23 January 2019

Dear Dr. Abbatt,

Thank you again for the opportunity to revise our manuscript for further consideration by Atmospheric Measurement Techniques. The suggestions made by the reviewer were fair and have further improved our manuscript. Below are the original reviewer comments and suggestions (in italics) and our responses. Accompanying this letter are the: 1) manuscript with edits tracked for easier review, 2) manuscript with all edits incorporated and not tracked, and 3) revised 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

Reviewer 1:
GENERAL COMMENTS:
I believe the supplementary experiments that tested the pyrolyzer up to 1000 °C are of great benefit to this manuscript as it provide the necessary evidence that it is likely the responsible party for the higher recoveries. While a safe and operational 1000 °C pyrolyzer would have been ideal for all the experiments I can understand concerns if it was not entirely stable or safe for on-going operation.

I will now accept the manuscript for publication if the following minor corrections and updates are made:

SPECIFIC COMMENTS:
Line 29: Please write the actual value (127%) and not >100%

We have added the actual value to this sentence.

Lines 30-32: Please rephrase this sentence to:
"The low HgBr2 breakthrough on the downstream CEMs (<1%), suggest that the elevated recoveries are more likely related to sub-optimal pyrolyzer conditions or inefficient collection on the Tekran 2537 gold trap."
The low breakthrough is what suggests the pyrolyzer likely being responsible for the elevated recoveries, not the elevated recoveries suggesting poor pyrolyzer conditions.

We have reworded this sentence using the reviewer's suggested sentence.

Lines 38-39: The authors have now removed any and all discussion on the concerns of using the more general terminology RM, which was my concern in the original round of reviews "More

caution should be used in the definition of the term reactive mercury (RM)."
The "Often" (or perhaps sometimes) use of RM is by one or maybe two research groups. This does not qualify as often.
Since the authors are struggling for a descriptive terminology due to their own interchanging use of GOM and RM in their literature I suggest the following simple and clear addition:
"While the term RM does dilute some specific information in regard to the state of oxidized Hg in the atmosphere it does remove some of uncertainty as whether or not PBM contributes to the Hg collected by the CEMs."

This qualifying statement has been added.

Lines 117-118: Should be "We attempted to explain…"

The error has been corrected.

Lines 200-202: Please do not use "pretty" in a scientific paper. It is a colloquial and very unspecific term. Can the authors be more quantitative here? Use the data form SI Figure 4. What was the collection efficiency compared to 1000 °C? State this. This doesn't mean this value describes the exact inefficiency of the existing system (which should be mentioned), but it does a better job than "pretty".

A more quantitative discussion of the pyrolyzer efficiency has been added.

Lines 276-280: Linearity of the first filters remains poorly addressed. Fit both a linear and exponential curve to the data with equations and r2 values (as suggested below). The authors say in their response:
"There are only five data points, so we feel any assertion about this relationship being linear or exponential is not robust."
The authors seems to be using this as some form excuse as to why this should not be discussed, but on the contrary why did this again not sound some alarm bells and why was this set-up not re-tested? This goes specifically with the sentiments of myself and one other reviewer that experiments were rushed and less conclusive than they should have been. The authors are happy to conclude the linearity of the relationship based on limited data, but seem to not want to make conclusions if they pose a problem. This is and has been a concern of mine because if it is a exponential relationship then it would pose a problem for lower concentrations. Some form of description or discussion on this point IS necessary.

Linear and exponential models equations and r^2 values have been added to SI Figure 5 for both sets of membranes, and more discussion has been added to the end of section 3.1.

Line 369-371: This sentence should be changed to:
"Although further work is required to more definitively determine detection and quantification limits of the various CEM methodologies, based on the mean total Hg mass of 50 ± 20 pg observed in this study, the artifact of GEM uptake to the CEMs would be below the detection limit observed here."
This sentence finally provides an (albeit subtle) mention that work is still required on defining

detection and quantification limits of the CEM methodologies that I have suggested in all rounds of review.

The requested revision has been made.

Line 406: Please add the following after the sentence concluding on line 406:
"Evidence for this conclusion can be seen in by the XX % increase in Hg collection by the pyrolyzer at 1000 °C (see SI Figure 4) in supplementary experiments."

The sentence has been added.

SUPPLEMENTAL
In the current supplemental information that caption to SI Figure 5 has a caption. This caption should obviously be removed for publication.
BUT, it makes a perfect point. Add both linear and exponential curves with their appropriate equations and r2 values. This is something I have been inquiring about throughout the reviews and even co-authors have asked for its inclusion.

The linear and exponential curve equations and r^2 values have been added to the Figure, and the mentioned comment on the figure caption has been removed.

1 **Evaluation of cation exchange membrane performance under exposure to high Hg^0 and**

2 **HgBr$_2$ concentrations**

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

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13 **Abstract**

14 Reactive mercury (RM), the sum of both gaseous oxidized Hg and particulate bound Hg, is an

15 important component of the global atmospheric mercury cycle, but measurement currently

16 depends on un-calibrated operationally-defined methods with large uncertainty and demonstrated

17 interferences and artifacts. Cation exchange membranes (CEM) provide a promising alternative

18 methodology for quantification of RM, but method validation and improvements are ongoing.

19 For the CEM material to be reliable, uptake of gaseous elemental mercury (GEM) must be

20 negligible under all conditions, and RM compounds must be captured and retained with high

21 efficiency. In this study, the performance of CEM material under exposure to high

22 concentrations of GEM (1.43×10^6 to 1.85×10^6 pg m^{-3}) and reactive gaseous mercury bromide

23 (HgBr$_2$ ~ 5000 pg m^{-3}) was explored, using a custom-built mercury vapor permeation system.

24 Quantification of total permeated Hg was measured via pyrolysis at 600 °C and detection using a

25 Tekran$^®$ 2537A. Permeation tests were conducted for 24 to 72 hours in clean laboratory air, with

26 absolute humidity levels ranging from 0.1 to 10 g m^{-3} water vapor. GEM uptake by the CEM

27 material averaged no more than 0.004% of total exposure for all test conditions, which equates to

28 a non-detectable GEM artifact for typical ambient air sample concentrations. Recovery of HgBr$_2$

29   on CEM filters was ~~>100~~on average 127 % compared to calculated total permeated HgBr$_2$ based

30   on the downstream Tekran® 2537A data. The low HgBr$_2$ breakthrough on the downstream CEMs

31   (<1%) suggest that the elevated recoveries are more likely related to sub-optimal pyrolyzer

32   conditions or inefficient collection on the Tekran® 2537A gold traps. ~~These results suggest~~

33   ~~incomplete thermal decomposition due to the pyrolyzer or the gold trap in the Tekran 2537, as~~

34   ~~the CEM demonstrated a high collection efficiency for HgBr$_2$, as indicated by less than 1%~~

35   ~~downstream breakthrough on average~~.

