

Interactive comment on “Evaluation of cation exchange membrane performance under exposure to high Hg^0 and HgBr_2 concentrations” by Matthieu B. Miller et al.

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Response to Major Issues:

1. In response to the concern that no standard reference material is used during the acid-digestion analysis:

Mercury standards were in fact analyzed repeatedly during every CEM filter analysis. In the described method, standard additions of known mercury concentration are analyzed after every batch of 10-12 samples, in what are known as Ongoing Precision and Recovery (OPR) samples. This includes a mercury standard analyzed immediately

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following generation of the calibration curve, and at least one standard analyzed at the end of the entire analysis. Acceptable recovery for these OPR standards is $\pm 10\%$.

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

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

We will address this concern in the text by including a more thorough description of the analytical procedure and providing the specific OPR data for the analyses performed during this study.

2. In response to concerns about pyrolyzer efficiency:

Referee #2 highlights Lynam and Keeler (2002), who suggest that 800 C pyrolysis was perhaps insufficient for determining total mercury from particulate mercury filters, based on lower total Hg recoveries from thermal desorption and pyrolysis versus an acid digestion method.

Firstly, the Lynam and Keeler study deals primarily with particulate mercury, for which pyrolysis temperatures are necessarily higher in order to insure decomposition of the larger masses involved compared to pure gas-phase samples. Secondly, Lynam and Keeler (2002) also suggest that sample matrix interferences may have played a more important role in lower total Hg recoveries during thermal desorption and pyrolysis, via passivation of the analytical gold traps or interference with detection.

Additionally, for determination of RGM Lynam and Keeler (2002) use only a Tekran 1130 denuder module without an attached 1135. Consequently, RGM was determined

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

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

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

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

3) In response to concerns over removal of first in-series CEM filter during GEM permeations:

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

In regard to concerns about undemonstrated GEM sorption at low ambient concentrations, the authors are unfamiliar with any isothermal sorption mechanism whereby lower concentrations of an analyte result in higher rates of sorption compared to higher concentrations. If such a mechanism exists, we would appreciate guidance to the relevant literature.

However, any debate on this point is purely academic. Even when including the first CEM the observed GEM uptake would still be negligible (0.006% overall, 0.017% first filters only). If necessary, the authors see no difficulty including the first CEM in the analysis of GEM uptake, and this discussion can be moved into the text rather than the SI.

4. In response to the concern over unheated Teflon sample tubing length between Line 1 and Line 0:

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

However, the authors maintain that the more important results are obtained from the configuration shown in Figure 1C, in which the length of Teflon tubing from the per-

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meation vial to each of the filter assemblies is exactly the same. In this configuration potential line-loss would be equivalent. Indeed, this is shown by the consistent HgBr₂ loading on the CEM filters on Line 1 and Line 0.

5. In response to a desire for additional experimentation:

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

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

6. In response to concerns about high CEM filter blanks:

It is unclear to the authors how this constitutes a 'major issue' with the work presented in this manuscript.

The authors acknowledge that long sample periods are currently required when using the CEM filters in ambient air sampling. We did not specifically discuss ambient air sampling time requirements because this is not an ambient air sampling study, and the CEM filters are not used exclusively for ambient sampling. Previous work, which is referenced in this manuscript, clearly indicates that the CEM filters are deployed for 2-week (336 hour) sample periods in ambient air.

Putting aside the non-relevance of this concern in regard to the present manuscript, the authors would like to point out that filter blanks reported in this study are in fact lower than in previously published studies using the CEM methodology, and so constitute an improvement in methodology that should alleviate concerns about detection limits rather than exacerbate them.

Response to Other General Concerns:

1. In response to the concern that more caution should be used in the definition of the term reactive mercury (RM):

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

2. In response the concern over the use of HgBr₂ as a surrogate for all “RM”:

The authors acknowledge that the use of HgBr₂ as a lone surrogate for GOM is a limitation of this manuscript. However, the results of the permeation tests using HgBr₂ are positive, and therefore justify ongoing and intensive validation using a host of GOM compounds, under a greater range of conditions. Unfortunately, such expanded experimentation was beyond the scope of this study, but is now the objective of an ongoing fully funded project. If the limited permeation tests described in this manuscript had failed to demonstrate adequate performance of the CEM material, the authors would have duly presented such results and discontinued further use.

The results presented in this manuscript also invite and encourage replication by other researchers and other labs.

3. In response to concerns that the review of the literature in the manuscript is skewed quite favourably to CEMs:

We will certainly round out the literature review to be more even-handed.

Response to Specific Comments:

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

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Correction made

Line 29: “. . .high collection efficiency.” Should be changed to: “. . .high collection efficiency of the target analyte.”

Correction made

Line 35-36: This is where a cautionary description of the use of the term RM should be included.

Correction made

Line 41-42: These reviews do provide a good critique of the Tekran based speciation measurement techniques, but they do not tell the whole story and more literature needs to be discussed here. For example, Maruszczak et al. 2017, describes how adding the zero flushes from GOM analysis to the actual GOM concentrations increases the derived concentrations to agree more closely with alternative measurement techniques and some modelled values. Such advancements as the latter with the previous system should also be discussed to ensure impartiality. Additionally Cheng and Zhang (2017) state: “Other measurements techniques such as mist chambers, nylon and cation exchange membranes [CEMs], and Detector for oxidized Hg, were capable of collecting more GOM than KCl-denuders. However, similar to the Tekran instrument, these alternative methods are not immune to sampling artefacts caused by high water vapour and other gases and aerosols.” A similar degree of impartiality would greatly benefit this review of the literature.

Will revise the literature review with greater impartiality

Line 78: The analytical information in parenthesis should be deleted. This is describing another paper in too much detail and not needed here.

Correction made

Line 88: Again as per the comment on lines 41-42 this is ignoring advancements in

other methods and caveats of the CEM methodology.

Will revise

Line 93-95: This information is extremely important and I credit the authors for its inclusion.

Thank you

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

Correction made

Line 121-122: “Each of these materials is known to be chemically inert, virtually non-porous, and to have a low coefficient of friction.” This needs to be referenced.

Reference included

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

Will provide details

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

Both flows were controlled by MFC

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

Can include if necessary

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

Noted

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

Noted

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

Cautionary note added

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

No solar radiation, but fluorescent room lighting during working hours. Anecdotally, more Hg observed downstream of the filters on the Tekran 2537 when lights turned on.

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

Correction made

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

Will revise conclusions

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

Because the main experiments described in this manuscript did not hinge on pyrolyzer performance SI Lines 14-15: What are the reported recoveries of the internal injections compared to the external injections, please provide details (%) and number of checks (n)

Details provided

SI Lines 60-62: This is purely speculation based on almost no evidence. Just as likely is it may be coming off the lines or indeed a little GEM is sorbing either to the CEMs or to something else on the CEMs. None of these scenarios can be fully ruled out using the data presented in these experiments. This statement is too speculative and should be removed

Statement removed

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2018-127, 2018.

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