Response to Reviewer #2

We greatly appreciate this reviewer's constructive criticisms that have improved the quality of this paper. We have addressed all of the comments carefully in the revised paper, as detailed below. The original comments are in black and our responses are in blue.

The paper attempts to review the present understanding of mercury dry deposition and Hg flux through litterfall and throughfall. Overall, the manuscript appears to be put together in short order and there are numerous issues that need to be addressed before consideration for publication.

R: Below is a summary of the major revisions that we have done in the revised paper.

- We have added the mean litterfall and throughfall values in the Abstract.
- We have revised two sentences in the Introduction as per the reviewer's suggestions.
- We have combined the first two paragraphs in Section 2.1 and added an additional reference to the bi-directional GEM model of Wang et al., 2014.
- We have added three sentences to the end of Section 3.4 to discuss why length of sampling is important and the differences caused by sampling frequency.
- Section 4 has been revised so that the focus is on North America, with explanations for the observed differences in this region, followed by a short discussion on GOM/PBM dry deposition in Asia.
- The median and mean values for litterfall Hg in Asia have been adjusted in Section 5 and four additional sentences have been added throughout this section for clarification.
- The mean and median values for throughfall Hg in Asia have been adjusted in Section 6 and an additional sentence comparing the reported values between Asia and North America has been added.
- Two sentences have been added to Section 7 to increase clarification of Figure 1.
- Changes have been made to the litterfall and throughfall values in Table 1 and an additional column, *n*, has been added to each region to indicate the number of sites used in the calculation of the values.
- An additional reference has been added to the reference section (Ma et al., 2015).

Specific Comments:

Title: The paper has an unbalanced coverage of topics. For the most part, the manuscript mainly discusses dry deposition and Hg deposition caused by the litterfall/throughfall/rainfall is a very small part. The title should be changed to reflect the context of presentation.

R: We feel that the title should be as short as possible, which is likely imbalance for each and every sub-topic covered in the paper. The length and content for each sub-topic are partly decided by the information available from the literature, besides their relevance to the main

topic/goal of the present study. We thus prefer to keep the original title for simplicity while trying our best to revise the paper to make it more balanced.

Line 5-9: What is the reason of using the median instead of the mean value?

R: The mean is particularly susceptible to the influence of outliers, therefore in order to get a more accurate view of the central tendency of the data, we use median in this study. Since the measurement data does not reflect a normal distribution, we have opted to discuss the results in terms of the median rather than the mean. But to be more inclusive, we have included the mean values in the abstract as well.

How many sites in Asia/America/Europe are included in the review?

R: For GOM and PBM, we have 17 sites for Asia and 41 sites for North America. For litterfall, there are 29 sites in Asia, 23 sites in the Amazon region, 16 in Europe, and 69 for North America. For throughfall, we have 11 sites in Asia, 1 in the Amazon region, 20 in Europe, and 29 in North America. Also see more information in our response to the next comment.

From the Table 1 and Figure 1, there are many studies that authors left out in this manuscript. For example, there are at least 70 sites that have the litterfall Hg deposition flux documented in America and Europe, while only about 20 sites are reviewed by authors.

R: While we have 108 sites for North and South America and Europe that have litterfall data, not all of these studies have enough data available to be able to calculate the annual Hg deposition flux from litterfall. In Figure 1, we have only included the sites that have measurements for litterfall, throughfall, and wet and dry deposition. We have added a sentence in the discussion for Figure 1 to inform the readers of our justifications for the number of sites provided in the Figure. This sentence reads “Figure 1 includes sites for which measurements for litterfall, throughfall, and dry and wet deposition have all been measured. This figure is provided to give a representation of the range of values for the various measurement methods”.

For Table 1, we had included 20 litterfall measurements for Asia, 14 litterfall measurements for Europe, and 92 litterfall measurements for North America. With the addition of the data from Ma et al. (2015; 2016), we now have 20 litterfall measurements for Asia. The data used to compile Table 1 are shown in detail in Tables S2-S5 in the SI document. Our intention was to present a clear and concise paper, therefore we focused our discussion on the major findings from our research. The details of the extensive datasets and studies reviewed are provided in the SI document. To make this clearer for the reader, we have added a column in Table 1 for each region that shows the number of data values, *n*, used in the calculations for each variable.

