Response to comments on “Global Observations and Modeling of Atmosphere-Surface Exchange of Elementary Mercury – A Critical Review” *by* W. Zhu et al.

We thank the reviewers for their thoughtful and constructive comments that help improve the quality of our manuscript. We have incorporated the reviewers’ suggestions in the revised manuscript. Our point-to-point response to the reviewers’ comments are shown below.

Anonymous Referee #1:

Overall comments:

Overall this is a very well written and fully researched review paper. In addition to simply reviewing existing studies, this paper performs original analysis of the compiled datasets in order to make large scale observations. This paper provides a comprehensive assessment of the current understanding of the atmospheric surface exchange of Hg and recommend it for publication in Atmospheric Chemistry and Physics.

The only complicating factor with the publication of this paper is that a separate group published a fairly similar paper very recently: Agnan et al., New Constraints on Terrestrial Surface-Atmosphere Fluxes of Gaseous Elemental Mercury Using a Global Database. ES&T 2016.

Given the similarities in objective and scope, I think this paper by Zhu et al, needs to: 1) acknowledge this separate paper in results and discussion, and 2) specifically identify how their paper is unique from Agnan et al., 2016, and 3) discuss similarities and differences in the two papers findings.

Response: We deeply appreciate the reviewer for the supportive comments and constructive suggestions to our manuscript. We have recognized and review the paper by Agnan et al. (ES&T 2016); and agree with the reviewer that a more robust discussion pointing the specific contribution of this paper in addition to the paper by Agnan et al. The similarity of the two papers are mainly on the overlap on existing literature on Hg flux measurement. The major differences between the two papers are: (1) approaches in the data compilation and synthesis (e.g., the statistical treatments), (2) the coverage of flux data over different landuses (soil, forest, snow, freshwater, and ocean in this paper as compared to terrestrial surfaces in Agnan et al.), (3) the inclusion of mechanistic discussion on flux quantification approaches (e.g., enclosure and micromet measurements) and air-surface exchange processes (e.g., confounding influences by environmental factors), (4) the inclusion of flux modeling approaches and scale-up of flux data for global cycle implications, and (5) the inclusion of more up-to-date field data and exclusion of laboratory data in the synthesis.

In the revised manuscript, we have provided an additional section to recognize the contribution by Agnan et al (2016) and laid out the differences of the two papers, cf. line 82-88. We have also cited Agnan et al. (2016) in other parts of our manuscript (line 284-293, line 498-501, line 603-605, line 648-649).

Specific comments:

Comment #1: Line 261: Very interesting result. Glad to see this analysis. A little more information is needed. The samples sizes are 229 and 39, but it is not clear if these numbers represent daily average values, hourly values, etc. A little more discussion about what constitutes a measurement would be helpful. Also, within the <0.3 ug/g cutoff, were there significant differences in the Hg concentrations between DFC and MM areas? If not, this would help build the case for the analysis.

Response: We thank the reviewer for pointing this out. The information regarding the measurement conditions have been added (line 271-272). Because the total Hg concentrations in soil substrates are frequently not reported in the literatures, particularly in those studies from background sites, it is not reliable to compare the substrate Hg concentrations between DFC and MM measurements due to the small available sample sizes.

Comment #2: Line 262: Why was 0.3 ug/g used as a cut-off point?

Response: The use of 0.3 $\mu g\ g^{-1}$ as the threshold of less human activity influenced background surfaces is based on investigation of background concentration from literatures and in line with the criteria used in Agnan et al. (2016). More important, Hg in a relatively low level surfaces are in general homogeneous than contaminated sites (Gustin et al., 1999), which reduced the uncertainty raised by footprint differences in comparing DFC and MM techniques.

Agnan, Y., Le Dantec, T., Moore, C. W., Edwards, G. C., and Obrist, D.: New constraints on terrestrial surface–atmosphere fluxes of gaseous elemental mercury using a global database, Environ. Sci. Technol., 50, 507-524, 2016.

Gustin, M. S., Lindberg, S., Marsik, F., Casimir, A., Ebinghaus, R., Edwards, G., Hubble-Fitzgerald, C., Kemp, R., Kock, H., Leonard, T., London, J., Majewski, M., Montecinos, C., Owens, J., Pilote, M., Poissant, L., Rasmussen, P., Schaedlich, F., Schneeberger, D., Schroeder, W., Sommar, J., Turner, R., Vette, A., Wallschlaeger, D., Xiao, Z., and Zhang, H.: Nevada STORMS project: Measurement of mercury emissions from naturally enriched surfaces, J. Geophys. Res.-Atmos., 104, 21831-21844, 1999.

