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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Estimating mercury emission outflow from East Asia using CMAQ-Hg" *by* C.-J. Lin et al.

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The authors greatly appreciate the thoughtful review and constructive comments from the anonymous reviewer, and will incorporate the reviewer's suggestions in the revised manuscript. Our point-by-point response to the reviewer's comments is given below.

Comment #1: This paper describes an interesting and informative modeling study of East Asian mercury emissions to the atmosphere and their contribution to the global mercury cycle. The authors appear to have applied the Community Multi-scale Air Quality (CMAQ) model in a reasonable manner in general, but there appears to be some margin for improvement. I also have some questions about the calculation of the regional mercury budget based on the simulation outputs. I am not sure that the simulated chemical and physical transformations of mercury after emission but before

export from the modeling domain have been taken into account properly in the mass balance assessment or in the conclusions drawn from it. The assessment assumes a conservation of mercury mass by the model that has not been substantiated, but could be with a more detailed analysis of the CMAQ simulation. Finally, I am concerned about statements made regarding the implications of the model simulation on inter-continental and trans-boundary transport, specifically the impact of Chinese emissions on mercury deposition in Korea. The simulation modeling results are definitely worthy of publication, but I believe some further discussion and consideration of the mass balance assessment is needed.

Response: The reviewer's comments are well received and we appreciate the reviewer's recognition of the merits of this work. These points are also mentioned in the specific comments, which are addressed in details in this document.

Comment #2: In Section 2.1.2., the treatment of dry deposition of particulate mercury (PHg) in CMAQ is said to use sulfate aerosols as a surrogate. This was true for the original adaptation of CMAQ version 4.1 to simulate mercury described in Bullock and Brehme (2002). However, the treatment of particulate mercury in CMAQ version 4.6 (the version used in this work) is not based on a surrogate. Instead, mercury is treated as a separate trace component which does not affect aerosol dynamics. Nonetheless, mercury mass is subject all aerosol processes, including dry deposition. CMAQ treats aerosols in each of its three size modes as internally mixed particles. Any component of a particular size mode, including trace components, are simulated to dry deposit in the same manner as all other components of that mode. The overall effective dry deposition velocity for a particular aerosol species will vary depending on how its mass is distributed among the size modes. In CMAQ version 4.6, mercury aerosol is not constrained to the same mass distribution as sulfate.

Response: This was our overlook and we thank the reviewer for catching this. In CMAQ v4.6, PHg is assigned into Aitken and accumulation modes, and the dry deposition velocities are calculated explicitly in the models. We will make sure that the description

is changed in the revised manuscript.

Comment #3: In Section 2.1.3., the authors wrote “The emission speciation followed the recommendations of Streets et al. (2005), with 56% as GEM, 32% as RGM, and 12% as PHg.” Are these the domain-average percentages of total mercury mass emitted for each mercury species or was this one speciation profile applied across the entire modeling domain? Since the only figure showing mercury emissions is Figure 1 and it appears to show only total mercury with no speciation, I assume that one speciation profile was indeed applied across the domain. If so, this is a simplification that detracts from the accuracy of the simulation and the reliability of the results, especially for source-receptor relationships within the modeling domain. The global mercury emission inventory published by the Arctic Monitoring and Assessment Programme at http://www.amap.no/Resources/HgEmissions/HgInventor yDocs.html provides gridded emission rates for each mercury species referenced to the year 2005.

Response: The emission inventories reported in Streets et al. (2005) and used in the simulations had a specific speciation profile for each of the emission source categories. Therefore, the description "56% as GEM, 32% as RGM, and 12% as PHg" represented the averaged profile in China. We will modify the description in the revised manuscript to avoid this confusion. We chose to apply the emission inventories by Streets et al. (2005) because of two primary reasons: (1) the inventory data included detailed speciation profiles for different source categories, and (2) the data had a higher spatial resolution. Because mercury deposition strongly depends on emission speciation and a higher resolution is desirable for regional model application, we feel that the use of the emission data was appropriate.

Comment #4: Section 2.3 describes the calculation of a “transport budget” (TB in equation 2) as the incoming mercury mass minus the outgoing mercury mass. This use of the term “transport budget” implies import and export of mass due to atmospheric transport. However, TB is actually calculated from known mass quantities within the domain at the start and end of the simulation and known inputs by emis-

sion and outputs by deposition. To apply this calculation to estimate transport into and out of the domain assumes mercury mass conservation by the model which may have been demonstrated elsewhere. If so, this demonstration should be referenced. If not, the analysis would be more reliable if there were an actual accounting of simulated mercury advection into and out of the domain.

