May 5, 2016

Dear Editor,

We appreciate the reviewers' suggestions which have considerably improved the manuscript (**acp-2016-7**). Enclosed are point-by-point responses to the reviewers. We hope that with these changes the manuscript will be suitable for publication in "**Atmospheric Chemistry and Physics**"

Thank you very much.

Sincerely,

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Response to Reviewers' Comments

● Journal: ACP

● Title: Total Atmospheric Mercury Deposition in Forested Areas in Korea

● Author(s): Jin-Su Han, Yong-Seok Seo, Moon-Kyung Kim, Thomas M. Holsen, Seung-Muk Yi

● MS No.: acp-2016-7

● MS Type: Research article

● Special Issue: Data collection, analysis and application of speciated atmospheric mercury

Response to Referee 1:

Comment 1

Abstract: It's just a list of numbers. What's missing is why the authors did the study and why the results they found matter. The Abstract needs a punch line.

Response 1

As suggested, we revised the Abstract as follows on **Line 34 to Line 51**

"In this study, mercury *(Hg) in dry and wet deposition, throughfall and litterfall, and Hg volatilization from soil were measured from August 2008 to February 2010 to identify the factors influencing the amount of atmospheric Hg deposited to forested areas in a temperate deciduous forest in Korea. For this location there was no significant correlation between the estimated dry deposition flux (litterfall + throughfall – wet deposition) (6.7 $\mu g\ m^{-2}\ yr^{-1}$) and directly measured dry deposition (9.9 $\mu g\ m^{-2}\ yr^{-1}$) likely due primarily to Hg losses from the litterfall collector. Dry deposition fluxes in cold seasons (fall and winter) were lower than in warmer seasons (spring and summer). The volume-weighted mean (VWM) Hg concentrations in both precipitation and throughfall were highest in winter likely due to increased scavenging by snow events. Since Korea experiences abundant rainfall in summer, VWM Hg concentrations in summer were lower than in other seasons. Litterfall fluxes were highest in the late fall to early winter when leaves were dropped from the trees (September to November). The cumulative annual Hg emission flux from soil was 6.8 $\mu g\ m^{-2}\ yr^{-1}$. Based on these data, the yearly deposition fluxes of Hg calculated using two input approaches (throughfall + litterfall or wet deposition + dry deposition), were 6.8 and 3.9 $\mu g\ m^{-2}\ yr^{-1}$ respectively. This is the first reported study which measured the amount of atmospheric Hg deposited to forested areas in Korea and thus our results provide useful information related to Hg fate and transport in this part of the world."*

Comment 2.

Introduction: Could be greatly improved by including a clearer statement of the problem or scientific question they're trying to answer with this dataset. The logical progression of the Introduction is a little hard to follow and it doesn't build a clear storyline for the rest of the

paper.

Response 2

As suggested, the introduction has been modified as follows **Line 58 to Line 114**.

"Hg is a highly toxic pollutant and a threat to human health and ecosystems due to its ability to bioaccumulate and biomagnify through the food chain after it is methylated (Weiss-Penzias et al., 2016; Zhu et al., 2014 It is classified as a persistent bioaccumulative and toxic (PBT) chemical (U.S.EPA, 1997a). Atmospheric Hg exists in three different forms with different chemical and physical properties; gaseous elemental mercury (GEM, Hg^0), gaseous oxidized mercury (GOM, Hg^{2+}), and particulate bound mercury (PBM, Hg_p). GEM is the major form of Hg in the atmosphere and is relatively water insoluble and very stable with a long residence time of 0.5 - 2 years (Carpi and Lindberg, 1997; Cohen et al., 2004; Schroeder and Munthe, 1998; Zhu et al., 2014). GOM is water soluble, with relatively strong adhesion properties (Han et al., 2005) and can be scavenged by rain within precipitating and below clouds (Blackwell and Driscoll, 2015; Lin and Pehkonen, 1999). It has a very high dry deposition velocity similar to HNO_3 (1~5 cm sec-1) if it is assumed that all GOM is $HgCl_2$ (Petersen et al., 1995). PBM is created by GEM or GOM adsorbing to a particle (Lai et al., 2011). Atmospheric PBM transport is significantly affected by its particle size distribution and may contribute to both wet and dry deposition (Lynam and Keeler, 2002).

