Total Atmospheric Mercury Deposition in Forested Areas in Korea

Jin-Su Han[1], Yong-Seok Seo[1, 2], Moon-Kyung Kim[1, 2], Thomas M. Holsen[3], Seung-Muk Yi[1, 2, *]

[1] Department of Environmental Health Sciences, Graduate School of Public Health, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, South Korea

[2] Institute of Health and Environment, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, South Korea

[3] Department of Civil and Environmental Engineering, Clarkson University, Potsdam, NY13699, USA

*Address correspondence to Dr. Seung-Muk Yi, Graduate School of Public Health, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 088626, South Korea
E-mail) yiseung@snu.ac.kr
Telephone) 82-2-880-2736
Fax) 82-2-745-9104

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

121 **2.1. Site description**

122

123 The sampling sites were located at Yangsuri, Yangpyeong-gun, Gyeonggi-do, a
124 province in Korea where the Bukhan (North Han) and Namhan River (South Han River)
125 come together (Fig. 1). Gyeonggi-do has a population of 12 million (24% of the total
126 population and the most populated province in South Korea) and an area of 10,187 km^2 (10%
127 of the total area of South Korea). Yangpyeong-gun has a population of 83,000 (0.2% of the
128 total population in South Korea) and an area of 878.2 km^2 (0.9% of the total area in South
129 Korea). Wet deposition samples were collected at the Han River Environment Research
130 Center (Elevation 25 m, N37°32´, E127°18´) (site A in Fig. 1). Dry deposition, throughfall,
131 litterfall, volatilization from soils and total mercury (TM) in soil samples were determined in
132 a deciduous forest including primarily chestnut (Elevation 60 m, N37°32´, E127°20´) (site B
133 in Fig. 1) about 2 km away from site A. This area contains rivers, a flood plain, agricultural
134 land, residential areas, forests, and wetlands. Therefore, the study sites are appropriate for
135 identifying the in/out flow of Hg in a forested ecosystem typical for this part of the world.

136

137 **2.2. Sampling methods**

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

141

142 2.2.1. Dry deposition for GOM and PBM

143 Some studies have investigated the use of surrogate surfaces to directly measure Hg
144 dry deposition (Lyman et al., 2007; Peterson and Gustin, 2008). Surrogate surfaces allow
145 better control over exposure times than those provided with natural vegetation (Lai et al.,
146 2011). However, surrogate surfaces, being smooth, may not mimic Hg dry deposition to
147 natural rougher surfaces (Huang et al., 2011). Surrogate surfaces with cation exchange
148 membranes have been useful for measuring GOM however they may collect a very small
149 aerosol fraction by diffusion (Huang and Gustin, 2015; Lyman et al., 2007). Similar to
150 previous studies, in this project the dry deposition sampler was equipped with a knife-edge
151 surrogate surface (KSS) sampler with the collection media facing up. Forty seven-mm quartz
152 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

transformations on the leaf surface that aren't mimicked with the surrogate surface including re-emission (Rea et al., 2001).

3.8. Mercury budget

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: 6.4 $\mu g\ m^{-2}\ yr^{-1}$ 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 3.6 $\mu g\ m^{-2}\ yr^{-1}$. 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.

4. Conclusions

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 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 $\mu g\ m^{-2}\ yr^{-1}$ 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).

References

Bishop, K. H., Lee, Y.-H., Munthe, J., and Dambrine, E.: Xylem sap as a pathway for total mercury and methylmercury transport from soils to tree canopy in the boreal forest, Biogeochem., 40, 101-113, 1998.

Blackwell, B. D., Driscoll, C. T., Maxwell, J. A., and Holsen, T. M.: Changing climate alters inputs and pathways of mercury deposition to forested ecosystems, Biogeochem., 119, 215-228, 2014.

Blackwell, B. D., and Driscoll, C. T.: Deposition of mercury in forests along a montane elevation gradient, Environ. Sci. Technol., 49, 5363-5370, 2015.

Blanchard, P., Froude, F., Martin, J., Dryfhout-Clark, H., and Woods, J.: Four years of continuous total gaseous mercury (TGM) measurements at sites in Ontario, Canada, Atmospheric Environment, 36, 3735-3743, 2002.

Buehler, S., and Hites, R.: The Great Lakes' integrated atmospheric deposition network, Environ. Sci. Technol., 36, 354A-359A, 2002.

Carpi, A., and Lindberg, S. E.: Sunlight-mediated emission of elemental mercury from soil amended with municipal sewage sludge, Environ. Sci. Technol., 31, 2085-2091, 1997.

Choi, H.-D., Sharac, T. J., and Holsen, T. M.: Mercury deposition in the Adirondacks: A comparison between precipitation and throughfall, Atmos. Environ., 42, 1818-1827, 2008.

