Total Atmospheric Mercury Deposition in Forested Areas in Korea

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Abstract

In this study, mercury (Hg) in dry and wet deposition, throughfall and litterfall, and Hg volatilization from soil were measured from August 2008 to February 2010 to identify the factors influencing the amount of atmospheric Hg deposited to forested areas in a temperate deciduous forest in Korea. For this location there was no significant correlation between the estimated dry deposition flux (litterfall + throughfall – wet deposition) (6.7 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 (throughfall + litterfall or wet deposition + dry deposition), were 6.8 and 3.9 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 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 (Weiss-Penzias et al., 2016; Zhu et al., 2014). It is classified as a persistent bioaccumulative and toxic (PBT) chemical (U.S.EPA, 1997b). Atmospheric Hg exists in three different forms with different chemical and physical properties; gaseous elemental mercury (GEM, Hg^0), gaseous oxidized mercury (GOM, Hg^{2+}), and particulate bound mercury (PBM, Hg_p). GEM is the major form of Hg in the atmosphere and is relatively water insoluble and very stable with a long residence time of 0.5 - 2 years (Carpi and Lindberg, 1997; Cohen et al., 2004; Schroeder and Munthe, 1998; Zhu et al., 2014). GOM is water soluble, with relatively strong adhesion properties (Han et al., 2005) and can be scavenged by rain within precipitating and below clouds (Blackwell and Driscoll, 2015; Lin and Pehkonen, 1999). It has a very high dry deposition velocity similar to HNO_3 ($1\sim5$ cm sec^{-1}) if it is assumed that all GOM is $HgCl_2$ (Petersen et al., 1995). PBM is created by GEM or GOM adsorbing to a particle (Lai et al., 2011). Atmospheric PBM transport is significantly affected by its particle size distribution and may contribute to both wet and dry deposition (Lynam and Keeler, 2002).

Wet and dry deposition of atmospheric Hg is an important input to the aquatic and terrestrial ecosystems (Buehler and Hites, 2002; Fitzgerald et al., 1998; Landis and Keeler, 2002; Lindberg et al., 1998; Miller et al., 2005; Rolfhus et al., 2003; Selvendiran et al., 2008; Shanley et al., 2015). Hg deposited from the atmosphere can be transformed to methyl mercury (MeHg) which bio-accumulates in aquatic food chains, resulting in adverse health and ecological effects (Ma et al., 2013; Lindberg et al., 2007; Rolfhus et al., 2003; Selin et al., 2007; Weiss-Penzias et al., 2016; Zhu et al., 2014). Atmospheric Hg deposition to forests includes direct dry deposition, throughfall, and litterfall. Dry deposition to leaves compromises a large proportion of litterfall (Grigal, 2002; St. Louis et al., 2001). Previous investigations (Fu et al., 2009) estimated dry deposition to forested areas as litterfall + throughfall – wet deposition. However, there are many variables that can adversely influence this technique including reemitted Hg from beneath the canopy and sampling artifacts. Directly measuring dry deposition with a surrogate surface is an alternative approach, although there is no universally accepted method on how to make these measurements.

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

The deposition of Hg in the forest ecosystem is complicated because of complex interactions between atmospheric Hg and the canopy, including oxidation of Hg on leaf surfaces (Blackwell and Driscoll, 2015; Iverfeldt, 1991), deposition of GOM and PBM on leaf surfaces (Blackwell 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). Recycled Hg would increase throughfall and litterfall concentrations (St. Louis et al., 2001).

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

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 that are expected to actively methylate Hg. Therefore, the study sites are appropriate for identifying the in/out flow of Hg in a forested ecosystem typical for this part of the world.

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). 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. Filters exposed to the atmosphere for 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, 2009) 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 DFCs (3.78 L) were placed 2 cm under the soil. The DFCs were made of glass and polycarbonate which may block some UV light.

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.

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, 1997a)

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, 1997a). 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). Additional information is described in the 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). This suggests that GEM may contribute to the measured dry deposition (Zhang et al., 2012).