Wet and dry deposition of atmospheric Hg is an important input to the aquatic and terrestrial ecosystems (Buehler and Hites, 2002; Fitzgerald et al., 1998; Landis and Keeler, 2002; Lindberg et al., 1998; Miller et al., 2005; Rolfhus et al., 2003; Selvendiran et al., 2008; Shanley et al., 2015). Hg deposited from the atmosphere can be transformed to methyl mercury (MeHg) which bio-accumulates in aquatic food chains, resulting in adverse health and ecological effects (Ma et al., 2013; Lindberg et al., 2007; Rolfhus et al., 2003; Selin et al., 2007; Weiss-Penzias et al., 2016; Zhu et al., 2014). Atmospheric Hg deposition to forests includes direct dry deposition, throughfall, and litterfall. Dry deposition to leaves compromises a large proportion of litterfall (Grigal, 2002; St. Louis et al., 2001). Previous investigations (Fu et al., 2009) estimated dry deposition to forested areas as litterfall + throughfall – wet deposition. However, there are many variables that can adversely influence this technique including reemitted Hg from beneath the canopy and sampling artifacts. Directly measuring dry deposition with a surrogate surface is an alternative approach,

although there is no universally accepted method on how to make these measurements.

Hg deposited onto plant surfaces can be revolatilized, incorporated into tissue or washed off by precipitation (which is deemed throughfall) which often results in throughfall having higher Hg concentrations than precipitation (Iverfeldt, 1991; Kolka et al., 1999; Munthe et al., 1995; Choi et al., 2008; Grigal et al., 2000; Schwesig and Matzner, 2000). Litterfall is dead plant material such as leaves, bark, needles and twigs that has fallen to the ground. Litterfall carries new Hg inputs from the atmosphere to the forest floor and also Hg recycled from volatilization from soils and other surfaces. Throughfall and litterfall contribute to the biochemical recycling of atmospheric Hg in forest systems (St. Louis et al., 2001) and are important Hg inputs that result in Hg accumulation in forest systems (Blackwell and Driscoll, 2015).

The deposition of Hg in the forest ecosystem is complicated because of complex interactions between atmospheric Hg and the canopy, including oxidation of Hg on leaf surfaces (Blackwell and Driscoll, 2015; Iverfeldt, 1991), deposition of GOM and PBM on leaf surfaces (Blackwell et al., 2014; Blackwell and Driscoll, 2015; St. Louis et al., 2001), stomatal uptake of atmospheric GEM (Fu et al., 2010; Iverfeldt, 1991; Lindberg et al., 1991; St. Louis et al., 2001), root uptake of dissolved Hg in soil and soil water and stomatal uptake of GEM that was volatilized from soils (Bishop et al., 1998; Cocking et al., 1995; Ma et al., 2015; St. Louis et al., 2001). Recycled Hg would increase throughfall and litterfall concentrations (St Louis. et al., 2001).

To date there have been few studies that have estimated atmospheric Hg deposition to forested areas and none in Korea. Fully characterizing Hg deposition in forested areas is important for estimating environmental risks associated with Hg. Thus, the objectives of this study were to characterize total atmospheric Hg deposition in a temperate deciduous forested area in Korea by measuring Hg dry deposition, wet deposition, throughfall, litterfall and volatilization from soils and comparing directly measured and estimated dry deposition. Based on the collected data the annual Hg flux was estimated using two approaches to determine inputs (wet deposition + dry deposition, throughfall + litterfall) minus volatilization from soil.

Comment 3.

Methods, Site Description: The authors need a clear statement of why this particular location in Korea was selected. Lines 117-120 provided somewhat of an explanation, but it

feels too vague. what does this site tell us that other sites don't?

Response 3

As suggested, we added the following information about the sampling site as follows on **Line 127 to Line 133**.

"Dry deposition, throughfall, litterfall, volatilization from soils and TM in soil samples were determined in a deciduous forest including primarily chestnut (Elevation 60 m, N37°32´, E127°20´) (site B in Fig. 1) about 2 km away from site A. This area contains rivers, a flood plain, agricultural land, residential areas, forests, and wetlands that are expected to actively methylate Hg. Therefore, the study sites are appropriate for identifying the in/out flow of Hg in a forested ecosystem typical for this part of the world."