Choi, H.-D., and Holsen, T. M.: Gaseous mercury emissions from unsterilized and sterilized soils: the effect of temperature and UV radiation, Environmental Pollution, 157, 1673-1678, 2009a.

Choi, H.-D., and Holsen, T. M.: Gaseous mercury fluxes from the forest floor of the Adirondacks, Environ. Pollut., 157, 592-600, 2009b.

Cocking, D., Rohrer, M., Thomas, R., Walker, J., and Ward, D.: Effects of root morphology and Hg concentration in the soil on uptake by terrestrial vascular plants, Water, Air, Soil Pollut., 80, 1113-1116, 1995.

Cohen, M., Artz, R., Draxler, R., Miller, P., Poissant, L., Niemi, D., Ratte, D., Deslauriers, M., Duval, R., and Laurin, R.: Modeling the atmospheric transport and deposition of mercury to the Great Lakes, Environ. Res., 95, 247-265, 2004.

Deguchi, A., Hattori, S., and Park, H.-T.: The influence of seasonal changes in canopy structure on interception loss: application of the revised Gash model, J. Hydrol., 318, 80-102, 2006.

Demers, J. D., Driscoll, C. T., Fahey, T. J., and Yavitt, J. B.: Mercury cycling in litter and soil in different forest types in the Adirondack region, New York, USA, Ecol. Appl., 17, 1341-1351, 2007.

Fitzgerald, W. F., Engstrom, D. R., Mason, R. P., and Nater, E. A.: The case for atmospheric mercury contamination in remote areas, Environ. Sci. Technol., 32, 1-7, 1998.

Fu, X., Feng, X., Dong, Z., Yin, R., Wang, J., Yang, Z., and Zhang, H.: Atmospheric total gaseous mercury (TGM) concentrations and wet and dry deposition of mercury at a high-altitude mountain peak in south China, Atmos. Chem. Phys. Discuss, 9, 1-40, 2009.

Fu, X., Feng, X., Dong, Z., Yin, R., Wang, J., Yang, Z., and Zhang, H.: Atmospheric gaseous elemental mercury (GEM) concentrations and mercury depositions at a high-altitude mountain peak in south China, Atmos. Chem. Phys, 10, 2425-2437, 2010.

508 Gabriel, M. C., Williamson, D. G., Zhang, H., Brooks, S., and Lindberg, S.: Diurnal and
509 seasonal trends in total gaseous mercury flux from three urban ground surfaces, Atmos.
510 Environ., 40, 4269-4284, 2006.
511 Gratz, L. E., Keeler, G. J., and Miller, E. K.: Long-term relationships between mercury wet
512 deposition and meteorology, Atmos. Environ., 43, 6218-6229, 2009.
513 Gray, J. E., Theodorakos, P. M., Fey, D. L., and Krabbenhoft, D. P.: Mercury concentrations
514 and distribution in soil, water, mine waste leachates, and air in and around mercury mines
515 in the Big Bend region, Texas, USA, Environ. geochem. heal., 37, 35-48, 2015.
516 Graydon, J. A., St. Louis, V. L., Hintelmann, H., Lindberg, S. E., Sandilands, K. A., Rudd, J.
517 W., Kelly, C. A., Hall, B. D., and Mowat, L. D.: Long-term wet and dry deposition of total
518 and methyl mercury in the remote boreal ecoregion of Canada, Environ. Sci. Technol., 42,
519 8345-8351, 2008.
520 Grigal, D., Kolka, R. K., Fleck, J., and Nater, E.: Mercury budget of an upland-peatland
521 watershed, Biogeochem., 50, 95-109, 2000.
522 Grigal, D.: Inputs and outputs of mercury from terrestrial watersheds: a review, Environ.
523 Revie., 10, 1-39, 2002.
524 Guo, Y., Feng, X., Li, Z., He, T., Yan, H., Meng, B., Zhang, J., and Qiu, G.: Distribution and
525 wet deposition fluxes of total and methyl mercury in Wujiang River Basin, Guizhou, China,
526 Atmos. Environ., 42, 7096-7103, 2008.
527 Hall, B. D., and St. Louis, V. L.: Methylmercury and total mercury in plant litter
528 decomposing in upland forests and flooded landscapes, Environ. Sci. Technol., 38, 5010-
529 5021, 2004.
530 Han, Y.-J., Holsen, T. M., Hopke, P. K., and Yi, S.-M.: Comparison between back-trajectory
531 based modeling and Lagrangian backward dispersion modeling for locating sources of
532 reactive gaseous mercury, Environ. Sci. Technol., 39, 1715-1723, 2005.
533 Huang, J., Liu, Y., and Holsen, T. M.: Comparison between knife-edge and frisbee-shaped
534 surrogate surfaces for making dry deposition measurements: wind tunnel experiments and
535 computational fluid dynamics (CFD) modeling, Atmospheric environment, 45, 4213-4219,
536 2011.
537 Huang, J., and Gustin, M. S.: Uncertainties of Gaseous Oxidized Mercury Measurements
538 Using KCl-Coated Denuders, Cation-Exchange Membranes, and Nylon Membranes:
539 Humidity Influences, Environ. Sci. Technol., 49, 6102-6108, 2015.
540 Iverfeldt, Å.: Mercury in forest canopy throughfall water and its relation to atmospheric
541 deposition, Water Air Soil Pollut., 56, 553-564, 1991.
542 Jiskra, M., Wiederhold, J. G., Skyllberg, U., Kronberg, R.-M., Hajdas, I., and Kretzschmar,
543 R.: Mercury deposition and re-emission pathways in boreal forest soils investigated with
544 Hg isotope signatures, Environ. Sci. Technol., 49, 7188-7196, 2015.
545 Keim, R. F., Skaugset, A. E., and Weiler, M.: Temporal persistence of spatial patterns in
546 throughfall, J. Hydrol. , 314, 263-274, 2005.
547 Kerbrat, M., Pinzer, B., Huthwelker, T., Gäggeler, H., Ammann, M., and Schneebeli, M.:
548 Measuring the specific surface area of snow with X-ray tomography and gas adsorption:
549 comparison and implications for surface smoothness, Atmos. Chem. Phys. , 8, 1261-1275,
550 2008.
551 Kim, P.-R., Han, Y.-J., Holsen, T. M., and Yi, S.-M.: Atmospheric particulate mercury:
552 Concentrations and size distributions, Atmos. Environ., 61, 94-102, 2012.
553 Kim, S.-H., Han, Y.-J., Holsen, T. M., and Yi, S.-M.: Characteristics of atmospheric speciated
554 mercury concentrations (TGM, Hg (II) and Hg (p)) in Seoul, Korea, Atmos. Environ., 43,
555 3267-3274, 2009.

