

Response to reviewer comments: Estimates of mercury flux into the United States from nonlocal and global sources: Results from a 3-D CTM simulation
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We wish to express our sincere appreciation to the reviewers for their valuable comments and suggestions. In general the reviewers have suggested that (a) we haven't included more gas-phase chemistry and aqueous chemistry (b) there is not enough validation of upper atmospheric model predictions. The simulation was designed to answer a fairly narrow range of questions as described in the abstract and focused on calculating the impact of emissions of Hg in China over concentrations in USA and the Midwestern USA in particular. As such, the goal is to generate estimates of the outer envelope of the possibilities and not really address the subtleties in the chemical mechanism. We used well accepted reaction pathways and focused only on gas phase transformations. This does produce higher estimates of long-range transport as we would underestimate the removal of particulate mercury due to washout and settling. Future calculations can include particulate mercury to get a more accurate estimate of long-range transported elemental and reactive mercury and will be considered. This is one of the first calculations using state-of-the-art CTM with full gas-phase chemistry and elemental and reactive mercury with dynamics described by observed meteorology in the form of NCEP data set. Thus, it gives a great opportunity to evaluate data collected during the period of simulation near the source region and receptor region. As for additional validation, there is not enough speciated data in the upper troposphere for the period of our study to evaluate with the model. Below we provide specific responses to the reviewer comments.

Reviewer A:

Comment: As such, the authors need to focus more on demonstrating the realism of this new model. The only evidence of model accuracy given is comparisons of observed and simulated elemental mercury air concentration over one site in Ohio.

Response: We agree that there is more evaluation needed for the model and probably all models that have been used for performing global simulation of mercury cycle. The comment about having only one data point in Ohio is incorrect. We have shown correlation of the modeled and calculated total mercury to CO, measured and modeled in Okinawa, Japan. This is actually much stronger confirmation of our model than the Ohio data point.

Comment: The modeled data are relevant to the 950 mb pressure level while the observed data were taken at the surface.

Response: Not correct, the site is an elevated location approximately at the height used for model validation. Please refer to the description in the paper.

Comment: Little is known about vertical gradients of elemental mercury concentration in general, and no such information is provided for this one site in Ohio.

Response: There is no such data set from this site and as far as we are aware there are no profile measurements.

Comment: The emission inventory used only includes elemental mercury emissions and there are problems with the gridding of emissions data for input to MOZART in other locations. This suggests to me that the model simulations were faulty from the start.

Response: It seems like there is some misunderstanding about gridding. We have used Pacyna emissions for the world and patched Streets emissions for China into them for our sensitivity study. The discrepancies we cited in the emissions after we patched the emissions are at one single location in the southern hemisphere. Due to trivially small emissions in some of these grid locations (close to zero), decimal place errors result in big % changes in emissions. We have performed simulations again to fix these problems and here is a figure showing the differences between Pacyna and Streets emissions. This corrects the small problem we had in interpolating the emissions and doesn't have any impact on our conclusion.