36

1 Introduction

38   Mercury (Hg) is a persistent environmental contaminant with a significant atmospheric life time,

39   and the form and chemistry of Hg is an important determinant of its biogeochemical cycling.

40   Mercury in the atmosphere is found in three forms: gaseous elemental mercury (GEM), gaseous

41   oxidized mercury (GOM), and particulate bound mercury (PBM). PBM and GOM are often

42   quantified together as reactive mercury (RM = GOM + PBM); while the term RM dilutes some

43   specific information regarding the state of GOM in the atmosphere, it removes some uncertainty

44   as to whether or not PBM contributes to the Hg collected by the CEMs. Atmospheric GEM, at an

45   average global background concentration of 1 to 2 ng m^{-3}, can be reliably measured with

46   calibrated analytical instruments (Gustin et al., 2015; Slemr et al., 2015). The measurement of

47   GOM and PBM requires detection at part per quadrillion (pg m^{-3}) concentrations, and depends

48   currently on un-calibrated operationally defined methods with demonstrated interferences and

49   artifacts, and concomitant large uncertainty (Marusczak et al., 2017; Jaffe et al. 2014; McClure et

50   al. 2014; Gustin et al. 2013; Lyman et al. 2010). Recent reviews (Zhang et al., 2017; Gustin et

51 al., 2015) detail the shortcomings, difficulties, developments, and ongoing improvements needed

52 for atmospheric RM measurements.

53 One alternative methodology that may provide improved measurement of ambient RM involves

54 use of cation exchange membranes (CEM). CEM materials have been used to selectively

55 measure GOM concentrations in ambient air in previous studies (Huang et al., 2017; Marusczak

56 et al., 2017; Pierce and Gustin, 2017; Huang and Gustin, 2015a; Huang et al., 2013; Sheu and

57 Mason, 2001; Ebinghaus et al., 1999; Mason et al., 1997; Bloom et al., 1996). Use of CEM type

58 filters (then manufactured by Gelman Sciences and referred to as "ion exchange membranes")

59 for this purpose was first documented in the literature in a conference presentation (Bloom et al.,

60 1996), though these had also been deployed in an earlier field-based international comparative

61 study of RM measurement techniques in September, 1995 (Ebinghaus et al., 1999). In the

62 comparative study, one participating lab deployed a series of ion exchange membranes (for

63 GOM) behind a quartz fiber filter (for PBM) at a sample flow rate of 9 to 10 Lpm, for 24 h

64 measurements (filter pore sizes were not reported). Results for PBM and GOM were in similar

65 ranges of 4.5 to 26 pg m^{-3} and 13 to 23 pg m^{-3}, respectively (Ebinghaus et al., 1999).

66 The ion exchange membrane method was also applied in a 1995-96 field campaign for

67 determining the speciation of atmospheric Hg in the Chesapeake Bay area (Mason et al., 1997).

68 This study used a 5-stage Teflon filter pack system that included one up front quartz fiber filter

69 (0.8 μm pore size) to remove particles, and four downstream Gelman ion exchange membranes

70 (pore size not reported) to 1) capture GOM, 2) capture GOM breakthrough, 3) serve as

71 deployment blanks, and 4) isolate the filter train on the downstream side (Mason et al., 1997).

72 Concentrations of GOM were reported to be 5-10 pg m^{-3}, essentially at or below the method

73 detection limit and it was speculated that even this small amount may have been an artifact from

74   fine particulate Hg passing through the 0.8 µm quartz fiber filter (Mason et al., 1997). These low

75   concentrations are likely due to GOM being degraded on the quartz fiber filter or inefficient

76   uptake by the Gelman filter (see Supplemental Information Gustin et al. 2013). The 3rd-in-series

77   ion exchange membrane blanks were reported to be not significantly different in Hg

78   concentration from unused membrane material, indicating that breakthrough was not a

79   phenomenon that extended past the second ion exchange filter position.

80   The particulate Hg artifact problem was subsequently elaborated on in a further comparative

81   study focusing exclusively on RM measurement techniques (Sheu and Mason, 2001). Specific

82   concerns included physical particle breakthrough, re-evolution of gas-phase Hg^{2+} from PBM

83   captured on the upstream particulate filters passing downstream to the ion exchange membranes,

84   possible adsorption of GOM compounds to the particulate filters, or a GEM collection artifact on

85   the ion exchange membranes. None of these concerns were proven or disproven conclusively.

86   Recent CEM based sampling systems typically deploy a pair of CEM disc filters without a pre-

87   particulate filter, in replicates of 2 to 3 at a flow rate of 1.0 Lpm (Gustin et al., 2016). Each pair

88   of filters constitutes one sample, the first filter serving as the primary RM collection surface, and

89   the second filter capturing breakthrough. Filters are deployed for 1 to 2 weeks and then collected

90   for analysis (Huang et al., 2017). The CEM material consists of a negatively charged

91   polyethersulfone coated matrix (Pall Corporation), and at least one manufacturing evolution has

92   occurred (Huang and Gustin, 2015b). Prior CEM material versions (I.C.E. 450) had a pore size

93   of 0.45 µm, while the current CEM material (Mustang[®] S) has a manufacturer reported pore size

94   of 0.8 µm.

95   Previous work with the I.C.E 450 material indicated it does not adsorb significant quantities of

96   GEM in passive exposures, but selectively uptakes gas-phase Hg^{2+} species (Lyman et al., 2007).

97   The CEM material was subsequently adapted for use in active sample flow systems, with the

98   presumption of continued inertness to GEM and selectivity for GOM (Huang and Gustin, 2015a;

99   Huang et al., 2013). These studies and others (Lyman et al., 2016) have shown better GOM

100 recovery on CEM material compared to potassium chloride (KCl) coated denuder methods.

101 Despite these tests, the transparency of the CEM material to GEM uptake has not been

102 conclusively demonstrated for active sampling flow rates, nor for high GEM concentrations,

103 though limited data using low concentration manual Hg^0 injections through CEM filters suggests

104 little or no GEM uptake (Lyman et al., 2016). However, even small rates of GEM uptake by the

105 CEM material could result in a significant measurement artifact (e.g. a modest 1 to 2% GEM

106 uptake could easily overwhelm detection of typical ambient GOM concentrations). It is therefore

107 important that a GEM artifact be ruled out if the CEM material is to be successfully deployed for

108 ambient RM measurements.

109 Additionally, previous studies observed significant amounts of "breakthrough" GOM on the

110 secondary filter. The amount of breakthrough is not consistent, neither as a constant mass, with

111 total Hg ranging from zero to as high as 400 pg (Huang et al., 2017), nor as a percentage of Hg

112 collected on the primary filter, ranging from 0 to 40% (Pierce and Gustin, 2017). Similar variable

113 breakthrough issues were observed in the earliest field-based CEM measurements as well

114 (Mason et al., 1997). In contrast to ambient measurements, previous laboratory experiments have

115 reported only minor (0 to 16%) or no breakthrough Huang and Gustin, 2015a; Huang et al.,

116 2013). Limited experimental work with flow rates of 1.0 and 16.7 Lpm in ambient air could not

117 provide an explanation for differing breakthrough rates (Pierce and Gustin, 2017).