Line 7: The median value of Hg input through litterfall is not likely to be 22.3 c as authors suggested. This value falls in the lower range of the observed values in China. Much larger

values have been reported in earlier studies. [Fu et al., 2015; Ma et al., 2015a; Ma et al., 2015b; Niu et al., 2011; Z W Wang et al., 2009; Zhou et al., 2013; Zhou et al., 2015].

R: In our revised study, the calculated median is 34.8 μg m^{-2} y^{-1} and the mean value is 42.8 μg m^{-2} y^{-1}. Our range of values is from 4.2 to 219.9 μg m^{-2} y^{-1} based on data from 20 sites. These values include those reported in Wang et al., 2009; Fu et al., 2010a; 2010b; Niu et al., 2011; Zhou et al., 2013; Gong et al., 2014; Lang et al., 2014; Luo et al., 2015; and Ma et al. 2015; 2016. No values were taken from Fu et al., 2015 as all of the litterfall values reported in Fu et al., 2015 were from previous studies.

Line 9-11: It is questionable that GEM deposition to canopy has important contribution unless the authors regard the multiple processes of vegetative uptake as "dry deposition." This is because the Hg in litter is a result of multiple processes: uptake (most Hg0 and an amount of deposited Hg2+), oxidation, re-volatilization of chemically bounded Hg, etc. In addition, Hg deposition through litterfall is also closely linked to litter biomass production. In fact, the litterfall biomass production is the primary cause for elevated Hg deposition from litterfall in subtropical/tropical forests [Fostier et al., 2015; Zhou et al., 2013].

Answer: We agree that Hg in aged litter involves complex processes as listed by the reviewer. However, mercury contents from freshly collected leaves, which are commonly treated as litterfall mercury, are mostly from leaf uptake of atmospheric mercury. Besides, the dry deposition process is also very complex involving many meteorological, chemical, and biological interactions. This process is thus assumed as a simple mass loss to the surface in literature. Since litterfall mercury content is much higher than the possible maximum GOM+PBM dry deposition, it was thus concluded that GEM dry deposition contributed significantly to litterfall (see Zhang et al., 2012 for detailed discussion). Also see more information in our response to the next comment.

Line 37-44: Hg uptake from the atmosphere can translocate to braches, stems, and roots [Siwik et al., 2010; Yin et al., 2013], which is not accounted for based on the estimate using litterfall data. This is also the reason for the litterfall Hg likely represents the low-end of the Hg dry deposition.

Answer: We agree with the reviewer on this point, and we actually have published a more detailed explanation on this topic in one of our previous studies (Zhang et al., 2012) in which we explained: "To assess the reasonableness of these dry deposition estimates, and explore the sources of Hg in litterfall, estimated speciated and total Hg dry deposition were compared with collected litterfall Hg. The total net Hg dry deposition to a forest is the sum of the Hg in the litterfall, the Hg captured by the canopy and then emitted back to the atmosphere, the Hg washed off the canopy by precipitation (throughfall), and the Hg deposited directly to the underlying soils. Thus, litterfall deposition may be treated as the low-end estimation of the total Hg dry deposition to a forest, if Hg emission from the underlying soil is limited. On the other hand, if

soil Hg emissions are high and the ambient Hg concentrations above the forest are low, the litterfall Hg might be higher than the dry deposition above the canopy due to the interception of emitted Hg by the forest leaves. Based on the above arguments, it is reasonable to assume that total dry deposition and litterfall deposition should be similar on regional scales, although the differences can be very large at individual sites."

To emphasize this, we have revised the description as follows: "Mercury dry deposited to a forest canopy-soil system includes absorption of Hg by leaf stomata and cuticle, tree bark, and underlying soil. Some of the deposited Hg may emit back into the atmosphere while some may be translocated to the branches, stems, and roots. Mercury in litterfall includes a portion of the dry deposited Hg as well as capture of Hg emitted from the soil, although it may not account for the Hg that has been translocated. Mercury in throughfall includes wet deposited Hg above the canopy and a portion of dry deposited Hg washed off from the canopy. Thus, litterfall Hg likely represents the low-end of Hg dry deposition if Hg emission from the underlying soil is small, although it can be higher than the actual dry deposition above the canopy due to the interception of emitted Hg by forest leaves if soil Hg emissions are high and the ambient Hg concentrations above the forests are low."

