

1 **Point-by-Point Response to Referees**

2

3 **Authors Response to Anonymous Referee #1**

4 The authors thank Referee #1 for their positive assessment.

5

6 **Response to Minor Comments:**

7

8 *L40 Please provide references for the 'demonstrated interferences and artifacts' of current GOM and
9 PBM monitoring techniques.*

10

11 References are included for this statement.

12

13 *L181. ". . .by digestion in an oxidizing solution. . .(EPA)". I know that readers can look up the EPA
14 method, but it could be informative to add a few details on the digestion method, for ex. (IN HCl, 12h,
15 80oC).*

16

17 The methodology has been elaborated on and includes method calibration data as well.

18

19 **Authors Response to Anonymous Referee #2**

20 The authors thank Referee #2 for their incisive commentary.

21

22 **Response to Major Issues:**

23

24 1. *No standard reference material used to confirm recovery of the acid digestion C1 method. I have
25 a major concern about the lack of inclusion of reference materials for quality assurance and
26 control purposes. Especially given the elevated recoveries of RM above what measured by the
27 Tekran/pyrolyzer. Without any such assessment how can we rule out contamination from
28 instruments, handling equipment or even uptake of outside Hg into the acid digestates? Blank
29 filters could have easily been spiked with a sediment or soil SRM and analysed to confirm the
30 recovery of the analytical method. Also, in response to this comment, it is not acceptable simply*

31 quote another paper that has done this. It needs to be confirmed in the lab and experimental
32 settings used in these experiments.

33
34 Mercury standards were in fact analyzed repeatedly during every CEM filter analysis.
35

36 In the described method, standard additions of known mercury concentration are analyzed after
37 every batch of 10-12 samples, in what are known as Ongoing Precision and Recovery (OPR)
38 samples. This includes a mercury standard analyzed immediately following generation of the
39 calibration curve, and at least one standard analyzed at the end of the entire analysis. Acceptable
40 recovery for these OPR standards is $\pm 10\%$.
41

42 The mercury standards are prepared at the same time and with the same batch of reagents as used
43 for the sample filter digestion and analysis (i.e. ultrapure water, bromine monochloride, stannous
44 chloride, etc.). The calibration blanks and filter blanks rule out contamination of any of the
45 analytical equipment. No analysis proceeds where contamination is detected or suspected.
46

47 Prior publications and the Standard EPA Method 1631 is here referenced because it describes in
48 detail the way that acid digestions for total mercury are typically accomplished, and which are
49 followed in this manuscript.
50

51 This concern has been addressed in the text by including a more thorough description of the
52 analytical procedure and providing the specific OPR data for the analyses performed during this
53 study.
54

- 55 2. *Concerns with the pyrolyzer conditions used in analysis. There is no comment on the*
56 *performance of the pyrolyzer not being 100% efficient in reducing HgBr₂ to Hg₀ in the methods*
57 *section (only in the SI where the majority of readers will not see such a concern); a major issue*
58 *when discussing Hg recovery discrepancies on the filters and the Tekran analyser. If the*
59 *pyrolyzer is not performing at 100% how can we be certain the system is collecting all the*
60 *mercury? They go on to suggest higher pyrolyzer temperatures above 600 C would improve its*
61 *performance. Indeed Lynam and Keeler (2002) suggest that pyrolyzer temperatures up to 900 C*
62 *may be necessary. So why did the authors not repeat the experiments with higher pyrolyzer*
63 *temperatures as they suggest? The fact that they did not implies incompleteness of the*
64 *experiment. Results would be greatly improved with a more efficient pyrolyzer, and the exact*
65 *nature of CEM recoveries vs Tekran/pyrolyzer recoveries may have been revealed.*
66

67 Pyrolyzer efficiency is discussed in the conclusions, not just in the SI.
68

69 Referee #2 highlights Lynam and Keeler (2002), who suggest that 800 C pyrolysis was perhaps
70 insufficient for determining total mercury from particulate mercury filters, based on lower total
71 Hg recoveries from thermal desorption and pyrolysis versus an acid digestion method. However,
72 the Lynam and Keeler study deals primarily with particulate mercury, for which pyrolysis
73 temperatures are necessarily higher in order to insure decomposition of the larger masses
74 involved compared to pure gas-phase samples. Secondly, Lynam and Keeler (2002) also suggest
75 that sample matrix interferents may have played a more important role in lower total Hg

76 recoveries during thermal desorption and pyrolysis, via passivation of the analytical gold traps or
77 interference with detection.

79 Additionally, for determination of RGM Lynam and Keeler (2002) use only a Tekran 1130
80 denuder module without an attached 1135. Consequently, RGM was determined exclusively from
81 the standard 500 C denuder desorption temperature, with no further 800 C pyrolysis in the 1135
82 module. Lynam and Keeler are not alone in this practice, as many studies since have reported
83 RGM/GOM values using only the Tekran 1130 denuder module without the benefit of further
84 pyrolysis in the 1135 module (e.g. Temme et al., 2003; Weiss-Penzias et al., 2003; Soerensen et
85 al., 2010; Wright et al., 2014; Huang and Gustin, 2015). The fact that the 1130 denuder module
86 can even be operated without the inclusion of the 1135 and it's pyrolyzer is an implicit
87 declaration by an industry-leading mercury analytics company that 500 C is adequate to desorb
88 and decompose RGM/GOM.

90 Numerous publications have used lab-based pyrolyzer temperatures of 500-650 C when working
91 with GOM compounds (e.g. Swartzendruber et al., 2009; Lyman et al., 2010; Lyman and Jaffe,
92 2011; Huang et al., 2013). The 600 C pyrolyzer temperature used in this study was a compromise
93 based on what could realistically be achieved within the scope of this project and was within a
94 well-established range of pyrolyzer temperatures used in previous work. The fact that the 600 C
95 temperature appears to have been insufficient is an important result in and of itself and supports
96 the need for higher pyrolyzer temperatures in future work.

97 The authors acknowledge the limitations of the pyrolyzer used in this study, point to the fact that
98 these limitations are discussed in the text, and re-iterate that the main conclusions of this
99 manuscript do not hinge on pyrolyzer performance. In fact, the majority of experiments described
100 in this manuscript could have been successfully conducted with no pyrolyzer at all. Specifically,
101 the generation of GEM was not contingent on pyrolyzer performance. Permeated GEM was
102 generated using a new bead of analytically certified pure elemental mercury in a clean nitrogen
103 flow. The pyrolyzer was used only as a backup to attempt to insure that all mercury was indeed
104 GEM before reaching the CEM filters. HgBr₂ loading during the simultaneous CEM filter
105 deployments on Line 1 and Line 0 (per Figure 1C) was performed upstream of the pyrolyzer, and
106 consequently these results are also entirely independent of pyrolyzer performance.

107 We will address concerns about pyrolyzer efficiency in the manuscript by discussing pyrolyzer
108 needs and limitations at great depth.

- 111
- 112 3. Removal of 1st CEM traps from GEM breakthrough experiments. This I totally disagree with. The
113 teflon lines could easily be cleaned by (a) rinsing the lines in an acid solution then DI water and
114 allowing them to dry in zero or very low Hg air and (b) running zero Hg air through the system
115 with CEMs in place before the actual GEM permeation cycles. At this point there should be no
116 RM in the system. Thus for the GEM permeation runs why would you discard the first set of CEM
117 filters without this analysis? There should be no RM in the system and any collected Hg should be
118 assumed to be GEM inadvertently collected. Again the discussion in the SI is HIGHLY relevant
119 and ignored in the main body of the paper. The first set of CEMs were always higher and not
120 arbitrarily so (as the authors seem to suggest), but this is not mentioned in the main paper only

121 the SI. "We believe it is unlikely that the Hg observed on the first CEM filters results from GEM
122 uptake." The Hg uptake on the first set of filters is attributed to residual GOM in the lines, but if
123 lines were properly cleaned before analysis this would not be the case. This is something that
124 could have been ruled out one way or another through subsequent analysis and again no doing
125 so implies the experiments are incomplete. Furthermore if it the 1st CEMs were picking up
126 "residual RM" from the lines then they would not have seen the dramatic increase in the CEM
127 filter concentration under higher GEM concentrations. GOM was not produced under this
128 scenario and therefore the "residual RM" should not increase, but as SI Figure 4 shows it did
129 increase and exponentially, not linearly.
130

131 Teflon lines were of course acid cleaned and rinsed with DI water before GEM permeations
132 began, and zero air was run through the system in between permeations. The amount of Hg seen
133 on the filters was not large, and is not necessarily from residual line contamination. It may
134 represent a small amount of oxidized Hg coming from the Hg^0 bead, in which case we would
135 expect to see an increase with higher permeated GEM concentrations.
136

137 The authors disagree with the contention that the first CEM filter in a series of 6 could somehow
138 be sorbing GEM differently than the following 5 filters exposed to the same carrier flow and
139 GEM concentration. Given the aforementioned uncertainties about absolute pyrolyzer efficiency,
140 it seems much likelier that a small fraction of oxidized mercury, again perhaps from the Hg^0 bead
141 itself, is passing through the system and being scrubbed by the first CEM.
142

143 Even when including the first CEM the observed GEM uptake would still be negligible (0.006%
144 overall, 0.017% first filters only). If necessary, the authors see no difficulty including the first
145 CEM in the analysis of GEM uptake, and this discussion can be moved into the text rather than
146 the SI.
147

- 148 4. Teflon lines were not heated and line lengths not fully described. Higher recoveries on CEMs
149 could be associated with losses in $HgBr_2$ to the longer inlet line on line 1 as it appears in Figure
150 1(b). Description of the length of tubing between the switch valve and the pyrolyzer (line 1) and
151 the switch value and the CEMs on line 0 should be included. Any difference in length in unheated
152 lines may also be causing inconsistent recoveries. Heating the lines (common practice in
153 atmospheric Hg monitoring to include GOM in analysis) would reduce any such losses. This is
154 another simple adjustment that would have produced more complete experimentation.
155

156 For the configuration shown in Figure 1B, the authors acknowledge a difference in unheated
157 Teflon tubing length between the filter pack on Line 0 and the pyrolyzer on Line 1.
158

159 However, the authors maintain that the more important results are obtained from the
160 configuration shown in Figure 1C, in which the length of Teflon tubing from the permeation vial
161 to each of the filter assemblies is exactly the same. In this configuration potential line-loss would
162 be equivalent. Indeed, this is shown by the consistent $HgBr_2$ loading on the CEM filters on Line
163 1 and Line 0.
164

166 5. Sorption of all forms of Hg to CEMs are assumed to be the same at low concentrations as they
167 are in these high concentration experiments. Maybe this is the case, but it could have easily been
168 proven by repeating experiments (for longer time periods) at much lower concentrations and I
169 can't really see why such experiments would not be included once things were already set up.
170

171 The authors agree that more experimentation is both welcome and necessary, and indeed is now
172 ongoing within the scope of an expanded and fully funded NSF research project.