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, $HgBr_2$) was explored, and the collection efficiency for this compound was estimated. Wwe attempted to explain or rule out possible mechanisms of RM breakthrough for both dry and humid conditions.

2 Methods

2.1 System for sampling configuration

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. 12). 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).

139 Sample flow through the system was alternated between two PTFE sample lines (designated

140 Line 0 and Line 1) using a Tekran® Automated Dual Switching (TADS) unit. Sample air was

141 constantly pulled through each line at 1.0 Lpm by the internal pump and mass flow controller

142 (MFC) in the 2537A, or by an external flush pump (KNF Laboport® N86 KNP) and MFC (Sierra

143 Smart-Trak® 2). Laboratory air was pulled through a single inlet at the combined rate of 2.0

144 Lpm, passing through a 0.2 μm PTFE particulate filter and an activated charcoal scrubber

145 (granular activated carbon 6-12 mesh, FisherChemical®) to produce clean sample air.

146 Additionally, for dry air permeations sample air was pulled through a Tekran® 1102 Air Dryer

147 installed upstream of the particulate filter, and for elevated humidity permeations sample air was

148 pulled through the headspace of a distilled water bath (DIW, < 0.2 ng L^{-1} total Hg) that was

149 located upstream from the charcoal scrubber to eliminate the DIW being a potential Hg source to

150 the system. Temperature and relative humidity (RH) were measured in-line (Campbell Scientific

151 CS215) and used for calculation of absolute humidity.

152 Pure liquid Hg^0 and crystalline HgBr$_2$ (purity $> 99.998\%$ Sigma-Aldrich®) were used as Hg

153 vapor sources. The elemental Hg^0 bead was contained in a PTFE vial. Solid HgBr$_2$ crystals were

154 packed in thin-walled PTFE heat-shrink tubing (O.D. 0.635 cm) with solid Teflon plugs in both

155 ends to create a permeation tube with an active permeation length of 2 mm (Huang et al., 2013).

156 The HgBr$_2$ permeation tube was also placed in the bottom of a PTFE vial, and the permeation

157 vials were submerged in a temperature-controlled laboratory chiller (0.06 ± 0.13 °C, Cole Parmer

158 Polystat®). A low source temperature was favored, because higher temperatures would have

159 produced unacceptably high concentrations, and there is evidence that at higher temperatures a

160 small amount of Hg^0 can be evolved from Hg^{2+} compounds (Xiao et al., 1997).

161 An ultra-high purity nitrogen (N_2) carrier gas was passed through the permeation vials at 0.2

162 Lpm to carry the target Hg vapor into the main sample line through a PTFE T-junction. The main

163 sample line was split into Line 0 and Line 1 immediately downstream from the permeation flow

164 junction, with flow on each line controlled by MFC. Line 0 proceeded directly to the 2537A

165 without modification during GEM permeations (Fig. 1A), but housed CEM filters during the

166 HgBr$_2$ permeations (Fig. 1B, 1C). Line 1 contained an in-line pyrolyzer unit. The goal of the

167 pyrolyzer was to convert all Hg to GEM for detection on the Tekran® 2537A.

2.2 Pyrolyzer

169 The pyrolyzer used in the study (SI Fig. 3) consisted of a 25.4 cm long quartz glass tube of 0.625

170 cm diameter (custom, URG Corporation). A loosely packed 3 cm section of quartz wool was

171 lodged in the mid-section of the tube, and this 3 cm section was wrapped with 22 gauge

172 Nichrome wire (18 loops). The quartz tube was closely contained within 2.5 cm thick quartz

173 fiber insulation within a 1.6 mm aluminum casing, except for an enclosed air space around the

174 heated Nichrome coil section. The coil wire was connected to 16 AWG stranded copper wire

175 with all metal disconnects that were buried within the quartz fiber insulation to reduce thermal

176 fatigue on the connections. The copper wire insulation was stripped and replaced with higher

177 temperature heat-shrink insulation where the wiring passed through the pyrolyzer case to the

178 external power supply. The tip of a 150 mm long K-type thermocouple (Auber WRNK-191) was

179 inserted through the insulation into the heated air space next to the coil to provide a temperature

180 feedback for a PID controller (Auber SYL-1512A). Power to the Nichrome coil was supplied by

181 a 12 VDC transformer through a solid-state relay (Auber MGR-1D4825) switched by the PID

182 controller. It was found that the position of the feedback thermocouple in the airspace outside of

183 the heating coil caused a large discrepancy between nominal temperature setpoint and actual

184 temperature inside the heated section of pyrolyzer tube. In general, much higher temperatures are

185 achieved inside the coil than outside. To compensate for this, actual temperature at the heated

186 coil section was verified to 600°C by external IR sensor and internal thermocouple probe.

187 To test if higher pyrolyzer temperatures converted more GOM to GEM for detection by the

188 Tekran 2537, the pyrolyzer temperature was increased to 650, 800, and 1,000°C (SI Fig. 4).

189 Pyrolyzer temperatures were measured by placing a thermocouple inside the pyrolyzer. GOM

190 concentrations measured as GEM by the Tekran 2537A increased at 600 and 800°C relative to

191 375°C. There was no significant difference between the amount of mercury concentrations in the

192 downstream Tekran 2537A when the pyrolyzer was at 600 and 800°C C (t-test, $p = 0.08$),

193 indicating that the increased pyrolyzer temperature did not convert more GOM to GEM.

194 However, when the pyrolyzer temperature was increased to 1000 °C, significantly more mercury

195 was measured by the downstream Tekran 2537A relative to when the pyrolyzer was at 650°C (t-

196 test, $p = 0.00$), indicating that the higher temperature was more efficient at converting GOM to

197 GEM; however, the pyrolyzer design could not sustain the 1000 °C temperature and was deemed

198 unsafe to use in the experimental permeation system. Thus, all experiments were performed with

199 a pyrolyzer temperature of 600°C.

200 The residence time in the pyrolyzer tube was approximately 1.5 seconds. Quartz wool was added

201 to increase the amount of surface area available to facilitate reactions and maximize the amount

202 of GOM converted to GEM in the pyrolyzer. Based on supplemental experiments, the

203 downstream Tekran® 2537A Hg measurements when the pyrolyzer was at 650 °C was 75%

204 compared to the measurements when the pyrolyzer was at 1000 °C (SI Fig. 4), indicating a

205 higher GOM to GEM conversion efficiency with higher pyrolyzer temperatures. Though this

206 conversion efficiency value does not describe the exact inefficiency of the experimental system

207 in this study, it provides an estimate for the efficiency of the pyrolyzer design in this study.

208 ~~Because of the conversion rate (discussed below), this is a pretty efficient method for converting~~

209 ~~GOM to GEM.~~ Having an efficient pyrolyzer provides us with a means of constraining

210 permeation tube permeation rates.

