May 21, 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 Referee's Reports

● 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.

Page 3, lines 58-60. Weiss-Penzias et al. (2016) and Zhu et al. (2014) are not appropriate references. The toxicity of MeHg and threat to ecosystems was established long before these papers.

Response 1.

We revised references as follows on **Line 60 to Line 61**.

" ..... bioaccumulate and biomagnify through the food chain after it is methylated (Lindqvist, 1991; Schroeder and Munthe, 1998)"

Comment 2.

Page 4, lines 97-105. It would make sense to include the work of Risch et al. (2011) Environmental Pollution.

Reponse 2.

We revised line 97-105 as follows on **Line 105 to Line 108**.

".....that was volatilized from soils (Bishop et al., 1998; Cocking et al., 1995; Ma et al., 2015; St. Louis et al., 2001). Also, the Hg in forest canopies can be emitted and reemitted from beneath the canopy (Risch et al., 2012). The Hg mass in litterfall have orginated from a large portion of dry deposition (Risch et al., 2012; St. Louis et al., 2001)."

Comment 3.

Page 10, lines 283-285. Sigler et al. (2009) found a similar effect from snow scavenging in the northeastern US. A brief comparison to their work is perhaps worth including.

Response 3.

We added effect from snow scavenging refer to Sigler et al. (2009) as follows on **Line 283 to Line 284**.

"While, Sigler et al. (2009) reported that GOM is scavenged less efficiently during snow events."

Response to Referee 2:

Comment 1.

Line 35, monthly or weekly measurements?

Response 1.

We added measurement cycle as follows on **Line 34 to Line 36**.

"*In this study, mercury (Hg) was sampled weekly in dry and wet deposition and throughfall and monthly in litterfall, and as it was volatilized from soil from August 2008 to February 2010....****"***

Comment 2.

Line 37, monthly data for the correlation? How many data point?

Response 2.

We added as follows on **Line 37 to Line 38**.

"For this location there was no significant correlation between the estimated monthly dry deposition flux...."

Comment 3.

Line 49-51, how this would be useful for global mercury research?

Response 3

We added some information as follows on **Line 50 to Line 52**.

"... and thus our results provide useful information to compare against data related to Hg fate and transport in this part of the world."

Comment 4.

Line 68-70, re-write the sentence, it is difficult to understand.

Response 4.

We re-wrote the the sentence as follows on **Line 70 to Line 71**.

"The dry deposition velocity is similar to HNO_3 (1~5 cm sec^{-1}) if it is assumed that all GOM is in the form of $HgCl_2$ (Petersen et al., 1995)"

Comment 5.

Line 70, "created" use another word, I suggest to use formed.

Response 5.

We revised from "created" to "formed" as follows on **Line 71**.

"PBM is formed by GEM or GOM...."

Comment 6.

Line 106-107, references

Response 6.

We added some references as follows on **Line 109 to Line 110**.

"To date there have been few studies (Blackwell et al., 2014; Choi et al., 2008; Rea et al., 2001) that have estimated atmospheric Hg deposition to forested areas and none in Korea."

Comment 7.

Line 131, references, or probably delete it, Hg methylation is a very complicated process, it would be better to explain this in detail if possible.

Response 7.

We deleted about Hg methylation as follows on **Line 133 to Line 134**.

"This area contains rivers, a flood plain, agricultural land, residential areas, forests, and wetlands. Therefore, the study sites are....."

Comment 8.

Line 142, Huang et al., 2015 passive sampler review paper and 2011 Atmos. Env. wind tunnel tests.

Comment 8.

We added some information about surrogate surfaces refer to Huang et al., 2011 as follows on **Line 144 to Line 149**.

"Surrogate surfaces allow better control over exposure times than those provided with natural vegetation (Lai et al., 2011). However, surrogate surfaces, being smooth, may not mimic Hg dry deposition to natural rougher surfaces (Huang 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 (Huang and Gustin, 2015; Lyman et al., 2007).

Comment 9.

The authors need to talk about the field blanks for dry/wet deposition and all other measurements

Comment 9.

We mentioned field blank for dry/wet deposition in the SI as follows on **Line 35 to Line 42**.

"*.... Field blank for GOM (n = 51) and PBM (n = 46) were 0.21 and 0.19 ng* m^{-2} hr^{-1} *respectively..... Field blanks were collected monthly from September to December and yielded Hg concentrations of 0.36 ± 0.05 ng* L^{-1}.

Comment 10.

Line 179, DFCs were placed 2 cm under the soil? Re-write, I don't think this is possible, probably say "The bottom 2 cm of DFCs is covered by soil and soil surface to the chamber top is XX cm" something like this. The sentence sounds like the chamber is fully covered by soil.

Response 10.

We revised these sentence as follows on **Line 183**.

"The bottom 2 cm of DFCs (3.78L) were covered by soil."

Comment 11.

Line 180, UV light needs some references

Response 11.

We added some references as follows on **Line 184 to Line 185**.

"The DFCs were made of glass and polycarbonate which may block some UV light (Choi and Holsen, 2009; Skinner, 1998)."

Comment 12.

Line 192-193, explain what are the uncertainties here

Response 12.

We explained about uncertainties as follows on **Line 197 to Line 199**.

".....measured by the KCl-coated quartz filter minus the flux measured by the quartz filter. However, recent studies (Lyman et al., 2010) reported potential sampling artifacts in the presence of O_3. "

Comment 13.

Line 221, what is the RPD range? I expect that might be large, but it should be fine

What are the max capacity of these surface, in case you did not over load them?

Response 13.

We already mentioned RPD range in the SI as follows on **Line 41**.

".....respectively with an RPD of 3 ~ 13%."

Comment 14.

Line 257-258, previous studies show no GEM collected on KCl surface, and in Zhang et al 2012, they discussed the potential GEM uptaken by dry deposition measurements is due to the usage of acidified BrCl. Since BrCl was not used in this study, this is not a suitable statement.

Response 14.

We deleted this statement.

"This suggests that GEM may contribute to the measured dry deposition (Zhang et al., 2012)"

Comment 15.

Line 262-265, 269-272, if you have figures or tables to present the data, you don't need to repeat the data again in text.

