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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Sensitivity analysis of an updated bidirectional air-surface exchange model for mercury vapor" *by* X. Wang et al.

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We appreciate the helpful comments provided by the reviewers to our paper and have incorporated their recommendations in the revised manuscript. We particularly appreciate the second reviewer for providing the very detailed and constructive remarks. Our point-by-point response to the reviewers' comments is given below. The corresponding changes relating to the reviewers' comments have also been indicated in the response.

Anonymous Referee #2

1. This paper describes a scheme for estimating air-surface exchange of elemental mercury. The model relies on mechanistically based algorithms to a greater extent than many other models. This is an advantage, to a certain extent, but also means

that the model relies on a greater number of parameters. Since many of the needed parameters are relatively uncertain, its not clear if any increase in accuracy can be obtained, at least presently, in the use of this model. The model is applied over a large domain including the contiguous U.S. and surrounding region, and is also subjected to an extensive sensitivity analysis. I have noted a few issues below, primarily involving potential clarifications that could be made, but overall, this is an excellent contribution and should certainly be published.

Response: We thank the reviewer for recognizing the significance of our work and share the same view that there is a need to better understand the role of the model parameters. This is indeed the primary motivation of this work.

2. The "base case" simulation was carried out over a large domain including the continental U.S. (CONUS), nearby surrounding oceanic areas, and portions of Canada, U.S., and the Caribbean. Over this domain, the box model was applied using spatiotemporally varying meteorological data, atmospheric mercury concentrations, and landuse. The atmospheric mercury concentrations used were generated off-line by the regional model CMAQ-Hg. The authors briefly note that "the simulation does not directly incorporate the feedback of the air-surface exchange to the air concentration". It would be very helpful if the authors could clarify in this paper how Hg0 surface exchange was treated in the CMAQ-Hg simulation. If surface exchange was simulated in the CMAQ Hg runs by a different approach than this box model, applying the box model after the fact to each computational surface cell would appear to result in an inherent inconsistency. Also, was the CMAQ-Hg simulation carried out using the same WRF-generated meteorological data? If not, this would represent another inconsistency. In relation to this, I'm not sure I agree with the statement that "for a regional model domain, natural evasion and deposition of Hg0 does not significantly modify the ambient concentration". The estimated net emissions flux over the model domain is 94 Mg over the two months simulated. If this flux is scaled up by a factor of 5-6 to create an approximate annual total, this would be on the order of 500 Mg/yr. This is

a relatively large flux, e.g., likely much larger than the direct anthropogenic emissions over the model domain. I am skeptical that such a large net emissions flux would not have at least some non-trivial impact on Hg0 concentrations over the domain. To the extent that these concerns are valid, they do not invalidate the work by any means, but perhaps the authors could acknowledge the limitations to a greater extent. For example, it seems that a logical next step would be to incorporate this scheme into a comprehensive fate and transport model. Then the "feedback" would take place within the model and the resulting fluxes would be estimated in a more consistent manner.

Response: We appreciate the reviewer's insightful comment and would like to clarify the point. The WRF meteorology utilized to generate the CMAQ concentration field and the box model results was of the same dataset and therefore there is no concern for the meteorological inconsistency. Although we agree with the reviewer that coupling the box model and CMAQ-Hg simulation scheme has the benefit of directly incorporating the feedback on the concentration, the coupling does not change the simulation results because of the following two reasons:

(1) In the base case simulation, the mean flux in the domain is 2.7 ng m-2 h-1. Even in the absence of horizontal advection and assuming a low mixing height of 1 km, the forcing of the concentration change in each grid cell per hour is only 2.7$\times$10-3 ng m-3. In a regional model such as the CONUS domain, the time required for air turnover is relatively short (typically 3-4 days), and the air concentration of Hg is mainly controlled by the boundary conditions (Pongprueksa et al., 2008) instead of the evasion flux (Lin et al., 2005;Gbor et al., 2006) . Since the CMAQ-Hg output using in the simulation have been verified against and agree with the observational data, the Hg concentration field is representative of the typical Hg concentration in each grid cell. (2) For an initial box model development such as this work, our focus is to understand the sensitivity of each model parameter and refine the model algorithm. In the sensitivity runs, the result of sensitivity remained the same since the same Hg concentration field was utilized in the simulation. We share the reviewer's concern and have also clarified this point in

Section 2.5 of the revised manuscript (P10L212-216). The coupling of this box model to existing model (including CMAQ-Hg and WRF-Chem) is currently ongoing and we will report the result in a separate manuscript.