Response: We agree with the reviewer that the mass conservation by the transport algorithms of a model must be satisfied in order for Eq.(2) in Section 2.3 to sustain. In fact, we have performed two sets of tracer simulations in the East Asian domain as well as in a trans-Pacific domain to make sure that mercury mass is conserved in the transport calculations. This was done by assuming a fixed value of mercury concentration (1.5 ng m-3) as initial and boundary conditions without invoking the calculations for chemistry and deposition. After one month of simulation, we observed nearly no change of mercury concentration (<0.1 %) throughout the entire domains. We will incorporate this discussion in the revised manuscript.

Comment #5: In section 3.3, the transport budget for individual mercury species is discussed and it is stated “. . . there is a net mass of GEM transported out of the East Asian region and a net removal of RGM and PHg in the region...” It seems to me that the natural mercury cycle would make this true for just about any location since GEM is emitted and transported long distances before being oxidized in the atmosphere and deposited as RGM or PHg. Industrial emissions of GEM do not alter this situation at all. Industrial emissions of RGM and PHg do not typically transport long distances before deposition unless they are converted to GEM. The chemical conversions of mercury between the species confound the arguments made in this paper based on equation 2. While it is reasonable to talk about the transport balance of total mercury in this sense, I do not think this is so for the individual species. I suggest that the authors use a more complex framework than equation 2 to discuss the exchanges of individual mercury species between the East Asia region and the rest of the world.

Response: Due to the physical and chemical characteristics of GEM, RGM and PHg,

it is true that GEM tends to be transported out of a regional domain and RGM/PHg tend to be deposited locally. On the other hand, we want to point out that not all the emitted RGM/PHg deposited within the domain. Instead, a portion of the RGM/PHg emission from the anthropogenic sources left the domain because of the plumes aloft to the upper air. Take RGM budget in the July month as an example, of the 22.8 Mg of RGM emission, we calculated that 60 % (13.7 Mg) of emitted RGM deposited within the domain while the remaining 40 % (9.1 Mg) left the domain due to transport. Therefore, the overall mass budget of 11.6 Mg in Table 3 (estimated by Eq. (2)) does not mean that there are 11.6 Mg of emitted RGM leaving the domain, but indicate the transport balance after considering other atmospheric processes such as chemistry and deposition. We agree that the mass balance results obtained by Eq. (2) cannot separate the deposition caused by RGM/PHg emission from the deposition caused by GEM oxidation. However, it is still useful to use Eq. (2) to track the mass of each mercury species because it considers all the source and sink processes, and is capable of estimating the transport balance for a control volume (i.e., the study domain). We will make this clarification in the revised manuscript.

Comment #6: Near the end of section 3.3, I was interested to see that the estimated fraction of anthropogenic mercury emissions leaving the domain differed between the Base and Inferred cases. OutïňĆow of anthropogenic emissions in the Base case was 68% while outïňĆow in the Inferred case was only 62%. Were all species of Hg in the anthropogenic emission inventor y scaled up equally in the Inferred case relative to the Base case? If so, this would indicate that the transformation and fate of anthropogenic mercury emissions is dependent on the preexisting mercury burden in the atmosphere. If this is the case, then the linear relationship between source strength and impact does not hold. Again, I fear that equation 2 is not a sufficient framework with which to assess imports and exports of speciïňĄc mercury species given the complexities of atmospheric mercury transformations.

Response: Yes, all mercury species in anthropogenic emission inventory were scaled

up based on a same factor, and the outflow percentage changes from 68% in the Base case to 62% in the Inferred case is expected. We agree with the reviewer that there is a linear relationship between the mercury burden in a region and its impact on concentration/deposition in a remote receptor region. However, in this case, while the linear relationship between mercury emissions and GEM outflow still holds true, the linear relationship in terms of total mercury outflow does not. This is because RGM and PHg have a greater tendency of being deposited. In the inferred case, the much greater RGM and PHg concentrations near emission sources preferentially deposit a greater fraction of RGM and PHg compared to the Base case, leading to a smaller fraction of total mercury outflow. We'll make this clear in the revised manuscript.

Comment #7: In section 3.4, the authors write ". . .the dry deposition of mercury is linear with respect to the concentration of GEM. . ." I presume the intended message here is that the rate of dry deposition of GEM is linear with respect to its concentration. Dry deposition of mercury (all forms together) is certainly not linear with respect to GEM concentration when the fraction of mercury present as RGM is variable. RGM deposits much more readily than GEM. Even given the presence of GEM alone, there are quite a few published works that show evidence for dynamic two-way interactions between Hg0 in air and Hg0 in underlying water, soil and vegetation. The ïňĆux of GEM by dry processes can certainly be upward when its concentration is high enough in the underlying substrate to overcome the depositional forces of GEM in air.