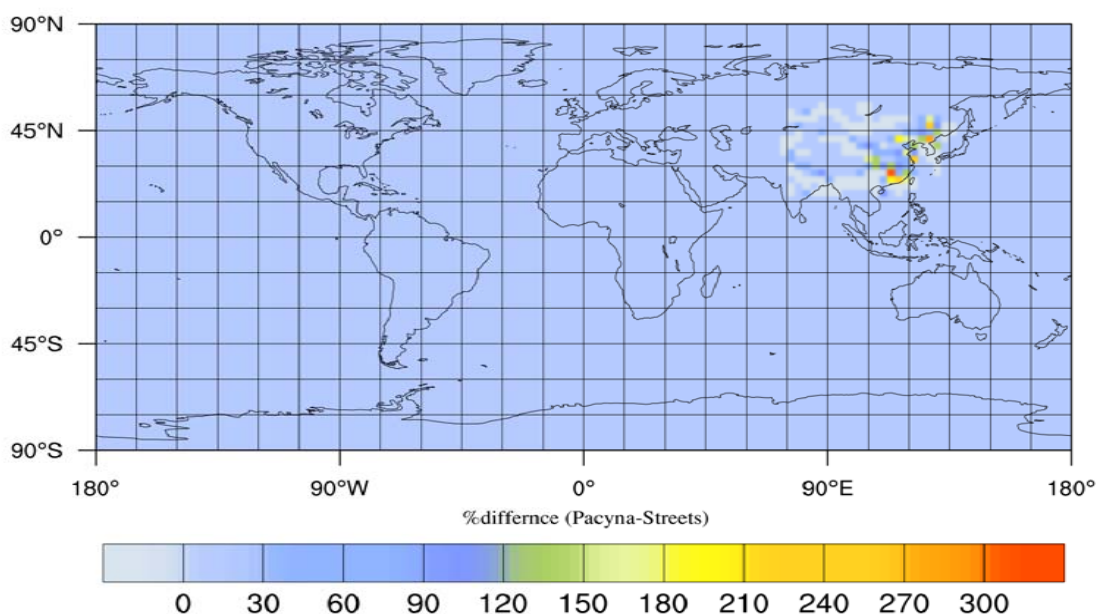


Figure 1: Percent differences in emissions between those prepared by Pacyna and from Streets as explained in the paper. Note that Streets emissions were available only for China and the rest of the domain is exactly the same as that from Pacyna.

Comment: The model does not treat aqueous-phase mercury chemistry. Given the general scientific uncertainties that all models suffer from in regard to atmospheric mercury chemistry, I can understand why the authors would want to keep things simple for their first try with MOZART. However, I am not aware of any published

atmospheric mercury model that completely neglects aqueous chemistry. I am left with the overall impression that this work does not provide much new information that can be taken with confidence.

Response: There are several global simulation of mercury cycle(Shia et al., for example) that haven't included aqueous chemistry. In fact, we are not aware of any global scale simulation that included aqueous chemistry for these types of calculations. The one study that used aqueous chemistry to test the sensitivity of aqueous chemistry on modeled mercury deposition. It was shown to be negligible (Seigneur et al.).

Comment: It does provide something of a progress report on the addition of mercury simulation within the MOZART model, but I am troubled by the use of the current model for assessment purposes. I do not believe the assessment provided here should be published without some significant evaluation relative to observed data.

Response: We are not advocating the use of our model for doing policy related assessments. This is still a research grade model and provides an additional data point for people involved in policy development and such issues.

Specific Comments:

Comment: use a better nomenclature

Response: the nomenclature can be fixed as suggested by the reviewer.

Comment: it is stated that reactions of HGE with HCl and Cl₂ are included in the model, but no reactions involving these species are listed.

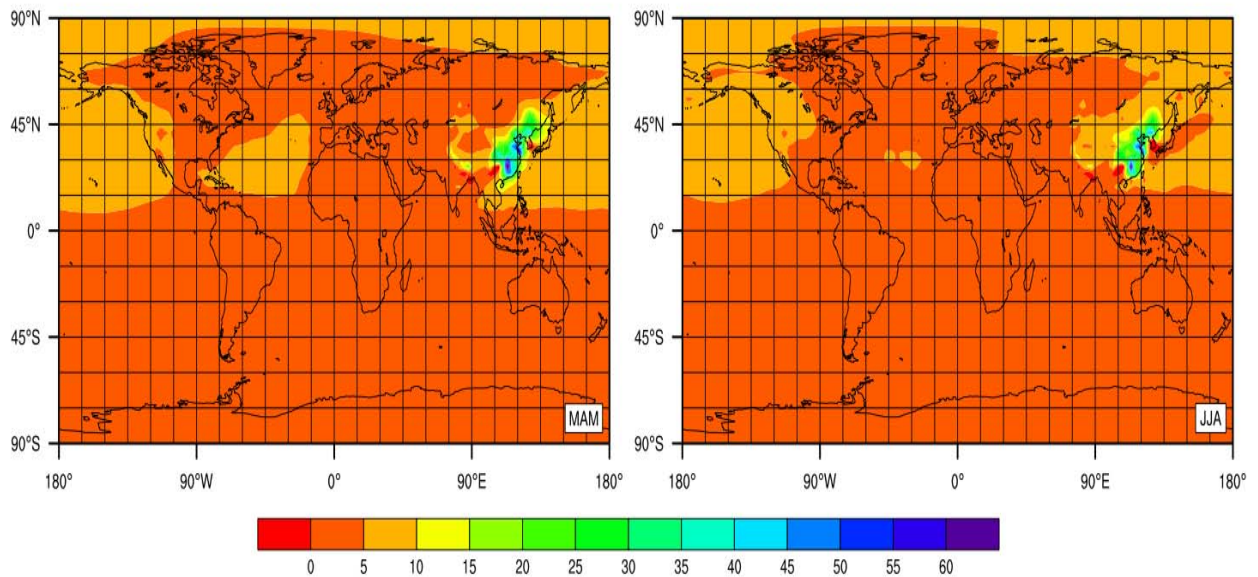
Response: We did perform some simulations with chlorine chemistry. Given the uncertainties in this chemistry and the nature of HCl/Cl in MOZART troposphere (fixed in altitude and time and needs additional validation) and we obtained insignificant impacts, we removed it from the final draft. We will remove the sentence from the text. Thanks for pointing this out, it was an editorial oversight.

