**Atmospheric
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Comment

Interactive comment on "Estimation of speciated and total mercury dry deposition at monitoring locations in Eastern and Central North America" *by* L. Zhang et al.

L. Zhang et al.

leiming.zhang@ec.gc.ca

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Responses To Referee #2

We greatly appreciate all of the comments, which have improved the paper. We have revised the paper by addressing all of the comments.

RC- Reviewer's Comments; AC – Authors' Comments

RC: Overall, I thought that this was a very good and well-organized manuscript. I believe that the authors provided a reasonable description of the previous work performed in this research field and they included references to a wide range of authors who have

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contributed to this field. The methodology section was well-written, though some improvements could be made as detailed below. While the presentation of results was a bit cumbersome at times given the significant quantitative results presented in the text, I was pleased to see that the authors provided information on the ranges of values obtained in the study, as this helped to put into perspective the large range of mercury dry deposition flux rates that are likely present in nature. Additionally, I was pleased to see a significant discussion of the uncertainties associated with the inferential modeling approach. This was underscored by the authors' discussion on how their estimates might vary due to the uncertainties in the input parameterizations.

I believe that this manuscript provides an important contribution to the understanding of science of mercury dry deposition in part because it addresses the sometimes ignored importance of gaseous elemental mercury (GEM) dry-deposition deposition to natural ecosystems. The assumption is often made that the dry deposition of gaseous elemental mercury is of lesser importance than that of gaseous oxidized mercury (GOM) and/or particulate bound mercury (PBM). The results of this modeling effort, and the information provided by litterfall measurements, suggest that modelers must seriously consider this process and not simply assume that GEM dry deposition is negligible due to is volatility and relative insolubility. Even small deposition rates could result in significant deposition due to the size of the GEM atmospheric pool. That said, the authors do a nice job of emphasizing differences in deposition and NET deposition of GEM. One issue that the authors might was to consider commenting upon (see below) is the bioavailability of GEM once taken up by vegetation and then deposited via litterfall.

While not the focus of this paper, I felt that the discussion on the relative importance of wet and dry deposition was too short. This is a very important issue in the attempt to obtain a better understanding of the environmental cycling of mercury. If the authors are going to include this section, they should expand discussion and provide a more complete and detailed comparison. I believe that this could be done relatively easily, without greatly expanding the length of the manuscript.

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Finally, "the Conclusions and Recommendations" section was a bit short, but was to the point and provided an adequate review of the manuscript's main findings.

AC: We have added discussions on the 'bioavailability of GEM' (more details below). We have added a more detailed comparison by listing the dry and wet deposition values at all of the collocated AMNeT/MDN sites (the new Table 3 in the revised paper). Related discussions have also been added in Section 3.6.

RC: My main concerns with the manuscript are:

RC: a)While the authors are correct in noting the importance of GEM to the total mercury dry deposition loading from the atmosphere, they neglect to discuss a second and related key issue: How bioavailable is the mercury taken up by the vegetation (presumed to be mostly GEM) and delivered to the surface as literfall? While from a numerical perspective GEM dry deposition is important (typically greater than GOM or PBM), if it is bound to organic matter and not released, are not GOM and PBM then more important in the overall cycling. Based upon recent work that shows that biomass burning is capable of releasing significant amounts of GEM to the atmosphere, it is quite possible that over longer time scales, the organically bound GEM may eventually be released back into the atmosphere. I think some very brief (one paragraph) discussion of this issue would make the manuscript be more complete.

AC: We have added a paragraph and several references at the end of Section 3.5 to address this comment. We have made the following points: (1) Litterfall can be an important source of organic matter to streams (Benfield, 1997). Hg bound to organic matter can be methylated in riparian wetlands and similar conditions in the stream or stream corridor, making it bioavailable; (2) Songbirds and bats that feed on invertebrates have been shown to accumulate methylmercury concentrations at levels of concern (Evers et al. 2012). The authors explained that methylmercury in the invertebrates is most likely from their consumption of either forest canopy foliage or leaf litter on the forest floor, or consumption of lower trophic level invertebrates that feed on fo-

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liage or leaf litter. This is indirect proof that some of the Hg in the foliage and litterfall must be bioavailable because it is in the terrestrial food chain; (3) Methylmercury was detected in all of the litterfall samples reported in Risch et al. 2012. Methylmercury is the bioavailable form of Hg.