Kolka, R. K., Nater, E., Grigal, D., and Verry, E.: Atmospheric inputs of mercury and organic carbon into a forested upland/bog watershed, Water Air Soil Pollut., 113, 273-294, 1999.
Lai, S.-o., Holsen, T. M., Hopke, P. K., and Liu, P.: Wet deposition of mercury at a New York state rural site: Concentrations, fluxes, and source areas, Atmos. Environ., 41, 4337-4348, 2007.
Lai, S.-O., Huang, J., Hopke, P. K., and Holsen, T. M.: An evaluation of direct measurement techniques for mercury dry deposition, Sci. Total Environ., 409, 1320-1327, 2011.
Landis, M. S., and Keeler, G. J.: Critical evaluation of a modified automatic wet-only precipitation collector for mercury and trace element determinations, Environ. Sci. Technol., 31, 2610-2615, 1997.
Landis, M. S., and Keeler, G. J.: Atmospheric mercury deposition to Lake Michigan during the Lake Michigan mass balance study, Environ. Sci. Technol., 36, 4518-4524, 2002.
Larssen, T., de Wit, H. A., Wiker, M., and Halse, K.: Mercury budget of a small forested boreal catchment in southeast Norway, Sci. Total Environ., 404, 290-296, 2008.
Lin, C.-J., and Pehkonen, S. O.: The chemistry of atmospheric mercury: a review, Atmos. Environ., 33, 2067-2079, 1999.
Lindberg, S., Turner, R., Meyers, T., Taylor Jr, G., and Schroeder, W.: Atmospheric concentrations and deposition of Hg to A deciduous forest atwalker branch watershed, Tennessee, USA, Water Air Soil Pollut., 56, 577-594, 1991.
Lindberg, S., Hanson, P., Meyers, T. a., and Kim, K.-H.: Air/surface exchange of mercury vapor over forests—the need for a reassessment of continental biogenic emissions, Atmos. Environ., 32, 895-908, 1998.
Lindberg, S., Bullock, R., Ebinghaus, R., Engstrom, D., Feng, X., Fitzgerald, W., Pirrone, N., Prestbo, E., and Seigneur, C.: A synthesis of progress and uncertainties in attributing the sources of mercury in deposition, J. H. Environ., 36, 19-33, 2007.
Lindqvist, O., Johansson, K., Bringmark, L., Timm, B., Aastrup, M., Andersson, A., Hovsenius, G., Håkanson, L., Iverfeldt, Å., and Meili, M.: Mercury in the Swedish environment—recent research on causes, consequences and corrective methods, Water, Air, and Soil Pollution, 55, xi-261, 1991.
Lyman, S. N., Gustin, M. S., Prestbo, E. M., and Marsik, F. J.: Estimation of dry deposition of atmospheric mercury in Nevada by direct and indirect methods, Environ. Sci. Technol., 41, 1970-1976, 2007.
Lyman, S. N., Gustin, M. S., and Prestbo, E. M.: A passive sampler for ambient gaseous oxidized mercury concentrations, Atmospheric Environment, 44, 246-252, 2010.
Lynam, M. M., and Keeler, G. J.: Comparison of methods for particulate phase mercury analysis: sampling and analysis, Anal. Bioanal. Chem., 374, 1009-1014, 2002.
Ma, M., Wang, D., Sun, R., Shen, Y., and Huang, L.: Gaseous mercury emissions from subtropical forested and open field soils in a national nature reserve, southwest China, Atmos. Environ., 64, 116-123, 2013.
Ma, M., Wang, D., Du, H., Sun, T., Zhao, Z., and Wei, S.: Atmospheric mercury deposition and its contribution of the regional atmospheric transport to mercury pollution at a national forest nature reserve, southwest China, Environ. Sci. Poll. Res., 22, 20007-20018, 2015.
Miller, E. K., Vanarsdale, A., Keeler, G. J., Chalmers, A., Poissant, L., Kamman, N. C., and Brulotte, R.: Estimation and mapping of wet and dry mercury deposition across northeastern North America, Ecotox., 14, 53-70, 2005.
Munthe, J., Hultberg, H., and Iverfeldt, Å.: Mechanisms of deposition of methylmercury and mercury to coniferous forests, in: Mercury as a Global Pollutant, Springer, 363-371, 1995.