Comment: This implies that the Streets and Pacyna emissions are the same, but they obviously are not. A much more clear explanation is needed.

Response: yes the emissions for the rest of the world are same except for China, where we use Streets emissions in place of Pacyna for this calculation.

Comment: In Section 3.1, it is stated "The variability of Hg concentrations in South Africa, Australia, and Europe (Fig. 5) is the result of differences in gridding the emission distribution input to MOZART". This technical error needs to be corrected. It detracts greatly from the confidence the reader is going to place in the model simulations and suggests a haphazard approach to the entire modeling effort.

Response: As explained earlier, these are small changes in emission that caused the error. Compared to emissions from China and USA, there are insignificant and unlikely to change the presentation. These calculations took considerable effort, to achieve a steady state atmosphere for mercury and then performing the perturbation runs. The confidence the model results comes from the ability of the model to perform simulations of a number of trace gases, ability to produce the mercury-CO observed correlations. The models main purpose is for looking at the perturbation results and these are robust. These problems have now been fixed and here is an updated figure 5. Note that there are no changes in the region of interest except for correcting the problems noted in the SH due interpolation errors in



emissions in the paper.

Figure 2: This is the same as figure 5 in the paper, with errors noted above corrected and model simulations repeated. Percent difference in Hg(0) concentrations in spring (left) and summer (right), as simulated with the *Pacyna* and *Streets* estimates of Hg emissions.