RC: b) Throughout the paper, the authors refer to the results from the model as "estimates". The truth is, surrogate surface measurements and litterfall measurements are also estimates. By not acknowledging this fact, the authors assign greater level of certainty to the measurement results than might be appropriate.

AC: We have rewritten the second paragraph of the Introduction (also based on one comment from Reviewer #3) and stated that surrogate surface measurements and litterfall measurements are all estimates. Besides, the uncertainties using different methods were discussed in many places in the paper. This should avoid any impression that the measurements are true deposition values.

RC: While there are a few sections within the manuscript which should be strengthened, I feel that this manuscript is worthy of publication following minor revisions.

RC: Specific Comments:

RC: Page 2788, Line 14: I believe that it is more appropriate to spell out numbers less than ten when not indicating a measured value. In other words, "two-hourly" is probably more appropriate than "2-hourly". Such corrections would be needed in other places within the manuscript.

AC: Corrected.

RC: Page 2788, Line 14: The authors note that individual hourly GEM and two-hourly GOM and PBM values were used. Were two Tekran speciation systems used at each site, with one system for GEM and a separate system for GOM and PBM? When a single system is employed, the typical operational procedure with these systems is to have a one-hour sampling cycle (during which time GEM is quantified using five minute

averages) and then a one-hour desorption cycle (during which time GOM and PBM are quantified). The result is to have what amounts to hourly average GEM, GOM and PBM data reported every other hour.

AC: The review is right about the procedure. This is why we stated in the abstract that two-hourly data were used in this study. However, two Tekran system have been used at two sites so hourly GEM data were available at these two sits. We have modified this sentence to: "Hourly and two-hourly observations, with intervening hours of instrument analysis"

RC: Page 2789, Line 12: The authors note that net GEM deposition was obtained using inferentially modeled GEM deposition, minus GRAHM estimated re-emission plus natural emissions. Were the GRAHM modeled re-emission values consistent with those reported by other regional chemical models?

AC: We have added the information in the revised paper that most mercury transport models use the same GEM emission model for natural surfaces.

RC: Page 2790, Line 3: What is the justification for the mesophyll resistance value assigned to GEM? Page 2790, Line 10: The authors should provide a more detailed description of their selection of scaling factors (alpha and beta) used for GEM. The explanation that "adjustments were based upon GRAHM-simulated GEM concentrations" does not provide much information for the reader to determine if such adjustments are appropriate.

AC: All of these are empirical parameters which were first assumed based on their solubility and/or reactivity. Model sensitivity tests were then conducted and compared with available measurements of Vd values, as described in Zhang et al. (2009). At a later time, when testing the dry deposition scheme in GRAHM, it was found that the GEM concentrations were somewhat underpredicted using the original beta value (0.2) (A. Dastoor, personal communication, also see Zhang et al., 2012a). We thus proposed to reduce the beta value to 0.1. We have rewritten this paragraph to explain

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the details.

RC: Page 2790, Line 25: Feddersen reference is listed as "to be submitted", but listing as in Line 25 would suggest that it is an accepted, peer reviewed publication. Perhaps it would be more appropriate to list this as "personal communication" or "unpublished data". I am not questioning the quality of the Feddersen work or the validity of its conclusions, but I am not sure that this a valid reference as listed.

AC: Reference modified.

RC: Page 2791, Line 17: The authors should specify the Canadian meteorological model used, which I assume to be the Global Environmental Multiscale (GEM) model.

AC: The model is now spelled out in the revised paper although we omit its abbreviation (GEM) to avoid confusion with the mercury name (GEM) used in this study.

RC: Page 2791, Line 21: The meteorological data used for the inferential model was obtained from a 15km x 15km resolution meteorological model. One might assume that the turbulence characteristics of the meteorological data were influenced by the description of the land use at this resolution. How might this have influenced results, when the inferential model only considered land use of the surrounding one kilometer?