3. It would be very helpful if the methodological details of the sensitivity analysis were described in a more straightforward way. For the simplest case (air-water exchange), it appears that four parameters were varied between two different levels (low and high). Did the analysis simply consist of running the a one-cell box-model for each possible combination of the variables? If this was the case, then what is the meaning of the "P values" given? The existence of the P-values suggest that some sort of more complicated, statistically-based analysis was carried out. A more detailed and transparent explanation of what was done would be extremely helpful. This also of course applies to the description of the sensitivity methodology in the more complex cases. In general, the description of the sensitivity methodology seems to be too terse and uses jargon that may be unfamiliar to some (at least it was to me..., e.g., "fractional design", "Resolution IV").

Response: We thank the reviewer for pointing this out and have clarified the methodology in the revised manuscript (P8L178-P9L196). Yes, for air-water exchange, the assessment was achieved by varying the levels of all four parameters. In other cases, due to the much more complicated parameter combinations, the factorial experimental design approach was applied and the P values infer the significance of the examined parameters. We have added a section in the Supplementary Material document that explains the factorial design approach and the terms used in the main text to maintain the succinctness of the manuscript.

4. It seems that there have been other efforts to create such a model. The authors cite, for example, the bi-directional model incorporated into CMAQ-Hg by Bash (JGR, 2010), and incorporate some of the algorithms from that model. I believe that other models have also implemented some sort of bi-directional scheme. What then, are the critical differences between the scheme described in this paper and those used in

other models?

Response: The main differences between the schemes described in this paper and in Bash (JGR, 2010) are (1) foliage storage effect is included (i.e., Hg from dry deposition is stored in the foliage), (2) parameterization of the resistance scheme is updated, and (3) photochemical reduction on foliage is considered. We have included the above discussion in the Section 2.3 (P5L107-110) and also describe other model treatments (GEOS-Chem and CMAQ-Hg, etc.) in the Introduction of the revised manuscript (P2L46-P3L64).

5. The scheme proposed here appears to be more mechanistically based than some previous, simpler schemes. This has obvious advantages but also some disadvantages. The problem is that there appear to be a larger number of parameters which are needed, some of which are highly uncertain. So, it appears we are trading the uncertainty of a less mechanistic model (with few parameters) with a more mechanistic model (with more parameters that are uncertain). The net effect may not be a reduction in uncertainty, at least in the beginning. But the authors are correct in asserting that this more mechanistic approach offers good suggestions as to which parameters need work. Could this scheme be "tested" by comparison with (a) other schemes and (b) with specific laboratory and field experiments? If this could be done, we'd have a much better idea of the uncertainties and differences.

Response: We recognize the reviewer's assessment regarding "a more complicated model may not necessarily reduce the uncertainty." One of the major drawbacks from the earlier, simpler model scheme is that the mathematical relationship was statistically based and therefore does not describe the scientific process. It is our view that a mechanistic model better represents the complex air-surface process. As long as the values of model parameters can be quantified or estimated through future studies, a mechanistic model can be applied to investigate the process being simulated and to advance the scientific understanding. In fact, this model study is part of a coordinated project effort to better quantify the air-surface exchange and new findings from other

published results and ongoing experimental efforts will be incorporated to calibrate the model. For example, we have improved the flux measurement platform and utilized isotopic tracer to better quantify Hg0 exchange flux (Sommar et al., 2013b;Sommar et al., 2013a;Lin et al., 2012;Cui et al., 2014) and plan to use the experimental results to make adjustment on the model parameters. Having a thorough mechanistic model allows efficient implementation of new scientific findings.

6. The authors use the term "natural emissions" numerous times in the paper. But isn't this scheme really an algorithm to estimate the net surface exchange resulting from natural emissions and re-emissions of previously deposited anthropogenic mercury. Indeed, Hg(II) (some of which would likely have been deposited) appears in some of the equations. It would help to clarify this terminology

Response: We appreciate the reviewer for pointing this out. The term "natural emission" in this study refers to the cumulative net release of Hg0 caused by the air-surface exchange process. We have clarified this in Section 3.1 of the revised manuscript (P10L224).

7. In the description of the individual components of the terrestrial exchange flux in Section 2.3, it would be helpful to describe the inter-relationships. For example, the total flux from the canopy is made up of the air-soil exchange flux and the air-foliar exchange flux (air-stomata and air-cuticle). This becomes clear in the discussion of Figure 7, but it would be helpful if this were explained earlier (e.g., in section 2.3). While first reading this section, I was concerned that mercury emitted from the soil would be adsorbed by the canopy, and that this was not being taken into account. It was only later that I realized that the soil-air flux for soil under the canopy apparently takes into account the deposition that might occur as the mercury is transported upward through the canopy. Given this, the air-foliar exchange is a little confusing to me. The foliage is encountering mercury coming up from the soil as well as mercury coming down from above the canopy. Is it possible that this flux is being double-counted or "double-simulated" along with the air-soil exchange flux?

