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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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Received and published: 10 February 2019 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

Response: We are sorry to hear this reviewer feels this way.

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.

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 Inorganic 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

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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."

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.

Response: Unfortunately, there is not currently a method to compare with ours since the only alternative is using KCl denuders that have been demonstrated to be inadequate for quantifying GOM.

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

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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 easily entrained.

Response: An adaptation of this response 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

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production for agricultural soils. Journal of Geophysical Research 93, 12645–12662.

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