Response 15.

We revised Section 3.2 as follows on **Line 267 to Line 272**.

"The average VWM concentration in precipitation (n = 35) and throughfall (n = 44) are shown Fig.3. Nonparametric Mann-Whitney U tests indicated that there were no statistically significant differences in the VWM TM concentration between winter 2009 and other seasons which is probably related with the small number of samples. The VWM TM concentration in winter 2009 was statistically significantly higher than fall 2009 (p = 0.007), spring 2009 (p = 0.035), and summer 2009 (p = 0.001) in throughfall."

Comment 16.

Line 276-278, could the author please do the analysis in detail? In the North American, we are seeing winter time low PBL, I agree GEM concentrations will increase, but I never see GOM concentrations increase in low PBL condition. The authors cited two papers here, Kim et al., 2009 and Seo et al., 2015, I went back to read these two papers, Seo et al., 2015 cited Kim et al., 2009 to make the statement, and Kim et al., 2009 cited Blanchard et al., 2002 to make the statement. None of Seo et al., 2015 and Kim et al., 2009 did a detail analysis on this. I just wonder could the authors do a detail analysis on how PBL decreasing impact atmospheric GOM concentrations?

Response 16.

Unfortunately we are not aware of a simple way to calculate the average PBL height by season. We revised reference and paragraph as follows on Line **273 to Line 275**.

"The high VWM Hg concentrations in precipitation and throughfall in winter were likely associated with the combined effects of reduced mixing heights (Blanchard et al., 2002)....."

Comment 17.

Line 312-315, could the authors discuss this in detail, is there any information measured at these sites supporting this statement?

Response 17.

We added some information measured at these sites as follows on **Line 311 to Line 315**.

"The rest of the variation is likely due to meteorological parameters that differ between events (Gratz et al., 2009), for example temperature(Table S3) and precipitation type (Rain, Snow, Mixed) and variations in ambient Hg speciation and PBM particle size distributions due to differing impacts of local and regional sources (Blackwell and Driscoll, 2015)."

Comment 18.

Line 320-321, do not understand

Response 18.

We revised this paragraph as follows on **Line 319 to Line 320**.

"However, a large rainfall depth does not affect wet deposition fluxes significantly if GOM and PBM concentrations are low (Zhang et al., 2012)"

Comment 19.

Line 379-380, what are the uncertainties?

Response 19.

We mentioned the uncertainties as follows on **Line 375 to Line 380**.

"The cumulative annual Hg emission flux was 6.8 $\mu g\ m^{-2}\ yr^{-1}$ (Fig. 5). 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. For comparison the annual Hg emission flux would be 4.8 $\mu g\ m^{-2}\ y^{-1}$ if only measured data were used."

Comment 20.

Line 384-402, re-write this paragraph. There are some things I suggest the authors can look into. Estimated dry deposition should less or equal to measured dry deposition due to no canopy resistance for KCl surface, no re-emissions for KCl surface. Similar concept for wet +

dry deposition and throughfull + litterfall should be considered. There is no (or very small) reemissions for wet + dry deposition; therefore, the numbers are totally making sense to me. However, the authors did not explain this in detail.

Response 20.

We added some texts as follows on **Line 384 to Line 407**.

"Fu et al. (2009) estimated dry deposition to be equal to litterfall + throughfall – wet deposition. Using the data presented here, the estimated dry deposition flux (6.7 $\mu g\ m^{-2}\ yr^{-1}$) was lower than measured dry deposition (9.9 $\mu g\ m^{-2}\ yr^{-1}$) and there was no significant correlation between the two methods ($r^2 = 0.22$) ($p = 0.65$). One of the reasons for the directly measured flux to be larger than the estimated flux is likely because there is no canopy resistance for, or re-emission from, the KCl coated surrogate surface. The differences in the estimates could be due to the loss of litter samples by wind or Hg losses from the collected litter due to meteorological conditions such as rainfall (Blackwell et al., 2014) due to relatively long sampling periods (1 month). However dry deposition collected with a surrogate surface doesn't include accumulation in leaf stomata which may underestimate dry deposition using this technique and since it is a smooth surface may collect less deposition than a rougher surface.

The annual input flux calculated by summing wet deposition plus measured dry deposition (14.3 $\mu g\ m^{-2}\ yr^{-1}$) was higher than the input flux calculated by summing throughfall + litterfall (12.8 $\mu g\ m^{-2}\ yr^{-1}$) (Fig. 6). This difference is likely, at least in part, due to the fact that no Hg is reemitted from wet and dry deposition as happens for litterfall. Nonparametric Mann-Whitney U tests indicated that there were not statistically significant differences ($r^2 = 0.14$) ($p = 0.98$). In general, wet + dry deposition was larger than throughfall plus litterfall except during fall when leaves were being actively dropped from the trees. The largest difference was in July during a period of significant precipitation (about 26.3 % of the total amount in 2009). This difference is most likely due to the many reactions and transformations on the leaf surface that aren't mimicked with the surrogate surface including re-emission (Rea et al., 2001)."

Comment 21.

Line 413-419, we know atmospheric GOM concentrations at this site are higher than the

numbers measured in Huntington Wildlife forest. However, the net flux in HWF is higher than the number at this site. Does this mean that Hg soil emissions are in Korea way higher the numbers in HWF? If this is true, what could be the reasons?

Response 21.

"Measured Hg soil emission fluxes in this study site (4.8 μg m^{-2} yr^{-1}) were lower than HWF (7.0 μg m^{-2} yr^{-1})."

Total Atmospheric Mercury Deposition in Forested Areas in Korea

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Abstract

In this study, mercury (Hg) was sampled weekly in dry and wet deposition and throughfall and monthly in litterfall, and as it was volatilized from soil 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 monthly dry deposition flux (litterfall + throughfall – wet deposition) (6.7 μg m^{-2} yr^{-1}) and directly measured dry deposition (9.9 μg 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 μg m^{-2} yr^{-1}. Based on these data, the yearly deposition fluxes of Hg calculated using two input approaches (wet deposition + dry deposition or throughfall + litterfall) were 6.8 and 3.6 μg 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 to compare against data related to Hg fate and transport in this part of the world.