603 Petersen, G., Iverfeldt, Å., and Munthe, J.: Atmospheric mercury species over central and
604 Northern Europe. Model calculations and nordic air and precipitation network for 1987 and
605 1988, Atmos. Environ., 29, 47-67, 1995.
606 Peterson, C., and Gustin, M.: Mercury in the air, water and biota at the Great Salt Lake (Utah,
607 USA), Sci. Total Environ., 405, 255-268, 2008.
608 Price, A., and Carlyle-Moses, D.: Measurement and modelling of growing-season canopy
609 water fluxes in a mature mixed deciduous forest stand, southern Ontario, Canada, Agric.
610 For. Meteorol., 119, 69-85, 2003.
611 Rea, A. W., Lindberg, S. E., and Keeler, G. J.: Dry deposition and foliar leaching of mercury
612 and selected trace elements in deciduous forest throughfall, Atmos. Environ., 35, 3453-
613 3462, 2001.
614 Risch, M. R., DeWild, J. F., Krabbenhoft, D. P., Kolka, R. K., and Zhang, L.: Litterfall
615 mercury dry deposition in the eastern USA, Environmental Pollution, 161, 284-290, 2012.
616 Rolfhus, K., Sakamoto, H., Cleckner, L., Stoor, R., Babiarz, C., Back, R., Manolopoulos, H.,
617 and Hurley, J.: Distribution and fluxes of total and methylmercury in Lake Superior,
618 Environ. Sci. Technol., 37, 865-872, 2003.
619 Schroeder, W. H., and Munthe, J.: Atmospheric mercury—an overview, Atmos. Environ., 32,
620 809-822, 1998.
621 Schwesig, D., and Matzner, E.: Pools and fluxes of mercury and methylmercury in two
622 forested catchments in Germany, Sci. Total Environ., 260, 213-223, 2000.
623 Selin, N. E., Jacob, D. J., Park, R. J., Yantosca, R. M., Strode, S., Jaeglé, L., and Jaffe, D.:
624 Chemical cycling and deposition of atmospheric mercury: Global constraints from
625 observations, Journal of Geophysical Research: Atmospheres, 112, 2007.
626 Selvendiran, P., Driscoll, C. T., Montesdeoca, M. R., and Bushey, J. T.: Inputs, storage, and
627 transport of total and methyl mercury in two temperate forest wetlands, J. Geophys. Res.,
628 113, 2008.
629 Seo, Y.-S., Han, Y.-J., Choi, H.-D., Holsen, T. M., and Yi, S.-M.: Characteristics of total
630 mercury (TM) wet deposition: scavenging of atmospheric mercury species, Atmos.
631 Environ., 49, 69-76, 2012.
632 Seo, Y.-S., Han, Y.-J., Holsen, T. M., Choi, E., Zoh, K.-D., and Yi, S.-M.: Source
633 identification of total mercury (TM) wet deposition using a Lagrangian particle dispersion
634 model (LPDM), Atmos. Environ., 104, 102-111, 2015.
635 Shanley, J. B., Engle, M. A., Scholl, M., Krabbenhoft, D. P., Brunette, R., Olson, M. L., and
636 Conroy, M. E.: High mercury wet deposition at a “clean air” site in Puerto Rico, Environ.
637 Sci. Technol., 49, 12474-12482, 2015.
638 Sigler, J., Mao, H., and Talbot, R.: Gaseous elemental and reactive mercury in Southern New
639 Hampshire, Atmospheric Chemistry and Physics, 9, 1929-1942, 2009.
640 Skinner, D.: UV curing through semi-transparent materials: the challenge of the DVD
641 bonding process, RADTECH-NORTH AMERICA-, 1998, 140-146.
642 St. Louis, V. L., Rudd, J. W., Kelly, C. A., Hall, B. D., Rolfhus, K. R., Scott, K. J., Lindberg,
643 S. E., and Dong, W.: Importance of the forest canopy to fluxes of methyl mercury and total
644 mercury to boreal ecosystems, Environ. Sci. Technol., 35, 3089-3098, 2001.
645 U.S.EPA: Persistent, bioaccumulative and toxic chemical program. http://
646 www.epa.gov/pbt, 1997a.
647 U.S.EPA: U.S. EPA Lake Michigan Mass Balance Methods Compendium.
648 http://nepis.epa.gov/, 1997b.
649 U.S.EPA: Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and
650 Cold Vapor Atomic Fluorescence Spectrometry, 2002.

