Atmos. Chem. Phys. Discuss., 14, C7398–C7410, 2014
www.atmos-chem-phys-discuss.net/14/C7398/2014/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Air–surface exchange of Hg^0 measured by collocated micrometeorological and enclosure methods – Part 1: Data comparability and method characteristics" *by* W. Zhu et al.

Anonymous Referee #2

Received and published: 25 September 2014

This manuscript presents field comparison of elemental mercury (Hg0) fluxes using micrometeorological (MM) and enclosure methods. The topic is relevant to ACP, and the scientific contribution is significant. However, there are some errors and a number of clarification issues. Moreover, the readability could be improved by further editing. Hopefully this revision will greatly strengthen the scientific contributions of your manuscript. More detailed comments can be found in the following sections.

I. Major comments/suggestions

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Interactive Discussion
Discussion Paper

1. The scientific contribution is of this manuscript is to some extend buried by the writing style, including unnecessary materials in Section 2 (Material and methods), redundancy in the Results and Discussion section, some general statements or incorrect statements, and overlap with Part 2 (Zhu, et al., 2014a). Some clarification and editorial issues are listed in sections II and III. My major concern is the structure of the manuscript. The detailed information of equations and repeated discussion in different sections would be appreciated for a thesis or a report, while a concise style might be more appropriate for a journal paper.

1.1 All general descriptions as well as equations and related explanation in pages 78-81 could be omitted. Interested readers can find detailed methodology descriptions in papers referenced within.

1.2 The manuscript could be shortened by removing sentences simply stating numbers presented in tables, e.g. pg 86, L7-9; pg 88, L20-24; pg 89, L11-14.

1.3 The authors may want to consolidate some subsections to remove redundancy regarding to results and discussion, thus to improve the readability. Some examples are listed below.

Item Occurrences

Correlation between DFC flux and meteorological parameters Pg 86, L11; pg 95, L19

Correlation between AGM and MBR fluxes Pg 90, L22; pg 93, L26

Comparison between TDFC and NDFC fluxes

Before correction similarity Pg 87, L14; pg 87, L26; pg 93, L24

After correction 3.5 times Pg 87, L18; pg 88, L1

Comparison of DFC and MM temporal variation Pg 86, L15-17; pg 92, L14-16

1.4 The overlap between this manuscript and Part 2 seems to be beyond a few lead-

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ins. Those overlaps hinder the ability of each manuscript (this and Part 2) to be a stand-alone paper. My impression is that the readers need to read Part 2 to understand some discussions presented in this manuscript, while the differences within and between DFC and MM methods will be repeated in Part 2 to facilitate the investigation of the causes of discrepancy. For example, the methodology of uncertainty analysis was not presented in this manuscript, but the results were (Fig 4). Similarly, there are conclusions in Part 2 presented in this manuscript without relevant methodology and discussion, for instance, reasons of dissimilarity in the DFC fluxes (pg 87, L1-3), reasons of variability in REA and other MM methods (pg 90, L2-5), reasons of disparate AGM and MRB fluxes (pg 91, 1-20), reasons of flipped AGM and fluxes in the two campaigns (pg 95, L3-13).

1.5 After shortening this manuscript, it would be great to incorporate content currently in Part 2.

2. The so-called NDFC has advantages over the TDFC. However, presentation of the NDFC in this manuscript is a bit confusing partially due to some unfounded statements, e.g.

2.1 Pg 74, L23, "This implicates that the NDFC technique, which accounts for internal friction velocity, effectively bridged the gap in measured Hg0 flux compared to MM techniques." Please provide the methodology to estimate internal friction velocity inside DFCs.