Response: We agree with the reviewer that describing the inter-relationships earlier help improve the clarity and have pointed it out in Section 2.3 of the revised manuscript (P5L106-107). The flux from the soil under canopy is NOT double counted because the landuse data separate the land area with vegetative coverage from the land area without vegetative coverage. The two fluxes were calculated independently based on their individual compensation points.

We thank the reviewer taking the time to make these editorial recommendations below:

8. The title of the article says "mercury vapor" but the article really deals only with Hg0. There are other forms of mercury in the vapor phase, e.g., gaseous oxidized mercury, that will behave differently. These other forms are not really discussed in the paper, and so maybe the title should be changed to say only Hg0 is being treated. Response: We agree - the title has been revised to “elemental mercury vapor.”

9. Page 32231, Line 9: While man-made emissions have been estimated... Response: The wording has been revised as suggested.

10. Page 32231, Line 16: Air-surface exchange is an important... Response: The wording has been revised as suggested.

11. Page 32232, Line 2: ... bidirectional flux through an Hg concentration gradient... Response: The wording has been revised as suggested.

12. Page 32232, Line 9: ... lack field data to estimate their values. Response: The wording has been revised as suggested.

13. Page 32232, Line 23: ... and their interconnections. Response: The wording has been revised as suggested.

14. Page 32234, Equation 3: Could mention that the individual compensation points are described by equations 6, 9, and 15 below. Response: The wording has been revised as suggested.

15. Page 32235, Lines 19-21: What value of Rac was used in this analysis? I could not find it in the paper. Response: Rac is used in Eq. [5]. We have moved the passage regarding Rac after Eq. [5].

16. Page 32237, Equation 15: What is KLA in the denominator? Response: We have made correction in Eq. [15] and clarified the value in Table 1 of the revised manuscript.

17. Page 32238, Line 3: ... higher order interactions are not significant. Response: The wording has been revised as suggested.

18. Page 32238, Line 15: ... to obtain the 5 most significant factors... Response: The wording has been revised as suggested.

19. Page 32239, Lines 21-24: The model domain includes land in Canada and Mexico and the Caribbean, and so can’t directly be compared to recent estimates for the contiguous U.S. On the other hand, if one multiplies the 2-month sum by 5-6, one gets 220-264 Mg/yr, significantly higher than the 95-150 Mg/yr in the recent contiguous U.S. estimates.

Response: This is a good point. The 43.9 Mg estimate is for the entire land surface in the domain. After excluding the emission from Canada, Mexico and Caribbean lands, the estimate in the contiguous US is 118-141 Mg yr-1. For clarification, the text have been revised to “Assuming the annual emission is 5-6 times of the two monthly sum and excluding the emission from Canada, Mexico and Caribbean lands, the model-estimated annual emission in the contiguous US is 118-141 Mg yr-1, comparable to the recent estimates (95-150 Mg yr-1) using flux scaling methods.” in the revised manuscript (P10L228-232).

20. Page 32240, Line 2: The mean simulated flux over water surfaces in the domain is...(And this same construct could be used elsewhere, in similar situations. The present language seems awkward to me.) Response: We agree - the wording has been revised to “Over water surface, the mean simulated flux ...” throughout the manuscript.

21. Page 32240, Line 3: Water bodies in the domain are a net source... Response: The wording has been revised as suggested.

22. Page 32240, Line 20: ... is largely from the southern portion of the domain. Response: The wording has been revised as suggested.

23. Page 32241, Line 2: Figure S8 was not in the Supplementary Materials that I was able to download. Response: We thank the reviewer for pointing this out. Figure S8 has been provided in the Supplementary Material document.

24. Page 32242, Line 6: 3.2 Sensitivity Analysis Response: We have checked and revised all subtitles' forms.

25. Page 32242, Line 7: 3.2.1 Sensitivity of exchange over water bodies Response: The wording has been revised as suggested.

26. Page 32242, Lines 24...: DGM is also "consumed" by some oxidation reactions, so its really the "net production" of DGM that is needed. And, if more DGM is produced on a net basis, the net evasion will be greater, leading to a lower DGM concentration. So, its not clear how much the variations in DGM concentration will be directly related to net DGM formation. Response: We agree and have revised the text accordingly. It is the DGM concentration (or net production) resulted from the redox chemistry that drives the evasion and deposition.