173
174 However, our original and primary concern within the more narrow scope of this manuscript was
175 with GEM uptake and HgBr₂ breakthrough at high loading rates. These questions were of
176 particular importance to a companion manuscript, also currently submitted to AMT.

177 6. High blank levels are a concern for background sampling. While blank levels of 50 ± 20 pg may
178 not seem high given the very high concentrations used in these experiments at background
179 concentrations of RM this could be an issue. Method Detection limits MDL = $3 * SD$ of blanks = 60
180 pg Method Quantification limits MQL = $10 * SD$ of blanks = 100 pg Assume background RM
181 concentration of 10 pg/m³ or 0.01 pg/L Flow rate = 1 L/m This translates to 0.6 pg/hr being
182 sorbed to the CEM, which would require 100 hours of sampling at background levels to exceed
183 just the MDL and about 330 hours to reach MQL. These issues are not currently discussed
184 adequately in the manuscript nor covered by the experimental design of the manuscript.
185

186
187 It is unclear to the authors how this constitutes a 'major issue' with the work presented in this
188 manuscript. The authors acknowledge that long sample periods are currently required when using
189 the CEM filters in ambient air sampling. We did not specifically discuss ambient air sampling
190 time requirements because this is not an ambient air sampling study, and the CEM filters are not
191 used exclusively for ambient sampling. Previous work, which is referenced in this manuscript,
192 clearly indicates that the CEM filters are deployed for 2-week (336 hour) sample periods in
193 ambient air.
194

195
196 The authors would like to point out that filter blanks reported in this study are in fact lower than
197 in previously published studies using the CEM methodology, and so constitute an improvement
198 in methodology that should alleviate concerns about detection limits rather than exacerbate them.

199 **Response to Other General Concerns:**
200

201 1. More caution should be used in the definition of the term reactive mercury (RM).
202 While it no doubt has some use, combining GOM and PBM as RM is diluting specific
203 information by grouping together two already very broad classes of atmospheric Hg
204 species. Our lack of knowledge and understanding of the molecules and complexes
205 that make up the specific forms of GOM and PBM is a major driving force behind
206 differences between global Hg transport and fate models and measured values, our
207 poor understanding of atmospheric Hg cycling and even terrestrial - atmospheric interactions.
208 Using RM to describe both species does little to improve that understanding.
209 Furthermore, while the use of the term does exist in the literature it is not widely applied
210 beyond one or two research groups. The sampling method applied in this manuscript
211 cannot distinguish between GOM and PBM, thus RM must be used here, but a much

212 greater description of this caution must be given in the manuscript.

213
214 This point is well taken, and the authors will elaborate on the limitations of using the term RM.
215 However, the authors also point out that no current measurement technique can always reliably
216 separate and quantify GOM and PBM, and there is uncertainty as to whether even total
217 atmospheric Hg is always accurately measured. We suggest that the ability to accurately quantify
218 total reactive mercury is a necessary first requirement to differentiating between GOM and PBM.
219

- 220 2. *The use of HgBr₂ as a surrogate for all “RM”. As I have just mentioned we do not*
221 *know nearly enough about what the exact species of GOM or PBM (let alone both*
222 *combined as RM) are. Different species of GOM and PBM are likely to behave quite*
223 *differently in the atmosphere and indeed on different sorption media. I have concerns*
224 *that using only HgBr₂ as a surrogate (do we even know if HgBr₂ is a common atmospheric GOM*
225 *constituent? ~~to~~ It has been suggested that Br acts as the primary*
226 *oxidant, but the very reactive HgBr (1+) product has a very short lifetime of less than*
227 *a second before other more stable Hg²⁺ compounds are produced through oxidation*
228 *by other atmospheric species (Horowitz et al. 2017)). The data from this manuscript*
229 *appear to show that CEMs effectively sorb HgBr₂, but how do we know they sorb ALL*
230 *species? Again this emphasizes the concern of using RM - a more generic term - to*
231 *define sorption of both GOM and PBM. We should be focusing on determining what*
232 *specific species and complexes that make up GOM and PBM rather than be even less*
233 *specific and defining everything as RM, based on only injection of HgBr₂. Again better*
234 *acknowledgement of this methodological short-coming is needed to proceed.*

Deleted:

235
236 The authors acknowledge that the use of HgBr₂ as a lone surrogate for GOM is a limitation of
237 this manuscript. However, the results of the permeation tests using HgBr₂ are positive, and
238 therefore justify ongoing and intensive validation using a host of GOM compounds, under a
239 greater range of conditions. Unfortunately, such expanded experimentation was beyond the scope
240 of this study, but is now the objective of an ongoing fully funded project. If the limited
241 permeation tests described in this manuscript had failed to demonstrate adequate performance of
242 the CEM material, the authors would have duly presented such results and discontinued further
243 use. The results presented in this manuscript also invite and encourage replication by other
244 researchers and other labs.
245

- 246 3. *The review of the literature in the manuscript is skewed quite favourably to CEMs*
247 *and quite negatively to existing methods. A more rounded approach would be less*
248 *evident of bias towards the CEMs (see specific comments).*

249 The literature review has been revised to be more even-handed.

250
251 **Response to Specific Comments:**

252 Line 12: “Reactive mercury (RM). . .” should be described here as: “Reactive mercury
253 (RM), the sum of both gaseous oxidised Hg and particulate bound Hg,...”

257
258 *Correction made.*
259
260 Line 29: "...high collection efficiency." Should be changed to: "...high collection efficiency
261 of the target analyte."
262
263 *Correction made.*
264
265 Line 35-36: This is where a cautionary description of the use of the term RM should be
266 included.
267
268 *Cautionary description of RM included in text.*
269
270 Line 41-42: These reviews do provide a good critique of the Tekran based speciation
271 measurement techniques, but they do not tell the whole story and more literature needs
272 to be discussed here. For example, Maruscak et al. 2017, describes how adding the
273 zero flushes from GOM analysis to the actual GOM concentrations increases the derived
274 concentrations to agree more closely with alternative measurement techniques
275 and some modelled values. Such advancements as the latter with the previous system
276 should also be discussed to ensure impartiality. Additionally Cheng and Zhang (2017)
277 state: "Other measurements techniques such as mist chambers, nylon and cation exchange
278 membranes [CEMs], and Detector for oxidized Hg, were capable of collecting
279 more GOM than KCl-denuders. However, similar to the Tekran instrument, these alternative
280 methods are not immune to sampling artefacts caused by high water vapour
281 and other gases and aerosols." A similar degree of impartiality would greatly benefit
282 this review of the literature.
283
284 *Revised text for greater impartiality.*
285
286 Line 78: The analytical information in parenthesis should be deleted. This is describing
287 another paper in too much detail and not needed here.
288
289 *Correction made.*
290
291 Line 88: Again as per the comment on lines 41-42 this is ignoring advancements in
292 other methods and caveats of the CEM methodology.
293
294 *Revised text to indicate that advancements are being made with other methods.*
295
296 Line 93-95: This information is extremely important and I credit the authors for its
297 inclusion.
298
299 *Thank you.*
300

301 Line 111: "...with a view to estimate the collection efficiency and..." this absolutely
302 should state: "...with a view to estimate the collection efficiency OF THIS ANALYTE
303 and..."

304

305 *Correction made in the text.*

306

307 Line 121-122: "Each of these materials is known to be chemically inert, virtually nonporous, and
308 to have a low coefficient of friction." This needs to be referenced.

309

310 *Reference included.*

311

312 Line 134: "...an activate charcoal scrubber..." Please provide details of this scrubber:
313 elemental imregnation (if any) and manufacturer. Different activated charcoal
314 scrubbers perform differently with regards to atmospheric Hg sorption with halogen
315 and sulphur impregnated charcoals performing better for Hg sorption (e.g. Vidic et al.
316 1998).

317

318 *Details of activated charcoal provided in the text.*

319

320 Line 152: Were flows measured downstream of both sampling lines to ensure pressure
321 differences across the CEM filters and the pyrolyzer did not cause flow rate differences
322 into the two lines? Any difference in flow may result in differing recoveries of the two
323 measurements.

324

325 *Both flows were controlled by MFC, as stated in the text.*

326

327 Line 201: These recovery values should be adjusted to include the first CEM filter.

328

329 *The authors do not feel that inclusion of the first filter is warranted, but this can be added if
330 necessary.*

331

332 Line 218: "4540 pg m⁻³" it should be noted here or in the methods that this concentration
333 is around 50-1000x higher than typical GOM concentrations and that behaviour
334 may be slightly different under lower concentrations.

335

336 *Noted in the text.*

337

338 Line 224-226: While this does mean the absolute uptake capacity of the CEMs
339 for HgBr₂ is very high, we must remember that this is likely to be a thermodynamic/equilibrium
340 parameter more than just a kinetic one and the uptake capacity will be higher under elevated
341 conditions than at ambient conditions. This should be noted.

342

343 *Noted in the text.*

344

345 Line 244-246: But again this is contamination for very high concentrations. If just a
346 small amount of this continues to be emitted during ambient sampling then this will
347 represent a very substantial contamination of HgBr₂. A cautionary note should be
348 made about sampling management; systems used for higher concentrations should
349 be only used for higher concentrations and likewise systems for lower concentrations.
350 This will prevent any contamination from systematic memory effects.