Comment 4.

Section 2.4. QA/QC: Too many acronyms are introduced. Makes the text difficult to follow.

Response 4.

As suggested, we revised section 2.4. QA/QC as follows on **Line 209 to Line 221**.

"A automated daily calibration of Tekran 2537 routinely operated was performed using an internal permeation source. Two-point calibrations (zero and span) were operated separately for each pure gold cartridge. A recovery of 102 ± 2.9% (r^2 > 0.9995) (n = 4) measured by directly injecting knowing amounts of five Hg standards which was connected to zero air. The Method Detection Limit (MDL) was by measuring the Hg concentration in zero air was 0.04 ng m^{-3}. More additional information is provied SI."

"Quality assurance and quality control were based on the U.S. EPA Methods 1631 version E (U.S.EPA, 2002) and LMMBMC (U.S.EPA., 1994a). The MDL (three times the standard deviation of seven sequential reagent blanks) for TM in wet deposition and throughfall was 0.05 ng L^{-1}. The standard curve was acceptable when r2 was greater than 0.9995 (linear). More additional information is described SI."

Comment 5.

The authors use a knife-edge surrogate surface for PBM and GOM dry deposition measurements (Section 2.2.1). It would be useful to provide some discussion on how this method compares to other surrogate surface methods (e.g., the work done by Mae Gustin's).

Response 5.

As suggested, we provied some additional discussion and refer to Gustin et al. (2016) as follows **on Line 141 to 154**. Additional changes were made to this section based on Reviewer 2 comments.

"Some studies have investigated the use of surrogate surfaces to directly measure Hg dry deposition (Lyman et al., 2007; Peterson and Gustin, 2008). Surrogate surfaces allow better control over exposure times than those provided with natural vegetation (Lai et al., 2011). Surrogate surfaces with cation exchange membranes have been useful for measuring GOM however they may collect a very small aerosol fraction by diffusion (Lyman et al., 2007; Huang and Gustin, 2015b). Similar to previous studies (Lai et al., 2011; Yi et al., 1996), in this project the dry deposition sampler was equipped with a knife-edge surrogate surface (KSS) sampler with the collection media facing up. Forty seven-mm quartz filters were used to measure PBM deposition and KCl-coated quartz filters were used to measure GOM + PBM deposition. The quartz filter and KCl-coated quartz filter (soaked in KCl solution for 12h and dried on clean bench) were pre-baked in a quartz container at 900 ºC for PBM and 525 ºC for GOM + PBM. Before weekly sampling, the filters were placed on a filter holder base and held in place with a retaining ring and then was deployed in the KSS. Filter exposed to the atmosphere from approximately one week and two side-by-side samples were deployed during each dry day."

Comment 6.

Page 8, lines 220-228: If all of these numbers are important, I suggest condensing into a table. It's difficult to parse text right now.

Response 6.

As suggested, we revised seasonal dry deposition data as follows on **Line 241 to Line 247**.

"*Weekly samples were collected using quartz filters (PBM) and KCl coated quartz filters*

(GOM). The average dry deposition fluxes for GOM (Table S1) and PBM (Table S2) were 5.4 μg m^{-2} yr^{-1} (range: 0.4 ~ 14.4 μg m^{-2} yr^{-1}) and 4.3 μg m^{-2} yr^{-1} (range: 0.8 ~ 19.4 μg m^{-2} yr^{-1}), respectively. The dry deposition fluxes for GOM were highest in spring 2009 (10.0 ± 2.0 μg m^{-2} yr^{-1}), lowest in fall 2009 (1.2 ± 1.4 μg m^{-2} yr^{-1}) while the dry deposition fluxes for PBM were highest in summer 2009 (9.6 ± 9.0 μg m^{-2} yr^{-1}), lowest in fall 2009 (1.2 ± 0.4 μg m^{-2} yr^{-1}) (Fig. 2)."

Comment 7.

Page 8, lines 240-243: The importance of this paragraph is unclear. Could it be deleted?

Response 7.

As suggested we deleted Page 8, lines 240-243

Comment 8.