Response: We totally agree with the reviewer on this comment. In essence, we meant that a linear relationship exists between the dry deposition of GEM and its gaseous concentration. We will revise the wording accordingly and also incorporate additional discussion regarding the dynamic air-surface exchange in the revised manuscript.

Comment #8: Later in section 3.4, the authors state that they "did not observe consistent transport events from China to Korea" based on two observations: 1) no simulated surface concentration gradient from industrial areas in China to the Korean region, and 2) similar observed GEM concentrations at the China-Korea border and Seoul, South

Korea. It seems that both of these pieces of evidence suffer from the same flaw. Neither takes into account the fact that lack of a concentration gradient does not prove lack of transport, especially when the substance in question may be cycling between the surface and the atmosphere. It is possible that emissions of mercury along the path of transport are simply compensating for deposition. Regarding point #1, the surface concentration gradient in question is apparently in terms of total gaseous mercury or total mercury (gas + aerosol). The authors need to be specific about this. Because of the different cycling behaviors of GEM versus RGM and PHg, this point of evidence is very weak. Regarding point #2, GEM does not deposit as readily as RGM or PHg and provides little support for the argument either. Given the apparent over-simplification of mercury speciation in the simulated emissions within the modeling domain (see section 2.1.3) and the weakness of the two points of evidence provided here, I feel the authors have little basis for conclusions regarding source-receptor relationships between China and Korea.

Response: We appreciate the reviewer's assessment regarding the trans-boundary transport and certainly agree with the reviewer that the description needs to be specific in terms of mercury species. In Section 3.4, we mainly tried to make the point that trans-boundary transport events are episodic instead of persistent, which was also shown by Kim et al. (2009). On the other hand, we would like to clarify that the emission speciation in this work is specific for each source category. In light of the long atmospheric lifetime of GEM, we still feel that there should be a concentration gradient if there are persistent winds carrying emitted GEM to a downwind location. At least this has been observed in our model results showing the gradient of total mercury concentration (dominated by GEM) from the China continent into the Pacific (Figure 3). To avoid the confusion, we will modify the discussion in this section so that the main point (trans-boundary transport events being episodic) is made without using the absence of concentration gradient as a direct evidence. We will also emphasize the emission outflow that enters global mercury pool increases global mercury burden, which will enhance the mercury concentration and deposition in other receptor regions.

Comment #9: Section 4 – "Removal" of RGM and PHg and "export" of GEM as described in the conclusions section and elsewhere in the paper are not simple transport issues. They are strongly affected by atmospheric oxidation of GEM to form RGM and PHg, both of which deposit rapidly to the surface. A significant part of the GEM said to be exported may have instead been converted to RGM or PHg and deposited within the domain. The authors' general statements about the contribution of East Asia emissions to mercury deposition in other regions (20∼30%) is reasonable given the evidence shown here. However, conclusions regarding the transport budgets of individual mercury species require the budget calculations to be done individually for each species and to be based on actually accountings of the inïňĆows and outïňĆows of each species as simulated by the model.

Response: We agree with the reviewer that the "removal" of RGM and PHg and "export" of GEM stated in the manuscript are not simple transport issues. In fact, this is the point that the authors attempted to make in this work: the atmospheric processes (emission, chemistry, dispersion, transport, and deposition, etc.) within a source region should be considered simultaneously in order to appropriately evaluate the influence of the regional emission. We recognize that the direct transport budget has been characterized by calculating the flux at each domain boundary traditionally. Here we are presenting an alternative mass balance approach to evaluate the outflow from a source region. Accordingly, we will revise the conclusion section to express this view with the greatest respect of the reviewer's comments.

Comment #10: There are quite a few errors in English grammar throughout the manuscript, but the intended message is clear in nearly all instances.

Response: We will go through another round of editorial revision to make sure that the errors are corrected before the submission of revised manuscript.

Comment #11: The caption for Figure 1 should specify that the emissions shown are for total mercury (GEM + RGM + PHg). Figure 2 has an error in the direction of the

arrow for deposition. It should be pointing down, not up.

Response: The emission values in Figure 1 are for total mercury. We will clarify it in the caption of the revised manuscript. We thank the reviewer for catching the direction of arrow in Figure 2 and will correct it in the revised manuscript.

Comment #12: The caption for Figure 3 should specify the species of mercury for the concentrations shown. Are the concentrations total Hg, total gaseous Hg, GEM?

Response: The concentration fields in Figure 3 are also for total mercury. This has been stated in the text and we will also clarify it in the caption of the revised manuscript.

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