2.2 Pg 76, L17, "a novel designed DFC (NDFC) based on surface wind shear condition (friction velocity) rather than on artificial fixed flow to account for natural shear conditions." Pg 78, L2, "a novel DFC (NDFC) design capable of controlling the internal shear flow over measurement surface (Lin et al., 2012). The NDFC internal flow condition was precisely controlled to relate to the applied flushing flow rate to the atmospheric boundary shear condition (therefore wind condition)". It is not clear how to implement this technique when the flow rate was indeed fixed in the NDFC operation (pg 78, L7)

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and the monitoring of atmospheric boundary shear condition is not mentioned. Even with the highly variable friction velocity available, the "precisely controlled" "internal flow condition" "to relate the applied flushing flow rate to the atmospheric boundary shear condition" would need a closed-loop system which was not available in this paper and the NFDC paper (Lin et at., 2012). Those statements also contradict equations 1 and 2 which have a fixed flow rate.

2.3 Pg 86, L16 "DFCs flux was derived from Hg0 mass balance calculation every 20 min, different from the MM flux that relied on atmospheric turbulence processes." This sentence contradicts other statements that the modified DFC taking into account turbulence, e.g. pg 76, "based on surface wind shear condition (friction velocity) rather than on artificial fixed flow to account for natural shear conditions", pg 87, "the well developed turbulence (higher friction velocity, Fig. 2) during daytime caused the corrected Hg0 flux from NDFC flux to be approximately 3.5 times higher than the TDFC flux".

2.4 Pg 88, L2-6, "Given that DFC of conventional types cannot reproduce atmospheric turbulence. . . NDFC is more preferable for the determination of net Hg0 gas exchange over soils." This sentence seems to be over-promoting the NDFC when in fact no DFCs can "reproduce atmospheric turbulence" regardless of corrections.

3. pg 86, L20, "Probability plots of both DFC datasets showed positive kurtosis (3.0 and 4.1) and skewness (1.6 and 2.1) (Fig. 5). As a consequence, the average flux is slightly positive". The reasoning here seems questionable; kurtosis and/or skewness themselves are not related to the sign (positive or negative) of a population or sample mean. The authors may want to clarify the meaning of positive kurtosis and skewness, and rephrase the sentence.

4. Pg 87, L18, "the corrected Hg0 flux from NDFC flux to be approximately 3.5 times higher than the TDFC flux". This assessment seems unfounded. Fig 6 had a slope of 2, i.e. one flux is twice as high as the other, or one time higher. Also, the slope of 1.1 indicates the two DFCs had similar fluxes, thus the corrected NDFC fluxes should

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be one time "higher than the TDFC flux" and the NDFC fluxes when flux >0, but lower when flux<0. Furthermore, Figure 6 caption seems incorrect regarding to the markers. If the discussion refers to Table 1 (2.2 vs. 7.6, 2.5 times higher), please clarify.

5. Pg 93, L23, correlation. Because of the substantial departure from normal distributions (Figures 5 &7; pg 98, L10), the use of Pearson correlation (in tables, figures and main body) should be justified. Alternatively, Spearman rank correlation and Kendall rank correlation could be employed.

6. Pg 94, L23, "Figure 11a and b shows scatterplots of hourly and cumulative flux specifically for MBR vs. NDFC, though the correlation between individual hourly data points is weak, the fluxes integrated over time show strong agreement." Perhaps it should read "Figure 12". Furthermore, the readers might be interested to see if the same could be said with the scatterplots of hourly and cumulative flux for MBR vs. TDFC. More importantly, the correlation of two cumulative fluxes may violate the independency requirement. Because the cumulative fluxes at time t+1 depend on fluxes at time t, the data points are not independent of each other. Consequently, the authors may want to remove the regression equation and r values and to include scatterplots of hourly and cumulative flux for MBR vs. TDFC.