651 Wallschläger, D., Herbert Kock, H., Schroeder, W. H., Lindberg, S. E., Ebinghaus, R., and
652 Wilken, R.-D.: Mechanism and significance of mercury volatilization from contaminated
653 floodplains of the German river Elbe, Atmos. Environ., 34, 3745-3755, 2000.
654 Wang, S., Feng, X., Qiu, G., Wei, Z., and Xiao, T.: Mercury emission to atmosphere from
655 Lanmuchang Hg–Tl mining area, southwestern Guizhou, China, Atmos. Environ., 39,
656 7459-7473, 2005.
657 Wang, Y., Peng, Y., Wang, D., and Zhang, C.: Wet deposition fluxes of total mercury and
658 methylmercury in core urban areas, Chongqing, China, Atmos. Environ., 92, 87-96, 2014.
659 Weiss-Penzias, P. S., Gay, D. A., Brigham, M. E., Parsons, M. T., Gustin, M. S., and ter
660 Schure, A.: Trends in mercury wet deposition and mercury air concentrations across the US
661 and Canada, Sci. Total Environ., 2016.
662 Zhang, L., Blanchard, P., Gay, D., Prestbo, E., Risch, M., Johnson, D., Narayan, J., Zsolway,
663 R., Holsen, T., and Miller, E.: Estimation of speciated and total mercury dry deposition at
664 monitoring locations in eastern and central North America, Atmos. Chem. Phys. , 12, 4327-
665 4340, 2012.
666 Zhu, J., Wang, T., Talbot, R., Mao, H., Yang, X., Fu, C., Sun, J., Zhuang, B., Li, S., and Han,
667 Y.: Characteristics of atmospheric mercury deposition and size-fractionated particulate
668 mercury in urban Nanjing, China, Atmos. Chem. Phys. , 14, 2233-2244, 2014.
669