AC: We do not use the turbulence characteristics-related parameters predicted by the model for the calculation of Vd. Instead, we use grid-averaged wind speed, temperature, relative humidity etc., to calculate friction velocity (and other parameters) for each land use category. Apparently, within the same model grid, the calculated friction velocity is larger over rough surfaces than over smooth surfaces. As long as the meteorological fields are reasonably forecasted, this approach should be theoretically appropriate. However, if a model grid was too big (as was the case for many early forecast models), using the grid-averaged wind speed might underpredict the turbulence intensity since the sub-grid scale turbulence was averaged out. A sub-grid scale velocity was parameterized in Zhang and Brook (2001) (A.E., 35, 3841-3850) to address this

issue a decade ago. Since then, the Canadian weather forecast model has increased its spatial resolution (to 15kmx15km). We thus think the approach is not needed here at such a high resolution.

RC: Page 2793, Line 1: The authors note that: "Dry deposition of GOM+PBM, net dry deposition of GEM, and litterfall measurements were also marked on a wet deposition map for easy comparison." Which map are they referring to?

AC: We referred to Figure 4. We did not specify the figure number at this place because we had not mentioned Figures 2 and 3 yet. In the revised paper, we have modified the sentence and moved it to the beginning of Section 3.5 and specified the figure number.

RC: Page 2793, Line 6: Ambient concentrations are reported here and in Figure 2. What are the instrument detection limits for the GOM and PBM species and how might this impact the interpretation of overall results?

AC: A recent study also using AMNet data by Baker and Bash (2012) stated that the detection limit is 1 pg/m3 for both GOM and PBM. This would have no impact on the interpretation of the results since annual GOM and PBM were 2 to 20 times higher than the detection limit. Besides, the highest concentration events dominated the total dry deposition budget. We have added the detection limit information and related references in Section 2.2

RC: Page 2793, Line 8: It is not clear what the authors mean be geographical ratios?

AC: We have rewritten this section including this statement.

RC : Page 2796, Line 11: Lombard et al. (2011) reference is missing in the "References" section at end of manuscript.

AC: Reference added.

RC: Page 2796, Line 24: What do the authors mean by "concentration adjustment"?

AC: Different study periods had different average concentrations. Comparing the model

estimated fluxes directly with measurement estimated fluxes would not make sense. We first adjusted the modeled flux by the same scale as the concentration ratio between the two study periods and then compared with the measurements.

RC: Page 2799, Line 1: Also, the authors later note that Huang et al (2012) used the same inferential model with observed meteorology. For the present study, were comparisons made between dry deposition velocities derived from modeled meteorology and observed meteorology at any of the sites? Just curious?

AC: We have added a brief comparison in the revised paper.

RC: Page 2799, Line 11: If the coarse fraction of PBM is assumed to be 30% of the total, why would the dry deposition of PBM need to be adjusted by a factor of two or more? Is this due to a the larger dry deposition velocity for coarse PM? The magnitude of adjustment seems extreme. Perhaps not, but a more detailed explanation would be helpful here.

AC: Two reasons: (1) the coarse fraction mass was not monitored; and (2) Vd for coarse particles can be 2 to 5 times higher, depending on if there is a small fraction of PM10+ (see Zhang et al., 2012, ACP, 12, 3405-3417). Thus, the flux ratio between total PM and PM2.5 $(0.7*Vd+0.3*2*Vd)/(0.7*Vd)$ is close to a factor of 2; $(0.7*Vd+0.3*5*Vd)/(0.7*Vd)$ is more than a factor of 3. If the majority of the coarse particles are close to 2.5 um (instead of > 5 um), then the Vd of the coarse particles would be similar to those of fine particles and the uncertainty would be less than a factor of 2. Another extreme case would be at coastal locations where 50% or more of the particles are in the coarse fraction. In this case, total fluxes can be underestimated dramatically, e.g., $(0.5*Vd+0.5*5*Vd)/(0.5*Vd)=6$, by a factor of 6. Combining all of the scenarios, a factor of 2 uncertainty is very likely.

RC: Page 2802, Line 22: The wording used in this line is awkward. I would suggest: "dry and wet depositional loadings".

AC: Corrected.

RC: Page 2803, Line 6: An example of what was noted earlier. Namely, the authors only refer to inferentially modeled values as estimates. In reality, surrogate surface measurements are only estimates, as well.

AC: This was made clear in the Introduction.

RC: Page 2805, Line 15: Engle reference out of alphabetical order.

AC: Corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 2783, 2012.