Keywords: Mercury budget; Dry deposition; Wet deposition; Throughfall; Litterfall; Hg emission flux

1. Introduction

Mercury (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 (Lindqvist et al., 1991; Schroeder and Munthe, 1998). 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). The dry deposition velocity is similar to HNO_3 (1 ~ 5 cm sec^{-1}) if it is assumed that all GOM is in the form of $HgCl_2$ (Petersen et al., 1995). PBM is formed 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 and Driscoll, 2015; Blackwell et al., 2014; 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). Also, the Hg in forest canopies can be emitted and reemitted from beneath the canopy (Risch et al., 2012). The Hg mass in litterfall have originated from a large portion of dry deposition (Risch et al., 2012; St. Louis et al., 2001).

To date there have been few studies (Blackwell et al., 2014; Choi et al., 2008; Rea et al., 2001) 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.

2. Materials and methods

2.1. Site description

The sampling sites were located at Yangsuri, Yangpyeong-gun, Gyeonggi-do, a province in Korea where the Bukhan (North Han) and Namhan River (South Han River) come together (Fig. 1). Gyeonggi-do has a population of 12 million (24% of the total population and the most populated province in South Korea) and an area of 10,187 km^2 (10% of the total area of South Korea). Yangpyeong-gun has a population of 83,000 (0.2% of the total population in South Korea) and an area of 878.2 km^2 (0.9% of the total area in South Korea). Wet deposition samples were collected at the Han River Environment Research Center (Elevation 25 m, N37°32´, E127°18´) (site A in Fig. 1). Dry deposition, throughfall, litterfall, volatilization from soils and total mercury (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. 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.

2.2. Sampling methods

Samples were collected from August 2008 to February 2010. Weekly samples for dry and wet deposition in an open area and throughfall were collected using a dry and wet deposition sampler (DWDS).

2.2.1. Dry deposition for GOM and PBM

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). However, surrogate surfaces, being smooth, may not mimic Hg dry deposition to natural rougher surfaces (Huang 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 (Huang and Gustin, 2015; Lyman et al., 2007). Similar to previous studies, 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. Filter exposed to the atmosphere from approximately one week and two side-by-side samples were deployed during each dry day.

2.2.2. TM in wet deposition and throughfall

The DWDS for wet deposition and throughfall was equipped with four discrete sampling systems that allows for two Hg and two trace elements sampling trains similar to what was used in previous studies (Lai et al., 2007; Landis and Keeler, 1997; Seo et al., 2012; Seo et al., 2015).

2.2.3. TM in soil and litterfall

Soil samples were collected every month from December 2008 to October 2010, except January 2009, January, July, and August 2010, at depths of 6 (A horizons) and 15 cm (B horizons).

Litterfall samples was collected every month from December 2008 to November 2010, except January 2010. Ten nylon-mesh-lined baskets (1.09 m^2 each) were acid cleaned and randomly placed under the canopy. All litter and soil samples were freeze-dried, sorted by tree species, weighed, and then homogenized by crushing manually prior to analysis.

2.2.4. Volatilization from soils

The gaseous mercury emission flux from soil was measured using a dynamic flux chamber (DFC) connected to the Tekran 2537A (Tekran Inc., Toronto, Canada) and Tekran 1110 dual sampling unit (allows alternate sampling from inlet and outlet) (Choi and Holsen, 2009b) under the deciduous forest area once a month. Daily automated calibrations were performed for the Tekran 2537A using an internal permeation source. Manual injections were used to evaluate these calibrations using a saturated mercury vapor standard. The flowrate was approximately 5 L min^{-1}. Four 1 cm diameter inlet holes were evenly placed around the chamber ensuring it was well mixed. The bottom 2 cm of DFCs (3.78 L) were covered by soil.

The DFCs were made of glass and polycarbonate which may block some UV light (Choi and Holsen, 2009a; Skinner, 1998).

2.3. Analytical methods

2.3.1. Dry deposition for GOM and PBM

The dry deposition samples for GOM and PBM samples were analyzed using a tube furnace connected to a Tekran 2537. The tube furnace was pre-heated (GOM: 525 °C, PBM: 900 °C) and zero air passed through until the Hg concentration was zero (Kim et al., 2009; Kim et al., 2012). After samples were placed inside the tube furnace, the tube furnace was purged with zero air until Hg level was again zero. The mass of Hg desorbed from the sample was determined using the product of concentration and flowrate (5 L min^{-1}). The system recovery was measured by injecting mercury vapor standards (0, 10, 20, 30, 50 μL) manually. 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. However, recent studies (Lyman et al., 2010) reported potential sampling artifacts in the presence of O_3.

2.3.2. TM in wet deposition and throughfall

TM in throughfall was measure using a Tekran Series 2600 equipped with cold vapor atomic fluorescence spectrometer (CVAFS) following the procedures outlined in the U.S. EPA Method 1631 version E (U.S.EPA, 2002) and the U.S. EPA Lake Michigan Mass Balance Methods Compendium (LMMBMC) (U.S.EPA, 1997b)

2.3.3. TM in soil and litterfall

TM concentrations in soil and litterfall samples were determined using a direct mercury analyzer (DMA-80, Milestone, Italy), which utilizes the serial process of thermal composition, catalytic reduction, amalgamation, desorption, and atomic absorption spectroscopy.

2.4. QA/QC

2.4.1 Dry deposition for GOM and PBM

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 provided in the SI.

2.4.2. TM in wet deposition and throughfall

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, 1997b). 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 r^2 was greater than 0.9995 (linear). More additional information is described SI.

2.4.3. TM in litterfall and soil

TM in litterfall and soil was reported on a dry-weight basis. Recovery (%) of standard reference materials (SRMs) (MESS3, marine sediment) purchased form the National Research Council of Canada and analyzed every 10 samples at the start of experiments was 104 ± 4%.

2.4.4. Volatilization from soil

The DFC was connected to the Tekran 2537A through Tekran 1110 sampling unit. Ten μL of vapor phase Hg was injected into the DFC (n = 10) before deployment in the field. Recovery was 86 ~ 110% and averaged 101% at a flow rate of 5 L min^{-1}. 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.