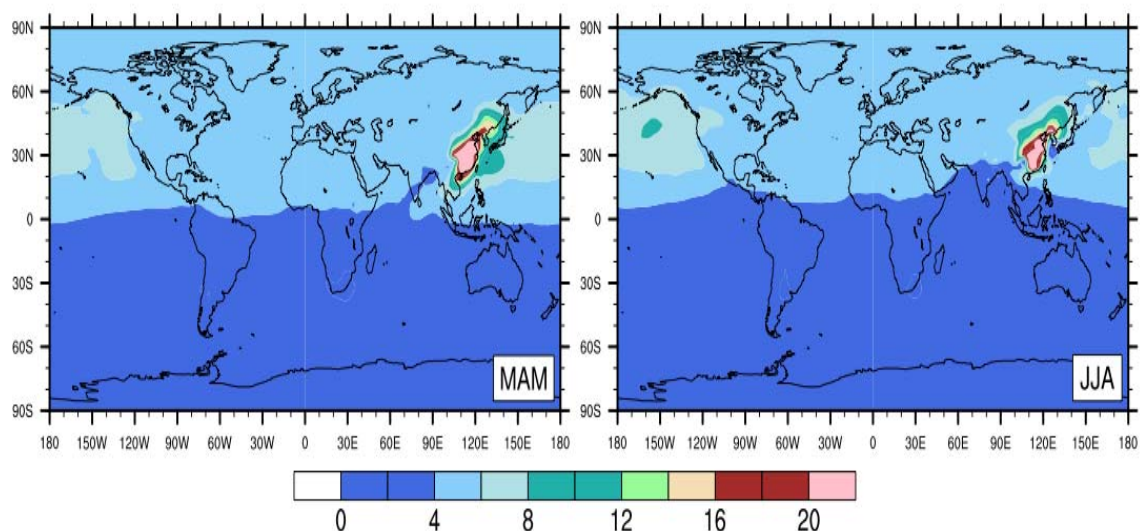


Figure 3: Same as figure 13 in the paper. Corrected for the small error in emissions differences in the SH noted above. Percent differences in HGO dry deposition in spring (left) and summer (right) for the *Pacyna* and *Streets* simulations.

Comment: In section 3.2.1, there is no attempt to compare the model simulations of mercury wet deposition with the many observations taken as part of the Mercury Deposition Network (MDN). The MDN data provide what I believe is the best opportunity to show realism in the MOZART simulations. The authors need to show some evidence that their model matches these observations to some degree.

Response: We have generated a mercury wet deposition map to compare with the MDN data set.

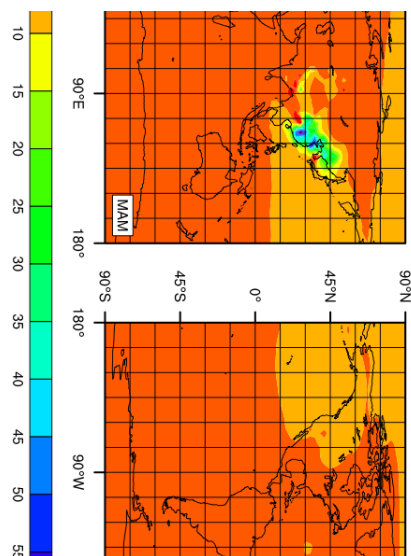


Figure 4: The wet deposition pattern follows the measurements from the MDN network and within the range measured. We don't reproduce some high measured wet deposition rates over Florida. These results are similar to the calculated results by Seignuer et al., (2001) using a global model and without any scaling for the

precipitation in the model with observations.

Comment: In section 3.2.2, it is stated <quote>Dry deposition patterns are very similar to the wet deposition patterns.</quote> However, there are no model results shown to support this statement. I would assume that what is meant here is that the differences in dry deposition between the modeling cases are similar to the differences in wet deposition between the cases. If any atmospheric mercury model showed similar patterns for wet and dry deposition, I would be very suspect of that model.

Response: We mean the differences and not the actual numbers. The sentence will be corrected to reflect the fact.

Comment: In the Conclusions section, Shetty et al. (personal communication) is cited. It appears that the Shetty et al. work published at <http://dx.doi.org/10.1016/j.atmosenv.2008.08.026> could be cited instead.

Response: Done.

Comment: In Figure 5, for comparison purposes, it would help to use the same color scale and to show all seasons as is done in Figure 4.

Response: Corrected to correspond to figure 4.

Seigneur et al., 2001 C. Seigneur, P. Karamchandani, K. Lohman, K. Vijayaraghavan and R.-L. Shia, Multiscale modeling of the atmospheric fate and transport of mercury, *Journal of Geophysical Research* 106 (2001) (D21), pp. 27,795–27,809.

Shia et al (1999). R.L. Shia, C. Seigneur, P. Pai, M. Ko and N.D. Sze, Global simulation of atmospheric mercury concentrations and depositions fluxes. *Journal of Geophysical Research* 104 D19 (1999), pp. 2747–23760.

