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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.

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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.

Response: Thank you.

Nonetheless, Flux measurements are difficult measurements to make and often produce variable results in regularly monitored gases (e.g. CO2) 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 han-

dling, 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, I have concerns about the validity of the results and the conclusion made.

Response: We would like to point out here that all experiments were done by one operator Matthieu Miller who has made many flux measurements from soils over many years and the same sampling procedure was carefully applied for each measurement.

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 Hg2+. This is difficult to envisage thermodynamically. There is substantial discussion in the literature of Hg2+ photoreduction or biotic reduction and re-emission from soils and aqueous bodies, but the flux of Hg is Hg0 not Hg2+ (e.g. 4,5,6). I cannot find literature describing the scenario required for the authors' conclusions, which leads to point (ii).

Response: The mechanism is volatilization. Volatilization of GOM compounds from pure salts has been demonstrated in many studies (see a few refs below). In fact, we can load membranes with salts of GOM compounds by placing them above a container holding them and then verify the compound emitted using an ion chromatograph. We have added some references that point to this in the paper in the introduction.

Finley, B. D.; Jaffe, D. A.; Call, K.; Lyman, S. N.; Gustin, M., Development, testing, and deployment of an air sampling manifold for spiking elemental and oxidized mercury during RAMIX. Submitted to Environ. Sci. Technol. 2013.

Landis, M. S.; Stevens, R. K.; Schaedlich, F.; Prestbo, E. M., Development and Characterization of an Annular Denuder Methodology for the Measurement of Divalent In-

organic Reactive Gaseous Mercury in Ambient Air. Environ. Sci. Technol. 2002, 36, (13), 3000-3009.

Lyman, Seth; Jones, Colleen; O'Neil, Trevor; Allen, Tanner; Miller, Matthieu; Gustin, Mae; Pierce, Ashley; Luke, Winston; Ren, Xinrong; Kelley, Paul (2016) Automated Calibration of Atmospheric Oxidized Mercury Measurements Environmental Science and Technology 50 12921-12927 DOI: 10.1021/acs.est.6b04211 Huang J., Miller M.B., Weiss-Penzias P., Gustin M.S. 2013 Comparison of Reactive Mercury Measurements Made with KCl-coated Denuders, Nylon Membranes, and Cation Exchange Membranes Environmental Science and Technology, 47: 7307-7316. DOI: 10.1021/acs.est.5b00098 McClure, C. D., Jaffe, D. A., Edgerton, E.S.: Evaluation of the KCl Denuder Method for Gaseous Oxidized Mercury using HgBr2 at an In-Service AMNet Site, Environ. Sci. Technol., 48 (19), 11437-11444, 2014. Here is the text added: "The potential for GOM volatilization from surfaces has not been quantified; however, we know that GOM can be emitted from salts of a variety of GOM compounds including HgCl2, HgBr2, HgO, HgSO4, and Hg(NO3)2 (Finley et al., 2013; Landis et al., 2002; Lyman et al., 2016; Huang et al., 2013; McClure et al., 2014). Because of rapid reactions observed during the Reno Atmospheric Mercury Intercomparison Experiment (RAMIX) (Gustin et al., 2013), methods to measure GOM at a short time resolution are needed."

(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 _m 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.

Response: An adaptation of the below has been added to the paper.

Based on the computational fluid dynamic modeling in Eckley at al. (2010), at 1 Lpm there is turbulence in the DFC, mainly near the entrances and exit. Based on the dimensions of the DFC, the friction velocity was on the order of 10-4 to 10-3 m s-1 in the flow range of 1 to 2 Lpm (Professor Jerry Lin, Lamar University-College of Engineering, Personal communication 18 February 2019). Gillette (1988) reported, in a paper that focused on trying to understand the generation of dust, threshold friction velocities for agricultural soils. Threshold friction velocity for wind erosion corresponds to the minimum wind stress needed to overcome forces holding soil particles in place. Experiments in Gillette (1988) were done using a portable wind tunnel using a variety of soils. (Dr. Heather Holmes, University of Nevada-Physics, Personal communication, 18 February 2019).