2.3 Sample deployment

212 CEM filters were deployed in 2-stage, 47 mm disc PFA filter holders (Savillex©). The primary

213 "A" filter in the 2-stage holder is the first to be exposed to the permeated Hg, with the secondary

214 "B" filter mounted immediately behind the A filter (A to B distance ~ 3mm) to measure potential

215 breakthrough. For GEM permeations, three 2-stage filter holders were placed in-series on Line 1

216 behind the pyrolyzer unit (Fig. 1A), while total Hg coming through the system was measured on

217 Line 0 with no filters in place. This allowed simultaneous exposure of 6 CEM filters in one GEM

218 sample exposure. The first CEM filter in-line served to scrub any small residual RM passing

219 through the system and pyrolyzer, and these first in-line filters were removed for the calculations

220 of mean GEM uptake rate, (SI. 5 and discussion). A controlled experiment was also performed to

221 ensure that both Lines 0 and 1 were conducting comparable concentrations of mercury under the

222 experimental conditions. Two-stage filter packs were deployed with CEM filters in each line at

223 equal distances from the permeation tube. The membranes were deployed for the same amount

224 of time in triplicate and analyzed to quantify the amount of total mercury sorbed to the

225 membranes. The average % deviation between lines was 2.9%, with a maximum deviation of

226 5.4%. These results indicated that though there may be some difference in the amount of

227 mercury passing through Lines 0 and 1, the difference was relatively small.

228 For determining the potential for GOM breakthrough, two system configurations were used. In

229 the first configuration (Fig. 1B), the total Hg concentration of air that passed through the

230 pyrolyzer on Line 1 was measured without any filters, while Line 0 held one 2-stage CEM filter

231 pair for $HgBr_2$ loading. This configuration allowed for 10 min interval quantification of the

232 $HgBr_2$ permeation concentration through Line 1 using the 2537A, and comparison with total Hg

233 loading on the CEM filters on Line 0.

234 In the second configuration, replicate filters were concurrently loaded with $HgBr_2$ by placing 2-

235 stage CEM filter holders on both Line 0 and Line 1 (upstream of the pyrolyzer, Fig. 1C). In all

236 $HgBr_2$ exposures, the filter holders were placed as close to the permeation vial as possible, with a

237 total distance from vial to filter surface of approximately 20 cm. Mercury bromide permeation

238 was conducted in dry air and elevated humidity air. The difference between one line being fully

239 open to the $HgBr_2$ permeation flow (configuration Fig. 1B) and then closed by deployment of the

240 CEM filters (configuration Fig. 1C) enabled a rough determination of the amount of $HgBr_2$ line-

241 loss within the system.

2.4 Analyses of cation exchange membranes

243 After permeation, CEM filters were collected into clean, sterile polypropylene vials and analyzed

244 for total Hg by digestion in an oxidizing acid solution, reduction to Hg^0, gold amalgamation, and

245 final quantification by cold vapor atomic fluorescence spectrometry (CVAFS, EPA Method

246 1631, Rev. E) using a Tekran® 2600 system. The system background Hg signal was determined

247 for every analytical run by analyzing pure reagent solution in the same vials and at the same

248 volume as used for actual filter samples. Total Hg standards (5 to 100 ppb) were analyzed before

249 and after each batch of 10 filter samples to check precision and recovery, and the mean recovery

250 for all Hg standards was 97.2 ± 5.0 % (n = 37). Analysis for total Hg on the CEM filters

251 provided for comparison of total Hg filter loading, and verification of in-line results. A to B filter

252 breakthrough was calculated by comparison of total Hg recoveries on the primary and secondary

253 CEM filters, using Eq. (1):

254 $$\% \ Breakthrough = 100 * CEM_{2nd}/(CEM_{1st} + CEM_{2nd}) \ (1)$$

255 Blank CEM filters were collected and analyzed in the same manner with every set of sample

256 filters deployed on the permeation system, and the overall mean filter blank value was subtracted

257 from all total Hg values to calculate the final blank-corrected Hg values used for data analysis.

258 All data were analyzed in Microsoft® Excel (version 16.12) and RStudio® (version 3.2.2).

259

260 3　Results

261 3.1 Elemental Mercury Uptake on CEM Filters

262 Elemental Hg uptake on CEM material was negligible for permeated Hg^0 vapor concentrations

263 ranging from 1.43×10^6 to 1.85×10^6 pg m^{-3} (Fig. 2). High GEM concentrations were employed in

264 this study under the logic that if no GEM uptake was observed at high concentrations, a similar

265 lack of GEM uptake can be expected for lower concentrations.

266 The mean Hg mass on blank CEM filters was 50 ± 20 pg (n = 28). For permeations into dry

267 sample air of 0.5 ± 0.1 g m^{-3} water vapor (WV), total mean Hg^0 permeation exposures of 2.7×10^6

268 pg (24 h) and 7.3×10^6 pg (72 h) resulted in total (blank-corrected) Hg recoveries on the CEM

269 filters of 100 ± 40 pg (n = 10) and 280 ± 110 pg (n = 5), respectively. These quantities of total

270 recovered Hg equate to a mean GEM uptake rate on the CEM filters of $0.004 \pm 0.002\%$ ($0.006 \pm$

271 0.006% including first in-line filter). For GEM permeations into ambient humidity sample air (2

272 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

273   (blank-corrected) Hg recoveries on the CEM filters were 55 ± 30 pg (n =10), equating to a GEM

274   uptake rate of 0.003 ± 0.001% (0.005 ± 0.005% including first in-line filter).

275   The first CEM filter in-~line during the GEM permeations always showed more total Hg than the

276   following 5 downstream filters, which that were not significantly different from each other (SI

277   Fig. 5). It is unlikely that the Hg observed on the first CEM filters resulted from GEM uptake.

278   Even at the highest GEM permeation rate, the first filter captured only ~1700 pg of Hg, out of a

279   total permeated amount of over 7.3 *million* pg (a 0.02 % uptake rate). This means that the

280   downstream CEM filters were still exposed to about 7.2985 *million* pg of GEM but captured less

281   total Hg. As we cannot entirely rule out the possibility of some small rate of *in-situ* oxidation of

282   GEM in the system, at the surface of the Hg^0 bead or in the vapor phase, the first in-line filters

283   were not included in the calculation of GEM uptake rates because of suspicion that some

284   component of the Hg captured on the first filter was GOM. Inclusion or removal of the first in-

285   line filters did not significantly alter calculations.

286   The overall GEM uptake rate was linear (r^2 = 0.9769, p = 0.0004; SI Fig. 5) for the range of

287   concentrations used in this study, indicating a similar low uptake rate can be expected down to

288   lower GEM concentrations. GEM uptake by first in-line filters was also linear (r^2 = 0.92, p =

289   0.00), though these results are based on 5 data points. Exponential models poorly fit the

290   experimental data for both the overall GEM uptake and uptake by first in-line filters (SI Fig. 5).