351
352 *Upon careful consideration, the authors have not addressed this comment in the text because it is*
353 *not applicable. The system described in the present manuscript is used only for high*
354 *concentration experimental tests and not for ambient sampling. A cautionary note is unneeded.*

355
356 Line 263: What would cause this reaction? Normally reduction in the presence of
357 water is driven by photochemistry. Are these lines exposed to solar radiation? Please
358 reference this suggested mechanism.

359
360 *No solar radiation, but there was fluorescent room lighting during working hours. Anecdotally,*
361 *more Hg observed downstream of the filters on the Tekran 2537 when lights turned on. The text*
362 *has been revised to indicate possible effect of fluorescent room lighting.*

363
364 Line 279: “ . . .(2 orders of magnitude above background). . .” This should be 3 orders of
365 magnitude. Background is ~1.5 ng/m³ the concentration used here is ~1500 ng/m³.

366
367 *Correction made.*

368
369 Line 305-308: So what does the difference in recoveries mean? Conclusions are meant
370 to summarise what was found, but here we are just getting a rehash of the numbers
371 without any explanation. Not sure I see any value in this.

372
373 *Corrected text to include a conclusion about differing recoveries.*

374
375 Line 317-320: Again, the authors state a problem with the pyrolyzer, so why wasn’t it
376 optimised and experiments repeated?

377
378 *Because the main experiments described in this manuscript did not hinge on pyrolyzer*
379 *performance.*

380
381 SI Lines 14-15: What are the reported recoveries of the internal injections compared
382 to the external injections, please provide details (%) and number of checks (n)

383
384 *Details provided.*

385
386 SI Lines 60-62: This is purely speculation based on almost no evidence. Just as likely
387 is it may be coming off the lines or indeed a little GEM is sorbing either to the CEMs or
388 to something else on the CEMs. None of these scenarios can be fully ruled out using

389 the data presented in these experiments. This statement is too speculative and should
390 be removed

391
392 *Statement removed.*

393 **Evaluation of cation exchange membrane performance under exposure to high Hg⁰ and**
394 **HgBr₂ concentrations**

395 Matthieu B. Miller¹, Mae S. Gustin², Sarrah M. Dunham-Cheatham², Grant C. Edwards^{1,3}

396 ¹Faculty of Science and Engineering, Department of Environmental Sciences, Macquarie University, Sydney, NSW,
397 2109, Australia

Deleted: 13

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

400
401 ³ Deceased 11 September 2018

402
403 Correspondence to: Matthieu B. Miller (matthieu.b.miller@gmail.com)

404
405 **Abstract**

406 Reactive mercury (RM), the sum of both gaseous oxidized Hg and particulate bound Hg, is an
407 important component of the global atmospheric mercury cycle, but measurement currently
408 depends on un-calibrated, operationally defined methods with large uncertainty and
409 demonstrated interferences and artifacts. Cation exchange membranes (CEM) provide a
410 promising alternative methodology for quantification of RM, but method validation and
411 improvement are ongoing. For the CEM material to be reliable, uptake of gaseous elemental
412 mercury (GEM) must be negligible for all conditions, and RM compounds must be captured and
413 retained with high efficiency. In this study the performance of CEM material under exposure to

414 high concentrations of GEM (1.43×10^6 to 1.85×10^6 pg m⁻³) and reactive gaseous mercury

Deleted: –

415 bromide (HgBr₂ ~ 5000 pg m⁻³) was explored, using a custom-built mercury vapor permeation
416 system, with quantification of total permeated Hg accomplished via pyrolysis at 600 °C and
417 detection using a Tekran® 2537A. Permeation tests were conducted for 24 to 72 hours in clean
418 laboratory air, with absolute humidity levels ranging from 0.1 to 10 g m⁻³ water vapor. Gaseous

Deleted: –

422 elemental mercury uptake by the CEM material averaged no more than 0.004% of total exposure
423 for all test conditions, which equates to a non-detectable GEM artifact for typical ambient air
424 sample concentrations. Recovery of HgBr₂ on CEM filters was >100 % compared to calculated
425 total permeated HgBr₂, suggesting incomplete thermal decomposition at the pyrolyzer, as the
426 CEM material collected HgBr₂ with less than 1% downstream breakthrough on average,
427 implying a high collection efficiency of the target analyte.
428

429 1 Introduction

430 Mercury (Hg) is a persistent environmental contaminant with a significant atmospheric life time,
431 and the form and chemistry of Hg is an important determinant of its biogeochemical cycling.
432 Mercury in the atmosphere is found in three forms: gaseous elemental mercury (GEM), gaseous
433 oxidized mercury (GOM), and particulate bound mercury (PBM). PBM and GOM are often
434 quantified together as reactive mercury (RM = GOM + PBM). a broad term that favors basic
435 accuracy of measurement over determination of specific compounds. Atmospheric GEM, at an
436 average global background concentration of 1 ~~to~~ 2 ng m⁻³, can be reliably measured with
437 calibrated analytical instruments (Gustin et al. 2015, Slemr et al. 2015). The measurement of
438 GOM and PBM requires detection at the part per trillion (pg m⁻³) level and depends on un-
439 calibrated operationally defined methods with demonstrated interferences and artifacts, and
440 concomitant large uncertainty (Jaffe et al. 2014, Lyman, Jaffe, and Gustin 2010, Gustin et al.
441 2013, McClure, Jaffe, and Edgerton 2014). Recent reviews (Gustin et al. 2015, Zhang et al.
442 2017) detail the shortcomings, difficulties, ~~developments, and ongoing improvements~~ for
443 atmospheric RM measurements.

Deleted: 4

Deleted: .

Deleted: –

Deleted: and needed

Deleted:

449 An alternative methodology ~~that might provide improved measurement of ambient RM involves~~
450 ~~use of~~ cation exchange membranes~~s~~(CEM). CEM materials~~s~~ have been used to selectively
451 measure GOM concentrations in ambient air ~~in previous studies~~(Huang et al. 2013, Huang and
452 Gustin 2015a, Huang et al. 2017, Sheu and Mason 2001, Pierce and Gustin 2017, Maruszczak et
453 al. 2017, Ebinghaus et al. 1999, Mason, Lawson, and Sullivan 1997, Bloom, Prestbo, and
454 VonderGeest 1996). The use of CEM type filters for this purpose was first documented in the
455 literature in a conference presentation (Bloom, Prestbo, and VonderGeest 1996), although such
456 membranes (then referred to as ‘ion exchange membranes’) were deployed earlier in a field-
457 based international comparative study of RM measurement techniques in September, 1995
458 (Ebinghaus et al. 1999). In the comparative study, one participating lab deployed a series of ion
459 exchange membranes (for GOM) behind a quartz fiber filter (for PBM) at a sample flow rate of
460 9-10 Lpm, for 24 h measurements (filter pore sizes were not reported). Results for PBM and
461 GOM were in similar ranges of 4.5 ~~to~~ 26 pg m⁻³ and 13-23 pg m⁻³, respectively (Ebinghaus et al.
462 1999).

Deleted: As a

Deleted: ,

Deleted: s

Deleted:

463 The ion exchange membrane method was also applied in a 1995-96 field campaign for
464 determining the speciation of atmospheric Hg in the Chesapeake Bay area (Mason, Lawson, and
465 Sullivan 1997). This study used a 5-stage Teflon filter pack system that included one up front
466 quartz fiber filter (0.8 µm pore size) to remove particulates~~s~~, and four downstream Gelman ion
467 exchange membranes (pore size not reported) to 1) capture GOM, 2) capture GOM
468 breakthrough, 3) serve as deployment blanks, and 4) isolate the filter train on the downstream
469 side (Mason, Lawson, and Sullivan 1997). Concentrations of GOM were reported to be 5 ~~to~~ 10
470 pg m⁻³, essentially at or below the method detection limit and it was speculated that even this
471 small amount may have been an artifact from fine particulate Hg passing through the 0.8 µm

Deleted: –

Deleted: –

478 quartz fiber filter (Mason, Lawson, and Sullivan 1997). The 3rd-in-series ion exchange
479 membrane blanks were reported to be not significantly different in Hg concentration from
480 unused membrane material, indicating that breakthrough was not a phenomenon that extended
481 past the second ion exchange filter position.

482 The particulate Hg artifact problem was subsequently elaborated on in a further comparative
483 study focusing exclusively on RM measurement techniques. Specific concerns included physical
484 particle breakthrough, re-evolution of gas-phase Hg²⁺ from PBM captured on the upstream
485 particulate filters passing downstream to the ion exchange membranes, possible adsorption of
486 GOM compounds to the particulate filters, or a GEM collection artifact on the ion exchange
487 membranes (Sheu and Mason 2001). None of these concerns were proven or disproven
488 conclusively.

489 Recent CEM based sampling systems typically deploy a pair of CEM disc filters without a pre-
490 particulate filter, in replicates of 2 to 3 at a flow rate of 1.0 Lpm (Gustin et al. 2016). Each pair
491 of filters constitutes one sample, the first filter serving as the primary RM collection surface, and
492 the second filter capturing breakthrough. Filters are deployed for 1-to-2 weeks and then collected
493 for analysis (Huang et al. 2017). The CEM material consists of a negatively charged
494 polyethersulfone coated matrix (Pall Corporation), and at least one manufacturing evolution has
495 occurred (Huang and Gustin 2015b). Prior CEM material versions (I.C.E. 450) had a pore size of
496 0.45 µm, while the current CEM material (Mustang® S) has a manufacturer reported pore size of
497 0.8 µm.

498 Previous work with the I.C.E 450 material indicated it does not adsorb significant quantities of
499 GEM in passive exposures, but can selectively uptake gas-phase Hg²⁺ species (Lyman et al.

