

Interactive comment on “Air–surface exchange of Hg⁰ measured by collocated micrometeorological and enclosure methods – Part 1: Data comparability and method characteristics” by W. Zhu et al.

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Anonymous Referee #1: We thank the reviewer for the thoughtful and constructive comments that improved the readability of our manuscript. We have incorporated the recommendations in the revised manuscript. Our point-to-point response to those comments and questions is given below (in blue). Corresponding revision was added in the manuscript.

Overall comments: The solar radiation was measured at 3-m height; we all know so
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lar radiation (here I am referring to UV light, especially for UV-B) is a critical factor for Hg emission from soil, and penetration of solar radiation under the chamber is not 100%. For thick poly-carbonate chamber, the UV penetration could be down to 30%. Do you think the solar radiation measured at 3-m height can represent the UV light intensity in the chamber? Different DFCs were made by different materials, quartz (I guess this should be the thick one) and poly-carbonate. I understand it might be complicated, is it possible for the authors to include discussions related to this question, and to report the penetration of UV-B under DFCs cover? Response: We agree with the reviewer that outside solar irradiation is not representative of the chamber internal irradiation condition. This is a limitation of DFC method because an ideal chamber material that allows both light transmission and manufacturability does not exist. The UV-B transmission for quartz chamber (5 mm) ~90%, and ~30% for polycarbonate. The application of polycarbonate sheet for our NDFC fabrication is due to the NDFC is designed with strict physical shape and dimension, which does not permit the use of thin Teflon film and quartz (Lin et al., 2010). For the point raised by the review of different material used here, we developed an algorithm based on total solar radiation to correct the flux bias due to light loss, which was presented in our companion paper Part 2. The flux bias has been corrected for the data published in this paper. Lin, C.-J., Zhu, W., Li, X., Feng, X., Sommar, J., and Shang, L.: Novel dynamic flux chamber for measuring air–surface exchange of Hg⁰ from soils, *Environ. Sci. Technol.*, 46, 8910–8920, 2012. Zhu, W., Sommar, J., Lin, C.-J., and Feng, X. B.: Air-surface exchange of Hg⁰ measured by collocated micrometeorological and enclosure methods - Part II: bias and uncertainty analysis, *Atmos. Chem. Phys.*, Submitted for publication.

Specific comments: Comment #1: The authors used many abbreviations in the manuscript, could the authors add an overall table to make this clear? Response: the abbreviations used in this paper was aimed to clarify the flux calculation from different methods. We have clearly explained the symbols below each equation in the revised manuscript, and those symbols were not frequently used in the discussion part.

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Comment #2: Page 22275, line 4, “Mercury(Hg).” a reference is needed
Response: a reference of Lindqvist et al., 1991 has been added.

Comment #3: Page 22276, line 3, suggest to use other word instead of “realized”
Response: the “realized” was changed to “accomplished”.

Comment #4: Page 22277, line 4, correct “per se” Response: the word “per se” was deleted, see the sentence “Measured fluxes are estimates of unknown quantities of air-surface exchange under field conditions and a reference technique for validating the estimates does not exist.”

Comment #5: Page 22278, line 20, friction velocity, does this mean the atmospheric boundary layer u^* or the u^* in the NDFC? Response: the u^* represents of “atmospheric boundary layer u^* ”, it has been clarified in the text.

Comment #6: Page 22279, line 3, “whole-air type” what does this mean? Response: the “whole-air type” refer to a type of REA systems where a single inlet line is used to draw (whole) air at a high speed to the REA apparatus, where sub-streams are conditionally sampled.

Comment #7: Page 22282, line 3, “DOY” spell out, is this day of year? Response: it is “day of year”. It has been added into the manuscript.

Comment #8: Line 2-11, can the authors make a clear table to include all the information? Response: we have revised Table 1 with added information. We reorganized this part to make it more concise. See the text.