3. Results and Discussion

3.1. Monthly and seasonal variations in dry deposition fluxes of GOM and PBM

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). Nonparametric Mann-Whitney U tests indicated that there were statistically significant differences in the dry deposition fluxes for GOM between spring 2009, fall 2008, and fall 2009 ($p < 0.05$) and there were statistically significant differences in the dry deposition flux for PBM between summer 2009 and fall 2009 ($p < 0.05$).

Zhang et al. (2012) reported that in eastern and central North America the GEM concentration in the colder seasons were generally higher than in warmer seasons. However, the dry deposition fluxes for GOM and PBM in spring and summer (warmer seasons) were higher than in the fall and winter (cold seasons) following the same pattern as average GEM concentrations (summer 2009: 2.7 ± 0.9 ng m^{-3}, spring 2009: 2.4 ± 0.6 ng m^{-3}, fall 2009: 2.3 ± 0.7 ng m^{-3}, winter 2008: 1.2 ± 0.2 ng m^{-3}) in Han River Environment Research Center (located approximately 2 km away).

3.2. Monthly and seasonal variations of TM wet deposition and throughfall flux

The average VWM concentration in precipitation (n = 35) and throughfall (n = 44) are shown Fig.3. Nonparametric Mann-Whitney U tests indicated that there were no statistically significant differences in the VWM TM concentration between winter 2009 and other seasons which is probably related with the small number of samples. The VWM TM concentration in winter 2009 was statistically significantly higher than fall 2009 ($p = 0.007$), spring 2009 ($p = 0.035$), and summer 2009 ($p = 0.001$) in throughfall.

The high VWM Hg concentrations in precipitation and throughfall in winter were likely associated with the combined effects of reduced mixing heights (Blanchard et al., 2002) 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). While, Sigler et al. (2009) reported that GOM is scavenged less efficiently during snow events.

Previous studies reported that rainfall depth in forested areas were approximately 8 ~ 24% smaller than that in an open area (Choi et al., 2008; Deguchi et al., 2006; Keim et al., 2005; Price and Carlyle-Moses, 2003) due to capture by the foliage and subsequent evaporation. In this study, rainfall depth in the forest was approximately 8% smaller than that in the open area. Regression analysis revealed that the TM concentration in throughfall was higher than in precipitation (statistically significant differences ($r^2 = 0.20$) ($p < 0.05$)) due to wash off of previously deposited Hg from the foliage (Grigal et al., 2000; Iverfeldt, 1991; Kolka et al., 1999; Schwesig and Matzner, 2000) and oxidation of Hg^0 to Hg^{2+} on the wet foliage surface by ozone and subsequent wash off (Graydon et al., 2008). Other possible sources of Hg in throughfall are leaching and biogeochemical recycling of Hg from foliage (St. Louis et al., 2001). 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 leaves since GOM is soluble and it is likely readily washed off during rain events (Blackwell and Driscoll, 2015).

3.3 Relationship between rainfall depth, VWM TM concentration, TM wet deposition and throughfall flux

There was a statistically significant negative correlation between rainfall depth and VWM TM concentrations in precipitation ($r^2 = 0.13$) ($p < 0.05$) (Fig. S1) and throughfall ($r^2 = 0.19$) ($p < 0.05$) (Fig. S2) due to dilution during the later stage of a precipitation event. This negative correlation has also been found in previous studies (Guo et al., 2008; Landis and Keeler, 2002; Seo et al., 2012; Seo et al., 2015; Wallschläger et al., 2000). About 19% of throughfall and 13% of precipitation variation in VWM concentration are explained by

precipitation depth. The rest of the variation is likely due to meteorological parameters that differ between events (Gratz et al., 2009), for example temperature (Table S3) and precipitation type (Rain, Snow, Mixed) 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 in previous studies (Choi et al., 2008; Gratz et al., 2009; 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 significantly if GOM and PBM concentrations are low (Zhang et al., 2012).

3.4. Leaf-on vs. Leaf-off

At this sampling site the leaf-on season is from March to the end of November. During leaf-on periods, the TM concentrations in throughfall (average 8.1 ng L^{-1}) were higher than that in precipitation (average 5.4 ng L^{-1}) and regression analysis suggested that they were significantly correlated ($r^2 = 0.59$) ($p < 0.05$). For leaf-off periods TM concentrations in throughfall (average 14.3 ng L^{-1}) were 1.7 times higher than in precipitation (average 8.6 ng L^{-1}) and concentrations were also significantly correlated ($r^2 = 0.56$) ($p < 0.05$) (Table 1). The concentration enhancement during leaf-off periods was probably due, at least in part, to snow on the branches that collected mercury due to dry deposition during dry periods that was subsequently collected by the sampler after being blown off by wind and/or after it melted.

The sample-by-sample flux of Hg in throughfall was similar to or lower than that of precipitation although the TM concentration in throughfall was higher than that in precipitation. However, the cumulative Hg fluxes in throughfall (leaf on: 7.0 μg Hg m^{-2}, leaf off: 3.1 μg Hg m^{-2}) were higher than in precipitation (leaf on: 4.9 μg Hg m^{-2}, leaf off: 0.6 μg Hg m^{-2}). As mentioned previously this may be a result of differences in rainfall depth (leaf-on periods) and snow events (leaf-off periods).

3.5. TM in litterfall and soil

Litterfall can be an important Hg input to soils under forested landscapes. The mean monthly TM concentrations in litterfall were 50.2 ± 16.5 ng g^{-1} (ranged from 28.2 to 76.4 ng g^{-1}) (Fig. 4). TM litterfall fluxes from winter 2009 to fall 2010 (one year) were 0.3 ± 0.4 μg m^{-2} (ranged from 0.01 to 1.9 μg m^{-2}). TM litterfall fluxes varied depending on the sampling periods; being lowest in summer, from June to August, and highest in fall, from September to November (Fig. 4) because litterfall production increases substantially over the growing season, from late fall to early winter. Hall and St. Louis (2004) reported the mean concentration of TM in leaf litter increased from 7.1 ng g^{-1} to a final value of 40.9 ng g^{-1} in deciduous litter. Demers et al. (2007) reported that the quantity of TM added to the decaying deciduous leaf litter was 5.1 ~ 5.5 μg m^{-2} during the growing season. In this study, TM litterfall fluxes were smaller than those in previous studies.