Page 9, lines 260-270: Which explanation do the authors think is most plausible? The text currently gives the impression the authors are just guessing. A more thoughtful scrutiny of the proposed explanations would be welcome.

Response 8.

As suggested, this section has been revised as follows on **Line 276 to Line 285**.

"The high VWM Hg concentrations in precipitation and throughfall in winter were associated with the combined effects of reduced mixing heights which increases atmospheric concentrations (Kim et al., 2009; Seo et al., 2015), low rainfall depth (11.7% of total rainfall depth) which is a typical pattern in Yangpyung, Korea (KMA, http://www.kma.go.kr/weather/climate/average_30years.jsp?yy_st&tnqh_x003D;2011&stn&tnqh_x003D;108&norm&tnqh_x003D;M&obs&tnqh_x003D;0&mm&tnqh_x003D;5&dd&tnqh_x003D;25&x&tnqh_x003D;25&y&tnqh_x003D;5 (accessed May 5, 2016) and the inclusion of snow events since scavenging by snow is more efficient than by rain due to the larger surface area of snow (snow: 700 cm^2/g, rain: 60 cm^2/g) (Kerbrat et al., 2008)."

Comment 9.

Page 10, line 282: "Therefore, all of the Hg deposited…" What fraction is lost? What

fraction is retained? This could be really interesting.

Response 9.

Unfortunately we did not make any direct measurements of what was collected on the leaves and how much remained after a precipiation event so we can not address this question. However we did add a bit more discussion on **Line 296 to Line 300**.

"Some of the deposited Hg can be washed off by rainfall and reemitted as GEM to the atmosphere (Jiskra et al., 2015; Rea et al., 2001). Therefore, all of the Hg deposited on the foliar surfaces is not in the throughfall. Throughfall also incorporates GOM and PBM that is adsorbed from the atmosphere by leave since GOM is soluble and it is likely readily washed off during rain events (Blackwell and Driscoll, 2015)."

Comment 10.

Page 10, lines 294-296: "… the rest of the variation is likely due to variations in local…" The "rest" here being >80%, correct? A more rigorous explanation of the majority of the variability seen in the data would be helpful. Being able to explain less than 20% does not give confidence in the interpretation.

Response 10.

As suggested we added further explanations as follows on **Line 312 to Line 321**.

"The rest of the variation is likely due to meteorological parameters that differ between events, for example temperature and precipitation type (Gratz et al., 2009) and variations in ambient Hg speciation and PBM particle size distributions due to differing impacts of local and regional sources (Blackwell and Driscoll, 2015). There was a statistically significant positive correlation between rainfall depth and TM deposition flux in precipitation (r^2 = 0.34) ($p < 0.05$), similar to what was found iiin previous studies (Choi et al., 2008; Gratz et al., 2009; Maremoto and Matsuyama, 2014; Shanley et al., 2015; Wang et al., 2014), suggesting that the TM deposition flux increased during large events even though continuous rain diluted the TM mass. However, a large rainfall depth does not affect wet deposition fluxes if atmospheric concentrations of GOM and PBM are low (Zhang et al., 2012)."

Comment 11.

Page 10, lines 307-309: Why is an r2=0.59 ($p<0.05$) "significantly correlated" and r2=0.56 ($p<0.05$) "moderately correlated"?

Response 11.

Those should be the same - we corrected "moderately correlated" to "significantly correlated" as follows on **Line 330**.

" .... concentrations were also significantly correlated ($r^2 = 0.56$) ($p < 0.05$) (Table 1)"

Comment 12.

Page 12: If you are missing data in January and February, the stated assumption that "fluxes were assumed to be equal to the average of the flux of the month before" doesn't make sense. How are you handling consecutive months of missing data?

Response 12.

We corrected this mistake about missing data as follows on **Line 377 to Line 380**.

"Due to sampler (Tekran 2537A) malfunctions in January, February and April, fluxes were assumed to be equal to the average of the flux of the previous and subsequent month. If only one month of data were available, it was assumed to be the same as the missing month"

Comment 13.

Page 13, lines 382-383: It would be useful here to be specific and describe what "both input approaches" are. It's not that clear what approaches you mean.

Response 13.