291   **3.2 Mercury Bromide Uptake on CEM Filters**

292   Breakthrough of $HgBr_2$ vapor from the primary (A) to secondary (B) CEM filters was low for all

293   conditions tested in this study (Table 1). These conditions included $HgBr_2$ permeated into clean

294   dry laboratory air with < 0.5 g m^{-3} WV, clean air at ambient room humidity (4 to 5 g m^{-3} WV),

295 and clean air at elevated humidity (10 to 11 g m^{-3} WV), at line temperatures between 17 to 19

296 °C. Overall, the mean A to B filter breakthrough ranged from 0 to 0.5%, and averaged 0.2 ± 0.2

297 % (n = 17), with no statistical difference observed in mean breakthrough rates for the three levels

298 of humidity (ANOVA, p = 0.124).

299 The first HgBr$_2$ permeation in clean dry (< 0.5 g m^{-3} WV) laboratory air was over a 96 h period,

300 using the system configuration in Fig. 1B to establish an approximate permeation rate (Fig. 3).

301 Total Hg reaching the 2537A through the pyrolyzer on Line 1 (red line, Fig. 3) indicated an

302 average HgBr$_2$ exposure concentration of 4540 pg m^{-3}, or about 4.5 pg min^{-1} from the permeation

303 tube. This permeated concentration of HgBr$_2$ was deliberately much higher than ambient in order

304 to test retention and break through at high levels. It should be noted that these concentrations are

305 50 – 1000 times above background ambient concentrations and the performance of the CEM

306 filters at low concentrations could be slightly different. After this permeation, total blank-

307 corrected HgBr$_2$ loading on the primary CEM filter on Line 0 was 49400 pg, but only 50 pg on

308 the secondary CEM filter, indicating a breakthrough rate of approximately 0.1%. Total Hg

309 reaching the 2537A through the CEM filters on Line 0 (black line, Fig. 3) over this time period

310 was 15 pg, mostly at the beginning of the deployment when some ambient Hg entered the

311 opened system. The low concentrations of Hg measured downstream in Line 0 on the 2537A

312 corroborates that breakthrough of HgBr$_2$ was low. These data also demonstrate that the CEM

313 material did not saturate with a HgBr$_2$ loading of ~ 50000 pg, a loading far higher than could be

314 expected in ambient conditions.

315 Subsequent replicate 24 h HgBr$_2$ permeations in clean dry air resulted in consistent total Hg

316 loading on CEM filters placed on both lines concurrently (8560 ± 320 pg, n = 6, Samples 2-7

317 Table 1), and mean total Hg on the secondary CEM filters was 20 ± 10 pg (average

318   breakthrough of 0.3%). On Line 0 (black line, Fig.3), which was never open to $HgBr_2$ vapor

319   downstream from the CEM filters at any point in the study, Hg measured at the 2537A was zero

320   for all three 24 h permeations, indicating no breakthrough (Samples 2, 4, & 6, Table 1).

321   However, on Line 1, ~~which~~ that had been exposed to the full $HgBr_2$ vapor concentration of 4540

322   pg m^{-3} over the duration of the 96 h permeation test, 1155 pg of Hg were measured downstream

323   in the first 24 h sample (Sample 3, Table 1). The amount of downstream Hg dropped to 10 pg in

324   the second 24 h, and 6 pg in the third 24 h (Samples 5 & 7, Table 1). This downstream Hg in

325   Line 1 (compared to the zero Hg simultaneously observed on Line 0) is attributed to

326   volatilization of $HgBr_2$ that had adsorbed to the line material during the open permeation flow.

327   At the moment CEM filters were deployed on Line 1 (red-to-blue transition, Fig. 3), a rapid

328   asymptotic decline in the Hg signal began. This decay curve supports drawdown and depletion of

329   a Hg reservoir on the interior line surfaces behind the CEM filters, and not a continuous source

330   such as breakthrough from the permeation tube that was still supplying $HgBr_2$ to both sample

331   lines. The total mass of Hg volatized from the interior line surfaces (1155 pg) represents 4 to 5%

332   of the total $HgBr_2$ that had passed through Line 1 (~25000 pg based on 2537A measurement).

333   Eventually, Hg reaching the 2537A through Line 1 decreased to zero during the same 24 h filter

334   deployment, indicating the majority of $HgBr_2$ line contamination in a high-concentration

335   permeation system can be expected to flush out within ~12 h. However, we caution that

336   materials used in high-concentration permeation systems, despite being flushed out, should not

337   be used for background ambient air work without at least a very thorough acid cleaning.

338   Additional $HgBr_2$ permeations were made at two levels of in-line humidity. At ambient room

339   humidity (4 to 5 g m^{-3} WV), mean total Hg measured on the CEM filters was 7910 ± 520 pg (n =

340   4; Samples H2-5, Table 1), with an average breakthrough to the secondary filters of 0.3%. When

341 normalized for sample volume, the mean $HgBr_2$ loading on CEM filters during ambient humidity

342 (5968 ± 125 pg) and dry air (5995 ± 188 pg) permeations was not statistically significantly

343 different (t-test $p = 0.790$). $HgBr_2$ breakthrough rates were also the same (0.3%) as during the

344 dry air permeations, indicating that the permeation system was operating similarly at the two

345 humidity levels, and suggesting that absolute humidity concentrations of 4 to 5 g m^{-3} WV had

346 insignificant effects on collection of $HgBr_2$ in clean laboratory air by the CEM material.

347 An increase in humidity resulted in an initial large increase in Hg measured at the 2537A

348 downstream of the CEM filters on Line 0 (Sample H1, Table 1), concurrently with an open

349 $HgBr_2$ permeation flow through Line 1 while both lines were subjected to increased RH. This

350 downstream Hg on Line 0 dropped substantially to zero in ~10 h in the first 24 h deployment

351 (Sample H2, Table 1), and was zero for the duration of the second 24 h deployment (Sample H4,

352 Table 1). Hg rapidly declined to zero, due to off-gassing from the tubing induced by the

353 increased humidity, which facilitated a heterogeneous surface reduction of $HgBr_2$ to GEM in the

354 short section of line between the permeation source and CEM filters. This phenomenon was also

355 observed during the Reno Atmospheric Mercury Intercomparison eXperiment (RAMIX; Gustin

356 et al., 2013). Reduced $HgBr_2$ then then passed through to the 2537A as GEM. As the

357 breakthrough rate and the mean $HgBr_2$ loading on the CEM filters did not change between the

358 dry air and ambient humidity permeations, the downstream Hg observed at the 2537A during the

359 ambient humidity permeations cannot be attributed to a loss of Hg from the CEM filters and is

360 more likely due to a process in the sample lines.

361 As a further test of possible humidity effects, two replicate 24 h CEM filter deployments were

362 conducted in elevated humidity conditions (10 to 11 g m^{-3} WV) created by an in-line water bath.