Deleted: (CVAFS, EPA Method 1631, modified)
Deleted: positively

502 2007). The CEM material was subsequently adapted for use in active sample flow systems, with
503 the presumption of continued inertness to GEM and selectivity for GOM (Huang et al. 2013,
504 Huang and Gustin 2015a). These studies and others (Lyman et al. 2016) have shown better GOM
505 recovery on CEM material compared to potassium chloride (KCl) coated denuder methods.

506 Despite these tests, the transparency of the CEM material to GEM uptake has not been
507 conclusively demonstrated for active sampling flow rates, nor for high GEM concentrations,
508 though limited data using low concentration manual Hg⁰ injections through CEM filters suggests
509 little or no GEM uptake (Lyman et al. 2016). However, even small rates of GEM uptake by the
510 CEM material could result in a significant measurement artifact (e.g. a modest 1 ~~to~~ 2% GEM
511 uptake could easily overwhelm detection of typical ambient GOM concentrations). It is therefore
512 of critical importance that such a GEM artifact be ruled out if the CEM material is to be
513 successfully deployed for ambient RM measurements, first and foremost under controlled
514 laboratory conditions in the absence of confounding variables.

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

Deleted: –

Deleted: –

Deleted: –

527 In this paper we investigate the potential for GEM uptake on CEM material using a custom-built
528 permeation system. In addition, the ability of the CEM material to capture and retain a
529 representative GOM compound (mercury bromide, HgBr₂) is discussed with a view to estimate
530 collection efficiency of this analyte and explain or rule out possible mechanisms of breakthrough
531 for both dry and humid conditions.

532

533 2 Methods

534 A Tekran® 2537A ambient mercury analyzer was integrated with a custom-built permeation
535 system designed to enable controlled exposures of GEM and GOM to CEM filters (Fig. 1). The
536 2537A analyzer was calibrated at the beginning and periodically throughout the study and
537 checked for accuracy by manual Hg⁰ injections (mean recovery 101.1% ± 4.3, n = 10, SI Fig. 1).
538 The entire system was checked for Hg contamination in clean air prior to permeation tests, and
539 periodically during sampling (SI Fig. 2). All tubing and connections used in the permeation
540 system were polytetrafluoroethylene (PTFE), except for the quartz glass pyrolyzer tube and
541 perfluoroalkoxy (PFA) filter holders. Each of these materials is known to be chemically inert,
542 virtually nonporous, and to have a low coefficient of friction and for these reasons, PTFE/PFA
543 plastic and quartz glass are the standard materials employed in almost all Hg sampling systems,
544 as GEM passes over or through these surfaces without loss (Gustin et al. 2015). Given its
545 reactive nature, some GOM inevitably adsorbs to internal line surfaces, but the capacity of these
546 materials to sorb and retain GOM is not infinite and a steady state of adsorption/desorption is
547 expected after 5-6 hours of exposure to a stable concentration (Xiao et al. 1997, Gustin et al.
548 2013).

Deleted: .

Deleted:

Deleted: F

552 Sample flow through the system was alternated between two PTFE sample lines (designated
553 Line 0 and Line 1) using a Tekran® Automated Dual Switching (TADS) unit. Sample air was
554 constantly pulled through each line at 1.0 Lpm by the internal pump and mass flow controller
555 (MFC) in the 2537A, or by an external flush pump (KNF Laboport® N86 KNP) and MFC (Sierra
556 Smart-Trak® 2). Laboratory air was pulled through a single inlet at the combined rate of 2.0
557 Lpm, passing through a 0.2 µm PTFE particulate filter and an activated charcoal scrubber
558 (granular activated carbon 6-12 mesh, FisherChemical[®]) to produce clean sample air.

Deleted: mass flow controller

Formatted: Superscript

559 Additionally, for dry air permeations sample air was pulled through a Tekran® 1102 Air Dryer
560 installed upstream of the particulate filter, and for elevated humidity permeations sample air was
561 pulled through the headspace of a distilled water bath (DIW, < 0.2 ng L⁻¹ total Hg) that was
562 located upstream from the charcoal scrubber to eliminate the DIW being a potential Hg source to
563 the system. Temperature and relative humidity (RH) were measured in-line (Campbell Scientific
564 CS215) and used for calculation of absolute humidity.

565 Pure liquid Hg⁰ and crystalline HgBr₂ (purity > 99.998% Sigma-Aldrich®) were used as Hg
566 vapor sources. The elemental Hg⁰ bead was contained in a PTFE vial. Solid HgBr₂ crystals were
567 packed in thin-walled PTFE heat-shrink tubing (O.D. 0.635 cm) with solid Teflon plugs in both
568 ends to create a perm tube with an active permeation length of 2 mm (Huang et al. 2013). The
569 HgBr₂ permeation tube was also placed in the bottom of a PTFE vial, and the permeation vials
570 were submerged in a temperature-controlled laboratory chiller (0.06 ± 0.13 °C, Cole Parmer
571 Polystat®). A low source temperature was favored both because higher temperatures would have
572 produced unacceptably high concentrations, and because there is evidence that at higher
573 temperatures a small amount of Hg⁰ can be evolved from Hg²⁺ compounds (Xiao et al. 1997).

575 An ultra-high purity nitrogen (N₂) carrier gas was passed through the permeation vials at 0.2
576 Lpm to carry the target Hg vapor into the main sample line through a PTFE T-junction. The main
577 sample line was split into Line 0 and Line 1 immediately downstream from the permeation flow
578 junction, with flow on each line controlled by MFC. Line 0 proceeded directly to the 2537A
579 without modification during GEM permeations (Fig. 1A), but housed CEM filters during the
580 HgBr₂ permeations (Fig. 1B, 1C). Line 1 held a pyrolyzer unit composed of a quartz glass tube
581 (O.D. 0.625 cm) packed with a 3 cm section of quartz wool heated to 600 °C using a nichrome
582 wire coil (SI Fig. 3 and discussion). The goal of the pyrolyzer was to convert all Hg to GEM for
583 detection on the Tekran® 2537A.

584 CEM filters were deployed in 2-stage, 47 mm disc PFA filter holders (Savillex®). The primary
585 “A” filter in the 2-stage holder is the first to be exposed to the permeated Hg, with the secondary
586 “B” filter mounted immediately behind the A filter (A to B distance ~3mm) to measure potential
587 breakthrough. For GEM permeations, three 2-stage filter holders were placed in-series on Line 1
588 behind the pyrolyzer unit (Fig. 1A), while total Hg coming through the system was measured on
589 Line 0 with no filters in place. This allowed simultaneous exposure of 6 CEM filters in one GEM
590 sample exposure. The first CEM filter in-line served to scrub any small residual RM passing
591 through the system and pyrolyzer, and these first in-line filters were removed for the calculations
592 of mean GEM uptake rate, (SI Fig. 4 and discussion).

593 For determining the potential for GOM breakthrough, two system configurations were used. In
594 the first configuration (Fig. 1B), the total Hg concentration of air that passed through the
595 pyrolyzer on Line 1 was measured without any filters, while Line 0 held one 2-stage CEM filter
596 pair for HgBr₂ loading. This configuration allowed for real time (10 min interval) quantification
597 of the HgBr₂ permeation concentration through Line 1 using the 2537A, and comparison with

Deleted:

599 total Hg loading on the CEM filters on Line 0. In the second configuration, replicate filters were
600 concurrently loaded with HgBr₂ by placing 2-stage CEM filter holders on both Line 0 and Line 1
601 (upstream of the pyrolyzer, Fig. 1C). In all HgBr₂ exposures, the filter holders were placed as
602 close to the permeation vial as possible, with a total distance from vial to filter surface of
603 approximately 20 cm. Mercury bromide permeation was conducted in dry air and elevated
604 humidity air. The difference between one line being fully open to the HgBr₂ permeation flow
605 (configuration Fig. 1B) and then closed by deployment of the CEM filters (configuration Fig.
606 1C) enabled a rough determination of the amount of HgBr₂ line-loss within the system.

607 After permeation, CEM filters were collected into clean, sterile polypropylene vials and analyzed
608 for total Hg by digestion in an oxidizing acid solution, reduction to Hg⁰, gold amalgamation, and
609 final quantification by cold vapor atomic fluorescence spectrometry (CVAFS, EPA Method
610 1631, Rev. E) using a Tekran® 2600 system. The system background Hg signal was determined
611 for every analytical run by analyzing pure reagent solution in the same vials and at the same
612 volume as used for actual filter samples. The background Hg value was used as a system
613 calibration blank and subtracted from all actual samples. Total Hg standards (5 to 100 ppb) were
614 analyzed before and after each batch of 10 filter samples to check precision and recovery, and
615 the mean recovery for all Hg standards was 97.2 ± 5.0 % (n = 37). Analysis for total Hg on the
616 CEM filters provided for comparison of total Hg filter loading, and verification of in-line results.
617 A to B filter breakthrough was calculated by comparison of total Hg recoveries on the primary
618 and secondary CEM filters, using Eq. (1):

$$619 \% \text{ Breakthrough} = 100 * \text{CEM}_{2nd}/(\text{CEM}_{1st} + \text{CEM}_{2nd}) \quad (1)$$

Deleted: This analysis

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

625 **3 Results**

626 **3.1 Elemental Mercury Uptake on CEM Filters**

627 Elemental Hg uptake on CEM material was negligible for permeated Hg⁰ vapor concentrations
628 ranging from 1.43×10^6 to 1.85×10^6 pg m⁻³ (Fig. 2). High GEM concentrations were employed in
629 this study under the logic that if no GEM uptake was observed at high concentrations, a similar
630 lack of GEM uptake can be expected for all lower concentrations.

