filters 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):

Deleted: The background Hg value was used as a system calibration blank and subtracted from all actual samples.

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

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

A controlled experiment was performed to ensure that both Lines 0 and 1 were conducting comparable concentrations of mercury under the experimental conditions. Two-stage filter packs were deployed with cation exchange membranes (CEM) in each line at equal distances from the permeation tube. The membranes were deployed for the same amount of time, in triplicate, and analyzed to quantify the amount of total mercury sorbed to the membranes. The average % deviation between lines was 2.9%, with a maximum deviation of 5.4%. These results indicated that though there may be some difference in the amount of mercury passing through Lines 0 and 1, but the difference was relatively small.

Formatted: Font: (Default) Times New Roman, 12 pt

Formatted: Normal, No bullets or numbering

Formatted: Font: (Default) Times New Roman, 12 pt

Formatted: Font: (Default) Times New Roman, 12 pt

Formatted: Font: (Default) Times New Roman, 12 pt

Elemental Hg uptake on CEM material was negligible for permeated Hg^0 vapor concentrations ranging from 1.43×10^6 to 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 lower concentrations.

Deleted: all

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% (0.006 ± 0.006% including first in-line filter).

The first CEM filter in line during the GEM permeations always showed more total Hg than the following 5 downstream filters, which were not significantly different from each other (SI Fig. 5). It is unlikely that the Hg observed on the first CEM filters resulted from GEM uptake. Even at the highest GEM permeation rate, the first filter captured only ~1700 pg of Hg, out of a total permeated amount of over 7.3 *million* pg (a 0.02 % uptake rate). This means that the downstream CEM filters were still exposed to about 7.2985 *million* pg of GEM but captured less total Hg.

We cannot entirely rule out the possibility of some small rate of *in-situ* oxidation of GEM in the system, at the surface of the Hg^0 bead or in the vapor phase. Therefore, the first in-line filters were not included in calculation of GEM uptake rates because of suspicion that some component of the Hg captured on the first filter was GOM. Inclusion or removal of the first in-line filters did not alter calculations.

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.

Commented [GM1]: Matthieu you need a p value and to give the equation since these data are not show in a figure.

Deleted: For GEM permeations into ambient humidity sample air (2 to 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% (0.005 ± 0.005% including first in-line filter).

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 to 5 g m^{-3} WV), and clean air at elevated humidity (10 to 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 Fig. 1B to establish an approximate permeation rate (Fig. 3). Total Hg reaching the 2537A through the pyrolyzer on Line 1 (red line, Fig. 3) indicated an average $HgBr_2$ exposure concentration of 4540 pg m^{-3}, or about 4.5 pg min^{-1} from the permeation tube. This permeated concentration of $HgBr_2$ was deliberately much higher than ambient in order to test retention and break through at high levels. It should be noted that these concentrations are 50 – 1000 times above background ambient concentrations and the performance of the CEM filters at low concentrations could be slightly different. 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.

Deleted: ure

Deleted: ly

Deleted: indicates

Deleted: ,

Deleted: but it

Formatted: Not Highlight

Deleted: ,

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 volatilization of $HgBr_2$ that had adsorbed 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 volatized from the interior line surfaces (1155 pg) represents 4 to 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 the majority of $HgBr_2$ line contamination in a high-concentration permeation system can be expected to flush out within ~12 h. However, we caution that materials used in high-concentration permeation systems, despite being flushed out, should not be used for background ambient air work without at least a very thorough acid cleaning.

Deleted: re-

Deleted: stuck

Deleted: re-

Deleted: a

Formatted: Not Highlight

Additional $HgBr_2$ permeations were made at two levels of in-line humidity. At ambient room humidity (4 to 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 of 4 to 5 g m^{-3} WV had insignificant effects on collection of $HgBr_2$ in clean laboratory air by the CEM material.