670

671 **Table List**

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

674

675

676

677 **Figure List**

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

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

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

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

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

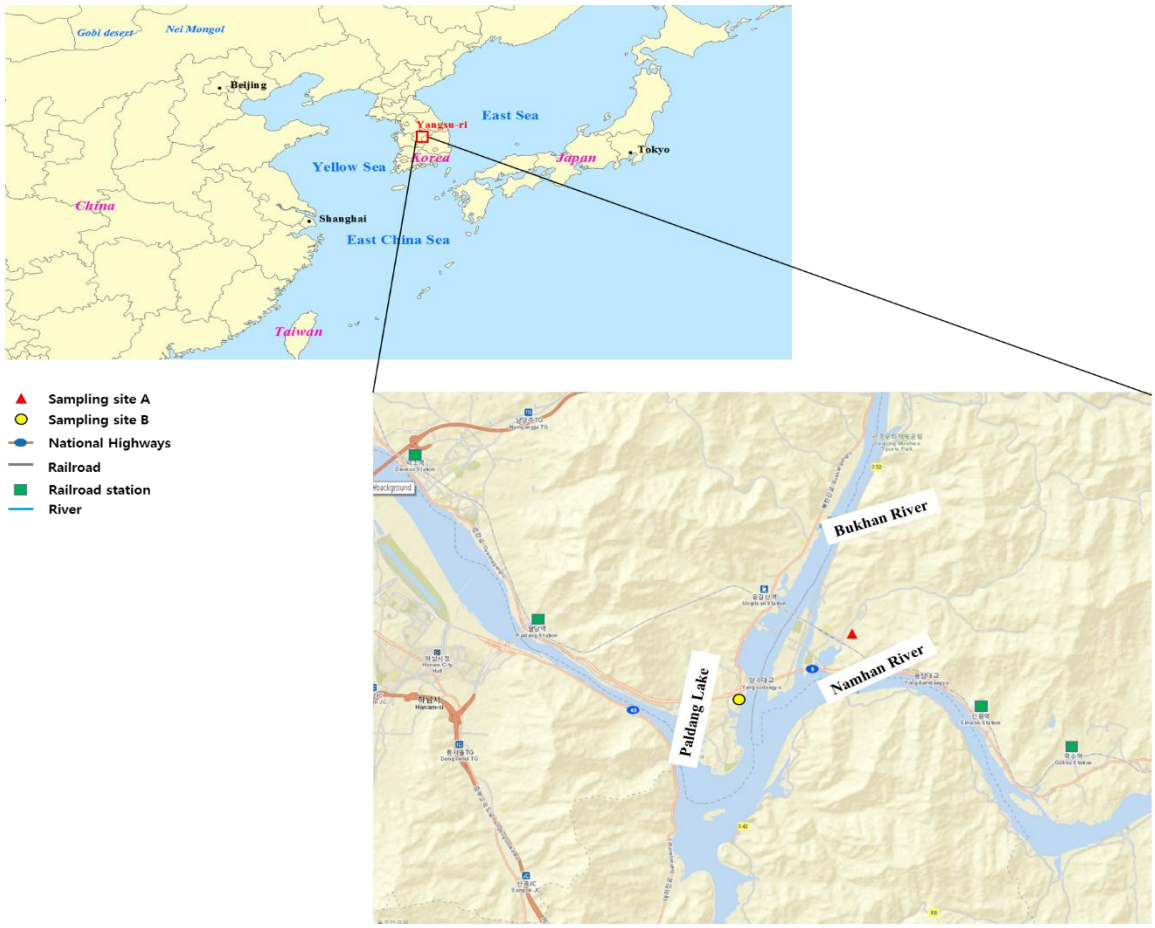
685 Fig. 6. Comparison of deposition flux calculated by summing wet deposition + dry deposition
686 and throughfall + litterfall

687

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

693

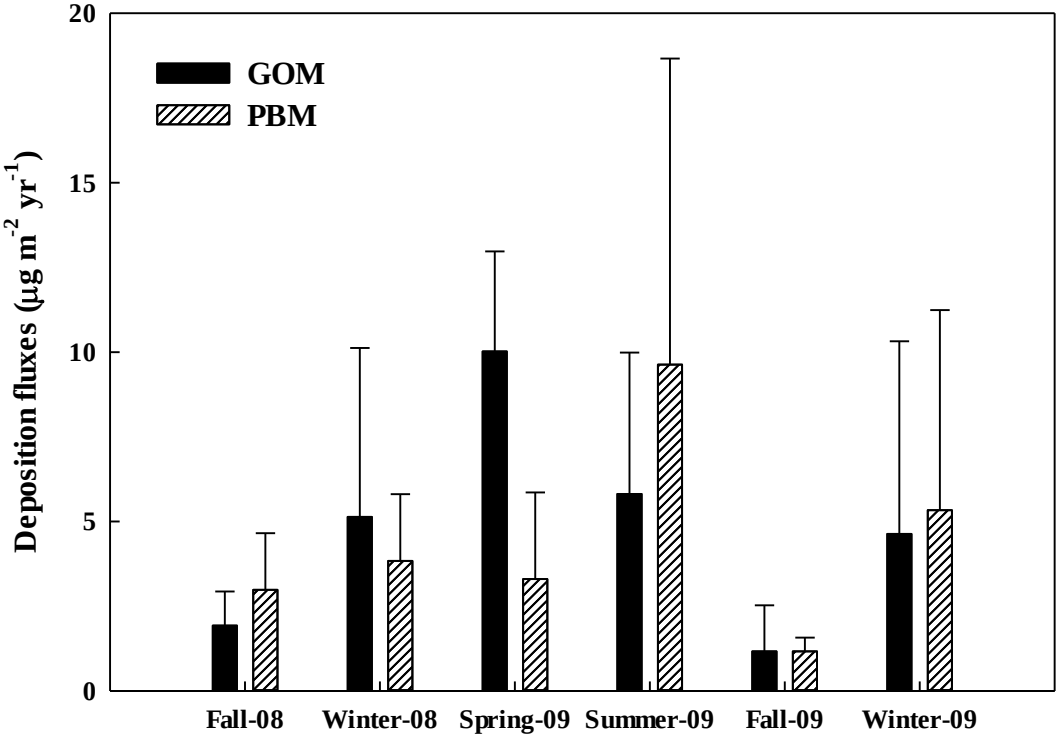


694

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

696

697



698

699 **Fig. 2. Seasonal variation in dry deposition flux for GOM and PBM under the**

