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Interactive comment on "Atmospheric wet and litterfall mercury deposition in typical rural and urban areas in China" *by* Xuewu Fu et al.

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

RC: This manuscript presents wet deposition and litterfall mercury (Hg) measurements from multiple sites across China. Samples were collected over varying time frames, ranging from one to four years for wet deposition and from one month to one year for litterfall. The objective of this study is to quantify Hg inputs to the ecosystem through these two processes, and inform the Hg budget for China. This is an important contribution to the scientific literature given the relatively limited understanding of Hg biogeochemical cycling, and given the relative contribution that emission sources in China apparently make to the global Hg pool. However, there are several major issues with the sampling methods as described here and also with the data interpretation that must

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Discussion paper

be addressed.

AC: We would like to thank the anonymous reviewer for their insightful comments on our manuscript. We have carefully assessed the comments and revised the manuscript according to the reviewers' recommendations. The corrections are shown in blue fonts in the revised manuscript.

RC: Section 2.2: The wet-only precipitation sampling and collection method needs significant clarification. This is probably the biggest issue I find with the manuscript. Specifically:

AC: we agree with the reviewer that sampling method should be specified. In line 145-168 on page 6 in the revised manuscript, we added descriptions of the sampling method and discuss the potential artifacts related to the sampling method.

RC: What type of wet-only collector was used? The name of a common commercial collector is not provided, so was the collector self-constructed? In this case more details should be provided if this particular collector has not already been described in the published literature.

AC: wet-only collectors used in this study were commercial collector made in China. The name and operational principle of the collector were added in line 148-155 on page 6 in the revised manuscript.

RC: Why were the samples collected into such large (15-L bottles) when most wet-only collectors employ 1-L or 2-L bottles? Why was the sample transferred to a 250 mL bottle? Was the sample acidified (i.e. with BrCl as a preservative) prior to this transfer? If not, then are the authors certain that no Hg was lost to the walls of the 15-mL bottle? Was a 250-mL bottle always sufficient to hold the entire sample that was collected into the 15-L bottle?

AC: the wet-only collector was a borosilicate glass bucket with a diameter of 25 cm. It works like the funnel that used in previous studies (Landis and Keeler, 1997;Prestbo

and Gay, 2009) to collect enough precipitation sampling during rain events. The borosilicate glass bucket was open during rain event and sealed at the end of the rain event using a cover controlled by a moisture sensor. The precipitation samples were generally kept inside the glass bucket for less than one day (transferred to the 250-mL bottle immediately after a precipitation event) and would have minor evaporation. After transferring to the 250-mL Teflon bottle, the precipitation samplings were kept in a refrigerator at 4 °C until Hg concentration analysis. We did not acidified the sample prior to this transfer. The precipitation was acidified using trace metal grade HCl (to 5‰ of total sample volume) after the transfer to the 250-mL Teflon bottle. We agree there might be loss of Hg to the wall of borosilicate glass bucket during the transfer. However, previous studies have verified that there is minor adsorption of Hg to the clean Teflon and borosilicate glass surface (Vermette et al., 1995;Landis and Keeler, 1997). During heavy rain events (e.g., accumulative precipitation depth of >6 mm), the 250-mL Teflon bottle can not hold the entire samples collected. In this case, Extra samples were transferred to another Teflon bottles for anion and trace element analysis or abandoned in the field. The description of the collector and the transfer of the samples are shown in line 150-168 on page 6 in the revised manuscript.

RC: The text says that before each new sample the borosilicate glass sampler was rinsed with Milli-Q water. Does this mean the sample funnel and the 15-L bottle were not replaced between samples? Milli-Q would not be sufficient to clean the funnel or other parts of the sampling train appropriately between samples. New sampling materials should be installed or the materials should be cleaned with a dilute acid. This needs significant clarification. The authors should discuss any potential uncertainties or carryover introduced with this method and/or discuss their collection of field blanks to determine a lack of carryover.

AC: the sample funnel (a borosilicate glass bucket) was not replaced between samples. We agree with the reviewer that it will be better using diluted HCl solution rather than Milli-Q water to the clean the collector. In this study, the collector was a borosilicate

glass bucket. It is characterized by simple structure and was clean during field sampling (was baked for one hour in a muffle furnace at a temperature of 500 °C before field sampling and kept sealed during dry period). We therefore suggest it may have a minor adsorption of Hg and small cross contamination between samples. The filed blank was not conducted in this study, but a previous study using the similar collector observed a low filed blank (≈0.36 ng L-1) (Burke et al., 1995). We therefore speculate that the sampling method used in this study would have minor artifacts.

RC: Section 2.3: Are the litterfall collectors described here similar to or modeled after others reported in the literature? It would be helpful to know if this is a common method, or a new method developed by the authors.

AC: the litterfall collectors used in this study were similar to previous studies. We added the description of the collectors in line 197-198 on page 8 in the revised manuscript. References were also added in line 196 on page 7 in the revised manuscript.

RC: In several places it is stated that samples were handled or analyzed in a “clean environment”. What does this mean? Is this referring to a certified clean room or some other trace metal clean environment? Please elaborate.

AC: we specified the “clean environment” in line 209-210 on page 8 in the revised manuscript.

RC: Section 3.1 The paragraph on lines 224-234 is confusing. The paragraph starts by saying that higher concentrations are found in the summer wet season and lower concentrations are found in the winter dry season. But the rest of the paragraph says the opposite. Perhaps this was just a typographical area but it should be addressed.