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). Hg rapidly declined to zero, due to off-gassing from the tubing induced by the increased humidity that facilitated a heterogeneous surface reduction of $HgBr_2$ to GEM in the short section of line between the perm source and CEM filters. This phenomena was also observed during the Reno Atmospheric Mercury Intercomparison eXperiment (RAMIX; Gustin et al., 2013). Reduced $HgBr_2$ then then passed through to the 2537A as GEM. 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 to 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

Deleted: around

Deleted: have

Deleted: We observed that a

Deleted: As this downstream

Deleted: we believe this was also

Deleted: an

Deleted: effect

Deleted: , which

Deleted: perhaps

Deleted: photochemical

Formatted: Not Highlight

Deleted: ,

Deleted: with the photochemistry driven by room fluorescent lighting…

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 Discussion

Deleted: Conclusions

GEM uptake on the CEM material was negligible under the laboratory conditions and high GEM loading rates (3 orders of magnitude above ambient) tested in this study, with an overall linear uptake rate of 0.004% (SI Fig. 5). This uptake rate would be insignificant at typical ambient atmospheric Hg concentrations (1 to 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. Given that blank filters have a mean total Hg mass of 50 ± 20 pg, this amount would be below the detection limit. 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 to 6000 pg.

Deleted: for permeated GEM concentrations between 1.43×10^6 to 1.85×10^6 pg m^{-3}

Deleted: and

Deleted: g

Mean $HgBr_2$ breakthrough from primary to secondary CEM filters averaged 0.2 ± 0.2% over all test conditions. 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 under laboratory conditions applied in this study. 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

Deleted: , using $HgBr_2$ as a test GOM compound permeations in dry air, and 0 to 40 pg in humid air, for filter deployments at 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), $HgBr_2$ recovery on the CEM filters averaged 127%. Adjusting the expected permeated $HgBr_2$ mass for our estimated line-loss (~4-5%) changed the recoveries to ~123%. Still, $HgBr_2$ loading on the CEM filters was ~23% higher than expected based on the pyrolyzed total measurement on the 2537A, indicating not all $HgBr_2$ was converted to GEM.

This can be explained by the pyrolyzer design used in this study not being 100% efficient at thermally reducing $HgBr_2$ to Hg^0, based on the higher total Hg recoveries on the CEM filters versus total Hg measured through the pyrolyzer on the Tekran 2537.

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 (Temme et al., 2003; Landis et al., 2002; Schroeder et al, 1995; Dumarey et al., 1985; Schroeder and Jackson, 1985). 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). This would 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

Deleted: those

Deleted: than can be considered

Deleted: ,

Deleted: the

Deleted: improves

Deleted: therefore

Moved down [1]: Further testing and optimization of the pyrolyzer parameters (e.g., temperature, volume) should be done to allow for a more accurate, quantitative comparison between the CEM and Tekran® 2537 results.

Deleted: . This indicates that

Deleted: was

Deleted: may have been

Deleted: being

Deleted: , suggesting that the pryolyzer was not 100% efficient and that higher pyrolyzer temperatures may be needed

Formatted: Font: Not Italic

Deleted: , which

Deleted: likely

Deleted: ,

pyrolyzer and during the best-case 500 °C desorption of the 2537 gold traps, contributed to the ~20% non-detection of total permeated $HgBr_2$ as it passed through the CVAFS optical path.

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.

Future work needed.

Further testing and optimization of the pyrolyzer parameters (e.g., temperature, volume) should be done to allow for a more accurate quantitative comparisons between the CEM and Tekran® 2537 results.

Permeation rates of $HgBr_2$ varied and these need to be precisely controlled. A stable permeation system that is standardized needs to be developed.

This study was done using controlled laboratory conditions. CEM performance needs to be further tested in ambient air.

Deleted: may have

Deleted: resulted in

Deleted: without generating the necessary fluorescence signal

Commented [DS3]: Mae, what do you think about this instead of building a brand new “Future Work Needed” section?

Moved (insertion) [1]

Deleted: ,

Formatted: Subscript

Lastly, the reason for breakthrough observed for CEM data collected in ambient air needs to be determined.