7. Pg 96, L1-15. As presented, the use of PCA seems unnecessary and the interpretation of the PCA results seems questionable. The discussion was focused on correlation among variables which is presented in Table 2, instead of identifying major factors affecting the air-surface exchange processes. In addition, the authors seem to have reached contradicting conclusions, "The environmental variables also significantly modified the gradient-MM fluxes (factor loading > 0.3)", and "Two separate PCA was resolved for gradient fluxes variance (factor 2) .... The two factors are not contributed from the environmental variables (factor loading < 0.1), suggesting that the MM fluxes and their temporal characteristics are likely influenced by turbulent transport processes ..." Furthermore, in both IC1 and IC2, only the first two factors had more than one loading > 0.4. In other words, factors 3-5 in IC1 and factors 3-4 in IC2 failed to

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be valid factors when there is one loading > 0.4 hence that factor only represents one variable. In cases like this, all 4 or 5 factors may become uncertain. This is likely due to the limitation of the dataset. Consequently, I would suggest remove this paragraph.

8. Fig 3. Wind rose. The height of 3 m above ground for meteorological measurements could be too low to represent regional movement of air mass. An alternative could be datasets from a nearby airport or air flow directions from trajectory models with small grids.

9. Fig 3. The pollutant rose as presented offers little information about the distribution of directional concentrations. The authors may want to consider the use of percentiles (e.g. 25%, 50%, 75% and 95%, see Figure 4b in http://www.mdpi.com/2073-4433/4/4/472).

II. Clarification issues

1. Pg 74, L13 & Pg 95, L14, the reviewer did not find any results or discussion about "sensitivity". Perhaps "correlation" is more appropriate.

2. Pg 75, L9-13, "Hg0 is subject to bi-directional exchange between atmosphere and natural surfaces through complex and yet not well understood processes, re-emitting previously deposited Hg back to the atmosphere (Bash, 2010; Gustin and Jaffe, 2010). Recent estimation indicates that annual natural emission accounts for two-thirds of global release of atmospheric Hg (Pirrone et al., 2010)." It is not clear whether "re-emitting previously deposited Hg" is part of the "natural emission". The authors may want to tidy up those loosely defined terms.

3. Pg 75, L19, "representing the smallest scale (< 0.1m2)". 1) in case you were not sure that areas covered any DFCs ever existed were < 0.1 m2, perhaps "in the order of 0.1 m2" could be more conservative, 2) perhaps "representing the smallest scale as the areas covered by the devices are typically in the order of 0.1 m2" could be more appropriate.

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4. Pg 77, last paragraph before section 2. “Real fluxes are per se unknown under field conditions and it is impossible to validate flux measurements by any (reference) technique”. In that case, the reviewer is curious on how to “quantify the bias of the examined flux measurement methods using statistical analyses”.

5. Pg 78, L5, please explain the meaning of “wind condition”.

6. Pg 78, L7, and other places, the term “footprint” in environmental studies often refers to an area much larger than what is covered by a DFC because the inlet lines sample air outside the chambers.

7. Pg 81, L19, “350 km from Beijing”. It would be more informative to state the province and distance to any nearby Hg sources, instead of distance to the capital.

8. Pg 83, L13, the reviewer could not find any description of “EC flux corrections” in this or any other sections.

9. Pg 83, L26, “low blank were observed for both DFCs”, please state whether the DFC fluxes were blank corrected.

10. Pg 84, L20 and Fig 2, precipitation, please clarify mm (cumulative) or mm/time (precipitation rate).

11. Pg 84, L24, “every 20 min”, if once “every 20 min”, please provide sampling duration (e.g. 1 min); if continuous monitoring, please provide sampling frequency (e.g. 1 hz) and averaging intervals (e.g. 1 min). Also in this paragraph, soil temperature is missing. Furthermore, please 1) identify measurements that were not carried out at 3 m above ground if any, 2) provide the distance between the weather station and the DFCs, 3) consider move this section to 2.1, in case the friction velocity is needed but not estimated by the DFCs.

12. Pg 85, L24, “The medians were elevated compared to the hemispheric background, but nevertheless appeared representative of a semi-rural area of North China plain (Zhang et al., 2013).” Please provide range of hemispheric background values and

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semi-rural area of North China plain Hg levels.