Line 74-75: X Wang et al. [2014] should be included.

R: The text has been revised to include Wang et al., 2014.

Line 59-86: It is better to incorporate two paragraphs into one paragraph because of similar contents. It is also better to present the scheme in each model by a table for clarity.

R: We agree with the reviewer and have revised the paper so that the first two paragraphs in Section 2.1 have been integrated into one. A summary of the dry deposition schemes for each model is provided in Table S1 in the SI document and the statement referring readers to the SI document has been modified in the revised manuscript as follows: "A summary of the various model schemes and their algorithms is provided in Table S1."

Section 2.1: An earlier review by [Gustin et al., 2015] have discussed the limits of modeling to simulate the GOM/PBM dry deposition, and another review by [Zhu et al., 2016] also discussed the simulation of dry deposition of GEM. What is the difference in the manuscript compared to these earlier reviews? At the present form presented by authors, there does not seem to be any new information.

R: In Section 2.1 of our paper, we discuss the current knowledge of dry deposition schemes in chemical transport models. This includes a review of recent model inter-comparison studies, which are not included in either the study by Gustin et al. (2015) or by Zhu et al. (2016). As discussed in the following comment, we have directed the focus of our study to be on GOM and PBM, which differentiates our study with that of Zhu et al., 2016. Modelling studies that are included in our study that were not included in the review by Gustin et al., 2015 include the

modelling work by Baker and Bash, 2012; Zhang et al., 2012a; Wang et al., 2014; Chen et al., 2015; Cheng et al., 2014; 2015; and Travnikov et al., 2015.

Section 3.2-3.3: The earlier review papers by [Gustin et al., 2015] and [Zhu et al., 2016] have clearly presented and discussed. I cannot find any new information in current manuscript.

R: We agree with the reviewer that the reviews by Gustin et al., 2015 and Zhu et al., 2016 are clearly presented and discussed. The review by Gustin et al., 2015 provides an in-depth review of GOM and PBM measurement techniques but does not include analysis of available measurements. The review by Zhu et al., 2016 focuses on GEM, which is why we do not go into great depth on GEM in this paper. In this paper, our intention for this section is to provide the reader with a general overview of the various sampling techniques that were used for the measurements of the data reviewed in this study. In terms of new information that our paper provides, a new sampling technique that was not discussed in either of the other two reviews, the turf surrogate sampler technique (Lynam et al., 2015), is discussed in this manuscript.

Line 372-388: Why this information is important, and what is the difference among different methods? Can the results from different methods be compared?

R: This information is important as it provides the reader with a general understanding of how the litterfall is collected. There is still limited data available and the measurement and collection methods for litterfall studies are still being investigated. Some of the differences among the different methods include whether the litter was collected as fresh leaves taken directly from the tree or if it was take from decomposing leaf litter; if the leaves were taken from the outside branches or the inside branches (i.e. if the leaves were grown in the sunlight or in the shade); or if the leaves were sampled from the top or the bottom of the canopy, among others. Yes, the results from the different methods can be compared with an understanding that there are associated uncertainties and factors that need to be taken into consideration during data inter-comparisons. It is anticipated that as the number of field measurements increases, the efficiencies and uncertainties among the various methods will be more understood.

Line 397-402: It is necessary discuss why the time schedule is important and the difference caused by sampling frequency.

R: We agree with the reviewer and have added an additional three sentences to this section in order to provide the reader with an understanding of why the length of the sample collections is important and how the measurements are affected by the sampling frequency. For example, Kalicin et al. (2008) collected on an event basis and observed differences in the throughfall Hg concentrations varied throughout the growing season and showed a negative relationship between throughfall Hg and quantity of rainfall. The new sentences read “The time schedule for throughfall collection is important as there is the opportunity for coniferous forests to scavenge atmospheric Hg outside of the growing season if the field studies last for longer than just the growing season (Fisher et al., 2012). The sampling frequency can affect the measured throughfall

Hg as there is the possibility of contamination by Hg dry deposition occurring if the samplers are not covered during extensive dry periods (Rea et al., 1996). Over long-term studies however, sample-to-sample throughfall Hg concentrations may vary on a smaller timescale (i.e. one month) using different sampling frequencies but the differences in the cumulative Hg throughfall deposition will be statistically insignificant (Choi et al., 2008)".