Comment #9: Line 21, why is the flow rate 0.75 Lpm? The 2537 cycle here is 5-mins, why not use 2.5 mins to obtain higher resolution data than 5 mins? Response: MM-derived flux require averaging times of 20 min and up depending on the site settings (topography, meteorological conditions etc.). At this site, we have identified 20 min as a suitable time (Sommar et al., 2013). As described in the same paper, coupling our REA system with 2537 only allows the analyser to be operated at 0.75 L/min due to

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back pressure. To get as robust samples as possible given the premises, 5-min is the sampling duration of choice for the REA and gradient-based system. Sommar, J., Zhu, W., Shang, L., Feng, X., and Lin, C.-J.: A whole-air relaxed eddy accumulation measurement system for sampling vertical vapour exchange of elemental mercury, *Tellus B*, 65, 19940, 2013.

Comment #10: Page 22283, line 6-10, could the authors add some details for the operation of synchronized DFCs? If I understand this correctly, one 2537 was used to measure Hg concentration in following processes: 1. inlet of TDFC for 5 mins (2.5-min cycle) 2.outlet of TDFC for 5 mins. 3. inlet of NDFC for 5 mins. 4. inlet of NDFC for 5 mins. Response: Yes, it is. We have reorganized this part in the manuscript.

Comment #11: Line 26-27, did the authors measure Hg concentrations at same location to determine system blank for MM methods? Response: We did very careful and thorough work on evaluating all the systems blanks. Not mentioned, the MM system blanks were evaluated by sampling zero air before and after the experiments (line 21-23). No significant contamination/carry-over bias was present in either MM-system. More important is the evaluation of MM systematic channel bias (including blanks) that is accounted for in Part I and II.

Comment #12: Page 22284, line 15-17, what parameters were used in this study? Response: we used flux observed from different methods and environmental parameters.

Comment #13: Line 20, “oC” for temperature? Response: thank you for correcting, we changed o to oC.

Comment #14: Page 22285, line 26, I understand this might need additional work; however, conditional probability function (CPF) can better present the data than Hg concentration wind rose. This is just a suggestion. Response: We agree with the reviewer that conditional probability function can better address the Hg concentration variability. For this study, we focus on flux method comparison to present the characteristic of each method. We thank the reviewer for the great suggestion, we will do

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conditional probability function analysis in the further work on atmospheric Hg distribution in the North China Plain.

Comment #15: Page 22286, line 10-11 and 14-15, these two sentences are similar please rephrase. Response: thank you for pointing out this. The sentence of line 10-11 has been removed and incorporated into line 14-15.

Comment #16: Line 16, the temporal variation of what? Response: the temporal variation of Hg⁰ flux, it has been added to the manuscript.

Comment #17: Line 16-17, please re-write, it is difficult to follow. Response: to consolidate the explanation, Line 16-17 has been deleted and incorporated into pg 92, Line 14-16.

Comment #18: Line 24, what the IQR is? Please spell out. Response: the IQR means interquartile range, it has been spelled out in the manuscript.

Comment #19: Page 22288 line 1, was, however, 3.5 times higher than that “measured” by TDFC. Here, I have some questions in series. What are the penetration of UV-B through thick quartz chamber and thin polycarbonate film? If the numbers are different, how did the authors compare the data measured by these two different chambers? Is there any way to correct this influence? Can this help to explain that NDFC measured higher flux than the number measured by TDFC? Response: We agree with the reviewer that UV-B has a significant effect in stimulating Hg⁰ emission. Q1: The thickness of the quartz is ~5 mm, the UV-B transmission for such a chamber is ~90%. However, the UV-B transmission of the PC chamber is ~30% (Lin et al., 2010). Q2: The choice of chamber material is crucial in DFC measurement. For chamber fabrication quartz, thin Teflon film, and polycarbonate sheet have been used in the previous studies. For the novel chamber in this study, the physical shape is critical in obtaining an optimal performance. Quartz and thin Teflon film were found not suitable for fabrication. The data presented in this study (Part-1) was corrected for flux bias, a calculation algorithm presented in our Part-2 paper, albeit the solar radiation correction