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

The average VWM TM concentration in precipitation (n = 35) was highest in winter 2009 (7.8 ± 4.6 ng L^{-1}) (n = 3), followed by fall 2009 (6.7 ± 2.6 ng L^{-1}) (n = 8), winter 2008 (6.3 ± 5.7 ng L^{-1}) (n = 3), fall 2008 (5.8 ± 3.9 ng L^{-1}) (n = 5), spring 2009 (5.0 ± 3.5 ng L^{-1}) (n = 6), and summer 2009 (4.0 ± 2.5 ng L^{-1}) (n = 10) (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 average VWM TM concentration in throughfall (n = 44) was also highest in winter 2009 (32.4 ± 6.7 ng L^{-1}) (n = 7), followed by winter 2008 (21.6 ± 17.8 ng L^{-1}) (n = 3), fall 2008 (10.1 ± 6.1 ng L^{-1}) (n = 5), fall 2009 (9.1 ± 2.7 ng L^{-1}) (n = 9), spring 2009 (8.5 ± 5.1 ng L^{-1}) (n = 7), and summer 2009 (4.9 ± 4.5 ng L^{-1}) (n = 13). Nonparametric Mann-Whitney U tests indicate that 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 ($p = 0.001$).

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

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, for example temperature and precipitation type (Gratz et al., 2009) and variations in ambient Hg speciation and PBM particle size distributions due to differing impacts of local and regional sources (Blackwell and Driscoll, 2015). There was a statistically significant positive correlation between rainfall depth and TM deposition flux in precipitation ($r^2 = 0.34$) ($p < 0.05$), similar to what was found 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 if atmospheric concentrations of GOM and PBM 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, 2009; 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).

This result is similar to a previous study. Choi and Holsen (2009) reported that during leaf-off periods, the Hg emission flux was correlated with temperature and solar radiation. The cumulative annual Hg emission flux was 6.8 μg 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.

3.7 Estimated dry deposition at forest

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 μ*g* m^{-2} yr^{-1}) was lower than measured dry deposition (9.9 μ*g* m^{-2} yr^{-1}) and there was no significant correlation between the two methods ($r^2 = 0.22$) ($p = 0.65$). 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 dry deposition (14.3 μ*g* m^{-2} yr^{-1}) was higher than the input flux calculated by summing throughfall + litterfall (12.8 μ*g* m^{-2} yr^{-1}) (Fig. 6). 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).

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 μg m^{-2} yr^{-1} plus dry deposition in the forested area: 9.9 μg m^{-2} yr^{-1}) minus output (emissions from 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 μg m^{-2} yr^{-1}. 2) The alternative method yields input (throughfall: 6.7 μg m^{-2} yr^{-1} plus litterfall: 4.6 μg m^{-2} yr^{-1}) minus output (emissions from 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 3.9 μg m^{-2} yr^{-1}. For comparison at the Lehstenbach catchment in Germany, the estimated net fluxes were similar: 6.8 μg m^{-2} yr^{-1} (Schwesig and Matzner, 2000) and in the Experimental Lakes Area (ELA) watersheds in Canada, the flux was 3 ~ 4 μg m^{-2} yr^{-1} (St. Louis et al., 2001). However, for the Lake Langtjern spruce forest in southeast Norway (20.1 μg m^{-2} yr^{-1}) (Larssen et al., 2008) and Huntington Wildlife forest (15.9 μg m^{-2} yr^{-1} in deciduous, 26.8 μg 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 μg m^{-2} yr^{-1} of GEM.

Based on this all data, the yearly accumulation of Hg in the deciduous forest was calculated using two input approaches (total input = throughfall + litterfall or wet deposition + dry deposition and total output: emission from soil + TM in soil). Using this approach the accumulation of Hg were 6.8 and 3.9 μg m^{-2} yr^{-1} respectively. There are several uncertainties associated with this study as discussed above. The primary ones include that fact that dry deposition measured with the surrogate surface does not account for accumulation in leaf stomata yet this technique yielded a larger flux than to litterfall + throughfall – wet deposition. Litterfall can be lost from the sampler by wind and Hg can be lost from the collected litter due to washoff from rainfall due to relatively long sampling periods. The differences in the approaches suggest that approximately half of the GEM stored in the leaf may be released to back to the atmosphere. DFCs can alter measured fluxes because they cover the soil potentially blocking some UV light. In addition, several months of measurements were missed. Finally grab samples for TM in soil may not capture the true variability in the forest. Additional work should focus on better quantifying dry deposition, TM in soil water, overflow rate and biogeochemical recycling within the forest canopy and understory.

