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Atmospheric Measurement Techniques Discussions

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.

Anonymous Referee #2

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While the quality of writing within this manuscript is very good (a major reason for accepting the quick review), upon a more detailed analysis there are some fundamental concerns with the quality of the science within the manuscript. The experimental design appears rushed and incomplete, to the point that some methodological issues were even brought up by the authors themselves, which could have easily been addressed and experiments repeated were not done. As such I cannot accept it for publication in its current state.

Major issues that require addressing:

1. No standard reference material used to confirm recovery of the acid digestion

method. I have a major concern about the lack of inclusion of reference materials for quality assurance and control purposes. Especially given the elevated recoveries of RM above what measured by the Tekran/pyrolyzer. Without any such assessment how can we rule out contamination from instruments, handling equipment or even uptake of outside Hg into the acid digestates? Blank filters could have easily been spiked with a sediment or soil SRM and analysed to confirm the recovery of the analytical method. Also, in response to this comment, it is not acceptable simply quote another paper that has done this. It needs to be confirmed in the lab and experimental settings used in these experiments.

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

3. Removal of 1st CEM traps from GEM breakthrough experiments. This I totally disagree with. The teflon lines could easily be cleaned by (a) rinsing the lines in an acid solution then DI water and allowing them to dry in zero or very low Hg air and (b) running zero Hg air through the system with CEMs in place before the actual GEM permeation cycles. At this point there should be no RM in the system. Thus for the GEM permeation runs why would you discard the first set of CEM filters without this analysis? There should be no RM in the system and any collected Hg should be

assumed to be GEM inadvertently collected. Again the discussion in the SI is HIGHLY relevant and ignored in the main body of the paper. The first set of CEMs were always higher and not arbitrarily so (as the authors seem to suggest), but this is not mentioned in the main paper only the SI. "We believe it is unlikely that the Hg observed on the first CEM filters results from GEM uptake." The Hg uptake on the first set of filters is attributed to residual GOM in the lines, but if lines were properly cleaned before analysis this would not be the case. This is something that could have been ruled out one way or another through subsequent analysis and again no doing so implies the experiments are incomplete. Furthermore if it the 1st CEMs were picking up "residual RM" from the lines then they would not have seen the dramatic increase in the CEM filter concentration under higher GEM concentrations. GOM was not produced under this scenario and therefore the "residual RM" should not increase, but as SI Figure 4 shows it did increase and exponentially, not linearly.

4. Teflon lines were not heated and line lengths not fully described. Higher recoveries on CEMs could be associated with losses in HgBr2 to the longer inlet line on line 1 as it appears in Figure 1(b). Description of the length of tubing between the switch valve and the pyrolyzer (line 1) and the switch value and the CEMs on line 0 should be included. Any difference in length in unheated lines may also be causing inconsistent recoveries. Heating the lines (common practice in atmospheric Hg monitoring to include GOM in analysis) would reduce any such losses. This is another simple adjustment that would have produced more complete experimentation.

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

6. High blank levels are a concern for background sampling. While blank levels of 50 ± 20 pg may not seem high given the very high concentrations used in these experiments

at background concentrations of RM this could be an issue. Method Detection limits MDL= 3*SD of blanks = 60 pg Method Quantification limits MQL= 10*SD of blanks = 100pg Assume background RM concentration of 10 pg/m3 or 0.01 pg/L Flow rate = 1 L/m This translates to 0.6 pg/hr being sorbed to the CEM, which would require 100 hours of sampling at background levels to exceed just the MDL and about 330 hours to reach MQL. These issues are not currently discussed adequately in the manuscript nor covered by the experimental design of the manuscript.

Other general concerns:

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

2. The use of HgBr2 as a surrogate for all "RM". As I have just mentioned we do not know nearly enough about what the exact species of GOM or PBM (let alone both combined as RM) are. Different species of GOM and PBM are likely to behave quite differently in the atmosphere and indeed on different sorption media. I have concerns that using only HgBr2 as a surrogate (do we even know if HgBr2 is a common atmospheric GOM constituent? – It has been suggested that Br acts as the primary oxidant, but the very reactive HgBr (1+) product has a very short lifetime of less than a second before other more stable Hg2+ compounds are produced through oxidation

by other atmospheric species (Horowitz et al. 2017)) . The data from this manuscript appear to show that CEMs effectively sorb HgBr2, but how do we know they sorb ALL species? Again this emphasizes the concern of using RM - a more generic term - to define sorption of both GOM and PBM. We should be focusing on determining what specific species and complexes that make up GOM and PBM rather than be even less specific and defining everything as RM, based on only injection of HgBr2. Again better acknowledgement of this methodological short-coming is needed to proceed.

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

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,..."

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

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

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, Marusczak 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

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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.

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

Line 88: Again as per the comment on lines 41-42 this is ignoring advancements in other methods and caveats of the CEM methodology.

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

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..."

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.

Line 134: "...an activate charcoal scrubber..." Please provide details of this scrubber: elemental imgregnation (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).

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.

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

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.

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.

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.

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.

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.

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.

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

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)

SI Lines 60-62: This is purely speculation based on almost no evidence. Just as likely

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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

References:

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