Deleted: –

631 The mean Hg mass on blank CEM filters was 50 ± 20 pg (n = 28). For permeations into dry
632 sample air of 0.5 ± 0.1 g m⁻³ water vapor (WV), total mean Hg⁰ permeation exposures of 2.7×10^6
633 pg (24 h) and 7.3×10^6 pg (72 h) resulted in total (blank-corrected) Hg recoveries on the CEM
634 filters of 100 ± 40 pg (n = 10) and 280 ± 110 pg (n = 5), respectively. These quantities of total
635 recovered Hg equate to a mean GEM uptake rate on the CEM filters of $0.004 \pm 0.002\%$ ($0.006 \pm$
636 0.006% including first in-line filter). For GEM permeations into ambient humidity sample air (2
637 to 4 g m⁻³ WV), at a slightly lower total mean permeated Hg⁰ 24 h exposure of 2.1×10^6 pg, total
638 (blank-corrected) Hg recoveries on the CEM filters were 55 ± 30 pg (n = 10), equating to a GEM
639 uptake rate of $0.003 \pm 0.001\%$ ($0.005 \pm 0.005\%$ including first in-line filter). The overall GEM
640 uptake rate was linear ($r^2 = 0.97$) for the range of concentrations used in this study, indicating a
641 similar low uptake rate can be expected down to lower GEM concentrations.

Deleted: 004

Deleted: 002

Deleted: –

Deleted: 003

Deleted: 001

642 **3.2 Mercury Bromide Uptake on CEM Filters**

649 Breakthrough of HgBr₂ vapor from the primary (A) to secondary (B) CEM filters was low for all
650 conditions tested in this study (Table 1). These conditions included HgBr₂ permeated into clean
651 dry laboratory air with < 0.5 g m⁻³ WV, clean air at ambient room humidity (4.~~to~~ 5 g m⁻³ WV),
652 and clean air at elevated humidity (10.~~to~~ 11 g m⁻³ WV), at line temperatures between 17 to 19
653 °C. Overall, the mean A to B filter breakthrough ranged from 0 to 0.5% and averaged 0.2 ± 0.2
654 % (n = 17), with no statistical difference observed in mean breakthrough rates for the three levels
655 of humidity (ANOVA, p = 0.124).

656 The first HgBr₂ permeation in clean dry (< 0.5 g m⁻³ WV) laboratory air was over a 96 h period,
657 using the system configuration in Figure 1B to establish an approximately permeation rate (Fig.
658 3). Total Hg reaching the 2537A through the pyrolyzer on Line 1 (red line, Fig. 3) indicates an
659 average HgBr₂ exposure concentration of 4540 pg m⁻³, or about 4.5 pg min⁻¹ from the permeation
660 tube. This permeated concentration of HgBr₂ was deliberately much higher than ambient in order
661 to test retention and break through at high levels, but it should be noted that the performance of
662 the CEM filters at low concentrations could be slightly different. After this permeation, total
663 blank-corrected HgBr₂ loading on the primary CEM filter on Line 0 was 49400 pg, but only 50
664 pg on the secondary CEM filter, indicating a breakthrough rate of approximately 0.1%. Total Hg
665 reaching the 2537A through the CEM filters on Line 0 (black line, Fig. 3) over this time period
666 was 15 pg, mostly at the beginning of the deployment when some ambient Hg entered the
667 opened system. The low concentrations of Hg measured downstream in Line 0 on the 2537A
668 corroborates that breakthrough of HgBr₂ was low. These data also demonstrate that the CEM
669 material did not saturate with a HgBr₂ loading of ~ 50000 pg, a loading far higher than could be
670 expected in ambient conditions.

Deleted: –

Deleted: –

673 Subsequent replicate 24 h HgBr₂ permeations in clean dry air resulted in consistent total Hg
674 loading on CEM filters placed on both lines concurrently (8560 ± 320 pg, n = 6, Samples 2-7
675 Table 1), and mean total Hg on the secondary CEM filters was 20 ± 10 pg (average
676 breakthrough of 0.3%). On Line 0 (black line, Fig.3), which was never open to HgBr₂ vapor
677 downstream from the CEM filters at any point in the study, Hg measured at the 2537A was zero
678 for all three 24 h permeations, indicating no breakthrough (Samples 2, 4, & 6, Table 1).
679 However, on Line 1, which had been exposed to the full HgBr₂ vapor concentration of 4540 pg
680 m⁻³ over the duration of the 96 h perm test, 1155 pg of Hg were measured downstream in the first
681 24 h sample (Sample 3, Table 1). The amount of downstream Hg dropped to 10 pg in the second
682 24 h, and 6 pg in the third 24 h (Samples 5 & 7, Table 1). This downstream Hg in Line 1
683 (compared to the zero Hg simultaneously observed on Line 0) is attributed to re-volatilization of
684 HgBr₂ that had stuck to the line material during the open permeation flow. At the moment CEM
685 filters were deployed on Line 1 (red-to-blue transition, Fig. 3), a rapid asymptotic decline in the
686 Hg signal began. This decay curve supports drawdown and depletion of a Hg reservoir on the
687 interior line surfaces behind the CEM filters, and not a continuous source such as breakthrough
688 from the permeation tube that was still supplying HgBr₂ to both sample lines. The total mass of
689 Hg re-volatized from the interior line surfaces (1155 pg) represents 4 to 5% of the total HgBr₂
690 that had passed through Line 1 (~25000 pg based on 2537A measurement). Eventually, Hg
691 reaching the 2537A through Line 1 decreased to zero during the same 24 h filter deployment,
692 indicating a majority of HgBr₂ line contamination in a high-concentration permeation system can
693 be expected to flush out within ~12 h.
694 Additional HgBr₂ permeations were made at two levels of in-line humidity. At ambient room
695 humidity (4 to 5 g m⁻³ WV), mean total Hg measured on the CEM filters was 7910 ± 520 pg (n =

Deleted: –

Deleted: –

698 4; Samples H2-5, Table 1), with an average breakthrough to the secondary filters of 0.3%. When
699 normalized for sample volume, the mean HgBr_2 loading on CEM filters during ambient humidity
700 (5968 ± 125 pg) and dry air (5995 ± 188 pg) permeations was not statistically significantly
701 different (t-test $p = 0.790$). HgBr_2 breakthrough rates were also the same (0.3%) as during the
702 dry air permeations, indicating that the permeation system was operating similarly at the two
703 humidity levels, and suggesting that absolute humidity concentrations around 4 to 5 g m^{-3} WV
704 have insignificant effects on collection of HgBr_2 in clean laboratory air by the CEM material.

Deleted: –

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

Deleted: , likely

Deleted: GEM

Deleted: passing

719 As a further test of possible humidity effects, two replicate 24 h CEM filter deployments were
720 conducted in elevated humidity conditions (10 to 11 g m^{-3} WV) created by an in-line water bath.

Deleted: –

726 Mean total Hg loading on the primary CEM filters was higher compared to the previous
727 permeations (11700 ± 720 pg, n = 4, Samples H9-12, Table 1), indicating an increase in the
728 effective HgBr_2 permeation rate, possibly due to the perturbation caused by a poor filter seal and
729 small leak in the preceding deployment (Sample H7-8, Table 1). However, mean total Hg on the
730 secondary CEM filters was 20 ± 20 pg, indicating an average breakthrough of 0.1%, less than the
731 breakthrough observed for the lower humidity permeations.

732 4 Conclusions

733 GEM uptake on the CEM material was negligible under the laboratory conditions and high GEM
734 loading rates (3 orders of magnitude above ambient) tested in this study, with an overall linear
735 uptake rate of 0.004% for permeated GEM concentrations between 1.43×10^6 to 1.85×10^6 pg m⁻³.
736 This uptake rate would be insignificant at typical ambient atmospheric Hg concentrations (1 to 2
737 ng m⁻³). As a hypothetical example, a CEM filter sampling ambient air at an average GEM
738 concentration of 2 ng m⁻³ for a typical 2-week sample period would have a total Hg^0 exposure of
739 ~40000 pg. At the calculated uptake rate of 0.004%, a maximum 1.6 pg of Hg observed on the
740 sample filter could be attributed to GEM artifact and given that blank filters have a mean total
741 Hg mass of 50 ± 20 pg, this amount would be below detection. This corroborates the lack of
742 GEM uptake seen by Lyman et al. (2016) for manual Hg^0 injections on CEM filters at lower total
743 mass loadings of 300 to 6000 pg.

744 Mean HgBr_2 breakthrough from primary to secondary CEM filters averaged $0.2 \pm 0.2\%$ over all
745 test conditions, using HgBr_2 as a test GOM compound. A to B filter breakthrough was derived
746 from a comparison between the large amount of HgBr_2 permeated onto the primary CEM filters,
747 to the small amount of HgBr_2 that collected on the secondary CEM filters, 3 mm immediately

Deleted: 2

Deleted: 004

Deleted: –

Deleted: –

Deleted: 004

Deleted: 1

Deleted: 6

Deleted: –

756 downstream. The measurement of 1000s of pg of Hg on the primary filter, and only 10s of pg on
757 the secondary filter, leads to the conclusion that the primary filter removed the majority of HgBr₂
758 from the sample air stream. In addition, low breakthrough was corroborated by downstream
759 measurement of the air stream passing through the CEM filters, using the Tekran® 2537A. The
760 average breakthrough to the 2537A was 0 pg for 24 h permeations in dry air and 0 ~~to~~ 40 pg in
761 humid air, for those filter deployments than can be considered steady-state (> 24 h without large
762 perturbations).

Deleted: –

763 While the permeation system was not specifically optimized for a quantitative mass balance
764 between permeated HgBr₂ and HgBr₂ recovered on the CEM filters, a rough estimation of the
765 CEM collection efficiency is possible. Using the HgBr₂ permeations conducted in clean dry air
766 (mean loading 8560 pg) and comparing this to the mean Hg concentration measured at the
767 2537A analyzer during the last 24 h of the 96 h permeation measurement (4680 pg m⁻³, or 6739
768 pg per 24 h), the HgBr₂ recovery on the CEM filters averaged 127%. Adjusting the expected
769 permeated HgBr₂ mass for our estimated line-loss (~4-5%) improves the recoveries to ~123%.
770 Still, HgBr₂ loading on the CEM filters was therefore ~23% higher than expected based on the
771 pyrolyzed total measurement on the 2537A. This indicates that not all HgBr₂ was being converted
772 to GEM, suggesting that the pyrolyzer was not 100% efficient and that higher pyrolyzer
773 temperatures may be needed.