Reviewer B

We again thank the reviewer for the comments and suggestions. The model (MOZART) has been used extensively for trace gas simulations and a number of papers published showing the performance of the model, export across boundaries for CO, ozone and other pollutants and evaluated with measurements. We are, as suggested by the reviewer, added mercury chemistry to this model and reporting the results. Though, this may seem like a trivial exercise, there indeed are only a few global scale simulations of mercury using CTMs. The primary issue being the large amount of computing resources and analysis time required for such simulations. We observe that the model typically needs to run between 4 and 5 years to reach a steady-state distribution. We defined steady-state here as modeled concentrations of all tracers for a particular day being insignificantly different from the same day from a previous year (we used $< 0.01\%$). In additional when performing perturbation studies resulting from emission changes this makes it even more expensive and time consuming using a relatively high-resolution model as we have done here. Many papers in the literature of global scale simulations used a 4 x 5 degree resolution model developed using the GISS climate model framework. Thus, we consider this a worthwhile effort and suited for publication.

Specific Comments:

Comment: The authors could use more discussion of previous studies that quantify Asian long-range transport (of mercury and other substances). The authors note the study of Seigneur et al. that Asian anthropogenic emission of Hg contributed 21% of total Hg deposition in the contiguous US in 1998. In addition the authors should discuss

Strode et al. (2008), who found that Asian anthropogenic sources contributed 15% in the Western U.S. and 12% in the eastern U.S. Some discussion of other long-range transport studies of mercury and other species would be warranted here.

Response: If a revised paper is acceptable, we will add this information.

Comment: Mercury Chemistry: the authors should at least acknowledge Calvert and Lindberg (2005) and the likelihood that the reactions with OH and O₃ do not occur in the atmosphere, and discuss how using e.g. Br as an oxidant may change their results if at all.

(I suspect not much, but it should be addressed). They should additionally acknowledge and discuss how omitting Hg(0) dry deposition may change results (see Lin et al., 2007; Selin et al., 2008).

Response: As explained in response to a comment from reviewer A, we included Cl related reactions and haven't obtained any noticeable difference in the model. This was not discussed in the model as a result. We suspect, adding Br chemistry will yield similar impacts.

Comment: Emissions: the authors should make it clearer throughout that they are only looking at Hg(0) emissions in China (and not Hg(II) or Hg(P) emitted directly). It is obvious when comparing the numbers to the Pacyna reference, but readers not familiar with total Hg emissions in China may confuse this as it is not stated in the paper. It is not, as stated, that "All surface emissions are assumed to be in all the form of Hg(0)"; but that emissions in the inventories from Hg(II) and Hg(P) are omitted [correct?]. The uniform distribution of Hg(0) emissions from land and ocean is problematic, as land emissions are likely to have been affected by previous deposition and ocean emissions vary latitudinally. Though I agree with the authors that it plays little role in the present application, it would dramatically affect the agreement of model to measurements and thus may need to be improved for this purpose.

It would also be helpful in this section (perhaps in a table?) to detail the actual (Mg) emission from China under the different scenarios and include a few words about why they are different.

Response: The reviewer is correct in his conclusion. However, as far as we can tell, the direct emissions of Hg(II) and Hg(P) are not significant and in particular for this study. Figure 1 above addresses the last point of the above comment and shows the differences between Pacyna and Streets emissions for China in terms of % difference.

Comment: Elemental Mercury It is impossible to see in Figure 2, given the color scale, whether the Hg(0) concentrations are remotely reasonable. The green color covers a range from 1.0-2.5 ng m⁻³. In addition, the authors do not give a global mean Hg(0) value or compare with any seasonal or annual mean data except for Athens, Ohio (Figure 3). It is also unclear in Fig 3 which is the data and what the circles and barplots represent. Thus, as a reviewer I have no way of knowing whether the simulation is remotely reasonable. Key information which would be necessary in this regard are the following: a) the global budget of mercury in the model, including the lifetime of Hg(0) in the atmosphere; b) comparison with annual average Hg(0); c) whether there is an interhemispheric gradient and if so how large.

Response: Here is figure 2 using a wider scale.