Acknowledgements

The authors would like to acknowledge funding from Macquarie University iMQRES 2015148 and NSF Grant 629679. Valuable input and assistance was received from Dr. Ashley Pierce, Dr. Seth Lyman, and the students of Dr. Gustin's laboratory. The surviving authors bid an untimely farewell to Dr. Grant C. Edwards, who was ever a cheerful friend, mentor, and colleague. Dr. Edwards passed away unexpectedly on September 10, 2018.

References

Bloom, N., Prestbo, E., and VonderGeest, E.: Determination of atmospheric gaseous Hg(II) at the pg/m 3 level by collection onto cation exchange membranes, followed by dual amalgamation/cold vapor atomic fluorescence spectrometry, 4th International Conference on Mercury as a Global Pollutant, Hamburg, 1996.

Dumarey, R., Dams, R., and Hoste, J.: Comparison of the collection and desorption efficiency of activated charcoal, silver, and gold for the determination of vapor phase atmospheric mercury, Analytical Chemistry, 57, 2638-2643, 10.1021/ac00290a047, 1985.

Ebinghaus, R., Jennings, S. G., Schroeder, W. H., Berg, T., Donaghy, T., Guentzel, J., Kenny, C., Kock, H. H., Kvietkus, K., Landing, W., Muhleck, T., Munthe, J., Prestbo, E. M., Schneeberger, D., Slemr, F., Sommar, J., Urba, A., Wallschlager, D., and Xiao, Z.: International field intercomparison measurements of atmospheric mercury species at Mace Head, Ireland, Atmospheric Environment, 33, 3063-3073, 1999.

Gustin, M. S., Huang, J., Miller, M. B., Peterson, C., Jaffe, D. A., Ambrose, J., Finley, B. D., Lyman, S. N., Call, K., Talbot, R., Feddersen, D., Mao, H., and Lindberg, S. E.: Do We Understand What the Mercury Speciation Instruments Are Actually Measuring? Results of RAMIX, Environmental Science & Technology, 47, 7295-7306, 10.1021/es3039104, 2013.

Gustin, M. S., Amos, H. M., Huang, J., Miller, M. B., and Heidecorn, K.: Measuring and modeling mercury in the atmosphere: a critical review, Atmos. Chem. Phys., 15, 5697-5713, 10.5194/acp-15-5697-2015, 2015.

Gustin, M. S., Pierce, A. M., Huang, J., Miller, M. B., Holmes, H. A., and Loria-Salazar, S. M.: Evidence for Different Reactive Hg Sources and Chemical Compounds at Adjacent Valley and High Elevation Locations, Environmental Science & Technology, 50, 12225-12231, 10.1021/acs.est.6b03339, 2016.

Huang, J., Miller, M. B., Weiss-Penzias, P., and Gustin, M. S.: Comparison of Gaseous Oxidized Hg Measured by KCl-Coated Denuders, and Nylon and Cation Exchange Membranes, Environmental Science & Technology, 47, 7307-7316, 10.1021/es4012349, 2013.

Huang, J., and Gustin, M. S.: Uncertainties of Gaseous Oxidized Mercury Measurements Using KCl-Coated Denuders, Cation-Exchange Membranes, and Nylon Membranes: Humidity Influences, Environmental Science & Technology, 49, 6102-6108, 10.1021/acs.est.5b00098, 2015a.

Huang, J., and Gustin, M. S.: Use of Passive Sampling Methods and Models to Understand Sources of Mercury Deposition to High Elevation Sites in the Western United States, Environmental Science & Technology, 49, 432-441, 10.1021/es502836w, 2015b.

Huang, J., Miller, M. B., Edgerton, E., and Sexauer Gustin, M.: Deciphering potential chemical compounds of gaseous oxidized mercury in Florida, USA, Atmos. Chem. Phys., 17, 1689-1698, 10.5194/acp-17-1689-2017, 2017.