13. Pg 86, L2-4, “The angular dependence of the ambient Hg0 level indicates the relative impact of regional anthropogenic Hg sources in mainland China (Zhang et al., 2013).” This sentence is rather ambiguous. Mainland China is enormous in terms of geographic coverage. Please comment on the locations of major Hg sources nearby or in the region, and whether the directional distribution of Hg0 reflects the transportation by air flows.

14. Pg 86, L10-15, “fluxes positively correlated with solar irradiation and soil temperature”, “flux was gradual and similar to irradiation and soil temperature”, I would suggest to 1) consolidate those two sentences, 2) reference a table/figure or provide r and p values, because solar radiation and soil temperature are not plotted in Fig 4.

15. Pg 87, L11, “the surface soil Hg content within the methodological footprint range”, please specify such a range, or did you mean the “the surface soil Hg content under the two DFCs placed 2 m apart is largely homogeneous”.

16. Pg 87, L13, “In addition, NDFC measured flux calculated from Eq. (1) was presented in gray squares. The data were significantly positive correlated (R = 0.93, R = 0.95 for NDFC fluxes calculated with Eq. (2) and Eq. (1) $p < 0.01$)”. The first sentence could be removed. Please rephrase the second sentence to clarify the correlations among the three datasets, TDFC, NDFC and DNDFC after correction.

17. Pg 87, L22, please clarify the meaning of “positive influence”.

18. Pg 88, L17, “an higher scale of gradient variability”, please provide statistical support, e.g. coefficient of variation.

19. Pg 89, L2, please explain “low quality turbulence”. If you have assessed the quality of turbulence, please provide the methodology. If you have assessed the quality of the turbulence measurements, please rephrase.

20. Pg 89, L6-7, suggest provide the net fluxes in Table 1.

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21. Pg 89, L17, please explain how the “MBR method giving the most confined distribution” while other methods had less confined distribution, by range or by coefficient of variation.

22. Pg 89, L25-27, the reasoning is confusing, you may want to 1) cite average air or soil temperatures to support the claim of “warmer IC2”, 2) clarify whether Baya and Van Heyst, 2010; Gustin, 2011, assumed “that the soil Hg0 efflux was higher during the warmer IC#2”.

23. Pg 90, L17, please explain why “changes in concentration with time” would affect the MBR but not AGM.

24. Pg 90, L20-24, please explain whether “small sensible heat fluxes” were associated with “periods at dawn, dusk and during nighttime” in your IC1 and/or IC2.

25. Pg 90, L26-27, “The MBR method becomes uncertain and may significantly overestimate flux”, please explain why “AGM fluxes were on an average 26.1% lower than MBR fluxes during IC #1, but 13.8% higher during IC #2.”

26. Pg 91-92, first paragraph of section 3.4.1. This passage is a bit hard to follow. Suggest remove general statements (e.g. L25) and rephrase long sentences (e.g. pg 92, L1-5) to make clear the estimated footprint of each method.

27. Pg 92, L27, “The pattern resembles to extent that of latent heat flux”, please reference a table or figure where latent heat flux is presented.

28. Pg 93, L3-11. The point of this passage is not very clear. The challenge in qualifying air-surface exchange of Hg is well understood. Therefore, the authors may want to support the discussion with new findings in this study or remove this passage.

29. Pg 93, last line, when $p>0.05$, the correlation becomes statistically not significant, i.e. the hypothesis of “no correlation between X and Y” could not be rejected, instead of a “weak correlation”.

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30. Pg 94, L17, “This was likely due to the presence of high eddy diffusivity of heat.” It is unclear what “this” refers to and why high eddy diffusivity of heat would cause “a large increase” of one flux or a stable flux of another.

31. Pg 95, L10-13, please reference a figure to support your discussion.

32. Pg 96, L27, “the diurnal variation of MM fluxes were biased under the low turbulence condition”, there is a lack of support in Section 3 about factors that bias the diurnal variation, suggest remove.

