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Atmospheric Chemistry and Physics Discussions

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.

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We greatly appreciate all of the comments, which have improved the paper. Our point-by-point responses are detailed below.

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

RC: This manuscript addresses some of the shortcomings of previous inferred dry deposition studies by comparing their dry deposition estimates to measurements of Hg in environmental media. The results presented in this manuscript are important.

The limitations of GOM measurements using KCl denuders is not sufficiently dis-

cussed. In particular there needs to be a discussion of GOM measurement artifacts when using KCl denuders in the presence of oxidants and how that uncertainty may impact the results (see Lyman et al. 2010b, it is cited in the manuscript but not discussed).

AC: In the revised paper, we have added this statement and have referred to previous studies for more details: "For example, a lower efficiency for capturing GOM was recently found by using KCl-coated quartz denuders, a standard method in Tekran speciation systems for GOM measurements. The GOM concentration was likely biased low, e.g., up to 55% under high ozone concentration conditions (Lyman et al., 2010b)." The purpose of the present study is to estimate dry deposition using the inferential method making use of the recently-available monitored speciated ambient Hg concentration data at multiple locations. Thus, the impact of the measurement uncertainties in the monitored concentrations on the estimated dry deposition was discussed in detail using available information from the literature (including the one mentioned by this reviewer). We believe that a detailed discussion on the limitations of the instruments used to measure the Hg concentrations is out of the scope of the present study. Such discussions are more appropriate in studies focusing on instrument inter-comparisons, or even in studies focusing on the measurements of speciated Hg concentrations. In a study using the modeling approach to estimate dry deposition, knowing the magnitude of the uncertainty in the measured concentration should be enough.

RC: In several areas the manuscript describes results as "significant", describes results as "better" and quantifies errors and uncertainty but the statistical metrics used to assess these results are not given. In general this manuscript would benefit from a better quantification of the results and the use appropriate statistical metrics.

There are some typos and some of the language used in this manuscript is incorrect and the manuscript could benefit from a thorough proof reading.

The magnitude of the GEM re-emissions and dry deposition velocity appear to be crit-

ical in determining the net GEM flux and the magnitude of the total Hg deposition. The uncertainty in the total Hg deposition to these variables should be discussed more given the uncertainties in them.

The comparison with throughfall measurements is a strong point in this manuscript. However, I would like to see a more quantitative presentation and discussion of these results, e.g. plotting throughfall deposition totals, and modeled totals as a function of the GEM, GOM, PBM concentrations or plotting the throughfall deposition totals as a function of the number of Hg sources in a 100 km radius. If GEM dry deposition is driving the total Hg dry deposition to these ecosystems, then the throughfall measurements should be better correlated with the ambient GEM concentrations than GOM or PBM.

AC: In the revised paper, wherever possible, we have replaced the qualitative descriptions with quantitative descriptions. Thorough proofreading has also been done by English-native speakers. Uncertainties in the GEM reemission have been briefly mentioned in the revised paper; however, at the present stage we cannot quantify the uncertainties. We have pointed out that several well-known mercury transport models in North America all use the same approach in estimating the GEM reemission. In our opinion, comparison of litterfall measurements with speciated and total Hg dry deposition is quantitative because all of the values were both marked on the same map and provided in Table 2. Litterfall measurements have been published in a previous study (Risch et al., 2012a). Here, the litterfall measurements were only used to asses if the model-estimated dry deposition is reasonable. Besides, plotting litterfall deposition against speciated Hg concentration gives little knowledge on Hg dry deposition. Litterfall Hg is the Hg that is retained in the leaves at the end of the season. Constant Hg cycling happens all the time. Plotting the throughfall deposition against Hg sources in a 100 km radius also gives no information at all since the litterfall Hg was most likely primarily from GEM (as demonstrated in the present study) and GEM is more evenly distributed globally. In other words, the canopy characteristics (e.g, LAI)

and meteorology play more important roles in the litterfall measurements than the GEM concentration itself.

Specific comments:

RC: Page 2791 Line 5: What exactly are the input parameters scaled by LAI?

AC: The sentences following Line 5 (Lines 10-14) explain all of the parameters.

RC: Page 2792 Lines 5-8: Is there a means of placing a bounds on the error that soil emissions may cause in net GEM flux, e.g. a model sensitivity?

AC: Several well-known mercury transport models in North America all use the same approach in estimating the GEM reemission. At the present stage, we cannot quantify the uncertainties with reasonable effort. It is possible to study this as a separate effort by the Hg modeling community. This statement has been added in the revised paper.

