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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 deeply appreciate the thoughtful review and constructive comments from the reviewer, and will incorporate the reviewer's suggestions in the revised manuscript once approved by the editor. Our point-by-point response to the reviewer's comments is given below:

General: This is a useful contribution to a very important subject and it merits publication, subject to revisions requested below. Specific: Three points need to be addressed before it is published.

Response: We thank the reviewer's assessment of the value of our work. The three specific comments raised by the reviewer are addressed in details as followed.

Comment #1: In the context of reducing global health hazards, one of the most useful results obtainable from this paper is the anthropogenic contribution to mercury outïňĆow, because this can be changed, whereas the natural contribution cannot. The study by (Shetty, et al., 2008) on which the natural emissions in this work were based, concludes that in East Asia, on average, the natural emissions are comparable to (∼80 % of) the anthropogenic emissions and exceed the latter considerably in the summer a result that is reflected in Figure 6. The abstract and conclusions, however, discuss only the total outïňĆow and deposition in the context of global values of these parameters, emphasizing the very large absolute amounts involved. I think it would be helpful to provide a better breakdown of natural vs. anthropogenic outïňĆow and deposition in these more prominent parts of the paper.

Response: This is a valuable comment and we agree with the reviewer in this regard. In our estimate, natural/re- emissions contribute to 50-60 % of the total mercury outflow and about 25 % of the total deposition caused by mercury emissions (i.e., anthropogenic plus nature/re- emissions), mainly in the form of GEM. We will incorporate the quantitative information in the Abstract and Conclusions of the revised manuscript.

Comment #2: BC/IC: The method purportedly is independent of the BCs because it relies on a subtraction (equation 3) that has BCs in both sides of the equation. It is useful to compare the outïňĆow calculated by this method (i.e. equation 3) with the net flux at the boundaries obtained from the GEOS/Chem BCs. Are these different?

Response: Boundary conditions have a very strong influence on the results of regional mercury simulations as demonstrated in Pongprueksa et al. (2008). IC has a similar but much weaker influence. The use of Eq. (3) was to isolate the impact caused by mercury emissions from the boundary effects such that the role of mercury emissions can be understood. The authors understand that traditionally the transport budget was calculated by integrating the flux at each boundary. We anticipate the result obtained from Eq. (3) to be the same as the value obtained from the direct flux calculation, because the air mercury mass within the domain is subject to the same atmospheric

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processes in both cases.

Comment #3: It is curious that the model has such a large over-prediction of the PHg and RGM at Seoul and Cape Hedo, but at the same time gets the GEM in these locations right. The authors postulate that this might be caused by too much GEM leaving the mainland (and getting oxidized in transit) or too little deposition of the reactive species to the water. They also refer to the possibility of incorrect oxidation rates by NOx/VOC chemistry, which raises an important source of error: The emissions of criteria pollutants such as VOCs and NOx in this region are not well known, so the possibility is very real that the oxidation rate of GEM to RGM and PHg might be wrong. If the model over-predicts RGM and PHg at a remote site due to an oxidation rates that are too high because of poorly known emissions of VOCs and/or NOx, then the oxidation rates might be too high in the domain as well. This would lead to a high removal rate of GEM, which is consistent with the observation that nearly all mainland measurements are higher than the model predictions. This is a different explanation than the common one that the emissions must be diluted over the grid square. While the latter is certainly true, it is difficult to quantify and thus one should use it cautiously and not as a catch-all for model failures. Moreover, this point can be tested easily by comparing the ozone levels obtained from the model with measurements. Such a comparison is extremely useful as a reality check for any work that is sensitive to atmospheric oxidation, which is the case here. We read on page 21297 "In the absence of mercury emission input, the mercury mass entering the model domain from the boundaries is readily removed due to chemical oxidation of GEM followed by dry and wet deposition." This shows that oxidation in the domain is an important process and will influence the outflow significantly. Thus I agree with the last line in the paper: "Major uncertainties of this assessment include mercury chemical mechanisms and mercury speciation of the anthropogenic emission estimates. Further understanding of mercury chemistry and emission processes will greatly reduce the uncertainties." Since both the authors and the referee agree that this is a problem, I suggest that a comparison with ozone be included in the work to assess the importance to the result of oxidation due to lack

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of information about the NOx/VOC emissions.

Response: We appreciate the reviewer's insightful comment and agree that the oxidant concentration needs to be check. In fact, we did. The monthly average surface ozone concentration in the mainland ranged from 30 to 70 ppbv, very typical of regional model results at this spatial resolution. Hydroxyl radical concentration was also within the reasonable range (in the order of 106 - 107 molec cm-3 midday). Compared to the limited available ozone data in Beijing and surrounding areas, the fractional mean bias was within $\pm$30 %. Therefore, we feel that the VOC and NOx emission inventories were representative, and the photochemistry was simulated appropriately. This was also demonstrated in another published work by one of the co-authors (Streets et al., 2007, doi:10.1016/j.atmosenv.2006.08.046). On the other hand, we feel that the original discussion (Lines 17-24 on page 21294) over-emphasizes the off-coast photochemistry and should be modified. What we meant was that the over-prediction of RGM/PHg may be attributed to a combination of the stated three reasons (uncertainty in emission speciation, the lower dry deposition over water surface and the residual photochemical activities off the continent), with the emission speciation uncertainty being the most important one. We thank the reviewer for pointing this out and will modify the text to avoid the confusion in the revised manuscript.

Comment #4: Technical: The grammar should be reviewed and improved. Also, there seems to be a confusion between "removal" and "export". On pg 21291, line 25: "A positive value of transport budget indicates a net removal of mercury mass in the domain (what's coming in is greater than what's going out); while a negative value indicates a net export of mercury from the domain. The mercury outïňĆow caused (or enhanced) by the mercury". This is confusing. I guess it means a removal of mass from air that is coming into the domain, not a removal IN the domain? This occurs later as well.

Response: We will go through another round of editorial revision to make sure that the grammatical errors are corrected. And yes, "removal" means "the removal of mercury

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mass from air coming into the domain"; and "export" means "the increase of mercury mass in air leaving the domain." Both will be made clear in the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 21285, 2009.