700 **deciduous forest.**

701

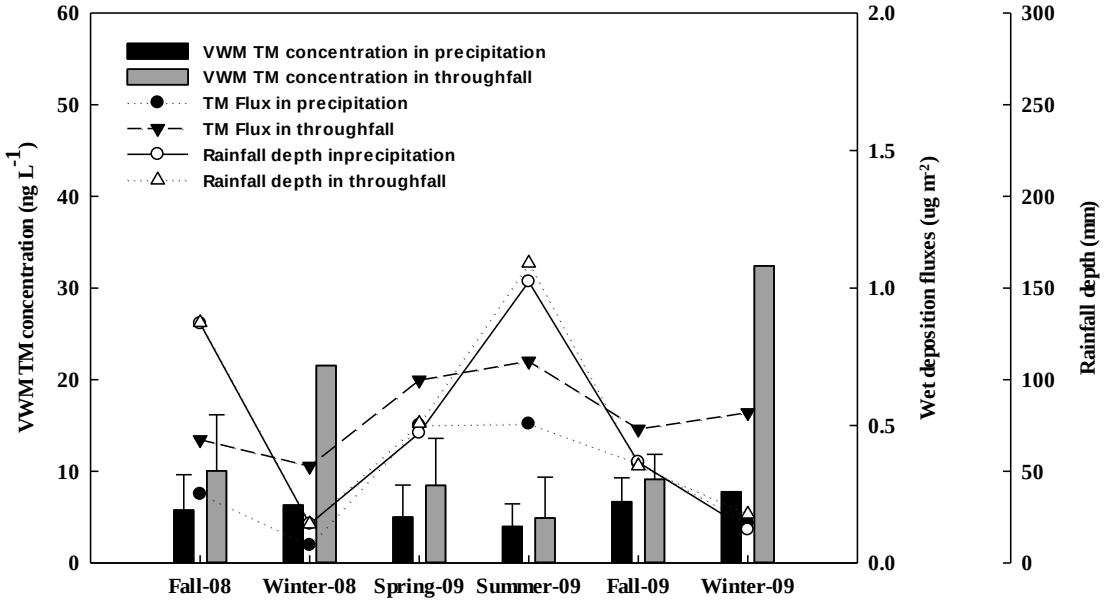


Fig. 3. Seasonal variation in VWM TM concentration, rainfall depth and TM flux in precipitation and throughfall.

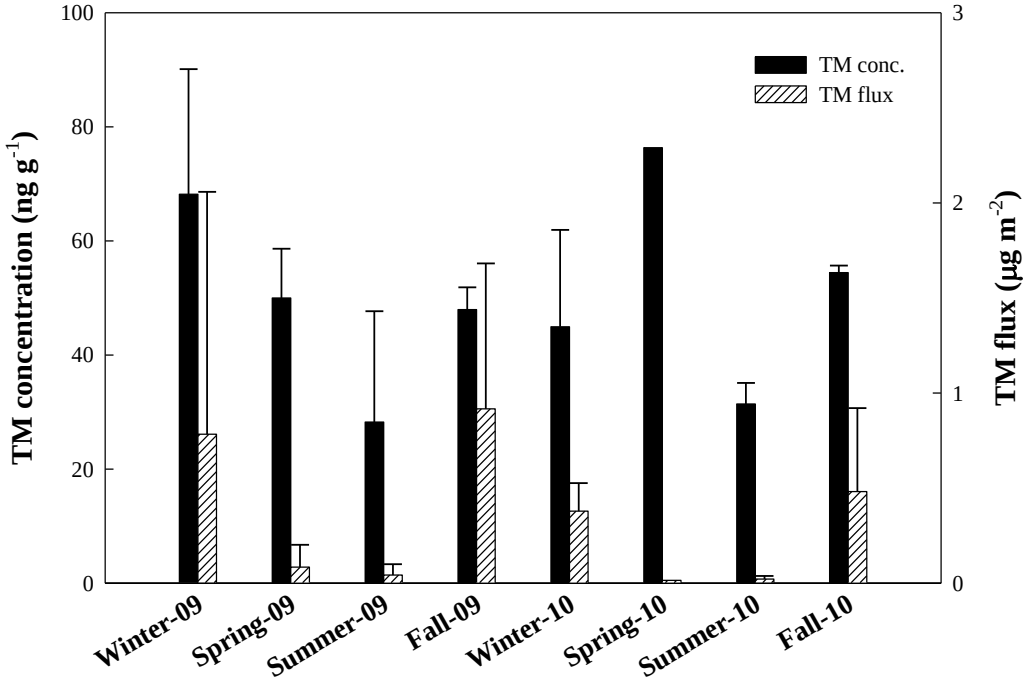
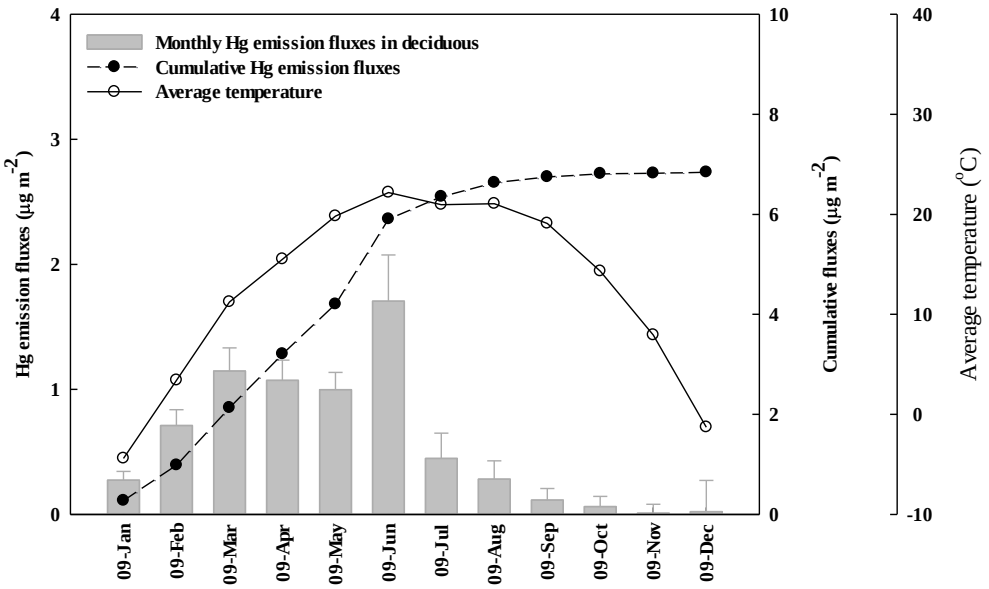