As suggested, we added further explanations as follows on **Line 406 to Line 408**.

"The yearly estimated budget of Hg was calculated using both input approaches (Total input = wet deposition + dry deposition or Total input = throughfall + litterfall) as follows..."

Comment 14.

Section 3.8: This section is disjointed and lacks cohesion. Revision strongly encouraged, with a focus on building a logical progression.

Response 14.

As suggested this section has been revised as follows on **Line 406 to Line 419**.

"The yearly estimated budget of Hg in this study site was calculated using both input approaches (Total input = wet deposition + dry deposition or Total input = throughfall + litterfall) as follows. 1) Input to the forest canopy (wet deposition in an open area: 4.3 $\mu g\ m^{-2}\ yr^{-1}$ plus dry deposition in the forested area: 9.9 $\mu g\ m^{-2}\ yr^{-1}$) minus output (emissions from soil 6.8 $\mu g\ m^{-2}\ yr^{-1}$ plus accumulation in the soil 0.6 $\mu g\ m^{-2}\ yr^{-1}$) resulting in a net flux of 6.8 $\mu g\ m^{-2}\ yr^{-1}$. 2) The alternative method yields input (throughfall: 6.7 $\mu g\ m^{-2}\ yr^{-1}$ plus litterfall: 4.6 $\mu g\ m^{-2}\ yr^{-1}$) minus output (emissions from soil: 6.8 $\mu g\ m^{-2}\ yr^{-1}$ plus accumulation in the soil: 0.6 $\mu g\ m^{-2}\ yr^{-1}$) resulting in a net flux of 3.9 $\mu g\ m^{-2}\ yr^{-1}$. For comparison at the Lehstenbach catchment in Germany, the estimated net fluxes were similar: 6.8 $\mu g\ m^{-2}\ yr^{-1}$ (Schwesig and Matzner, 2000) and in the Experimental Lakes Area (ELA) watersheds in Canada, the flux was 3 ~ 4 $\mu g\ m^{-2}\ yr^{-1}$ (St. Louis et al., 2001). However, for the Lake Langtjern spruce forest in southeast Norway (20.1 $\mu g\ m^{-2}\ yr^{-1}$) (Larssen et al., 2008) and Huntington Wildlife forest (15.9 $\mu g\ m^{-2}\ yr^{-1}$ in deciduous, 26.8 $\mu g\ m^{-2}\ yr^{-1}$ in conifer) (Blackwell et al., 2014), the estimated fluxes were higher than in this study."

Comment 15.

Conclusions: The manuscript needs a Conclusions section. Without Conclusions, the manuscript incomplete and doesn't seem mature enough for publication. A couple of strong synthesis statements from the authors about why their results add to our knowledge in the Hg field would really help the paper.

Response 15.

As suggested, we added a conclusions section as follows on **Line 423 to Line 451**.

"Hg in dry and wet deposition, throughfall and litterfall and Hg volatilization from soil were measured from August 2008 to February 2010 to identify the factors influencing the amount of atmospheric Hg deposited to forested areas in a temperate deciduous forest in Korea. In

addition measured and theoretical dry deposition were compared. The GOM fluxes were low in fall and increased towards the spring. PBM fluxes were lowest in fall and peaked in summer. The estimated and directly measured deposition fluxes were not significantly correlated likely due to loss of litter samples by wind or wash-off by rainfall and the fact that accumulation in leaf stomata was not characterized in the direct dry deposition measurement technique. The average VWM Hg concentration in throughfall was approximately 2.4 times higher than in precipitation due to wash off of previously deposited Hg from the foliage. Both were higher in winter due to increased concentrations in snow events relative to rain events likely due to enhanced scavenging of GOM and PBM. TM in litterfall fluxes were highest in fall when the leaves were dropped and lowest in summer from June to August. Hg emission fluxes from soil resulted in a cumulative annual volatilization of 6.8 $\mu g\ m^{-2}\ yr^{-1}$ of GEM.

Based on this all data, the yearly accumulation of Hg in the deciduous forest was calculated using two input approaches (total input = throughfall + litterfall or wet deposition + dry deposition and total output: emission from soil + TM in soil). Using this approach the accumulation of Hg were 6.8 and 3.9 $\mu g\ m^{-2}\ yr^{-1}$ respectively.

