

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

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This is a well-written study in mercury chemistry and geochemical cycling across the atmosphere-terrestrial boundary, an area of much uncertainty and debate. Nonetheless, Flux measurements are difficult measurements to make and often produce variable results in regularly monitored gases (e.g. CO<sub>2</sub>) due to variability in the measurements of micro- and macro- movement of air (vertically and horizontally) and the gases themselves (1,2,3). The measurement concerns of these parameters stem from differing instruments (and their quality assurance and control protocols), data handling, corrections, and calculations, and even differing personnel (1,2,3). Considering the current study focusses the ultra-trace level fluxes of GOM (ppqv) that the authors themselves discuss as being notoriously difficult to measure just in terms of concentrations,

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I have concerns about the validity of the results and the conclusion made. As such, for the following reasons I would have to reject the study:

(i). What is the mechanism for GOM emissions from the substrate? There is no discussion on what might be driving low-volatility GOM compounds from a relatively stable state in the solid phase, sorbed (physically or chemically) to the substrate into the gaseous phase as Hg<sub>2</sub><sup>+</sup>. This is difficult to envisage thermodynamically. There is substantial discussion in the literature of Hg<sub>2</sub><sup>+</sup> photoreduction or biotic reduction and re-emission from soils and aqueous bodies, but the flux of Hg is Hg<sub>0</sub> not Hg<sub>2</sub><sup>+</sup> (e.g. 4,5,6). I cannot find literature describing the scenario required for the authors' conclusions, which leads to point (ii).

(ii). In lines 161-163 the authors state that particle entrainment is not expected. While the ideal modeled scenario shows reasonable laminar flow within the flux chamber itself (7), perfectly laminar, non-turbulent flow is less likely real deployments due to substrate, chamber, and flow imperfections. Furthermore, the ideal modeled scenario in Eckley et al. (7) shows the highest flow rates within the chamber are always at the surface of the substrate. These factors suggest there is potential for the chamber to generate suspension of particles. These particles (potentially carrying mercury) can then stick to the CEMs. This may include particles finer than 0.8 μm if they display any affinity for the CEM. If this occurs then the CEMs are not measuring GOM fluxes, but are instead measuring a GOM/PBM signal generated by the chamber itself. Only a small number of particles from these heavily contaminated substrates will cause a significant artefact in the flux signal. This must be categorically confirmed or denied before these fluxes can be discussed further. High resolution microscopy to observe the surface of the CEMs before and after deployment may present a means to determine the presence of any particles.

(iii). The uncertainty of the sampler is not rigorously described for GOM air concentrations, let alone for flux measurements. Uncertainty in this study seems to be based solely on the median and confidence intervals of the CEM filter blanks. This in itself is a

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problem. Figure 3 shows, as stated by the authors, the blank data to be heavily skewed to the right (as would be expected for blanks). There are blank CEMs with over 200 pg, which would cause a flux measurement with a CEM carrying this much residual Hg to be overstated. The median results in a lower value than the mean in determining the central tendency of the blanks. The mean would be more appropriate to capture the elevated blank concentrations that do exist on some CEMs. All the data on the mass of Hg in blanks and the samples (not just fluxes, but include pg of Hg per CEM) should be included in the supplemental so readers can make a better assessment of the data as a whole. Moving on, what is the overall uncertainty of the CEMs for measuring GOM? What is the accuracy and precision of these measurements? Without this overall uncertainty (and solely the blank uncertainty) we cannot be sure the differences do not fall within the uncertainty of the full sampling methodology.

(iv). I do not agree with the removal of 44% (7/16) of measurements for LTL and TCC sediments because the results were below detection limits. These remain results and should be included in the analysis and discussion.

(v). GOM or RM? There are references to both these descriptors within the manuscript. All the figure captions and axes labels refer to RM, yet throughout the text the authors make the case for GOM. Maybe this is an oversight, but quite an important one considering the context of the study and does suggest the authors have had some back-and-forth on which term is most appropriate.

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