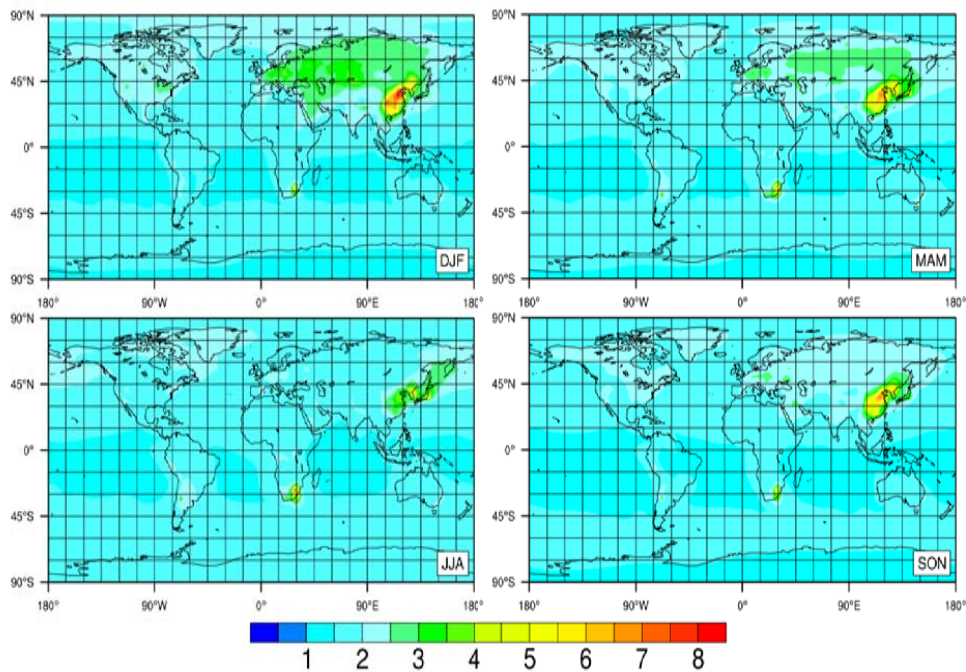


Figure 5: Same as figure 2 in the paper reproduced using a different color scheme. Model-calculated background Hg(0) concentrations (ngm⁻³) at the model surface for the Northern Hemisphere in winter (upper left), spring (upper right), summer (lower left), and fall (lower right), in the *Pacyna* emissions case.

As the caption for figure 3 says, the red boxes are observations and the model results are presented in green. This is known as a box-whisker plot, the boxes cover the middle 50% of the distribution and lines cover the lower and upper quartiles. The circles represent data that is not in the 90% of the distribution or outside. The global burden of mercury in the base case is (*Pacyna* emissions) is calculated as 5386Mg and given total emissions (anthropogenic+ background) of 6207Mg/y, the

lifetime of Hg(0) is approximately 0.9 years at steady state. The inter-hemispheric gradient is miniscule in the model and differences in burden between the NH and SH is approximately 1% higher in the NH compared to SH. As for the annual average Hg(0), we can't find any estimates from 'measurements' of annual average Hg(0) due to few available measurements.

Comment: Page 19868 lines 12+: I am very confused as to why "gridding distributions" would cause differences in the Southern hemisphere. As is stated earlier, all of the simulations used the same inventories outside of China, so why should they be gridded differently other than due to human error? Also, why are there differences in the U.S.?

Response: Yes, there was a minor error in gridding, small changes in numbers, which are close to zero, produced some of the errors. These have now been fixed as explained earlier and in response to reviewer 1.

Comment: Page 19869 lines 1-15: It would be helpful to show the total concentrations which can be compared directly to the Jaffe data, to convince the reader that the model is reasonably simulating these concentrations, in addition to the China component.

Response: Here is a figure of the modeled Hg(0) at a location near Seattle from the model. The data is from the surface level of the model and not elevated as in Jaffe's data set.