There are several uncertainties associated with this study as discussed above. The primary ones include that fact that dry deposition measured with the surrogate surface does not account for accumulation in leaf stomata yet this technique yielded a larger flux than to litterfall + throughfall – wet deposition. Litterfall can be lost from the sampler by wind and Hg can be lost from the collected litter due to washoff from rainfall due to relatively long sampling periods. The differences in the approaches suggest that approximately half of the GEM stored in the leaf may be released to back to the atmosphere. DFCs can alter measured fluxes because they cover the soil potentially blocking some UV light. In addition, several months of measurements were missed. Finally grab samples for TM in soil may not capture the true variability in the forest. Additional work should focus on better quantifying dry deposition, TM in soil water, overflow rate and biogeochemical recycling within the forest canopy and understory."

Comment 16.

Supporting Information: I encourage the authors to make their data available in the SI. This will make it easier for other interested scientists, especially modelers, to compare against the data in Korea. The mercury community will be excited about this dataset and want to weave

it into their comparisons – make it easy for them!

Response 16.

As suggested, we revised SI as follows on **Line 31 to Line 50**.

Response to Referee 2:

Comment 1

Abstract is written in the way with number reporting, there is no significant conclusions and any new discovery.

Response 1

As suggested, we revised the Abstract as follows on **Line 34 to Line 51**.

"In this study, mercury *(Hg) in dry and wet deposition, throughfall and litterfall, and Hg volatilization from soil were measured from August 2008 to February 2010 to identify the factors influencing the amount of atmospheric Hg deposited to forested areas in a temperate deciduous forest in Korea. For this location there was no significant correlation between the estimated dry deposition flux (litterfall + throughfall – wet deposition) (6.7 $\mu g\ m^{-2}\ yr^{-1}$) and directly measured dry deposition (9.9 $\mu g\ m^{-2}\ yr^{-1}$) likely due primarily to Hg losses from the litterfall collector. Dry deposition fluxes in cold seasons (fall and winter) were lower than in warmer seasons (spring and summer). The volume-weighted mean (VWM) Hg concentrations in both precipitation and throughfall were highest in winter likely due to increased scavenging by snow events. Since Korea experiences abundant rainfall in summer, VWM Hg concentrations in summer were lower than in other seasons. Litterfall fluxes were highest in the late fall to early winter when leaves were dropped from the trees (September to November). The cumulative annual Hg emission flux from soil was 6.8 $\mu g\ m^{-2}\ yr^{-1}$. Based on these data, the yearly deposition fluxes of Hg calculated using two input approaches (throughfall + litterfall or wet deposition + dry deposition), were 6.8 and 3.9 $\mu g\ m^{-2}\ yr^{-1}$*

respectively. This is the first reported study which measured the amount of atmospheric Hg deposited to forested areas in Korea and thus our results provide useful information related to Hg fate and transport in this part of the world."

Comment 2.

Line 69-71, the original papers were not cited and PBM is particle-bound Hg, how can it be adsorbed on PM? You could say oxidized Hg or GOM.

Response 2

As suggested, we revised text and reference as follows on **Line 70 to Line 71**.

"PBM is created by GEM or GOM adsorbing to a particle (Lai et al., 2011)."

Comment 3.

Line 72-74, re-write.

Response 3

As suggested, we revised as follows on Line **71 to Line 74**.

"..... Atmospheric PBM transport is significantly affected by its particle size distribution and may contribute to both wet and dry deposition (Lynam and Keeler, 2002). Wet and dry deposition of atmospheric Hg is an important input to the aquatic and terrestrial ecosystems"

Comment 4.

Line 84-86, not clear, also update the reference here Line 88-89

Response 4

As suggested, we revised and updated this text as follows on **Line 80 to Line 105**.

"Dry deposition to leaves compromises a large proportion of litterfall (Grigal, 2002; St. Louis et al., 2001). Previous investigations (Fu et al., 2009) estimated dry deposition to

forested areas as litterfall + throughfall – wet deposition. However, there are many variables that can adversely influence this technique including reemitted Hg from beneath the canopy and sampling artifacts. Directly measuring dry deposition with a surrogate surface is an alternative approach, although there is no universally accepted method on how to make these measurements.