33. Pg 97, L4-6, please explain the association between the “ poor to moderate” “ comparability between individual DFC and MM fluxes” and “the risk of utilizing sporadic (non-diurnally resolved) flux measurements as representative of an ecosystem.”

34. Pg 97, last paragraph. The discussion seems to be general and lacking a direct linkage to the data and analysis presented in this paper, suggest remove.

35. Table 1. please clarify “NDFC” or “NDFC after correction”. It might help your discussion to include net fluxes, median absolute deviation or coefficient of variation, dry deposition velocities, kurtosis, skewness, and the results of normality tests, instead of those numbers popping in the main body.

36. Fig 8 caption, please explain “those plots under sensible heat flux Wm$-$2 (filled circles)”. The unit of H should be provided too.

37. Fig 9 caption seems incorrect, 5th and 95th percentiles should be lower/higher than the 10th and 90th percentiles, respectively. Also, whiskers are missing for fluxes over wheat canopy in all three MM subplots.

38. Please report p values in any figures where correlation coefficient (r) is presented.

III. Editorial suggestions

The use of English language is largely satisfactory. However, the overall writing style has much room for improvement. The reviewer found many examples of awkward

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sentence structure, run-on sentences, ambiguous references (not citations, but use of words like “this”, “both”), and unusual word choices. Some examples are listed below. Furthermore, a proof reading by a native speaker could help.

1. The term NDFC was defined at least twice in the main body.

2. Suggest avoiding the use of first person, i.e. “we”.

3. Significant numbers, e.g. wind speed and Hg0 concentrations, perhaps one decimal is sufficient; for percent differences, integers could be adequate.

4. Citation in the main body, the number of papers seems a bit excessive especially in sections 1 and 2, which hinders the readability of the paper. The authors may want to list a few examples each time, perhaps citing the original methodology papers and the most recent applications. When there is more than one paper, you may want to order them by year of publication.

5. In quite a few incidents, a review of others’ work (e.g. pg 87, L4; pg 87, L20; pg 95, L15) was placed before your results. You may want to present your results first, followed by a discussion.

6. Pg 74, L13, please define DFC.

7. Pg 76, L17, could read “Lin et al. (2012)”.

8. Pg 76, L21, “4-day” or “4 days”

9. Pg 83, L15, a reference is needed for the SOP by NADP.

10. Pg 88, L15 and other places in some tables and the main body, the range expressed as e.g. “-2 –4 m/s” is hard to follow, suggest using e.g. “-2 to 4 m/s”

11. Pg 94, L5-7, those #s could be reported in Table 1.

12. Pg 96, L20-27, the switches from temporal trends to median values of the three MM method then back to temporal trends make the passage hard to follow, please

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rephrase.

13. There is little need to repeat in the main body the content of figure captions regarding to the meanings of some markers.

14. Fig 3, please provide units.

15. Fig 4, the plots and fonts are a bit too small to read; also the “black bars given in corresponding plots represent absolute flux uncertainties” make the plots even harder to read. You may want to remove the black bars and enlarge the charts.

16. Figs 5&7, the reviewer could not find the “filled diamond”.

17. Examples of unusual word choices:

Pg Line Words Comments/Suggestions

74 16 driving rephrase

77 6 benefits “advantages”

77 19 sophisticated remove

82 1 spatial homogeneously rephrase

83 20 limited rephrase

85 18 integral rephrase or remove

86 22 As a consequence consequently

87 3 foundation rephrase

89 16 It is obvious remove

90 24 approximately remove

92 14 many up to x

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92 19 there is an obvious lag there is a 2-hr lag

93 5 So they not thus they do not

95 18 statistical correlation Pearson correlation

97 10 next to REA in scale remove

97 13 behavior rephrase

97 13 in turn remove

Fig 5 Caption unbroken solid

Fig 8 Caption empty open

18. Examples of awkward sentences:

Pg Line

74 24

86 27

87 23-25

97 19

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