27. Page 32243, Line 28: use of term "reactivity" seems awkward... its not a chemical reaction, but really a scaling factor of sorts... maybe just say "... including temperature, Hg scaling factor..." Response: We agree and have revised the text accordingly.

28. Page 32248, Line 2: there's a question mark in one of the names... Response: It was possible generated during online document conversion and has been removed.

Anonymous Referee #3

1. This paper may have been lack of a proper motivation for their study. The authors

developed a very detailed model and run this model for hundreds of times to answer a very trivial question. The authors may need a better review of the previous observations and model efforts for air-surface exchange of mercury vapor in the introduction. I'm not convinced that we really need this study. Do the observations support your model assumptions, especially for such a detailed and complex one? Did previous model studies fail to capture some important features in the observations? It will easily bore your reader if without a proper motivation for your study.

Response: We appreciate that the reviewer spending the time to skim through our manuscript. Although we respectfully disagree with the reviewer on his/her views, we have included additional references including Strode et al. (2007) and Soerensen et al. (2010), and focused more on air-land exchange as the reviewer recommended. This model study is part of a coordinated project effort to better quantify the air-surface exchange. There are published results and ongoing experimental efforts to understand the complex and yet insufficiently understood air-surface exchange process. The model presented in this work attempts to build a thorough mechanistic model and use the model to understand the impact of the process parameters so that the experimental effort can be prioritized. For example, we have improved the flux measurement platforms and utilized isotopic tracer to better quantify Hg0 exchange flux (Sommar et al., 2013b;Sommar et al., 2013a;Lin et al., 2012;Cui et al., 2014) and plan to use the experimental results to make adjustment on the model parameters. This allows efficient implementation of new scientific findings. So the motivation our study is genuine and there is indeed a research need.

2. The authors may need to connect their model results more with empirical evidence. My feeling of reading this paper is that the authors develop a model and run sensitivity runs, but rarely interpret their model results in a broader picture of mercury biogeochemical cycle. The lack of evaluation of the accuracy of the model against observations is another issue. The authors probably need to compare their results with those predicted by previous models, too, especially they declare they are presenting an

UPDATED air-surface exchange model. They need to convince the readers that their model is somehow better than previous ones. To my knowledge, there is nothing new for the air-water exchange of mercury in this study. The authors use an old scheme to calculate the piston velocity and assume uniformly DGM concentrations in the surface ocean. This is even worse than the state of the art air-sea exchange model for mercury which considers the spatial distribution and chemical reactions of mercury in the surface ocean (e.g. Strode et al., 2007; Soerensen et al. 2010). The discussion of the influencing factors for air-sea exchange flux is also very superficial, and can be directly deduced from equation (1). I suggest the authors focus on air-land exchange only.

Response: Perhaps it was the reviewer's overlook, the model results were indeed compared to published data for the CONUS coverage in the manuscript. This is presented in the results of the base-case simulation (Section 3.1). The focus of this modeling work is mainly on the net flux exchange and the sensitivity of the modeling parameters in terrestrial system. This is in contrast to the focus in Soerensen et al. (2010), which was primarily to simulate the global air-sea exchange, the DGM concentration and its global distribution using a mixed layer slab model. For a regional simulation, we did not attempt to answer the global biogeochemical cycle question. Instead, we are developing model that can be better estimate the quantity of air-surface exchange of Hg0. We have followed the reviewer's recommendation to focus more on the air-land exchange. In the revised manuscript, more than 85% of the Results and Discussion is devoted to the air-land exchange.

For the air-land exchange, the advances of this model are (1) foliage storage effect is included (i.e., Hg from dry deposition is stored in the foliage), (2) parameterization of the resistance scheme is updated, and (3) photochemical reduction on foliage is considered. We have included the above discussion in the Section 2.3 (P5L107-110) and also describe other model treatments (GEOS-Chem and CMAQ-Hg, etc.) in the Introduction of the revised manuscript (P2L46-P3L64).

Regarding the depth of the discussion in the air-water exchange, we would like to point

out that (1) this is the only model assessment that analyze the interaction between model parameters, (2) the effect of model parameters and the interactions are quantified with statistical significance. We have also included the assessment by Strode et al. (2007) and Soerensen et al. (2010) in the discussion of air-water exchange (P14L315-317).

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Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/13/C13373/2014/acpd-13-C13373-2014-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 32229, 2013.