774 The technique of gold amalgamation in general, and specifically including the Tekran® 2537
775 analyzer, is widely considered to provide a quantitative *total gaseous Hg* measurement, at or
776 very near 100% collection efficiency for Hg⁰ and Hg compounds (Dumarey, Dams, and Hoste
777 1985, Schroeder and Jackson 1985, Landis et al. 2002, Temme et al. 2003, Schroeder et al.
778 1995). However, to our knowledge collection and desorption efficiencies on gold traps have not

780 been demonstrated for HgBr₂. The stated desorption temperature of the Tekran® 2537A gold
781 traps is 500 °C, but temperatures as low as 375 °C have been reported (Gustin et al. 2013), which
782 would likely cause reduced thermal decomposition efficiency for all captured GOM compounds,
783 including HgBr₂. We speculate that a combination of incomplete thermal decomposition to Hg⁰,
784 at both the 600 °C pyrolyzer and during the best-case 500 °C desorption of the 2537 gold traps,
785 resulted in ~20% non-detection of total permeated HgBr₂ as it passed through the CVAFS optical
786 path without generating the necessary fluorescence signal.

787 While our results validated some basic performance metrics for the CEM material, they did not
788 provide data that could fully explain the higher levels of breakthrough observed for CEM filters
789 deployed in ambient air over the 1-to-2 week sample periods in previous studies. Increasing
790 humidity by itself did not affect observed HgBr₂ breakthrough. A HgBr₂ loading of ~50000 pg
791 also did not lead to increased breakthrough, indicating there is no saturation effect on CEM filter
792 capacity at a GOM loading far greater than expected from ambient concentrations. It remains
793 unclear, though, whether breakthrough results from different collection efficiencies for GOM
794 compounds other than HgBr₂, or whether breakthrough results from a degradation of GOM
795 retention capacity in the CEM material when exposed to ambient air chemistries not simulated in
796 this study. Also, our experiments were conducted in particulate-free air, which leaves open the
797 possibility that breakthrough is related to capture (or lack thereof) of PBM by the CEM material.

798 Acknowledgements

799 The authors would like to acknowledge funding from Macquarie University iMQRES 2015148
800 and NSF Grant 629679. ~~Valuable input and assistance was received~~ from Dr. Ashley Pierce, Dr.
801 Seth Lyman, and the students of Dr. Gustin's laboratory. ~~The surviving authors bid an untimely~~

Deleted:

Deleted:

Deleted: , as well as

Deleted: v

806 farewell to Dr Grant C. Edwards, who was ever a cheerful friend, mentor, and colleague. Dr
807 Edwards passed away unexpectedly on September 11, 2018.

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

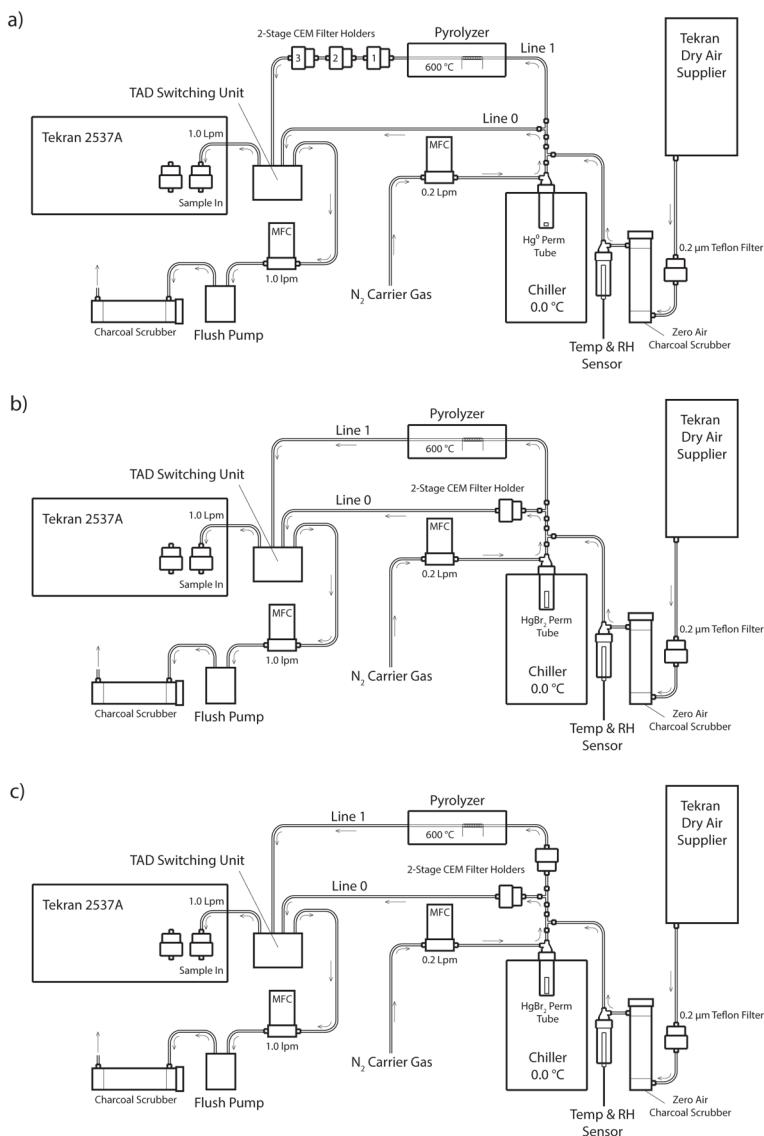
808
809
810
811
812
813
814
815
816
817

818 References

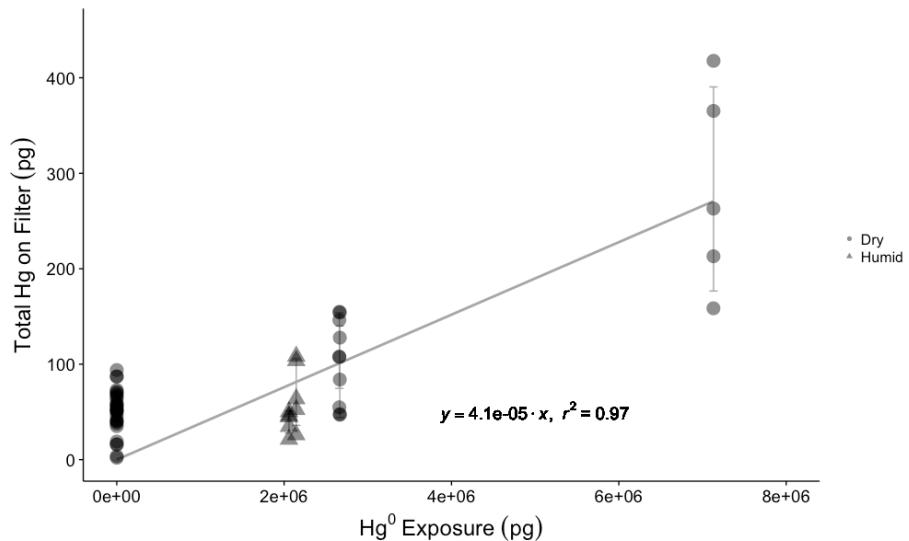
- 819
820 Bloom, NS, EM Prestbo, and E VonderGeest. 1996. "Determination of atmospheric gaseous
821 Hg(II) at the pg/m³ level by collection onto cation exchange membranes, followed by
822 dual amalgamation/cold vapor atomic fluorescence spectrometry." 4th International
823 Conference on Mercury as a Global Pollutant, Hamburg.
824 Dumarey, R, R Dams, and J Hoste. 1985. "Comparison of the collection and desorption
825 efficiency of activated charcoal, silver, and gold for the determination of vapor phase
826 atmospheric mercury." *Analytical Chemistry* 57 (13):2638-2643. doi:
827 10.1021/ac00290a047.
828 Ebinghaus, R., S. G. Jennings, W. H. Schroeder, T. Berg, T. Donaghy, J. Guentzel, C. Kenny, H.
829 H. Kock, K. Kvietkus, W. Landing, T. Muhleck, J. Munthe, E. M. Prestbo, D.
830 Schneeberger, F. Slemr, J. Sommar, A. Urba, D. Wallschlager, and Z. Xiao. 1999.
831 "International field intercomparison measurements of atmospheric mercury species at
832 Mace Head, Ireland." *Atmospheric Environment* 33 (18):3063-3073.
833 Gustin, M. S., H. M. Amos, J. Huang, M. B. Miller, and K. Heidecorn. 2015. "Measuring and
834 modeling mercury in the atmosphere: a critical review." *Atmos. Chem. Phys.* 15
835 (10):5697-5713. doi: 10.5194/acp-15-5697-2015.
836 Gustin, Mae Sexauer, Jiaoyan Huang, Matthieu B. Miller, Christianna Peterson, Daniel A. Jaffe,
837 Jesse Ambrose, Brandon D. Finley, Seth N. Lyman, Kevin Call, Robert Talbot, Dara
838 Feddersen, Huiting Mao, and Steven E. Lindberg. 2013. "Do We Understand What the
839 Mercury Speciation Instruments Are Actually Measuring? Results of RAMIX."
840 *Environmental Science & Technology* 47 (13):7295-7306. doi: 10.1021/es3039104.
841 Gustin, Mae Sexauer, Ashley M. Pierce, Jiaoyan Huang, Matthieu B. Miller, Heather A. Holmes,
842 and S. Marcela Loria-Salazar. 2016. "Evidence for Different Reactive Hg Sources and
843 Chemical Compounds at Adjacent Valley and High Elevation Locations." *Environmental*
844 *Science & Technology* 50 (22):12225-12231. doi: 10.1021/acs.est.6b03339.