Jaffe, D. A., Lyman, S., Amos, H. M., Gustin, M. S., Huang, J., Selin, N. E., Levin, L., ter Schure, A., Mason, R. P., Talbot, R., Rutter, A., Finley, B., Jaeglé, L., Shah, V., McClure, C., Ambrose, J., Gratz, L., Lindberg, S., Weiss-Penzias, P., Sheu, G.-R., Feddersen, D., Horvat, M., Dastoor, A., Hynes, A. J., Mao, H., Sonke, J. E., Slemr, F., Fisher, J. A., Ebinghaus, R., Zhang, Y., and Edwards, G.: Progress on Understanding Atmospheric Mercury Hampered by Uncertain Measurements, Environmental Science & Technology, 48, 7204-7206, 10.1021/es5026432, 2014.

Landis, M. S., Stevens, R. K., Schaedlich, F., and Prestbo, E. M.: Development and characterization of an annular denuder methodology for the measurement of divalent inorganic reactive gaseous mercury in ambient air, Environmental Science & Technology, 36, 3000-3009, 10.1021/es015887t, 2002.

Lyman, S., Jones, C., O'Neil, T., Allen, T., Miller, M., Gustin, M. S., Pierce, A. M., Luke, W., Ren, X., and Kelley, P.: Automated Calibration of Atmospheric Oxidized Mercury Measurements, Environmental Science & Technology, 50, 12921-12927, 10.1021/acs.est.6b04211, 2016.

Lyman, S. N., Gustin, M. S., Prestbo, E. M., and Marsik, F. J.: Estimation of Dry Deposition of Atmospheric Mercury in Nevada by Direct and Indirect Methods, Environmental Science & Technology, 41, 1970-1976, 10.1021/es062323m, 2007.

Lyman, S. N., Jaffe, D. A., and Gustin, M. S.: Release of mercury halides from KCl denuders in the presence of ozone, Atmospheric Chemistry and Physics, 10, 8197-8204, 10.5194/acp-10-8197-2010, 2010.

Marusczak, N., Sonke, J. E., Fu, X., and Jiskra, M.: Tropospheric GOM at the Pic du Midi Observatory—Correcting Bias in Denuder Based Observations, Environmental Science & Technology, 51, 863-869, 10.1021/acs.est.6b04999, 2017.

Mason, R., Lawson, N., and Sullivan, K.: The concentration, speciation and sources of mercury in Chesapeake Bay precipitation, Atmospheric Environment, 31, 3541-3550, 10.1016/S1352-2310(97)00206-9, 1997.

McClure, C. D., Jaffe, D. A., and Edgerton, E. S.: Evaluation of the KCI Denuder Method for Gaseous Oxidized Mercury using HgBr2 at an In-Service AMNet Site, Environmental Science & Technology, 48, 11437-11444, 10.1021/es502545k, 2014.

Pierce, A. M., and Gustin, M. S.: Development of a Particulate Mass Measurement System for Quantification of Ambient Reactive Mercury, Environmental Science & Technology, 51, 436-445, 10.1021/acs.est.6b04707, 2017.

Schroeder, W., and Jackson, R.: An instrumental analytical technique for speciation of atmospheric mercury, International Journal of Environmental Analytical Chemistry, 22, 1-18, 10.1080/03067318508076405, 1985.

Schroeder, W., Keeler, G., Kock, H., Roussel, P., Schneeberger, D., and Schaedlich, F.: International field intercomparison of atmospheric mercury measurement methods, Water Air and Soil Pollution, 80, 611-620, 10.1007/BF01189713, 1995.

Sheu, G. R., and Mason, R. P.: An examination of methods for the measurements of reactive gaseous mercury in the atmosphere, Environmental Science & Technology, 35, 1209-1216, 10.1021/es001183s, 2001.

Slemr, F., Angot, H., Dommergue, A., Magand, O., Barret, M., Weigelt, A., Ebinghaus, R., Brunke, E., A Pfaffhuber, K., Edwards, G., Howard, D., Powell, J., Keywood, M., and Wang, F.: Comparison of mercury concentrations measured at several sites in the Southern Hemisphere, 3125-3133 pp., 2015.