363 Mean total Hg loading on the primary CEM filters was higher compared to the previous

364 permeations (11700 ± 720 pg, n = 4, Samples H9-12, Table 1), indicating an increase in the

365 effective $HgBr_2$ permeation rate, possibly due to the perturbation caused by a poor filter seal and

366 small leak in the preceding deployment (Sample H7-8, Table 1). However, mean total Hg on the

367 secondary CEM filters was 20 ± 20 pg, indicating an average breakthrough of 0.1%, less than the

368 breakthrough observed for the lower humidity permeations.

369

370 **4   Conclusions**

371 GEM uptake on the CEM material was negligible under the laboratory conditions and high GEM

372 loading rates (3 orders of magnitude above ambient) tested in this study, with an overall linear

373 uptake rate of 0.004% (SI Fig. 5). This uptake rate would be insignificant at typical ambient

374 atmospheric Hg concentrations (1 to 2 ng m^{-3}). As a hypothetical example, a CEM filter

375 sampling ambient air at an average GEM concentration of 2 ng m^{-3} for a typical 2-week sample

376 period would have a total Hg^0 exposure of ~40000 pg. At the calculated uptake rate of 0.004%, a

377 maximum 1.6 pg of Hg observed on the sample filter could be attributed to GEM artifact. ~~Given~~

378 ~~that blank filters have a mean total Hg mass of 50 ± 20 pg, this amount would be below the~~

379 ~~detection limit~~Although further work is required to more definitively determine detection and

380 quantification limits of the various CEM methodologies, based on the mean total Hg mass of 50

381 ± 20 pg observed in this study, the artifact of GEM uptake ~~to~~by the CEMs would be below the

382 detection limit observed here. This corroborates the lack of GEM uptake seen by Lyman et al.

383 (2016) for manual Hg^0 injections on CEM filters at lower total mass loadings of 300 to 6000 pg.

384 Mean $HgBr_2$ breakthrough from primary to secondary CEM filters averaged 0.2 ± 0.2% over all

385 test conditions. A to B filter breakthrough was derived from a comparison between the large

386 amount of HgBr$_2$ permeated onto the primary CEM filters, to the small amount of HgBr$_2$ that

387 collected on the secondary CEM filters, 3 mm immediately downstream. The measurement of

388 1000s of pg of Hg on the primary filter, and only 10s of pg on the secondary filter, leads to the

389 conclusion that the primary filter removed the majority of HgBr$_2$ from the sample air stream

390 under laboratory conditions applied in this study. In addition, low breakthrough was corroborated

391 by downstream measurement of the air stream passing through the CEM filters, using the

392 Tekran® 2537A. The average breakthrough to the 2537A was 0 pg for 24 h permeations in dry

393 air, and 0 to 40 pg in humid air, for filter deployments at steady-state (> 24 h without large

394 perturbations).

395 While the permeation system was not specifically optimized for a quantitative mass balance

396 between permeated HgBr$_2$ and HgBr$_2$ recovered on the CEM filters, a rough estimation of the

397 CEM collection efficiency is possible. Using the HgBr$_2$ permeations conducted in clean dry air

398 (mean loading 8560 pg), and comparing this to the mean Hg concentration measured at the

399 2537A analyzer during the last 24 h of the 96 h permeation measurement (4680 pg m^{-3} or 6739

400 pg per 24 h), HgBr$_2$ recovery on the CEM filters averaged 127%. Adjusting the expected

401 permeated HgBr$_2$ mass for our estimated line-loss (~4-5%) changed the recoveries to ~123%.

402 Still, HgBr$_2$ loading on the CEM filters was ~23% higher than expected based on the pyrolyzed

403 total measurement on the 2537A, indicating not all HgBr$_2$ was converted to GEM. This can be

404 explained by the pyrolyzer design used in this study not being 100% efficient at thermally

405 reducing HgBr$_2$ to Hg^0, based on the higher total Hg recoveries on the CEM filters versus total

406 Hg measured through the pyrolyzer on the Tekran 2537.

407 The technique of gold amalgamation in general, and specifically including the Tekran® 2537A

408 analyzer, is widely considered to provide a quantitative total gaseous Hg measurement, at or very

409　near 100% collection efficiency for Hg^0 and Hg compounds (Temme et al., 2003; Landis et al.,

410　2002; Schroeder et al, 1995; Dumarey et al., 1985; Schroeder and Jackson, 1985). However, to

411　our knowledge collection and desorption efficiencies on gold traps have not been demonstrated

412　for $HgBr_2$. The stated desorption temperature of the Tekran® 2537A gold traps is 500 °C, but

413　temperatures as low as 375 °C have been reported (Gustin et al., 2013). This would cause

414　reduced thermal decomposition efficiency for all captured GOM compounds, including $HgBr_2$.

415　We speculate that a combination of incomplete thermal decomposition to Hg^0 at both the 600 °C

416　pyrolyzer and during the best-case 500 °C desorption of the 2537A gold traps contributed to the

417　~20% non-detection of total permeated $HgBr_2$ as it passed through the CVAFS optical path.

418　Evidence for this conclusion can be seen in the 134% increase in Hg collection by the Tekran®

419　2537A when the pyrolyzer was at 1000 °C, as compared to at 650 °C (SI Fig. 4), in

420　supplementary experiments.

421　While our results validated some basic performance metrics for the CEM material, they did not

422　provide data that could fully explain the higher levels of breakthrough observed for CEM filters

423　deployed in ambient air over the 1-to-2 week sample periods in previous studies. Increasing

424　humidity by itself did not affect observed $HgBr_2$ breakthrough. A $HgBr_2$ loading of ~50000 pg

425　also did not lead to increased breakthrough, indicating there is no saturation effect on CEM filter

426　capacity at a GOM loading far greater than expected from ambient concentrations. It remains

427　unclear, though, whether breakthrough results from different collection efficiencies for GOM

428　compounds other than $HgBr_2$, or whether breakthrough results from a degradation of GOM

429　retention capacity in the CEM material when exposed to ambient air chemistries not simulated in

430　this study. Also, our experiments were conducted in particulate-free air, which leaves open the

431　possibility that breakthrough is related to capture (or lack thereof) of PBM by the CEM material.

432 Further testing and refinements are necessary, beginning with optimization of the pyrolyzer

433 parameters (e.g., temperature, volume) to allow for a more accurate quantitative comparisons

434 between the CEM and Tekran® 2537A results. Permeation rates of $HgBr_2$ were variable and need

435 to be more precisely controlled, a standardized and stable GOM permeation system being needed

436 in general. This study was undertaken using controlled laboratory conditions, but CEM

437 performance needs to be further validated in ambient air. Specifically, the reasons for RM

438 breaking through CEM filters deployed in ambient air still need to be determined.

446

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.