Section 4: Maybe a better presentation is to discuss the GOM/PBM dry deposition in America, then Europe, Asia, followed by the reasons for the observed differences in these regions.

R: We agree with the reviewer and appreciate this insightful suggestion. We have revised this section so that the focus is on North America first and foremost, with explanations for the observed differences in this region, followed by a short discussion on GOM/PBM dry deposition in Asia.

Line 482-484: It is questionable because the foliage from different tree species has distinctly different lifespan. Just multiplying the Hg concentration in fresh foliage by 1.5 for Hg deposition from litterfall may produce a large error.

R: We agree with the reviewer that there is a potential for large errors when simply multiplying the fresh foliage value by 1.5. We have added a sentence to this paragraph that reads: "It is important to note that a litterfall deposition value estimated through multiplying the fresh foliage value by 1.5 does have associated over- and under-estimated error factors that come with it, including possible interannual variations, variations in the accumulation of Hg with time, and the different growth characteristics between the species (Fu et al., 2010), ."

Line 495-499: Please add the site number in each region.

R: We have revised the text to include the number of sites in each region. These numbers for litterfall measurements are: Asia=19, Europe=14, North America=92.

Line 501-510: Although Hg concentrations in foliage are correlated with atmospheric Hg0 concentrations, the difference in litter Hg concentration cannot be solely explained by the disparity in atmospheric Hg_0 concentration. For example, at comparable atmospheric Hg0 concentrations (1-1.5 ng m^{-3}) [Fostier et al., 2015], mean litter Hg concentration in remote Amazon rainforest is 70% higher than the value in America. There are many factors to influence Hg accumulation in foliage.

R: We agree with the reviewer and have added a sentence in the revised manuscript to address this. The revised sentences read "Atmospheric Hg concentrations can affect the levels of Hg concentrations in foliage and leaf litter with higher litterfall Hg in urban forests than remote forests (Fostier et al., 2003, 2015; Wang et al., 2009; Fu et al., 2010a; 2010b; Gong et al., 2014); higher Hg concentrations in close proximity to degassing vents and during eruption activity of volcanoes (Martin et al., 2012); and higher Hg concentrations at intermediate altitudinal

mountain zones (Szopka et al., 2011). It is important to note, however, that the atmospheric Hg concentration is not the only factor that affects the levels of Hg concentrations in foliage and leaf litter, as discussed below."

Line 520-521: Wang et al. (2009) show date for 3 sites only; and these sites are with very high GEM. How these data can be represented the data in entire Asia?

R: We agree with the reviewer that this sentence is misrepresentative of the data. We have revised the manuscript accordingly. The new sentence reads "In three urban forests in Asia, annual litterfall Hg deposition was found to account for up to 75% of the total Hg input fluxes to the forests (Wang et al., 2009)."

Line 520-533: These information have been presented by [Fu et al., 2015], and there does not seem to be any new information.

R: In the paragraph including Lines 520-533, there is a discussion of litterfall data from the following studies that are not included in the Table 3 in Fu et al., 2015: Iverfeldt et al., 1991; Rea et al., 1996; Grigal et al., 2000; Schwesig and Matzner, 2001; Johnson, 2002; Silva-Filho et al., 2006; da Silva et al., 2009; and Jiskra et al., 2015. We have added a sentence in the revised manuscript to refer to the review by Fu et al., 2015. This sentence reads "A detailed review of litterfall, throughfall, and precipitation studies in China can be found in Fu et al., 2015."

Line 521-546: What is the difference between the observations reported in Asia and USA?

R: For litterfall, the median and mean litterfall Hg values in Asia are both three times larger than those reported for North America. For throughfall, the median and mean throughfall Hg in Asia are eight and five times larger, respectively, than those reported in North America.