Temme, C., Einax, J. W., Ebinghaus, R., and Schroeder, W. H.: Measurements of Atmospheric Mercury Species at a Coastal Site in the Antarctic and over the South Atlantic Ocean during Polar Summer, Environmental Science & Technology, 37, 22-31, 10.1021/es025884w, 2003.

Xiao, Z., Sommar, J., Wei, S., and Lindqvist, O.: Sampling and determination of gas phase divalent mercury in the air using a KCl coated denuder, Fresenius Journal of Analytical Chemistry, 358, 386-391, 1997.

Zhang, L., Lyman, S., Mao, H., Lin, C. J., Gay, D. A., Wang, S., Sexauer Gustin, M., Feng, X., and Wania, F.: A synthesis of research needs for improving the understanding of atmospheric mercury cycling, Atmos. Chem. Phys., 17, 9133-9144, 10.5194/acp-17-9133-2017, 2017.

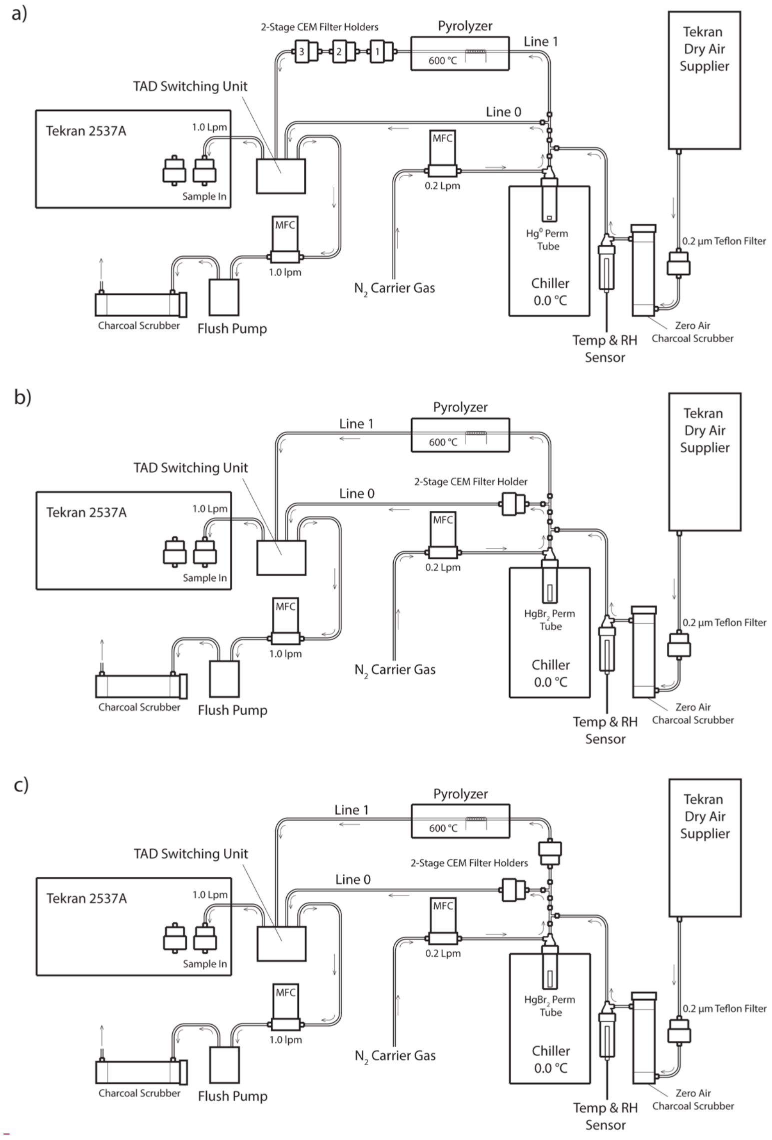

Figure 1. Schematic of the Hg vapor permeation system configurations for: a) GEM permeations b) $HgBr_2$ permeations c) Simultaneous $HgBr_2$ loading on two sample lines. Note dry air supplier disconnected for ambient and elevated humidity $HgBr_2$ permeations, with sample path starting at 0.2 µm Teflon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