- 845 Huang, J., M. B. Miller, E. Edgerton, and M. Sexauer Gustin. 2017. "Deciphering potential
846 chemical compounds of gaseous oxidized mercury in Florida, USA." *Atmos. Chem.
847 Phys.* 17 (3):1689-1698. doi: 10.5194/acp-17-1689-2017.
- 848 Huang, Jiaoyan, and Mae Sexauer Gustin. 2015a. "Uncertainties of Gaseous Oxidized Mercury
849 Measurements Using KCl-Coated Denuders, Cation-Exchange Membranes, and Nylon
850 Membranes: Humidity Influences." *Environmental Science & Technology* 49 (10):6102-
851 6108. doi: 10.1021/acs.est.5b00098.
- 852 Huang, Jiaoyan, and Mae Sexauer Gustin. 2015b. "Use of Passive Sampling Methods and
853 Models to Understand Sources of Mercury Deposition to High Elevation Sites in the
854 Western United States." *Environmental Science & Technology* 49 (1):432-441. doi:
855 10.1021/es502836w.
- 856 Huang, Jiaoyan, Matthieu B. Miller, Peter Weiss-Penzias, and Mae Sexauer Gustin. 2013.
857 "Comparison of Gaseous Oxidized Hg Measured by KCl-Coated Denuders, and Nylon
858 and Cation Exchange Membranes." *Environmental Science & Technology* 47 (13):7307-
859 7316. doi: 10.1021/es4012349.
- 860 Jaffe, Daniel A., Seth Lyman, Helen M. Amos, Mae S. Gustin, Jiaoyan Huang, Noelle E. Selin,
861 Leonard Levin, Arnout ter Schure, Robert P. Mason, Robert Talbot, Andrew Rutter,
862 Brandon Finley, Lyatt Jaeglé, Viral Shah, Crystal McClure, Jesse Ambrose, Lynne Gratz,
863 Steven Lindberg, Peter Weiss-Penzias, Guey-Rong Sheu, Dara Feddersen, Milena
864 Horvat, Ashu Dastoor, Anthony J. Hynes, Huiting Mao, Jeroen E. Sonke, Franz Slemr,
865 Jenny A. Fisher, Ralf Ebinghaus, Yanxu Zhang, and Grant Edwards. 2014. "Progress on
866 Understanding Atmospheric Mercury Hampered by Uncertain Measurements."
867 *Environmental Science & Technology* 48 (13):7204-7206. doi: 10.1021/es5026432.
- 868 Landis, M. S., R. K. Stevens, F. Schaedlich, and E. M. Prestbo. 2002. "Development and
869 characterization of an annular denuder methodology for the measurement of divalent
870 inorganic reactive gaseous mercury in ambient air." *Environmental Science &
871 Technology* 36 (13):3000-3009. doi: 10.1021/es015887t.
- 872 Lyman, S. N., D. A. Jaffe, and M. S. Gustin. 2010. "Release of mercury halides from KCl
873 denuders in the presence of ozone." *Atmospheric Chemistry and Physics* 10 (17):8197-
874 8204. doi: 10.5194/acp-10-8197-2010.
- 875 Lyman, Seth, Colleen Jones, Trevor O'Neil, Tanner Allen, Matthieu Miller, Mae Sexauer
876 Gustin, Ashley M. Pierce, Winston Luke, Xinrong Ren, and Paul Kelley. 2016.
877 "Automated Calibration of Atmospheric Oxidized Mercury Measurements."
878 *Environmental Science & Technology* 50 (23):12921-12927. doi:
879 10.1021/acs.est.6b04211.
- 880 Lyman, Seth N., Mae Sexauer Gustin, Eric M. Prestbo, and Frank J. Marsik. 2007. "Estimation
881 of Dry Deposition of Atmospheric Mercury in Nevada by Direct and Indirect Methods."
882 *Environmental Science & Technology* 41 (6):1970-1976. doi: 10.1021/es062323m.

- 883 Maruszczak, Nicolas, Jeroen E. Sonke, Xuewu Fu, and Martin Jiskra. 2017. "Tropospheric GOM
884 at the Pic du Midi Observatory—Correcting Bias in Denuder Based Observations."
885 *Environmental Science & Technology* 51 (2):863-869. doi: 10.1021/acs.est.6b04999.
- 886 Mason, RP, NM Lawson, and KA Sullivan. 1997. "The concentration, speciation and sources of
887 mercury in Chesapeake Bay precipitation." *Atmospheric Environment* 31 (21):3541-
888 3550. doi: 10.1016/S1352-2310(97)00206-9.
- 889 McClure, C. D., D. A. Jaffe, and E. S. Edgerton. 2014. "Evaluation of the KCl Denuder Method
890 for Gaseous Oxidized Mercury using HgBr₂ at an In-Service AMNet Site."
891 *Environmental Science & Technology* 48 (19):11437-11444. doi: 10.1021/es502545k.
- 892 Pierce, Ashley M., and Mae Sexauer Gustin. 2017. "Development of a Particulate Mass
893 Measurement System for Quantification of Ambient Reactive Mercury." *Environmental
894 Science & Technology* 51 (1):436-445. doi: 10.1021/acs.est.6b04707.
- 895 Schroeder, WH, and RA Jackson. 1985. "An instrumental analytical technique for speciation of
896 atmospheric mercury." *International Journal of Environmental Analytical Chemistry* 22
897 (1-2):1-18. doi: 10.1080/03067318508076405.
- 898 Schroeder, WH, G Keeler, H Kock, P Roussel, D Schneeberger, and F Schaedlich. 1995.
899 "International field intercomparison of atmospheric mercury measurement methods."
900 *Water Air and Soil Pollution* 80 (1-4):611-620. doi: 10.1007/BF01189713.
- 901 Sheu, G. R., and R. P. Mason. 2001. "An examination of methods for the measurements of
902 reactive gaseous mercury in the atmosphere." *Environmental Science & Technology* 35
903 (6):1209-1216. doi: 10.1021/es001183s.
- 904 Slemr, Franz, Hélène Angot, Aurélien Dommergue, O. Magand, Manuel Barret, Andreas
905 Weigelt, Ralf Ebinghaus, Ernst Brunke, K. A Pfaffhuber, Grant Edwards, Dean Howard,
906 J. Powell, M. Keywood, and Feiyue Wang. 2015. *Comparison of mercury concentrations
907 measured at several sites in the Southern Hemisphere*. Vol. 15.
- 908 Temme, Christian, Jürgen W. Einax, Ralf Ebinghaus, and William H. Schroeder. 2003.
909 "Measurements of Atmospheric Mercury Species at a Coastal Site in the Antarctic and
910 over the South Atlantic Ocean during Polar Summer." *Environmental Science &
911 Technology* 37 (1):22-31. doi: 10.1021/es025884w.
- 912 Xiao, Z., J. Sommar, S. Wei, and O. Lindqvist. 1997. "Sampling and determination of gas phase
913 divalent mercury in the air using a KCl coated denuder." *Fresenius Journal of Analytical
914 Chemistry* 358 (3):386-391.
- 915 Zhang, L., S. Lyman, H. Mao, C. J. Lin, D. A. Gay, S. Wang, M. Sexauer Gustin, X. Feng, and
916 F. Wania. 2017. "A synthesis of research needs for improving the understanding of
917 atmospheric mercury cycling." *Atmos. Chem. Phys.* 17 (14):9133-9144. doi:
918 10.5194/acp-17-9133-2017.
- 919



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



926

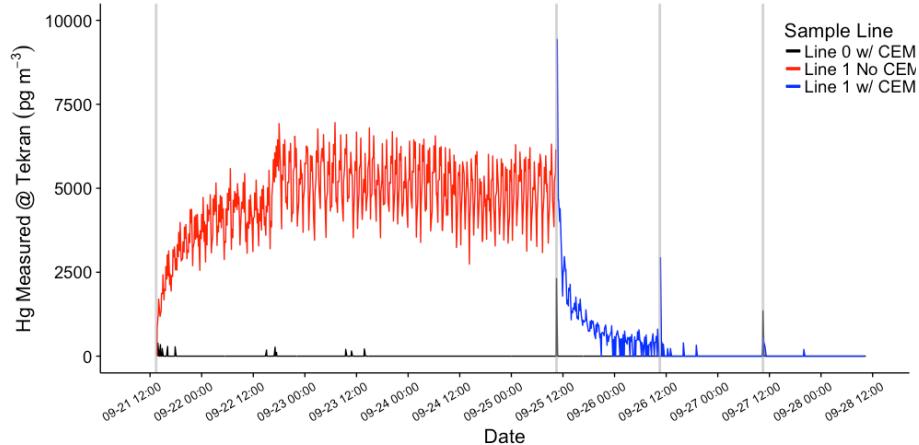
927 **Figure 2.** Total Hg recovered on CEM material for blank filters (Hg exposure = 0 pg)
 928 and different Hg⁰ vapor permeations in dry ($0.5 \pm 0.1 \text{ g m}^{-3}$ WV) and humid air ($2\text{-}4 \text{ g m}^{-3}$ WV). Circles represent dry air permeations,
 929 triangles represent humid air exposures, and all permeation exposures were blank-corrected. The regression line
 930 shows the relationship between total Hg⁰ exposure and blank-correct mean total Hg recovered on CEM filters (error
 931 bars \pm one standard deviation), with a slope of 4.1×10^{-5} indicating a linear uptake rate of 0.004%.

932

933

934

935



936
937 **Figure 3.** HgBr₂ permeations in clean dry lab air using the configuration in Figure 1B (red line) and Figure 1C (blue line).
938 The red line indicates total Hg released from permeation tube and passing through pyrolyzer on Line 1 before
939 being measured by Tekran 2537A, black line indicates Hg reaching 2537A through CEM filters on Line 0.
940 Vertical grey lines indicate open system during filter deployments.

941
942
943
944
945
946
947
948
949
950
951
952
953
954

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 Brkthr (%)
Mean CEM Filter Blank									
54									
Clean Dry Air ($0.3 \pm 0.05 \text{ g m}^{-3} \text{ wv}$)									
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		
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 ($4.4 \pm .2 \text{ g m}^{-3} \text{ wv}$)									
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		
HgBr H7B						2672*	2618*	105	na
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 ($10.9 \pm 1.7 \text{ g m}^{-3} \text{ wv}$)									
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		

955

Table 1. Summary of CEM filter loading and breakthrough during HgBr₂ 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.