RC: Page 2792 Lines 20-21: Six sites have both dry deposition and litterfall measurements. Why not look at all the litterfall sites. If GEM is the predominant deposited species, we would expect relatively uniform litterfall deposition values because GEM has a relatively long atmospheric lifetime/or is constantly recycled resulting in relatively uniform concentration fields.

AC: The constant recycling of Hg results in a rather uniform GEM concentration (compared to RGM and PBM), but not necessarily for the litterfall deposition due to the dominant effects of LAI and the meteorological conditions on the litterfall Hg. Thus, first we look at the range of the litterfall values from all of the available sites, then we look at the sites that have both litterfall and ambient Hg (where dry deposition was estimated).

RC: Section 3.1: This section could generally benefit from a more quantitative discussion.

AC: This section has been rewritten in the revised paper to quantitatively discuss the

geographical and seasonal variations in the three forms of Hg.

Page 2794 Lines 2-3: "GOM and PBM where highly variable ... much larger than GEM" The authors should quantify this?

AC: This sentence is a follow-up to the major statement made at the beginning of the section where the spatial variation was quantitatively stated (lines 6-8 on Page 2793). The statement has been split into separate sentences in the revised paper to discuss GEM, GOM, and PBM separately.

RC: Page 2794 Lines 3-4: "concentrations in spring were much higher" How much higher?

AC: Due to the large number of sites shown in Figure S1 and Table S3, it is difficult to compare every season in a quantitative way. In the revised paper, we first present the general seasonal patterns, and then give the range of the seasonal variations by calculating the ratio of the highest to the lowest seasonal concentration for each site.

Page 2794 Lines 5-7: "At two other urban/suburban sites..." Which sites?

AC: Sites (NJ05, UT96) have been added in the revised paper.

RC: Page 2794 Line 8: "For PBM, the highest season concentrations..." This was also observed by Amos et al 2012 and they derived an empirical PBM - GOM partitioning model to describe this variability.

AC: Literature has been cited and information has been added in the revised paper.

RC: Page 2794 Line 15: "dry deposition theory" I have heard of that and if the authors are going to stick with it they need to provide a citation. The following discussion appears to discuss the precipices of boundary layer meteorology and similarity theory as they relate to air-surface exchange (see Stull 1988). Alternatively the authors could cite micormeteorological theory (see Baldocchi et al. 1988).

AC: The discussion in this paragraph was focusing on the dry deposition mod-

els/parameterizations constructed for mercury species, and based on these models, what parameters should control the Hg dry deposition velocities. We have removed the 'dry deposition theory' and replaced it with 'models/parameters constructed for mercury species'.

RC: Page 2795 Lines 2-3: "turbulence intensity (friction velocity)" The friction velocity, u*, is not turbulence intensity and is not defined in the manuscript or alluded to why it would be important. Mechanical turbulence intensity, what the authors are discussing, is often defined as the standard deviation of the mean wind speed divided by the mean wind speed. u* is the shear stress defined as the square root of magnitude of the surface Reynold's stress divided by the atmospheric density and is an important variable in deriving the aerodynamic and boundary layer resistances used in estimating dry deposition.

AC: To avoid confusion, the second half of this sentence was replaced with this statement: 'Note that Ra, Rb, Rns and Rs, defined in Section 2.4, are all smaller under stronger wind conditions.'

RC: Page 2796 Lines 1-2: "significant Hg emissions" What makes these Hg emissions significant?

AC: Figure 1 shows the point sources surrounding each site. Point sources larger than 200 kg/yr seem to have a direct impact on the estimated GOM and PBM dry deposition. We have added this annotation after "significant Hg emissions": "(e.g., point sources > 200 kg/yr)."

RC: Page 2796 Lines 6-8: Is this an artifact of estimating the new GEM flux and are there litterfall measurements to support this claim?

AC: We think the results can be reasonably examined. For example, in Section 3.5, the estimated GEM (and total) dry deposition are comparable with monitored litterfall and throughfall deposition at ELA.

RC: Page 2796 Line 29: "Good agreement between ..." What was used as a measure of good? How was this quantified. Because these estimates where within the range of surrogate surface measurements?

AC: Taking NY20 as an example, during the study period presented in Huang et al. (2012), the concentration was 1.9 ug/m3 and the deposition was 0.8 ug/m2/yr; during our study period, the concentration was 1.2 ug/m3, and the deposition was 0.4 ug/m2/yr. After the concentration adjustment, the percentage difference [(A-B)/A or (A-B)/B] and the absolute difference [2(A-B)/(A+B)] were all in the range of 20-27%. As for NY95, the study periods mostly overlapped each other and the measured and estimated depositions were also similar (4.4 versus 3.9 ug/m2/yr, or a 10% difference). We therefore think that the agreement was reasonable. We have rewritten a few sentences in the revised paper to make this clear.