Hg deposited onto plant surfaces can be revolatilized, incorporated into tissue or washed off by precipitation (which is deemed throughfall) which often results in throughfall having higher Hg concentrations than precipitation (Iverfeldt, 1991; Kolka et al., 1999; Munthe et al., 1995; Choi et al., 2008; Grigal et al., 2000; Schwesig and Matzner, 2000). Litterfall is dead plant material such as leaves, bark, needles and twigs that has fallen to the ground. Litterfall carries new Hg inputs from the atmosphere to the forest floor and also Hg recycled from volatilization from soils and other surfaces. Throughfall and litterfall contribute to the biochemical recycling of atmospheric Hg in forest systems (St. Louis et al., 2001) and are important Hg inputs that result in Hg accumulation in forest systems (Blackwell and Driscoll, 2015).

The deposition of Hg in the forest ecosystem is complicated because of complex interactions between atmospheric Hg and the canopy, including oxidation of Hg on leaf surfaces (Blackwell and Driscoll, 2015; Iverfeldt, 1991), deposition of GOM and PBM on leaf surfaces (Blackwell et al., 2014; Blackwell and Driscoll, 2015; St. Louis et al., 2001), stomatal uptake of atmospheric GEM (Fu et al., 2010; Iverfeldt, 1991; Lindberg et al., 1991; St. Louis et al., 2001), root uptake of dissolved Hg in soil and soil water and stomatal uptake of GEM that was volatilized from soils (Bishop et al., 1998; Cocking et al., 1995; Ma et al., 2015; St. Louis et al., 2001). Recycled Hg would increase throughfall and litterfall concentrations (St Louis. et al., 2001).”

Comment 5.

Line 77-79, add Selin et al., 2007 and Lindberg et al., 2007

Response 5

As suggested, we added Selin et al., 2007 and Lindberg et al., 2007 as follows on **Line 77 to Line 79**.

“…. , resulting in adverse health and ecological effects (Ma et al., 2013; Lindberg et al.,

2007; Rolfhus et al., 2003; Selin et al., 2007; Weiss-Penzias et al., 2016; Zhu et al., 2014).”

Comment 6.

how does uptake via roots impact Hg deposition. Also stomatal uptake of Hg^0 emitted from soils?

Response 6

As suggested, we added information as follows on **Line 102 to Line 105**.

“ …. root uptake of dissolved Hg in soil and soil water and stomatal uptake of GEM that was volatilized from soils (Bishop et al., 1998; Cocking et al., 1995; Ma et al., 2015; St. Louis et al., 2001). Recycled Hg would increase throughfall and litterfall concentrations (St Louis. et al., 2001).”

Comment 7.

I don’t understand this sentence. Line 133, please discuss problems from using KCl coated quartz surface. Lyman et al., 2010; Huang et al., 2013/2015, McClure et al., 2015, Lynam and Keeler 2006 Sampling method, what are the time periods?

Response 7

As suggested, We revised and discussed problems from using KCl coated quartz surface as follows on **Line 141 to Line 154**.

“Some studies have investigated using a surrogate surfaces to measure dry deposition (Lyman et al., 2007; Peterson and Gustin, 2008). Surrogate surfaces is better control over exposure times than those provided with natural vegetation (Lai et al., 2011). Surrogate surfaces with cation exchange membranes could be collected very small aerosol fraction by diffusion (Lyman et al., 2007; Huang and Gustin, 2015b). However, we collected direct dry deposition using a surrogate surfaces with quartz filters. Similar to previous studies (Lai et al., 2011; Yi et al., 1996), the dry deposition sampler was equipped with a knife-edge surrogate surface (KSS) sampler with the collection media facing up. Forty seven-mm quartz

filters were used to measure PBM deposition and KCl-coated quartz filters were used to measure GOM + PBM deposition. The quartz filter and KCl-coated quartz filter (soaked in KCl solution for 12h and dried on clean bench) were pre-baked in a quartz container at 900 ºC for PBM and 525 ºC for GOM + PBM. Before weekly sampling, the filters were placed on a filter holder base and held in place with a retaining ring and then were placed on the KSS. Filters exposed to the atmosphere for approximately one week and two side-by-side samples were deployed during each dry day."