Comment #3: Line 288: change matters to matter.

Response: It has been changes accordingly.

Comment #4: Line 285: Two factors that have been shown to affect soil-air Hg fluxes are grain size and soil disturbance. Only a couple of studies have shown this, but may want to consider including these two factors in the discussion if the goal is to be comprehensive as possible.

Response: We thank the reviewer for pointing out the two factors that are not as extensively studied: grain size and soil disturbance, and have provided the discussion in the revised manuscript, line 326-329.

Comment #5: Line 339. There is a paper by Mazur et al. 2014 in Science of the Total Environment that has a similar focus: the impact of forestry operations on surface-air Hg fluxes.

Response: The results of Mazur et al. (2014) has been incorporated in the discussion and the reference has been added in the citation list, cf. line 348-349.

Comment #6: Line 346: Suggest changing to "more recent" instead of just "recent". This idea has been around for more than a decade now.

Response: It has been changed.

Comment #7: Line 352: remove excess Hg0.

Response: The excess Hg^0 has been deleted.

Comment #8: Line 422: Need more information to support this statement. Earlier the text focuses on photo-pathways and this is a big jump without sufficient explanation.

Response: We agree with the reviewer on the suggestion. Previous statement was incorrect as showed in Fig.5, which has been corrected and reworded as "Both dark abiotic and biotic redox transformations are suggested to be involved (Fig. 5)", cf. line 435-436.

Comment #9: Line 472: remove "got flux calculation".

Response: It has been removed.

Comment #10: Line 476: in "the" literature

Response: It has been inserted into the text.

Comment #11: Line 558: This paragraph should also discuss the work of Kuiken et al, 2008 part 1, which shows the opposite trend....lower emission in summer due to drier conditions and lower light from more leaf cover. In the scaling paper, Hartman et al, 2009 comes to the same conclusion.

Response: We thank the reviewer for pointing this out. The phenomenon of low flux in summer as a result of low light and drier conditions has been added in the discussion, cf. line 578-580.

Comment #12: Line 601. Double check that Gustin et al, 2003 used a multivariate approach using soil Hg, flux and solar radiation. Or did that paper look at these variables separately.

Response: We thank the review for the cautionary remark. We have checked into Gustin et al. (2003) and discussed the influence of those environmental factors separately [page 345 and 347] with the citation.

Comment #13: Line 700. Remove "in"

Response: It has been removed from the text.

Comment #14: Line 713. This is a great summary of knowledge gaps, glad to see this in the paper.

Response: We thank the reviewer for the positive comment.

Anonymous Referee #2:

Overall comments:

This paper is a thorough review of measurement and modeling studies of elemental mercury. The depth and extent of the analyses of available data does indeed make this a critical review rather than just a literature review. The discussion on the advances in the measurement techniques is beneficial. This paper provides a necessary addition to the scientific community's GEM literature and aids in furthering our understanding of the air-surface exchange of atmospheric mercury. With some minor editing on a technical scale, I recommend the publication of this paper in Atmospheric Chemistry and Physics.

I agree with Reviewer #1's comments regarding the paper by Agnan et al. (2015). The only discussion on their paper was relating to the measurement method. It would be interesting to see a discussion on the findings of the two papers and how they complement each other.

Response: We deeply appreciate the reviewer for the supportive comments and constructive suggestions. Our special thanks to the reviewer for providing detailed editorial remarks. As discussed in our response to reviewer #1, we have recognized the review paper by Agnan et al. (ES&T 2016) and agree with the reviewer that a more robust discussion pointing the specific contribution of this paper in addition to the paper by Agnan et al. The similarity of the two papers are mainly on the overlap on existing literature on Hg flux measurement. The major differences between the two papers are: (1) approaches in the data compilation and synthesis (e.g., the statistical treatments), (2) the coverage of flux data over different landuses (soil, forest, snow, freshwater, and ocean in this paper as compared to terrestrial surfaces in Agnan et al.), (3) the inclusion of mechanistic discussion on flux quantification approaches (e.g., enclosure and micromet measurements) and air-surface exchange processes (e.g., confounding influence by environmental factors), (4) the inclusion of flux modeling approaches and scale-up of flux data for global cycle implications, and (5) the inclusion of more up-to-date field data and exclusion of laboratory data in the synthesis.