485 Jaffe, D. A., Lyman, S., Amos, H. M., Gustin, M. S., Huang, J., Selin, N. E., Levin, L., ter
486 Schure, A., Mason, R. P., Talbot, R., Rutter, A., Finley, B., Jaeglé, L., Shah, V., McClure, C.,
487 Ambrose, J., Gratz, L., Lindberg, S., Weiss-Penzias, P., Sheu, G.-R., Feddersen, D., Horvat, M.,
488 Dastoor, A., Hynes, A. J., Mao, H., Sonke, J. E., Slemr, F., Fisher, J. A., Ebinghaus, R., Zhang,
489 Y., and Edwards, G.: Progress on Understanding Atmospheric Mercury Hampered by Uncertain
490 Measurements, Environmental Science & Technology, 48, 7204-7206, 10.1021/es5026432,
491 2014.

492 Landis, M. S., Stevens, R. K., Schaedlich, F., and Prestbo, E. M.: Development and
493 characterization of an annular denuder methodology for the measurement of divalent inorganic
494 reactive gaseous mercury in ambient air, Environmental Science & Technology, 36, 3000-3009,
495 10.1021/es015887t, 2002.

496 Lyman, S., Jones, C., O'Neil, T., Allen, T., Miller, M., Gustin, M. S., Pierce, A. M., Luke, W.,
497 Ren, X., and Kelley, P.: Automated Calibration of Atmospheric Oxidized Mercury
498 Measurements, Environmental Science & Technology, 50, 12921-12927,
499 10.1021/acs.est.6b04211, 2016.

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

503 Lyman, S. N., Jaffe, D. A., and Gustin, M. S.: Release of mercury halides from KCl denuders in
504 the presence of ozone, Atmospheric Chemistry and Physics, 10, 8197-8204, 10.5194/acp-10-
505 8197-2010, 2010.

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

509 Mason, R., Lawson, N., and Sullivan, K.: The concentration, speciation and sources of mercury
510 in Chesapeake Bay precipitation, Atmospheric Environment, 31, 3541-3550, 10.1016/S1352-
511 2310(97)00206-9, 1997.

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

515 Pierce, A. M., and Gustin, M. S.: Development of a Particulate Mass Measurement System for
516 Quantification of Ambient Reactive Mercury, Environmental Science & Technology, 51, 436-
517 445, 10.1021/acs.est.6b04707, 2017.

518 Schroeder, W., and Jackson, R.: An instrumental analytical technique for speciation of
519 atmospheric mercury, International Journal of Environmental Analytical Chemistry, 22, 1-18,
520 10.1080/03067318508076405, 1985.

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

524 Sheu, G. R., and Mason, R. P.: An examination of methods for the measurements of reactive
525 gaseous mercury in the atmosphere, Environmental Science & Technology, 35, 1209-1216,
526 10.1021/es001183s, 2001.

527 Slemr, F., Angot, H., Dommergue, A., Magand, O., Barret, M., Weigelt, A., Ebinghaus, R.,
528 Brunke, E., A Pfaffhuber, K., Edwards, G., Howard, D., Powell, J., Keywood, M., and Wang, F.:
529 Comparison of mercury concentrations measured at several sites in the Southern Hemisphere,
530 3125-3133 pp., 2015.

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

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

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

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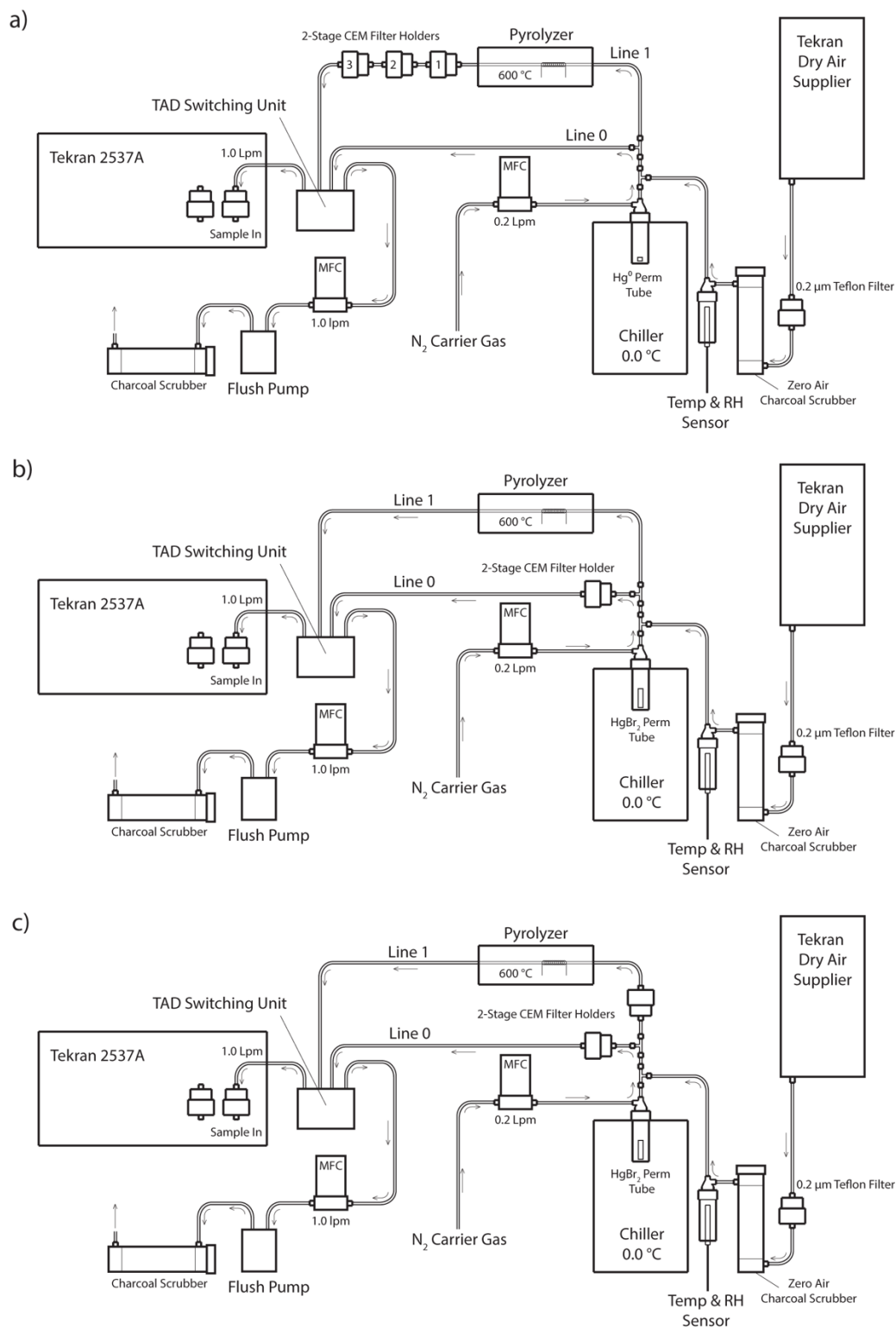
Figure 1. Schematic of the Hg vapor permeation system configurations for: a) GEM permeations b) $HgBr_2$ permeations c) Simultaneous $HgBr_2$ loading on two sample lines. Note dry air supplier disconnected for ambient and elevated humidity $HgBr_2$ permeations, with sample path starting at 0.2 μm Teflon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