Comment 8.

Analytical method, did the author develop the thermal desorption method? If not please cite references.

Response 8

As suggested, we added references as follows on **Line 187 to Line 188**.

"..... zero air passed through until the Hg concentration was zero (Kim et al., 2009; Kim et al., 2012)."

Comment 9.

If I understand this correctly, KCl QFF was heated to 525C and QFF was heated to 900C to separate GOM and PBM. Two questions here. 1. Is dry deposition collected up facing or down facing? and how up/down facing impact measurement? 2. Is this possible for GOM attach on QFF and quantified as PBM, and PBM attach on KCl-QFF and quantified as GOM?

Response 9

As suggested, we added information about sampling method of dry deposition as follows on **Line 141 to Line 154 and Line 192 to Line 193**.

Question 1 :

Some studies have investigated the use of surrogate surfaces to directly measure Hg dry deposition (Lyman et al., 2007; Peterson and Gustin, 2008). Surrogate surfaces allow better control over exposure times than those provided with natural vegetation (Lai et al., 2011).

Surrogate surfaces with cation exchange membranes have been useful for measuring GOM however they may collect a very small aerosol fraction by diffusion (Lyman et al., 2007; Huang and Gustin, 2015b). Similar to previous studies (Lai et al., 2011; Yi et al., 1996), in this project the dry deposition sampler was equipped with a knife-edge surrogate surface (KSS) sampler with the collection media facing up. Forty seven-mm quartz filters were used to measure PBM deposition and KCl-coated quartz filters were used to measure GOM + PBM deposition. The quartz filter and KCl-coated quartz filter (soaked in KCl solution for 12h and dried on clean bench) were pre-baked in a quartz container at 900 ºC for PBM and 525 ºC for GOM + PBM. Before weekly sampling, the filters were placed on a filter holder base and held in place with a retaining ring and then were placed on the KSS. Filters exposed to the atmosphere from approximately one week and two side-by-side samples were deployed during each dry day.

Question 2 :

It was assumed that GOM deposition was equal to the flux measured by the KCl-coated quartz filter minus the flux measured by the quartz filter.

Comment 10.

What is the recovery for the thermal desorption system? Recovery for Tekran 2537 direct injection 87% is too low usually from 93-107%. How many sampling time periods? Only 4 field blanks? Why? Volatilization from soil, what are MDL or blanks?

Response 10

As suggested, we revised section 2.4.1 and 2.4.4 as follows on **Line 209 to Line 214 and Line 232 to Line 235**.

"Automated daily calibration of Tekran 2537A routinely was performed using an internal permeation source. Two-point calibrations (zero and span) were performed separately for each pure gold cartridge. A recovery of 102 ± 2.9% (r^2 > 0.9995) (n = 4) was measured by directly injecting knowing amounts of five Hg standards which was connected to zero air. The Method Detection Limit (MDL) determined by measuring the Hg concentration in zero air was 0.04 ng m^{-3}. Additional information is described in the SI.....Before flux chamber measurements automated calibration was performed using the internal permeation

source connected to the Tekran 2537A and Tekran 1110 dual sampling unit. External calibration and MDLs for this instrument are described above."

Comment 11.

Section 3.1, if you only have a short time period during each season, how can you really see the seasonal pattern? Please add more detail information for sampling plan.

Response 11

As suggested, we added information about sampling plan as follows on **Line 241 to Line 242**.

"Weekly sample were collected using quartz (PBM) and KCl coated quartz filters (GOM)"

Comment 12.

What statistical test are you using, please add information for every place you mention significant difference.

Response 12

As suggested, we added information about significant difference as follows on **Line 247, Line 265, Line 272, Line 290, Line 327, Line 396.**

"Nonparametric Mann-Whitney U tests....."

Comment 13.

Line 281, what is mechanical weathering?

Response 13

As suggested, we revised as follows on **Line 294 to Line 296**.

"Other possible sources of Hg in throughfall are leaching and biogeochemical recycling of Hg from foliage (St. Louis et al., 2001)."

Comment 14.

Most references are also out of date.

Response 14

As suggested, we added recent references.