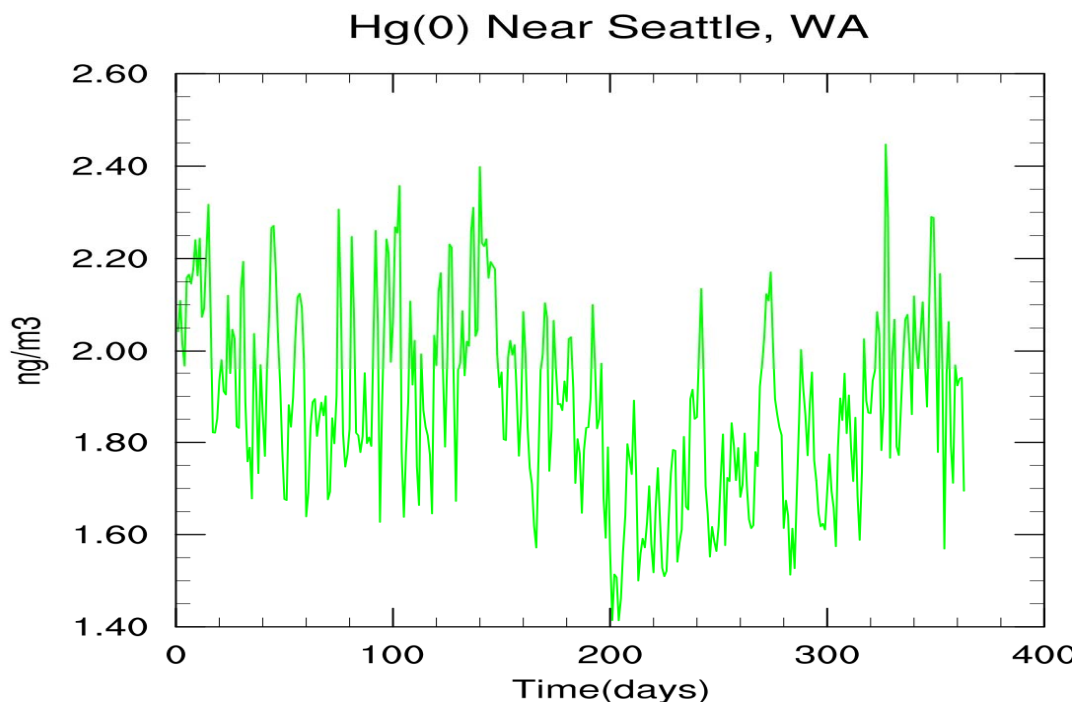


Figure 6: Model calculated Hg(0) concentrations for a location near Seattle, WA. The concentrations are in the same range as measured at Mt. Bachelor.

Comment: Wet deposition P. 19870 line 6: "Wet deposition is highly seasonal..."; I assume that the authors mean in the U.S. There is no data elsewhere (e.g. the tropics)

to support this statement. The authors do no comparisons with total wet deposition measurements, for which there is an extensive data set in the U.S. Further, the authors note that while measurement data is low in winter in the U.S., calculated deposition is high during that time. The authors should discuss their parameterization of scavenging of Hg in snow in particular (see Mason et al., 2000). If the model does not correctly represent the processes of wet deposition over the United States, it is unclear whether the analysis of Asian sources is to be believed, as previous model studies have shown the strong role of scavenging from the free troposphere (see Strode et al., 2008; Selin and Jacob, 2008). A better discussion of transport and mixing in the free troposphere is needed here.

Response: Please refer to figure 4. The comparison is shown for the data in US and is reasonable. We have essentially followed the wet scavenging scheme used in MOZART for highly soluble species and no other modifications.

Comment: Dry Deposition: Here, and above, it would be helpful to be clearer in the language

a) what the model predicts as the total Asian contribution, with a range between Streets and Pacyna, and b) what the uncertainty between Streets and Pacyna are. The way it is written with the differences between the two cases is confusing. I

would suggest, here and elsewhere, focusing the language on what these cases are diagnosing rather than merely reporting their difference.

Response: many of the figures in the paper and response here address this particular question. As can be seen from figure 12 emissions from China can change dry deposition fluxes in the US by about 8% during most of the year, except for winter, using a lower emission estimates from China generated by Streets. Using higher emissions from China by approximately 16% adds another 4-6% to the calculated dry deposition flux over the Western US (figure 13 and corrected figure 3 above).