Soil samples were collected from the near-surface A-horizon following the removal of any rock fragments and the B-horizon. The mean soil TM concentrations were higher within the A-horizon (66.9 ± 20.3 ng g^{-1}) than within the B-horizon (46.1 ± 17.5 ng g^{-1}). TM concentration in soil collected in this study was similar to TM concentration found in soil collected from uncontaminated baseline sites which ranged from 30 to 50 ng g^{-1} (Gray et al., 2015).

3.6. Volatilization from soils

Hg emission fluxes were estimated from directly measured soil volatilization of gaseous elemental mercury (GEM) using a dynamic flux chamber (DFC). The measured fluxes were the highest in June and the lowest in November. Emission fluxes were positively correlated with ambient air temperature however, they were not influenced by precipitation. For example, the ambient air temperature was higher in summer than other seasons, but were not higher in July, a period of several severe rain storms nor were they lower in August which had very little rain. This result may be because the relative humidity was high enough that the soil remained moist. This result is similar to previous studies that found that Hg emission fluxes were positively correlated with soil surface temperature and negatively correlated with humidity (Choi and Holsen, 2009b; Gabriel et al., 2006; Wallschläger et al., 2000; Wang et al., 2005). Hg emission fluxes during leaf-on periods (March to November) (0.65 ± 2.25 ng m^{-2} hr^{-1},16.9 °C) were higher than leaf-off periods (December) (0.02 ± 2.13 ng m^{-2} $hr^{-1,}$ -1.29 °C).

374 This result is similar to a previous study. Choi and Holsen (2009b) reported that during leaf-
375 off periods, the Hg emission flux was correlated with temperature and solar radiation. The
376 cumulative annual Hg emission flux was 6.8 μg m^{-2} yr^{-1} (Fig. 5). Due to sampler (Tekran
377 2537A) malfunctions in January, February and April, fluxes were assumed to be equal to the
378 average of the flux of the previous and subsequent month. If only one month of data were
379 available, it was assumed to be the same as the missing month. For comparison the annual Hg
380 emission flux would be 4.8 μg m^{-2} y^{-1} if only measured data were used.
381
382
383 **3.7 Estimated dry deposition at forest**
384 Fu et al. (2009) estimated dry deposition to be equal to litterfall + throughfall – wet
385 deposition. Using the data presented here, the estimated dry deposition flux (6.7 μg m^{-2} yr^{-1})
386 was lower than measured dry deposition (9.9 μg m^{-2} yr^{-1}) and there was no significant
387 correlation between the two methods (r^2 = 0.22) (p = 0.65). One of the reasons for the directly
388 measured flux to be larger than the estimated flux is likely because there is no canopy
389 resistance for, or re-emission from, the KCl coated surrogate surface. The differences in the
390 estimates could be due to the loss of litter samples by wind or Hg losses from the collected
391 litter due to meteorological conditions such as rainfall (Blackwell et al., 2014) due to
392 relatively long sampling periods (1 month). However dry deposition collected with a
393 surrogate surface doesn't include accumulation in leaf stomata which may underestimate dry
394 deposition using this technique and since it is a smooth surface may collect less deposition
395 than a rougher surface.
396 The annual input flux calculated by summing wet deposition plus measured dry
397 deposition (14.2 μg m^{-2} yr^{-1}) was higher than the input flux calculated by summing
398 throughfall + litterfall (11.0 μg m^{-2} yr^{-1}) (Fig. 6). This difference is likely, at least in part, due
399 to the fact that no Hg is reemitted from wet and dry deposition as happens for litterfall.
400 Nonparametric Mann-Whitney U tests indicated that there were not statistically significant
401 differences (r^2 = 0.14) (p = 0.98). In general, wet + dry deposition was larger than throughfall
402 plus litterfall except during fall when leaves were being actively dropped from the trees. The
403 largest difference was in July during a period of significant precipitation (about 26.3% of the
404 total amount in 2009). This difference is most likely due to the many reactions and
405 transformations on the leaf surface that aren't mimicked with the surrogate surface including

406 re-emission (Rea et al., 2001).
407
408
409 **3.8. Mercury budget**
410 The yearly estimated budget of Hg in this study site was calculated using both input
411 approaches (Total input = wet deposition + dry deposition or Total input = throughfall +
412 litterfall) as follows. 1) Input to the forest canopy (wet deposition in an open area: 4.3 μg m^{-2}
413 yr^{-1} plus dry deposition in the forested area: 9.9 μg m^{-2} yr^{-1}) minus output (emissions from
414 soil 6.8 μg m^{-2} yr^{-1} plus accumulation in the soil 0.6 μg m^{-2} yr^{-1}) resulting in a net flux of 6.8
415 μg m^{-2} yr^{-1}. 2) The alternative method yields input (throughfall: 6.4 μg m^{-2} yr^{-1} plus litterfall:
416 4.6 μg m^{-2} yr^{-1}) minus output (emissions from soil: 6.8 μg m^{-2} yr^{-1} plus accumulation in the
417 soil: 0.6 μg m^{-2} yr^{-1}) resulting in a net flux of 3.6 μg m^{-2} yr^{-1}. For comparison at the
418 Lehstenbach catchment in Germany, the estimated net fluxes were similar: 6.8 μg m^{-2} yr^{-1}
419 (Schwesig and Matzner, 2000) and in the Experimental Lakes Area (ELA) watersheds in
420 Canada, the flux was 3 ~ 4 μg m^{-2} yr^{-1} (St. Louis et al., 2001). However, for the Lake
421 Langtjern spruce forest in southeast Norway (20.1 μg m^{-2} yr^{-1}) (Larssen et al., 2008) and
422 Huntington Wildlife forest (15.9 μg m^{-2} yr^{-1} in deciduous, 26.8 μg m^{-2} yr^{-1} in conifer)
423 (Blackwell et al., 2014), the estimated fluxes were higher than in this study.
424
425 **4. Conclusions**
426 Hg in dry and wet deposition, throughfall and litterfall and Hg volatilization from
427 soil were measured from August 2008 to February 2010 to identify the factors influencing the
428 amount of atmospheric Hg deposited to forested areas in a temperate deciduous forest in
429 Korea. In addition. measured and theoretical dry deposition were compared. The GOM fluxes
430 were low in fall and increased towards the spring. PBM fluxes were lowest in fall and peaked
431 in summer. The estimated and directly measured deposition fluxes were not significantly
432 correlated likely due to loss of litter samples by wind or wash-off by rainfall and the fact that
433 accumulation in leaf stomata was not characterized in the direct dry deposition measurement
434 technique. The average VWM Hg concentration in throughfall was approximately 2.4 times
435 higher than in precipitation due to wash off of previously deposited Hg from the foliage. Both
436 were higher in winter due to increased concentrations in snow events relative to rain events
437 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 μg m^{-2} yr^{-1} of GEM.