956

957

958

960 **Supporting Information**

961 **Evaluation of cation exchange membrane performance under exposure to high Hg⁰ and**
962 **HgBr₂ concentrations**

963 Matthieu B. Miller^{1*}, Mae S. Gustin², Sarrah Dunham-Cheatham², Grant C. Edwards¹

964 ¹Faculty of Science and Engineering, Department of Environmental Science, Macquarie University, Sydney, NSW,

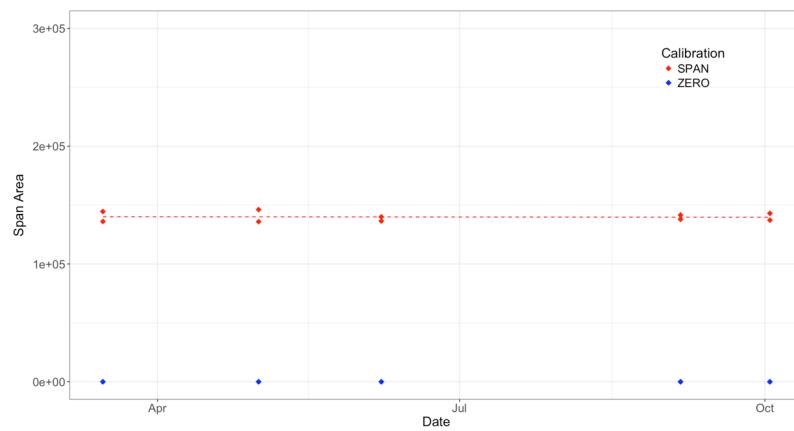
965 2113, Australia

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

968

969 **Tekran QA/QC**

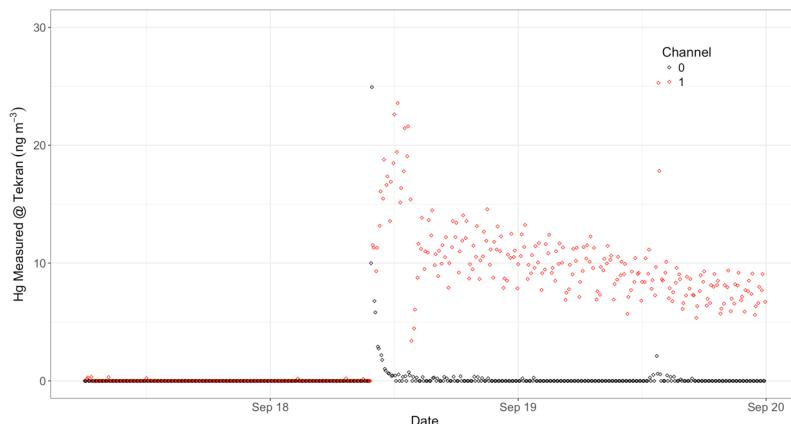
970 The Tekran 2537A unit operated consistently over the duration of study. All internal calibrations
971 showed good analyzer zeros, and stable span areas ($139875 \pm 2.7\%$) with no drift (SI Fig. 1). The
972 calibration data indicates that: 1) there was no Hg contamination within the 2537A unit, and 2)
973 there was no passivation of the gold traps. Every calibration was also checked by external Hg
974 vapor source injections (mean recovery $101.1\% \pm 4.3$, $n = 10$). The system was not operated with
975 a recurring automatic internal calibration, due to the variable timing of the experimental work.



976

977 **SI Figure 1.** Tekran 2537A internal calibration data for the duration of the study.

978 System blanks were performed by flowing scrubbed zero air through the entire path of the
979 permeation system, which produced blank values below the Tekran® 2537A detection limit (<
980 0.1 ng m⁻³, SI Fig. 2 as example). In addition, the system routinely zeroed out when deploying
981 CEM filters on both sample lines during HgBr₂ permeations.



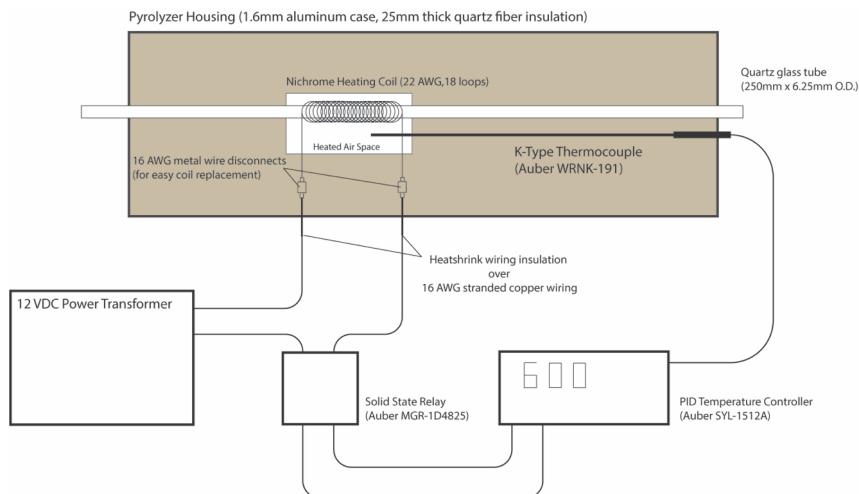
982
983 **SI Figure 2.** Example of system zero check prior to turning on HgBr₂ permeation source.
984

985 **Pyrolyzer Design**

986 The pyrolyzer used in the study (SI Fig. 3) consisted of a 25.4 cm long quartz glass tube of 0.625
987 cm diameter (custom, URG Corporation). A loosely packed 3 cm section of quartz wool was
988 lodged in the mid-section of the tube, and this 3 cm section was wrapped with 22 gauge
989 Nichrome wire (18 loops). The quartz tube was closely contained within 2.5 cm thick quartz
990 fiber insulation within a 1.6 mm aluminum casing, except for an enclosed air space around the
991 heated Nichrome coil section. The coil wire was connected to 16 AWG stranded copper wire
992 with all metal disconnects, which were buried within the quartz fiber insulation to reduce thermal
993 fatigue on the connections. The copper wire insulation was stripped and replaced with higher

994 temperature heat-shrink insulation where the wiring passed through the pyrolyzer case to the
995 external power supply. The tip of a 150 mm long K-type thermocouple (Auber WRNK-191) was
996 inserted through the insulation into the heated air space next to the coil to provide a temperature
997 feedback for a PID controller (Auber SYL-1512A). Power to the Nichrome coil was supplied by
998 a 12 VDC transformer through a solid-state relay (Auber MGR-1D4825) switched by the PID
999 controller.

1000 It was found that the position of the feedback thermocouple in the airspace outside of the heating
1001 coil caused a large discrepancy between nominal temperature setpoint and actual temperature
1002 inside the heated section of pyrolyzer tube. In general, much higher temperatures are achieved
1003 inside the coil than outside. To compensate for this, actual temperature at the heated coil section
1004 was verified to 600 °C by external IR sensor and internal thermocouple probe.



1005

1006

SI Figure 3. Detailed schematic of pyrolyzer design.

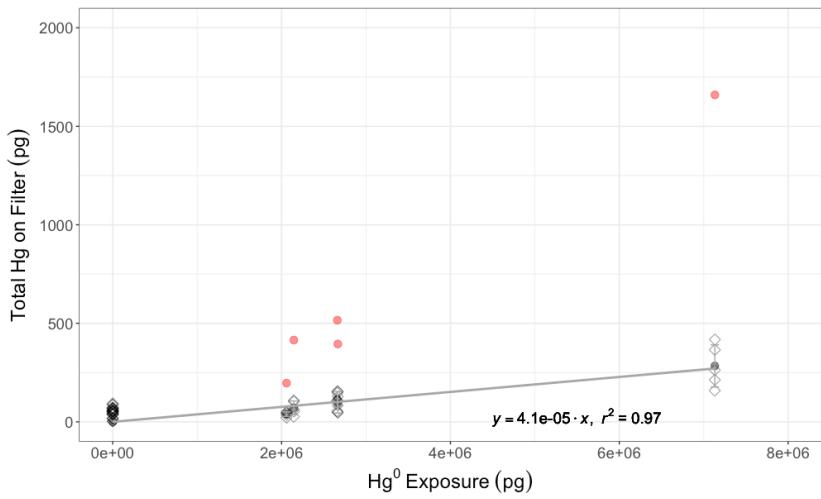
1007

1008 The pyrolyzer design used in this study was not 100% efficient at thermally reducing HgBr₂ to
1009 Hg⁰, based on the higher total Hg recoveries on the CEM filters versus total Hg measured
1010 through the pyrolyzer on the Tekran 2537. A larger heated section, and higher temperatures than
1011 600 °C would likely improve pyrolyzer efficiency.

1012 **GEM Permeation**

1013 The first CEM filter in line during the GEM permeations always showed more total Hg than the
1014 following 5 downstream filters, which were not significantly different from each other (SI Fig.
1015 4). We believe it is unlikely that the Hg observed on the first CEM filters results from GEM
1016 uptake. Even at the highest GEM permeation level, the first filter captured only ~1700 pg of Hg,
1017 out of a total permeated amount of over 7.3 *million* pg (a 0.02 % uptake rate). This means that
1018 the downstream CEM filters were still exposed to about 7.2985 *million* pg of GEM but captured
1019 less total Hg.

1020 We cannot entirely rule out the possibility of some small rate of *in-situ* oxidation of GEM in the
1021 system, at the surface of the Hg⁰ bead or in the vapor phase. Therefore, the first in-line filters
1022 were not included in calculation of GEM uptake rates because of suspicion that some component
1023 of the Hg captured on the first filter was GOM. Inclusion or removal of the first in-line filters did
1024 not materially alter calculations.



1025

1026 **SI Figure 4.** Hg on first in-line CEM filters (red circles) versus following downstream filters (open diamonds and
1027 regression line), during the 5 GEM permeations. These first filters were not used in calculations of GEM uptake, on
1028 the strong suspicion they were capturing a small component of residual RM.

1029