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Atmospheric Measurement Techniques Discussions

Interactive comment on "Reactive mercury flux measurements using cation exchange membranes" *by* Matthieu B. Miller et al.

Anonymous Referee #2

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General Comments

This manuscript details mercury flux measurements made over various mining waste materials using dynamic flux chambers (DFC). The main motivation for the paper involves the use of polysulfone cation exchange membranes on the DFC sample lines as a means of collecting gaseous oxidized mercury (GOM) and thereby making estimates of GOM flux from and to the mining waste materials.

After careful reading and consideration of the manuscript, I am afraid that I find the manuscript flawed and that the main conclusions of the paper are built around assumptions of potentially interfering processes that were unmeasured and/or are not as easily dismissed in reality as assumed by the authors.

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Discussion paper

Fundamentally, it is unclear to me how GOM can be emitted from these solid surface materials when nearly all studies find that GOM fluxes are dominantly in the deposition direction. The authors also do not explore in their paper a possible mechanism by which GOM emission could occur. The literature is rich in examples of how GOM is easily and quickly removed from the atmosphere to surfaces (deposited) because of its high reactivity and strong binding with surfaces. The authors point to previous work on GOM flux measurement in their introduction (lines 69-75), but even though a very small number of these studies (e.g., Skov et al. 2006) potentially found small GOM emissions, authors of previous works have attributed those emissions to measurement artifacts and/or the quick oxidation of gaseous elemental mercury emissions, making it merely appear that the fluxes are GOM. The Engle et al. (2005) paper does suggest that GOM emissions may occur with some sort of heterogeneous surface reaction. The authors state their findings are “a unique scientific finding” (line 363), but I feel there are too many confounding factors to confidently believe that this is likely the case. The specifics of why I would say this include: 1. As a first approximation to the suitability of this method for measurement of GOM fluxes, one would expect this method to be assessed against another relatively accepted method used in the published literature to assess fluxes. I could see this as unnecessary if all potentially uncontrolled variables were accounted for, but this is not the case in this paper. 2. The authors rely on assumptions based on previous modelling of the DFC that flow rates are too small to induce the entrainment and potential capture of particles. This seems an overly sweeping comment to me, especially since 1) smaller particles are more easily entrained than larger ones and thus the air flow rate to entrain particles would be particle size-specific and 2) there is no microscopic evidence given at all that particles were not trapped. To me, particle entrainment and capture is actually the most straightforward and most likely reason for what appeared to be, but quite possibly was not, GOM emission. In the paper, the authors have also labeled all of the GOM flux axes in their figures as “reactive mercury” (RM) fluxes, though they refer to the same fluxes in the text as GOM. As per the authors’ own definition, RM includes both GOM and particulate bound mercury

(PBM). This is again suggestive that particulate mercury fluxes may be what are pushing the seeming GOM fluxes. 3. The authors do not suggest a mechanism by which GOM emission could occur. 4. The authors' handling of detection limits is somewhat puzzling and thus it is difficult to be confident that what is portrayed as a detectable flux, really is above the detection limit. Specifically, the authors use the median mass of Hg on CEM filters to arrive at a "practical detection limit". Normally, one would use a measure of variability to arrive at a detection limit, not just a central tendency. From Figure 3, it is apparent that the blank variability is fairly high. If the authors used 3X (limit of detection) and 10X (quantification limit) standard deviation of blank measurements, I would be interested to know how the ability to detect differences in inlet and outlet concentrations would be affected.

Specific Comments

Is it the norm for this journal to not have a "Discussion" section? I found it odd for the Results section to be followed by a Conclusions section.

Line 52-53: "Deposition rates" for GEM are indeed quite variable and dependent on a number of things. This is sentence is oddly written. A low deposition rate does already infer a long residence time and vice versa. Why give a range in "atmospheric lifetime" (including 1 minute), but say that deposition is slow?

Line 55: Does just "rapid deposition of GEM" "suggests that deposition and re-emission on short time scales is an important process driving movement."?

Line 69-73: This is a very large number of articles to reference for a single point. Moreover, many of these articles do not actually directly measure GOM fluxes, but rather sometimes just deposition via passive surfaces and sometimes just concentrations.

Lines 77-79: Is the overall suggestion here that GOM fluxes in a specific direction are important outside of AMDE's but that we just don't know much about it? I'm not a big fan of vague ending sentences like this unless you are indeed going to improve our

"understanding of GOM air-surface exchange PROCESSES".

Line 85: What is the relevance of the unpublished work referenced here?

Lines 97-100: While I did not find the abbreviations overly used in the paper, I don't really see their use. Are the different places on lines 97-98 even important? They are not really differentiated by "place" in the paper. The different types of material are important, but for example, is it really all that difficult to write "cap material" or "heap leach material" or certainly "tailings"? I could see the usefulness of abbreviations in some of the figures, but that important abbreviations could simply be defined in the captions.

Line 114: The authors refer to "previous watering experiments". They should verify that these experiments do not (hopefully) impart any variability into their experimental design.

Line 178: Do you really mean REACTIVE Hg flux? Term mismatch?

Line 204: What mechanistically would cause this to happen in the winter but not the summer? This nuanced way of dealing with blanks does not provide much assurance about control.

Line 234: This is a fairly bold statement, without an explanation as to why it "moves us a step further for understanding GOM flux."

Line 279: Not sure what you mean here by "both in general and in detail".

Line 294: Was it really "much" lower? It would appear statistically insignificantly different from the period at line 289, for TCC measurements, which says it's about 70 +/- 20 pg/m3.

Line 317: After looking at this Eckley et al. (2011a) paper, it appears that they measured only total gaseous mercury fluxes and not anything to delineate GEM from GOM. I also do not see anything about GOM at all in the conclusions of this paper. Your state-

ment here therefore appears incorrect.

Line 335: Is this part about “generally sufficient” really a viable conclusion? Many of the 24-hour measurements on the lower concentration materials were not reconcilable (e.g., figure 5). There are also concerns about the handling of detection limits as per my previous comments.

Line 337: Until an absence of particles can be confirmed, I would not advocate for increasing the flow rate.

Line 343-344: That particles were not entrained is more an assumption than a conclusion in this paper. There were no direct measurements.

Line 344-345: GOM concentrations are dominated by GOM?

Line 346: The authors seem to be conflating PBM as a possible fraction of GOM, which it is not.

Line 347: I’m not sure I follow the writing in the paragraph exactly, because what about small particles (i.e. < 0.8 microns)? Is this paragraph about trying to extract out the possibility of a particulate Hg influence? It does not succeed as currently written.

Line 350: Just "unlikely"? This is a conclusions paragraph and none of these measurements were made.

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