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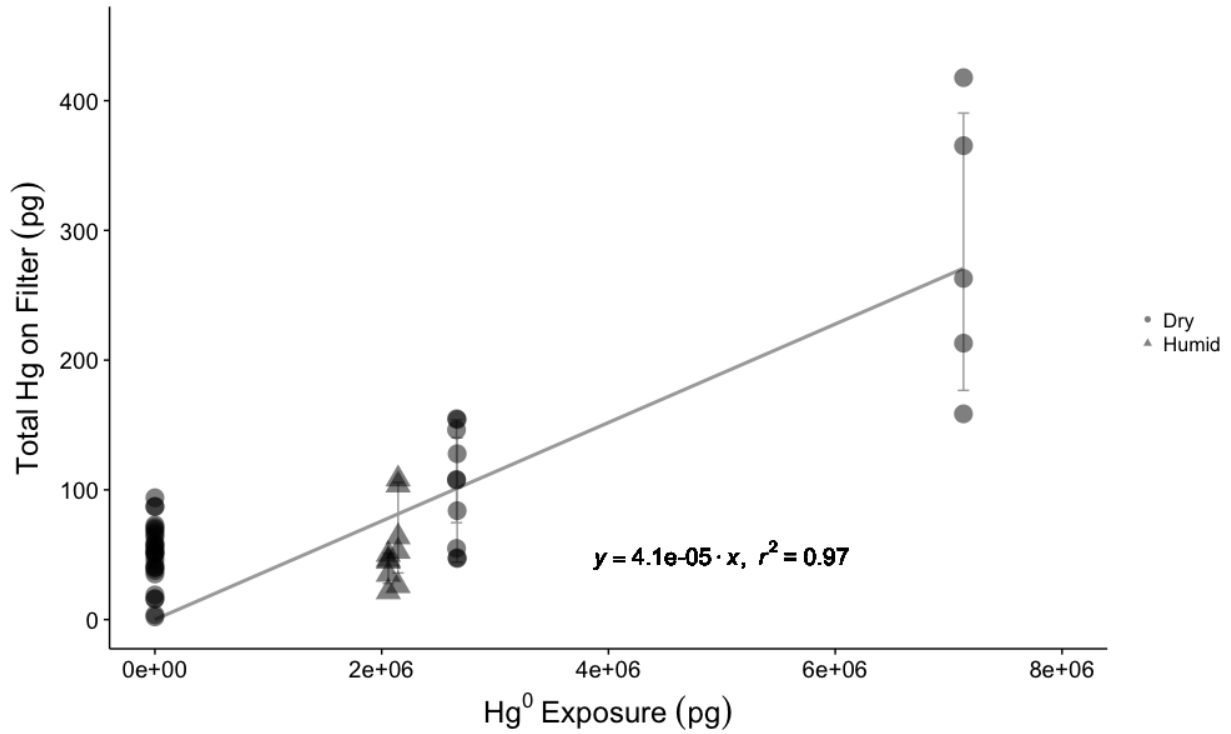
Figure 2. Total Hg recovered on CEM material for blank filters (Hg exposure = 0 pg) and different Hg^0 vapor
permeations in dry (0.5 ± 0.1 g m^{-3} WV) and humid air (2-4 g m^{-3} WV). Circles represent dry air permeations,
triangles represent humid air exposures, and all permeation exposures were blank-corrected.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

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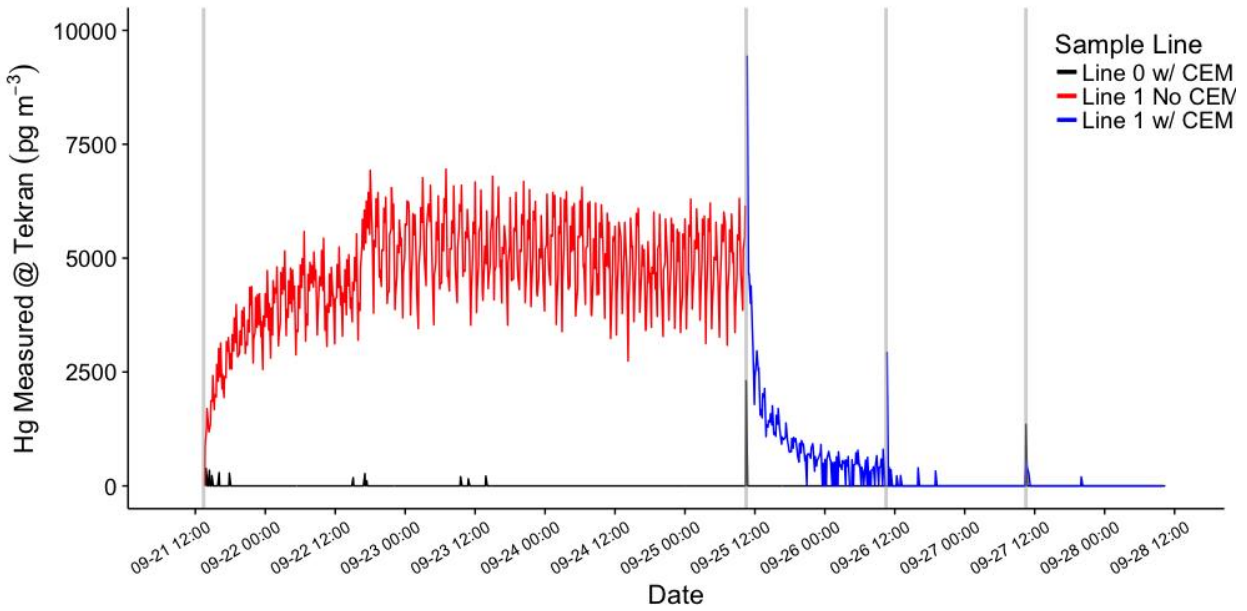
554
555 **Figure 3**. HgBr$_2$ permeations in clean dry lab air using the configuration in Figure 1B (red line) and Figure 1C (blue
556 line). The red line indicates total Hg released from permeation tube and passing through pyrolyzer on Line 1 before
557 being measured by Tekran 2537A, black line indicates Hg reaching 2537A through CEM filters on Line 0. Vertical
558 grey lines indicate open system during filter deployments.

559

Table 1.

Sample	Start	End	Sample Time (min)	Sample Flow (lpm)	Sample Volume (m³)	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		

560

561 **Table 1**. Summary of CEM filter loading and breakthrough during HgBr$_2$ permeations. Samples denoted P indicate
562 approximate permeation rate check through Line 1 via pyrolyzer and Tekran 2537A, italicized text indicates filter
563 deployments on Line 1, and * indicates high values due to leak around first filter seal.