AC: yes, this paragraph in line 224-234 in the original manuscript had the error. We changed it in line 254 on page 10 in the revised manuscript.

RC: The findings on lines 241-245 that wetter zones had more Hg wet deposition seem a little obvious. If there is more rain then, all else being equal, would we not expect

more Hg deposition? Please provide more information on what these findings imply.

AC: the implications of these findings were shown in line 279-280 on page 11 in the revised manuscript.

RC: Section 3.2: If TGM was not significantly correlated with Hg concentrations in litterfall at any site, this implies that of the possible factors controlling Hg concentrations in litterfall the ambient Hg concentration was not the most important here. In this case, what do the authors propose to be the driving factor controlling Hg concentrations in litterfall?

AC: atmospheric TGM is the dominant source of Hg in litterfall but the Hg concentration in litterfall is also affected by many other factors. We proposed several explanations for the lack of significant correlation between litterfall Hg concentrations and annual atmospheric TGM concentrations at the sampling sites in line 304-311 on page 11 and 12.

RC: Section 3.3 The statements on lines 308-310 contradict the findings discussed in Section 3.2 (referenced above). Here it is stated that Hg in litterfall is mostly due to uptake of atmospheric GEM, but previously you stated no correlation between litterfall Hg and ambient Hg. How do you resolve this?

AC: the statements in line 308-310 in the original manuscript did not contradict the finding in Section 3.2. The statements that Hg in litterfall is mostly from the uptake of atmospheric GEM did not mean a significant correlation between Littefall Hg and atmospheric TGM (or GEM), the concentration of Hg in litterfall could also depend on tree species, “leaf maintenance” period, and environmental factors as well as the mean atmospheric TGM concentration during the “leaf maintenance” period of each tree specie. The correlation established in section 3.2 used the annual mean atmospheric TGM at the sampling sites, and it was not equal to the mean atmospheric TGM concentration during the “leaf maintenance” period of each tree specie. There were many tree species at each sampling site and it is difficult to calculate the mean atmo-

spheric TGM concentration during the “leaf maintenance” period of each tree specie.

RC: Then, on lines 326-327 it is deduced that Hg deposition through litterfall played a predominant role in total Hg deposition in forested ecosystems in China. Is the “total” assumed to simply be wet deposition + litterfall? What about throughfall? Or dry deposition? Even if those two things were not measured they should be considered when drawing conclusions about total Hg input.

AC: the total deposition of Hg to forest ecosystems included direct wet deposition, litterfall deposition and dry deposition of GOM and PBM. The dry deposition of GOM and PBM to forests could be estimated using a comparison of precipitation and through fall data collected side by side (Gustin, 2012), and empirical model (Zhang et al., 2012). In this study, we calculated the dry deposition of GOM and PBM using both empirical model (Zhang et al., 2012) and throughfall in line 346-354 on page 13 in the revised manuscript.

RC: Conclusions: The manuscript ends with a statement that litterfall deposition contributes significantly to Hg deposition in China. Is this true for all of China? Or only for forested areas such as those sampled here? How much of China is forested compared to the total land area? Some clarification to these implications should be given.

AC: here we mean the Hg deposition in forest ecosystems in China. The wording has been corrected in line 490-491 on page 18 in the revised manuscript.

RC: Other comments: At no point in the text is the range of dates given for the sampling campaigns. It seems this can only be obtained from consulting Tables 1 and 2. Even though the sampling spanned different date ranges at each site, there should be at least some statement in the text describing the overall time frame. Also, any limitations of comparing sites to one another where the samples were not collected concurrently or even during overlapping years should be discussed.

AC: the overall time frame has been introduced in line 145-146 on page 6 in the revised

manuscript. Limitations of comparing sites to one another were shown in line 243-252 on page 9 and 10 in the revised manuscript.

RC: The manuscript title is a little misleading ("typical rural and urban areas") when in fact only one urban area was sampled. And what do the authors mean by "typical"?

AC: we agree with the reviewer the original title is a little misleading, and we changed it to 'Atmospheric wet and litterfall mercury deposition at urban and rural sites in China'.

RC: Figure 2: The data points for rain depth should not be connected to one another, especially if the record is not continuous. Lines connecting data points that are weeks or months apart imply that the values along that line are known, which they are not (or maybe it simply did not rain then). Rain depth measurements should be represented as bars rather than points on a line just as the THg concentrations are presented.

AC: we changed connecting line between data points of rain depth to dotted line. Using bars to present rain depth would make the Figure 2 difficult to be read.

RC: Figure 3: This graph is difficult to interpret in black and white. It is also a little misleading since samples were not collected at all sites in the same year(s). What is it that the authors want the reader to take away from this graph, and is there a way it could be presented more clearly?

AC: the Figure 3 shows the monthly variation in VWM Hg concentrations of precipitation at all the sampling sites, which were related to many factors as we discussed in line 256-264 on page 10 in the revised manuscript. Precipitation samples were collected continuously for at least one year at all the sampling sites, and therefore the monthly trend at each site could be depicted in this study. We agree with the reviewer that monthly trend may be slightly different at one sampling site, that will bring uncertainties to the monthly trend at the sampling sites. To present Figure 3 more clearly, we also added pattern in bars of Figure 3 in the revised manuscript.

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