Deleted: chemically inert

Deleted: ,

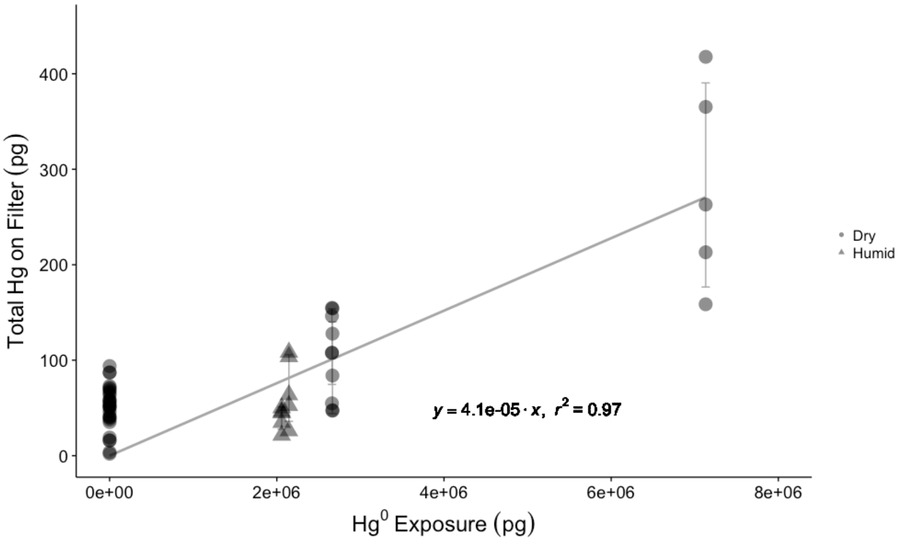

Figure 2. Total Hg recovered on CEM material for blank filters (Hg exposure = 0 pg) and different Hg^0 vapor permeations in dry (0.5 ± 0.1 g m^{-3} WV) and humid air (2-4 g m^{-3} WV). Circles represent dry air permeations, triangles represent humid air exposures, and all permeation exposures were blank-corrected. 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 4.1x10^{-5} indicating a linear uptake rate of 0.004%.

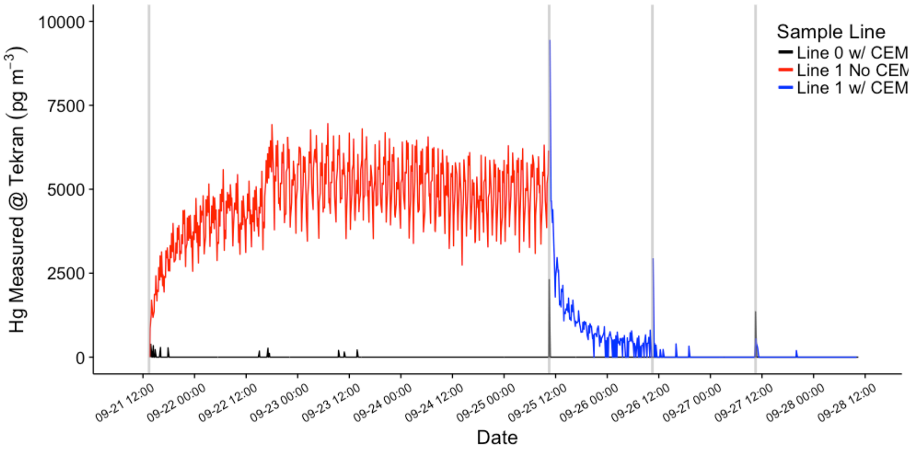

Figure 3. $HgBr_2$ permeations in clean dry lab air using the configuration in Figure 1B (red line) and Figure 1C (blue line). The red line indicates total Hg released from permeation tube and passing through pyrolyzer on Line 1 before being measured by Tekran 2537A, black line indicates Hg reaching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

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.