In the revised manuscript, we have provided an additional section to recognize the contribution by Agnan et al (2016) and laid out the differences of the two papers, cf. line 82-88. We have also cited Agnan et al. (2016) in other parts of our manuscript (line 284-293, line 498-501, line 603-605, line 648-649).

Specific comments:

Comment #1: Line 108: Is this a possible typo that <1 Hz is considered a higher frequency?

Response: We thank the reviewer for pointing it out and would like to clarify it. The text has been rephrased as "Later on, monitoring ambient air Hg0 with relative higher frequency (up to 1 Hz) was achieved by using

Lumex RA-915+ Zeeman atomic absorption spectrometry (AAS) analyzer operating without pre-concentration", cf. line 113-114.

Comment #2: Line 113: The use of "but" in this sentence suggests that the higher detection limit of 0.35 ng m^{-3} is a negative aspect, but could that sensitivity be considered a benefit of this sensor over previous ones?

Response: Yes, the detection limit at 0.35 mg m^{-3} is a negative aspect in terms of analytical accuracy for Hg vapor because of the low concentration gradient typically observed in most flux quantification techniques (typically <0.4 ng m^{-4}, Zhu et al., 2015). However, the high frequency of this sensor (25 Hz) is a benefit among available Hg vapor detection techniques because it offers the possibility of using eddy covariance method to measure Hg flux even it is limited over contaminated surfaces only, e.g., Pierce et al., 2015.

Pierce, A. M., Moore, C. W., Wohlfahrt, G., Hörtnagl, L., Kljun, N., and Obrist, D.: Eddy covariance flux measurements of gaseous elemental mercury using cavity ring-down spectroscopy, Environ. Sci. Technol., 49, 1559-1568, 2015.

Zhu, W., Sommar, J., Lin, C. J., and Feng, X.: Mercury vapor air–surface exchange measured by collocated micrometeorological and enclosure methods - Part I: Data comparability and method characteristics, Atmos. Chem. Phys., 15, 685-702, 2015.

Comment #3: Lines 185-187: This sentence, while accurate, discusses the lack of the ability of this sensor at background sites. This study however was over Hg-enriched soils and the sensor performed well over Hg-enriched sites. Would it be useful to note this as an advantage to this method considering the high number of sites that are Hg-enriched?

Response: We appreciate this insightful comment. It is indeed worth highlighting the possible application of CRDS-EC over Hg-enriched sites. The discussion has been revised to (cf. line 190-193):

Pierce et al. (2015) reported the first field trial of CRDS-EC flux measurement over Hg-enriched soils with a flux detection limit of 32 ng m^{-2} h^{-1}, offered the opportunity for high frequently monitoring Hg^0 flux from Hg-enriched surfaces. However, the present state of development of CRDS-EC must be further advanced for Hg^0 flux measurement at most, if not all, background sites.

Comment #4: Line 547: Perhaps consider mentioning why the fluxes would be higher in Europe than East Asia prior to 2002 and during summer and/or daytime.

Response: We agree with the reviewer on the suggestion. Detailed discussion of high fluxes over freshwater bodies in summer and daytime have been discussed in Section 3.3 and 4.3.2. We have also revised the sentence to (cf. line 561-563) “The flux over freshwater bodies in Europe is somewhat higher than those measured in East Asia (6.5 vs. 4.6 ng m^{-2} h^{-1}, p=0.40, ANOVA). These data were obtained mostly prior to 2002 (n=9) or during summer time and daytime (n=8) subject to higher blank larger extent of photo-reduction and evaporation.”

Comment #5: Line 558: There are some studies that suggest the opposite (e.g. Lee et al., 2000; Fristche et al., 2008).

Response: We thank the reviewer for the suggestion, the discussion of opposite seasonal flux variation has been provided in the revised manuscript with the corresponding references, cf. line 578-582.

Comment #6: Lines 577; 593; 612; 627: The titles of the subsections in Section 4.4 include statements. Does this possibly change the flow of the paper?

Response: We agree with the reviewer that the full statements in the titles are somewhat distracting. In the revised manuscript, the subtitles have been incorporated into the text to maintain the flow of the text.

Comment #7: editorial comments.

Response: We deeply appreciate the reviewer’s generous effort to provide the detailed editorial remarks, which significantly improved the readability of our paper. These specific technical corrections have been carefully addressed and added in the revised manuscript. The revised words/sentences have been marked in blue in the revised manuscript.