RC: Page 2797 Line 15: "Great Lakes region" This is also qualitatively shown for CMAQ and CAMx at AMNet sites in Baker and Bash 2012.

AC: This reference has been added in a few places in the revised paper.

RC: Section 3.4: The impact that oxidants have on GOM measurements using KCl denuders should be discussed in this section (see Lyman et al. 2010b).

AC: See our response at the top.

RC: Page 2798 Line 11: "lower than 40%" How was this determined?

AC: The uncertainty in the GOM concentration measurement is on the order of 40%. It is assumed that uncertainties should be lower than this percentage under high concentration conditions and may be higher than this percentage under very low concentration conditions. But the total dry deposition is decided by the high concentration cases.

RC: Page 2798 Line 20: "should be generally within a factor of 2" Why would that be? If GOM deposits like HNO3 then the uncertainty would be dominated by uncertainties in the aerodynamic boundary layer resistances because canopy resistances are believed

to be near zero (see Flechard et al. 2011). It is unclear how that equates to a factor of 2.

AC: The reviewer is right in that GOM dry deposition is dominated by the aerodynamic resistances. However, different formulas (although they differ slightly from model to model), different land-use dependent input parameters (e.g., roughness length), and meteorological data can cause the calculated Vd to differ significantly. Based on the results from Flechard et al. (2011), the estimated HNO3 dry deposition from using four different dry deposition models (including the Canadian dry deposition model used in the present study and three European models) were mostly within a factor of 2.

RC: Page 2798 Line 23: "within 30% differences" If this is just at several sites, which sites were included in the comparison and how does it compare to all the collocated sites.

AC: Surrogate surface measurements were only available at three sites and only for short periods. This '30%' applies to all the three sites (details were presented in Section 3.3 as pointed out in the text). There is no other collocated site.

RC: Page 2799 Line 2: "only slightly" Is this referring to the 30% difference mentioned on the previous page? If not, please quantify this statement.

AC: Three sites were discussed in Huang et al. (2012) and at one site three different samplers or surrogate surfaces were also used. The quantitative differences between the model estimates and the measurements cannot be described in one sentence. We have therefore modified the sentence to this: "Huang et al. (2012), on the other hand, found much closer agreements between model estimates and surrogate surface measurements, with model estimates lower by 10% to 50% (a factor of 2), depending on location and sampling method, than the measurements."

RC: Page 2799 Lines 27-29: Doubling GOM+PBM deposition may not change the conclusion but changing your GEM dry deposition due to inaccurate emission estimates

could. The net GEM flux should be discussed in more detail.

AC: If net GEM dry deposition was underestimated due to the overestimation of GEM emission, then the conclusions stay the same (because GEM dry deposition was even more important than presented here). If net GEM dry deposition was substantially overestimated (e.g., by a factor of 3 or larger) due to the underestimation of GEM emission, then the conclusion needs to be adjusted to some extent. However, this is very unlikely since a large portion of litterfall deposition would not be explained by the total estimated dry deposition. In theory, the total dry deposition should at least be in a similar range (if not much higher) to the litterfall deposition because the total of the litterfall and the throughfall might be a better indication of the total dry deposition. Some of the above discussions were already in the ACPD paper (such as the discussion on the ELA site). At the present stage, there is no information that can enhance the discussion of the GEM flux. In the revised paper, we have added a brief discussion that GEM emission cannot be quantified at this time and that most mercury transport models use the same emission scheme.

RC: Page 2800 Lines 23-24: How was significance determined?

AC: Considering the potentially large uncertainties in both model estimates and litterfall measurements, we think 10-20% differences were insignificant as noted in the bracket.

RC: Page 2801 Line 12: "with low soil Hg emissions" is unsupported by the cited literature or research presented in the manuscript. Graydon et al. 2009 used isotropically labelled Hg to show that the foliar Hg did not contain a large contribution from the soils at ELA.

AC: We made this assumption based on these indirect evidences (1) the ELA site is a remote site with few nearby Hg sources (Figure 1); (2) modeled GEM emission from natural surfaces at this site (ELA) and a few other remote sites (e.g., NS01) were among the lowest (see Figure 3 the difference between GEM and Net GEM deposition). We have added this explanation in the revised paper.

RC: Page 2802 Lines 1-2: "are at best model estimates with large uncertainties" Please quantify what large uncertainties means.

AC: The uncertainties for each Hg species are detailed in Section 3.4. Here we have simply added ‘a factor of 2 uncertainties in the estimated species and total dry deposition’ as our best guesses.

RC: Technical corrections

RC: References

AC: Technical corrections have been addressed and some of the suggested references have been added in the revised paper.

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