Fig. 4. Seasonal variation in TM concentration and flux in a deciduous forest.

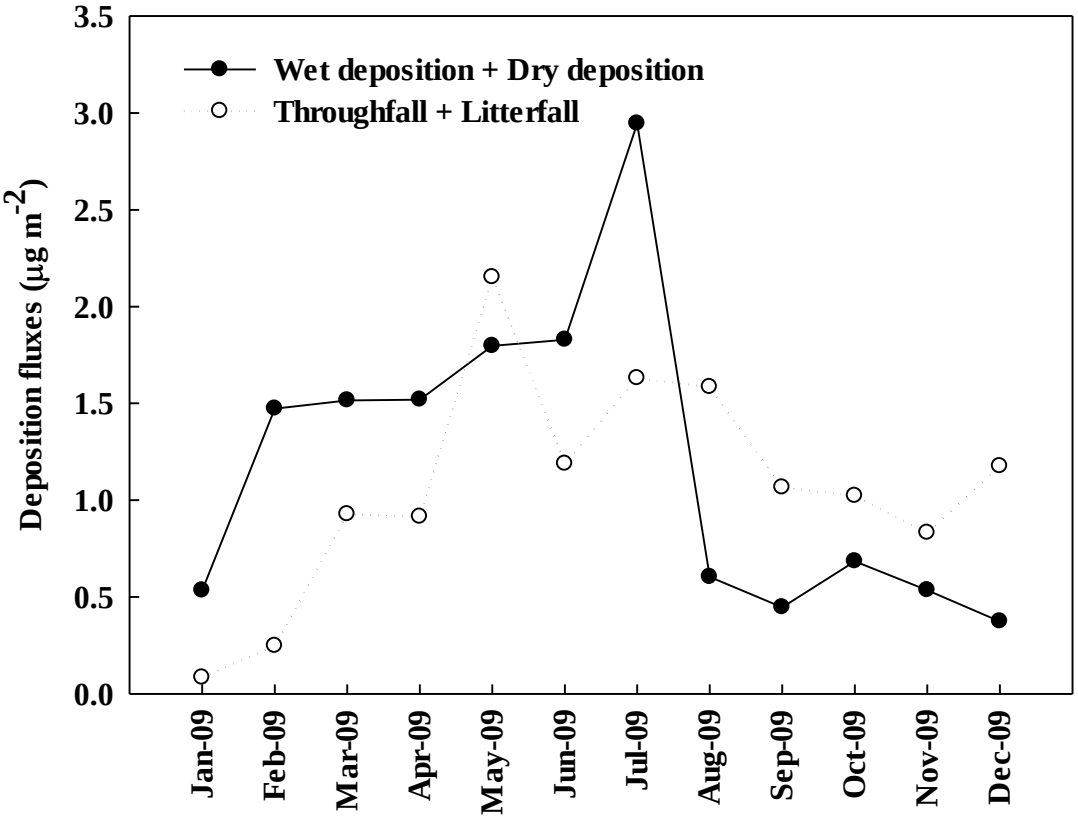


717
718

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

720

721



722

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