Based on these 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 μg m^{-2} yr^{-1} respectively. There are several uncertainties associated with this study as discuss 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 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 soil. Additional work should focus on better quantifying dry deposition, TM in soil water, overflow rate and biogeochemical recycling within the forest canopy and understory.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) of Korea (NRF-2008-0059001 and NRF-2012 R1A1A2042150), Korea Ministry of Environment (MOE) as “the Environmental Health Action Program (2015001370001)” and Brain Korea 21 (BK21) Plus Project (Center for Healthy Environment Education and Research).

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669

Table List

Table 1. Cumulative precipitation depths, VWM Hg concentration, cumulative Hg fluxes in precipitation and throughfall during leaf-on and leaf-off periods.

Figure List

Fig. 1. The locations of the sampling sites used in this study (Yangsu-ri, Korea)

Fig. 2. Seasonal variation in dry deposition flux for GOM and PBM under the deciduous forest.

Fig. 3. Seasonal variation in VWM TM concentration, rainfall depth and TM flux in precipitation and throughfall.

Fig. 4. Seasonal variation in TM concentration and flux in a deciduous forest.

Fig. 5. The estimated annual Hg emission fluxes in 2009 from soil.

Fig. 6. Comparison of deposition flux calculated by summing wet deposition + dry deposition and throughfall + litterfall

Table 1. Cumulative precipitation depths, VWM Hg concentration, cumulative Hg fluxes in precipitation and throughfall during leaf-on and leaf-off periods.

	Cumulative precipitation depth (mm)		VWM Hg Concentration (ng L^{-1})		Cumulative Hg fluxes (μg Hg m^{-2})	
	Leaf-on	Leaf-off	Leaf-on	Leaf-off	Leaf-on	Leaf-off
Precipitation	968.3	117.6	5.4	7.2	3.8	0.5
Throughfall	1009.7	114.7	8.1	18.3	4.9	1.8

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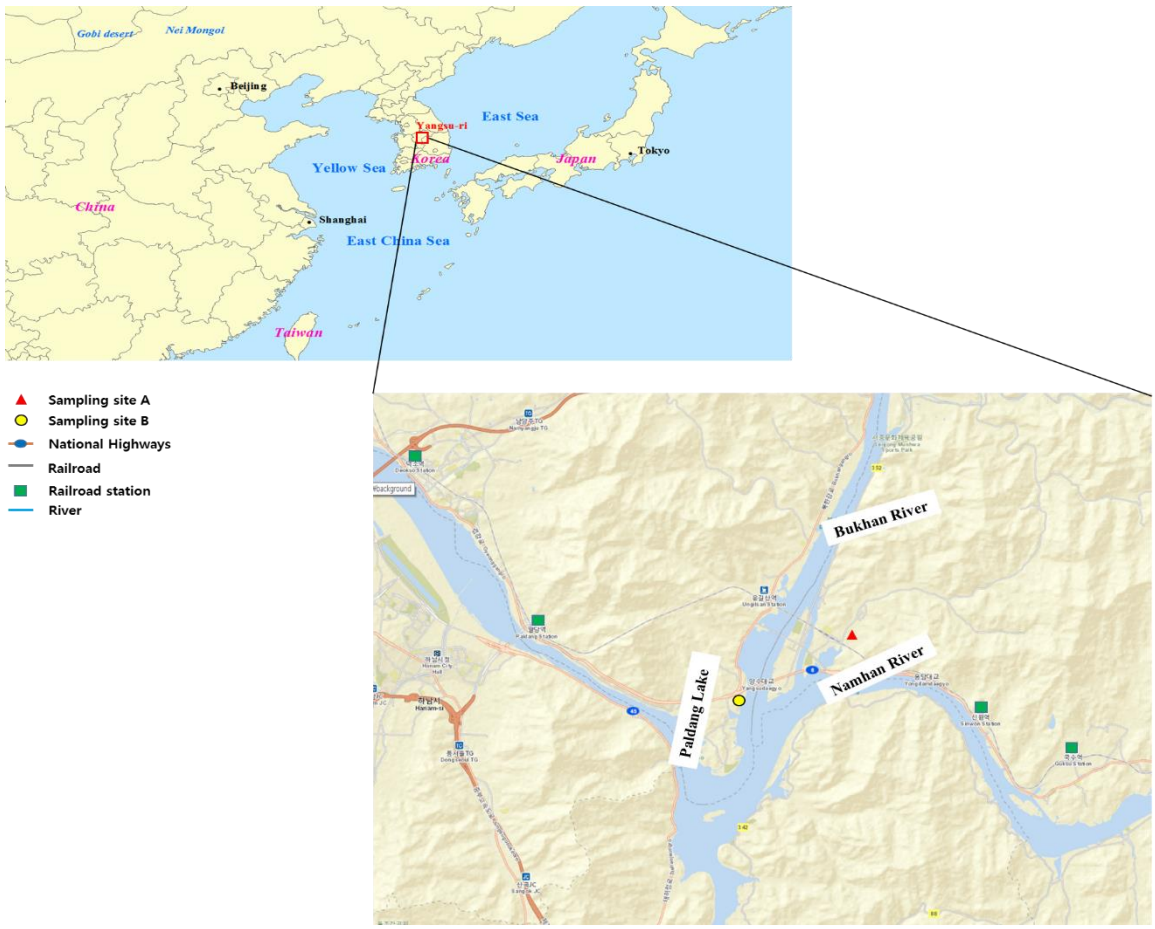

