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

Anonymous Referee #2

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Referee Comment for: Title: Sensitivity analysis of an updated bidirectional air-surface exchange model for mercury vapor Author(s): X. Wang et al.; MS No.: acp-2013-459; MS Type: Research Article

Jan 15, 2014

——————— General Comments ———————

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,

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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.

———————— Specific Comments ————————

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 spatio-temporally varying meteorological data, atmospheric mercury concentrations, and land use. 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 $\sim$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 per-

haps 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.

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").

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?

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 an reduc-

tion 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.

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.

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?

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.

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—————————— Technical Corrections ——————————

Page 32231, Line 9: While man-made emissions have been estimated...

Page 32231, Line 16: Air-surface exchange is an important...

Page 32232, Line 2: ... bidirectional flux through an Hg concentration gradient...

Page 32232, Line 9: ... lack field data to estimate their values.

Page 32232, Line 23: ... and their interconnections.

Page 32234, Equation 3: Could mention that the individual compensation points are described by equations 6, 9, and 15 below

Page 32235, Lines 19-21: What value of Rac was used in this analysis? I could not find it in the paper.

Page 32237, Equation 15: What is KLA in the denominator?

Page 32238, Line 3: ... higher order interactions are not significant.

Page 32238, Line 15: ... to obtain the 5 most significant factors...

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.

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.}

Page 32240, Line 3: Water bodies in the domain are a net source...

Page 32240, Line 20: ... is largely from the southern portion of the domain.

Page 32241, Line 2: Figure S-8 was not in the Supplementary Materials that I was able to download.

Page 32242, Line 6: 3.2 Sensitivity Analysis

Page 32242, Line 7: 3.2.1 Sensitivity of exchange over water bodies

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.

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..."

Page 32248, Line 2: there's a question mark in one of the names...

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