Based on this information, friction velocity for the flux chamber under operating conditions during our experiment were 2 orders of magnitude lower than those determined for a variety of soils (Gillette, 1988). In addition, as mentioned in the paper, at the onset of the GOM flux experiments, substrates were undisturbed for $\sim$3 years, and were completely dry and well compacted/consolidated from previous watering experiments. Lastly, similar values were obtained for repeated experiments. Based on these pieces of information the potential for particle entrainment and suspension in the chamber was unlikely, and it is thought volatilization of GOM was occurring. Future work should work on further investigating this. Gillette, D.A., 1988. Threshold friction velocities for dust production for agricultural soils. Journal of Geophysical Research 93, 12645–12662.

We do not need to respond to the rest of the comment, because the reviewer corrected his comment in a second response. McLagan second comment "CLARIFICATION: In my previous comment there was a mistake in point (ii). The highest flow rates were not observed at the surface of the substrate in Eckley et al. (2010). But the point remains ideal flow conditions are unlikely in real deployments and there is potential for some particle entrainment. The concern of artifacts from sorbed particles requires resolution by the suggested mechanism or otherwise; at the elevated Hg concentration of the substrate and ultra-trace GOM fluxes, any uptake of particulates to the CEMs would cause greatly effect the GOM flux data."

(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 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.

Response: We feel the median is more appropriate since the mean captures outliers and these were not very abundant as demonstrated in Figure 3. We have added the following regarding the accuracy and precision. GOM was determined after digestion in an oxidizing acid solution, reduction to Hg0, gold amalgamation, and final quantification

by cold vapor atomic fluorescence spectrometry (CVAFS, EPA Method 1631, Rev. E) using a Tekran® 2600 system. The system background Hg signal was determined for every analytical run by analyzing pure reagent solution in the same vials and at the same volume as used for actual filter samples. Total Hg standards (5 to 100 ppb) were analyzed before and after each batch of 10 filter samples to check precision and recovery, and the mean recovery for all Hg standards was 97.2 $\pm$ 5.0 %. Coefficient of variation in concentrations for triplicate filters is typically 1 to 10% with the low value being associated with concentrations > 100 pg.

(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.

Response: Since we were not focusing on scaling up fluxes, but instead were just attempting to understand GOM fluxes we felt removal of data below the detection limit was appropriate. We added a sentence to that affect.

(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-andforth on which term is most appropriate.

Response: We agree there is debate regarding this issue and it still needs work. We prefer to leave as RM in the paper; however, based on the calculations it is unlikely PBM was collected by the CEM sampling the outlet of the chamber; however, it is possible that some RM be it limited was collected by the inlet CEM.

Literature: 1. Foken, T., & Wichura, B. (1996). Tools for quality assessment of surface-based flux measurements. Agricultural and forest meteorology, 78(1-2), 83-105. 2. McGillis, W. R., Edson, J. B., Ware, J. D., Dacey, J. W., Hare, J. E., Fairall, C. W., & Wanninkhof, R. (2001). Carbon dioxide flux techniques performed during GasEx-98.

Marine Chemistry, 75(4), 267-280. 3. Massman, W. J., & Lee, X. (2002). Eddy covariance flux corrections and uncertainties in long-term studies of carbon and energy exchanges. Agricultural and Forest Meteorology, 113(1), 121-144. 4. Lindberg, S. E., Kim, K. H., Meyers, T. P., & Owens, J. G. (1995). Micrometeorological gradient approach for quantifying air/surface exchange of mercury vapor: tests over contaminated soils. Environmental science & technology, 29(1), 126-135. 5. Fritsche, J., Obrist, D., & Alewell, C. (2008). Evidence of microbial control of Hg0emissions from uncontaminated terrestrial soils. Journal of plant nutrition and soil science, 171(2), 200-209. 6. Yin, R., Feng, X., Chen, B., Zhang, J., Wang, W., & Li, X. (2015). Identifying the sources and processes of mercury in subtropical estuarine and ocean sediments using Hg isotopic composition. Environmental science & technology, 49(3), 1347-1355. 7. Eckley, C. S., Gustin, M., Lin, C. J., Li, X., & Miller, M. B. (2010). The influence of dynamic chamber design and operating parameters on calculated surface-to-air mercury fluxes. Atmospheric Environment, 44(2), 194-203.

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