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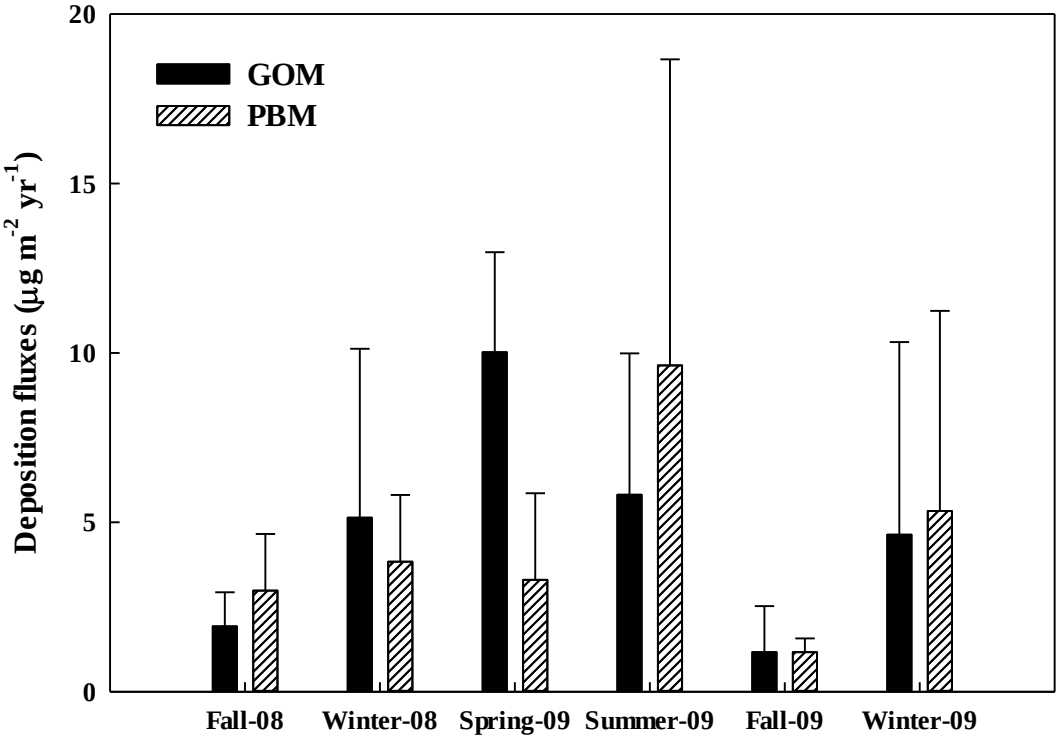

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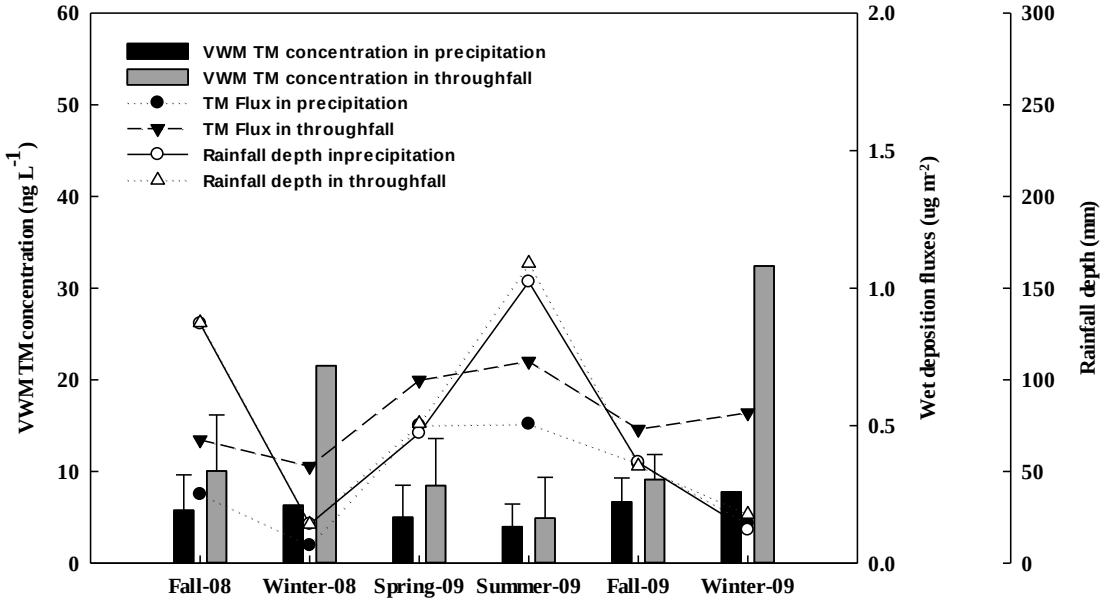
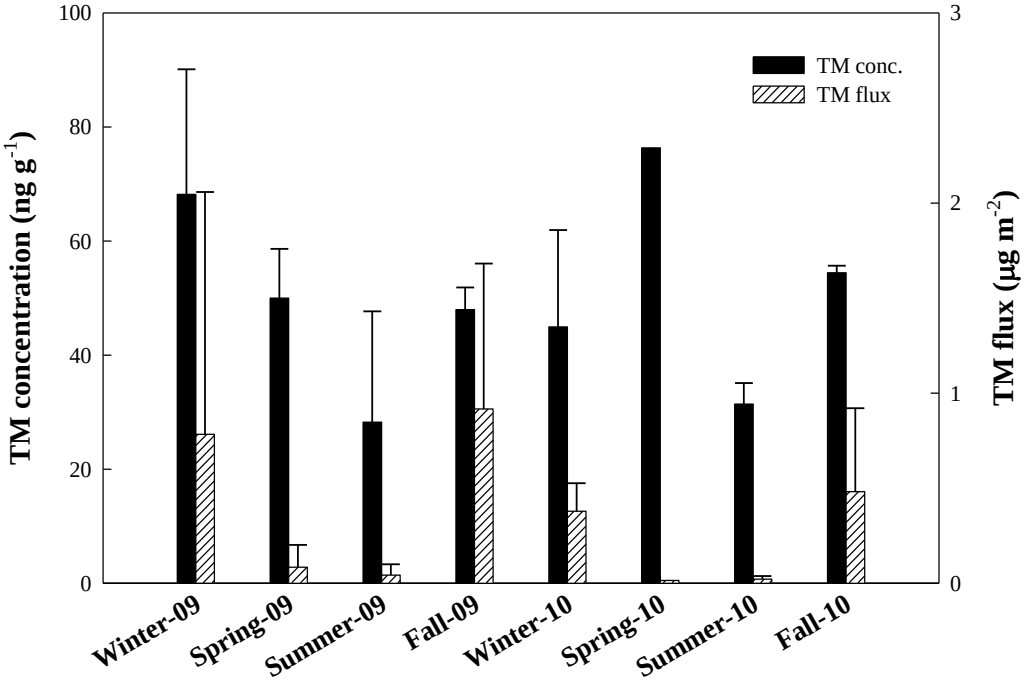