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was treated as total irradiation (not separated into UV-B and visible light) measured by a pyranometer, we think this is the most direct way to compare the chamber data. The measurement results presented in Fig. 6 demonstrated even if the NDFC UV-B penetration is lower than the TDFC, the measured fluxes were very comparable. Q3: We have developed an algorithm (multivariate regression model) to correct the flux for bias due to attenuation of radiation by the chamber material. Q4: The data presented here has been corrected for the flux bias (Zhu et al., 2014), it clearly demonstrated that NDFC tendency observe a higher flux due to the internal controlled flow condition, “In the present study, TOT of TDFC is 50% lower than that of the NDFC. Moreover, the footprint of the traditional type is in square measure merely two thirds of the NDFC and the mass transfer, an elevation in fluxes derived by this type is expected”, however, the direct measured flux is comparable. Lin, C.-J., Zhu, W., Li, X., Feng, X., Sommar, J., and Shang, L.: Novel dynamic flux chamber for measuring air–surface exchange of Hg⁰ from soils, *Environ. Sci. Technol.*, 46, 8910-8920, 2012. Zhu, W., Sommar, J., Lin, C.-J., and Feng, X. B.: Air-surface exchange of Hg⁰ measured by collocated micrometeorological and enclosure methods - part II: bias and uncertainty analysis, *Atmos. Chem. Phys.*, Submitted for publication.

Comment #20: Line 10, how did the authors normalize the data? Response: we normalized the Hg⁰ gradient using Hg⁰ concentration difference between the two sampling level divided by the corresponding height difference. The unit of the presented normalized gradient is ng m⁻⁴, i.e. ng m⁻³ m⁻¹.

Comment #21: Line 13, what does “marker’s color” mean? I understand the authors present the data in another paper; however, could the authors briefly discuss the uncertainties in this paper? Response: Thank you for the suggestion. The “marker’s color” means the turbulence data quality. We have described the data quality segregation in the manuscript and detailed those information in the Part 2 paper.

Comment #22: Line 21, is this real “observed flux” or estimated flux? Response: the “observed” has been corrected with “estimated”.

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Comment #23: Page 22289, line 5-7, based on the Agüres, the Hg emission wasn't enhanced when the precipitation occurred? This is different from previous Hg emission measurements; most studies have reported Hg emission was enhanced when water was applied, any thoughts? Response: The key component in all MM-flux system is the 3-D sonic anemometer. When its sending head or the receiving heads become wet, the sensors may not function properly (indicated by diagnostic warnings). It takes a while for the sensor to start to work again after a rainfall even if water droplets are manually wiped by the operator. There is therefore a gap in MM-data for this period. For the TDFC, during the shower, we did not move the chamber, so there is no tendency of increasing fluxes. After the rain stopped, we moved both NDFC and TDFC to the surrounding area. The shower lasts for ~10h, it was around midnight when the anemometer got dry and we relocated the DFCs, we did not observed large increase peak like those reported after immediate rain (Lindberg et al., 1997), this could be because of low temperature when relocate the chamber. Lindberg, S. E., Zhang, H., Gustin, M., Vette, A., Marsik, F., Owens, J., Casimir, A., Ebinghaus, R., Edwards, G., Fitzgerald, C., Kemp, J., Kock, H. H., London, J., Majewski, M., Poissant, L., Pilote, M., Rasmussen, P., Schaedlich, F., Schneeberger, D., Sommar, J., Turner, R., Wallschläger, D., and Xiao, Z.: Increases in mercury emissions from desert soils in response to rainfall and irrigation, *Journal of Geophysical Research-Atmospheres*, 104, 21879-21888, 1999.

Comment #24: Line 18, what does the sampling mean here? Sampling method? Sampler? Response: the "sampling" at here do mean "sampling method", we have corrected this in the revision paper.