Section 6-7: Need to a more in-depth discussion for the difference between the observations reported in Asia and USA.

R: For throughfall, the median and mean throughfall Hg in Asia are eight and five times larger, respectively, than those reported in North America, likely due to heavier atmospheric Hg loadings in Asia that North America due to industrial and urban pollution. Based on the reviewer's recommendation, we have added more in-depth discussion in the revised paper.

References

Fostier, A. H., J. J. Melendez-Perez, and L. Richter (2015), Litter mercury deposition in the Amazonian rainforest, Environ Pollut, 206, 605-610.

Fu, X. W., H. Zhang, B. Yu, X. Wang, C. J. Lin, and X. B. Feng (2015), Observations of atmospheric mercury in China: a critical review, Atmos Chem Phys, 15(16), 9455-9476.

Gustin, M. S., H. M. Amos, J. Huang, M. B. Miller, and K. Heidecorn (2015), Measuring and modeling mercury in the atmosphere: a critical review, Atmos Chem Phys, 15(10), 5697-5713.

Ma, M., D. Y. Wang, H. X. Du, T. Sun, Z. Zhao, and S. Q. Wei (2015a), Atmospheric mercury deposition and its contribution of the regional atmospheric transport to mercury pollution at a national forest nature reserve, southwest China, Environ Sci Pollut Res, 22(24), 20007-20018.

Ma, M., D. Y. Wang, T. Sun, Z. Zhao, and H. X. Du (2015b), Forest runoff increase mercury output from subtropical forest catchments: an example from an alpine reservoir in a national nature reserve (southwestern China), Environ Sci Pollut R, 22(4), 2745-2756.

Niu, Z. C., X. S. Zhang, Z. W. Wang, and Z. J. Ci (2011), Mercury in leaf litter in typical suburban and urban broadleaf forests in China, J Environ Sci-China, 23(12), 2042-2048.

Siwik, E. I. H., L. M. Campbell, and G. Mierle (2010), Distribution and trends of mercury in deciduous tree cores, Environmental Pollution, 158(6), 2067-2073, doi:10.1016/j.envpol.2010.03.002.

Wang, X., C. J. Lin, and X. Feng (2014), Sensitivity analysis of an updated bidirectional air-surface exchange model for elemental mercury vapor, Atmos Chem Phys, 14(12), 6273-6287.

Wang, Z. W., X. S. Zhang, J. S. Xiao, C. Zhijia, and P. Z. Yu (2009), Mercury fluxes and pools in three subtropical forested catchments, southwest China, Environ Pollut, 157(3), 801-808.

Yin, R. S., X. B. Feng, and B. Meng (2013), Stable Mercury Isotope Variation in Rice Plants (Oryza sativa L.) from the Wanshan Mercury Mining District, SW China, Environ Sci Technol, 47(5), 2238-2245.

Zhang L., Blanchard P., Gay D.A., Prestbo E.M., Risch M.R., Johnson D., Narayan J., Zsolway R., Holsen T.M., Miller E.K., Castro M.S., Graydon J.A., St. Louis V.L., and Dalziel J., 2012. Estimation of speciated and total mercury dry deposition at monitoring locations in eastern and central North America. Atmos Chem Phys, 12, 4327-4340.

Zhou, J., X. B. Feng, H. Y. Liu, H. Zhang, X. W. Fu, Z. D. Bao, X. Wang, and Y. P. Zhang (2013), Examination of total mercury inputs by precipitation and litterfall in a remote upland forest of Southwestern China, Atmos Environ, 81, 364-372.

Zhou, J., Z. W. Wang, X. S. Zhang, and J. Chen (2015), Distribution and elevated soil pools of mercury in an acidic subtropical forest of southwestern China, Environ Pollut, 202, 187-195.

Zhu, W., C. J. Lin, X. Wang, J. Sommar, X. Fu, and X. Feng (2016), Global observations and modeling of atmosphere–surface exchange of elemental mercury: a critical review, Atmos Chem Phys, 16(7), 4451- 4480, doi:10.5194/acp-16-4451-2016.