Fig. 3. Seasonal variation in VWM TM concentration, rainfall depth and TM flux in precipitation and throughfall.



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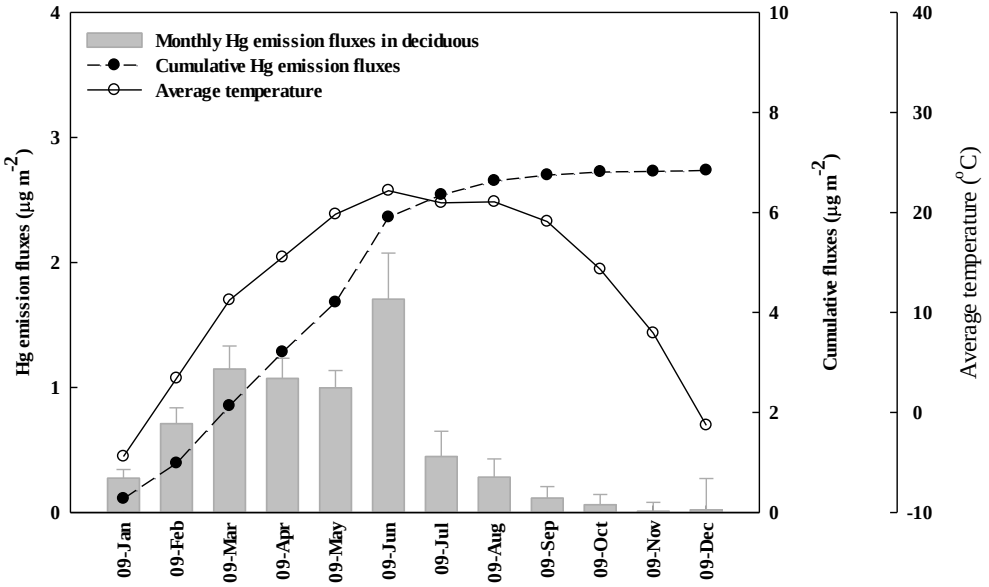

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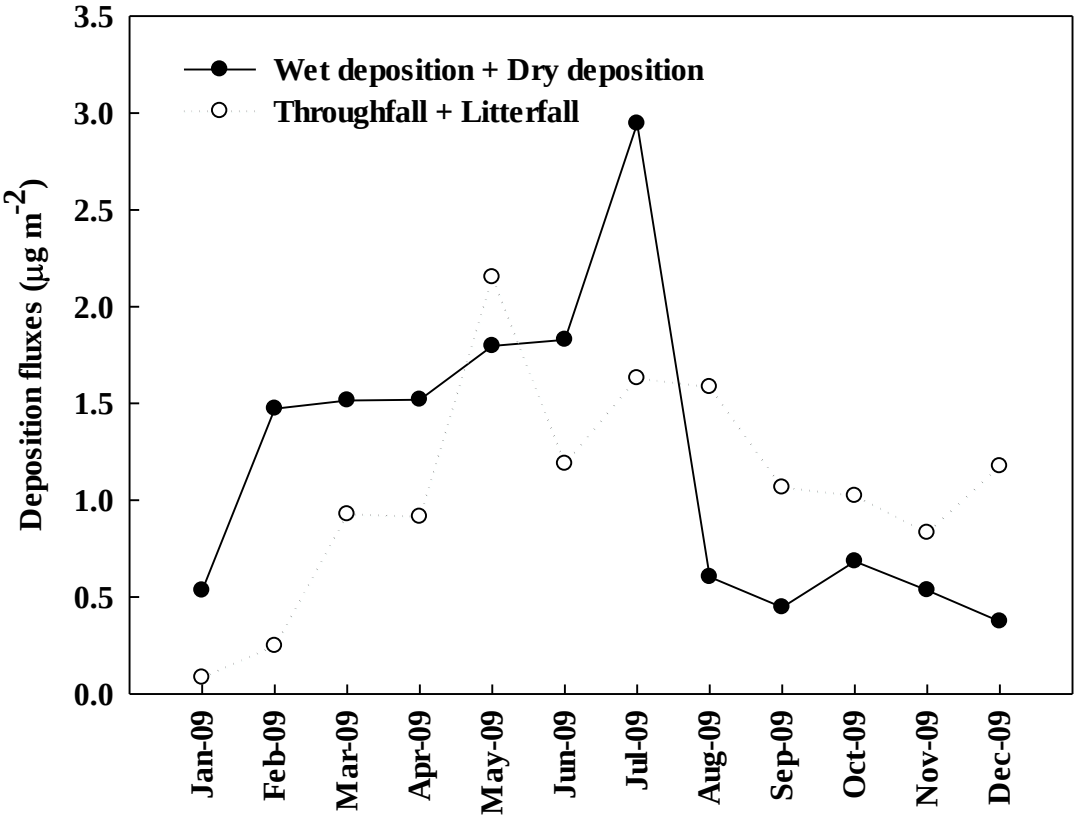

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724 **deposition and throughfall + litterfall**