Comment #25: Line 20-27, just a comment, sources and sinks of Hg from surfaces are related to surface types, surface conditions, Hg soil content, and the environmental conditions. Response: We do agree with the reviewer. That's why a large area with homogeneous surface was chosen for the experiment.

Comment #26: Page 22290, line 23-26, could the authors please explain this in more
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detail? Response: we have modified this part to make it clearer. It was revised following "However, when the sensible heat flux becomes small (small temperature gradient) approximately at $w m^{-2}$, the correlation coefficient diminishes drastically and the fall-off in slope () implying that MBR flux tendency to be significantly overestimated when the temperature gradient becomes very small. These MBR flux data during small scalar gradient time (often during dawn and dusk transition periods) are of questionable quality and should be considered for omission."

Comment #27: Page 22291, line 25, areal? Response: the "areal" has been corrected with "area".

Comment #28: Page 22294, line 25-27, the reason of a good correlation for integrated \dot{C}_{ux} over time is the way the integrated \dot{C}_{ux} was calculated. The integrated \dot{C}_{ux} at time t was calculated as the \dot{C}_{ux} from $t-1$ to t adding to the integrated \dot{C}_{ux} at $t-1$, therefore, both integrated \dot{C}_{ux} es (MBR and NDFC) are showing increasing trend. This might not be a good way to present the data, the better way to explain the data is to use longer time average (eg. daily, or every three hours) Response: we than the reviewer for the suggestion of compare DFC and MBR flux. In the revised paper, we using deviation of cumulative flux between DFC and MBR flux, see revised figure 12 and corresponding discussion the revised paper.

Comment #29: Page 22295 line 1-2, I am wondering is this possible due to the UV-B influence. Look at Hg₀ concentrations in detail, we can And this surface was functioned as a sink rather than source from 20:00-8:00. I am wondering is that possible the daytime emission was from night deposited? And At 10:00 am, the natural soil surface received enough solar radiation, and showed a peak at 11:00 am then Hg emission started to decrease after that due to lack of available Hg. However, because the penetration of UV-B under chambers was not high enough till 2:00 pm, it peaked at 2:00 pm. I know it is complicated, just some ideas. Response: The DFCs measurement demonstrated that Hg₀ exchange between soil and atmosphere at nighttime 20:00-8:00 is bidirectional. Even the ambient Hg₀ concentration shown a clear diel pat-

tern with decreasing from afternoon to night, we believe that this is primarily due to the regional source. We agree with the reviewer that nighttime deposition could contribute to daytime emission. We have given a hypothesis that MM P1 was emission from the night deposition via frost, dewfall and dry deposition. The processes could be complicated, we have incorporated the reviewer's suggestion into the discussion in section 3.4.2.

Comment #30: Line 15-18, the authors should read Choi and Holsen, 2009 *Environ Pollution*, page 1673-1678. Response: we have added the "Choi and Holsen, 2009".

Comment #31: Page 22296, there is a problem from their PCA results, in Table 3, some factors are only explained by one variable. For example, factor 4 IC#2, this factor is only correlated to REA \dot{C}_{ux} , this cannot help explain the data. People usually selected the factor number once the eigenvalue reaches to 0.9-1, and there is no factor explained by a single variable. It depends on the situation, to reduce the number of factor might not influence the meaning of factors; however, in some cases, in-properly using PCA might mislead the results. I suggest to redo the PCA or move all PCA to SI not emphases in this section. Response: we thank the reviewer for the comment. We agree that the data point may restricted the results of PCA, we have remove the PCA analysis in the revised paper.

Comment #32: Table 3, how many data points were used to run PCA? Response: the data point used for IC #1 and IC #2 is 1218 and 465, respectively. The Table 3 has been moved to supporting information, see Comments #31.

Comment #33: Figure 1, this figure is busy, and the resolution is low, could the authors provide a high resolution one. It is a very good figure, but cannot be read very well. Response: we thank the reviewer for the suggestion, the figure 1 resolution has been changed into a good reading condition.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 14, 22273, 2014.

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