**Atmospheric
Chemistry
and Physics
Discussions**

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

Anonymous Referee #1

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General Comments:

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 intercontinental 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.

Specific Comments:

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.

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/HgInventoryDocs.html provides gridded emission rates for each mercury species referenced to the year 2005.

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 emission 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.

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.

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. Outflow of anthropogenic emissions in the Base case was 68% while outflow in the Inferred case was only 62%. Were all species of Hg in the anthropogenic emission inventory 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 specific mercury species given the complexities of atmospheric mercury transformations.

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 flux 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.

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.

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 inflows and outflows of each species as simulated by the model.

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

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.

The caption for Figure 3 should specify the species of mercury for the concentrations

shown. Are the concentrations total Hg, total gaseous Hg, GEM?