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Table List

Figure List

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

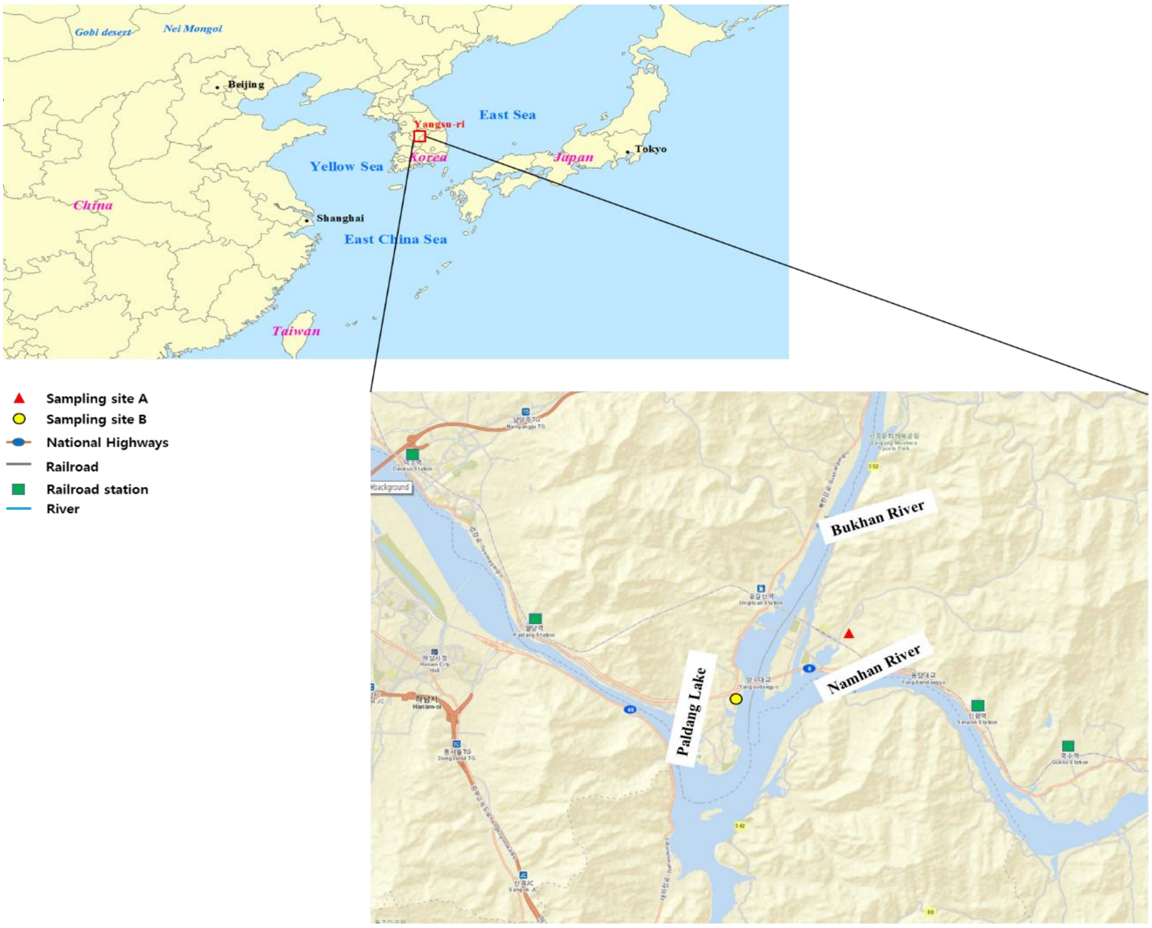

Fig. 1. The locations of the sampling sites used in this study (Yangsu-ri, Korea).

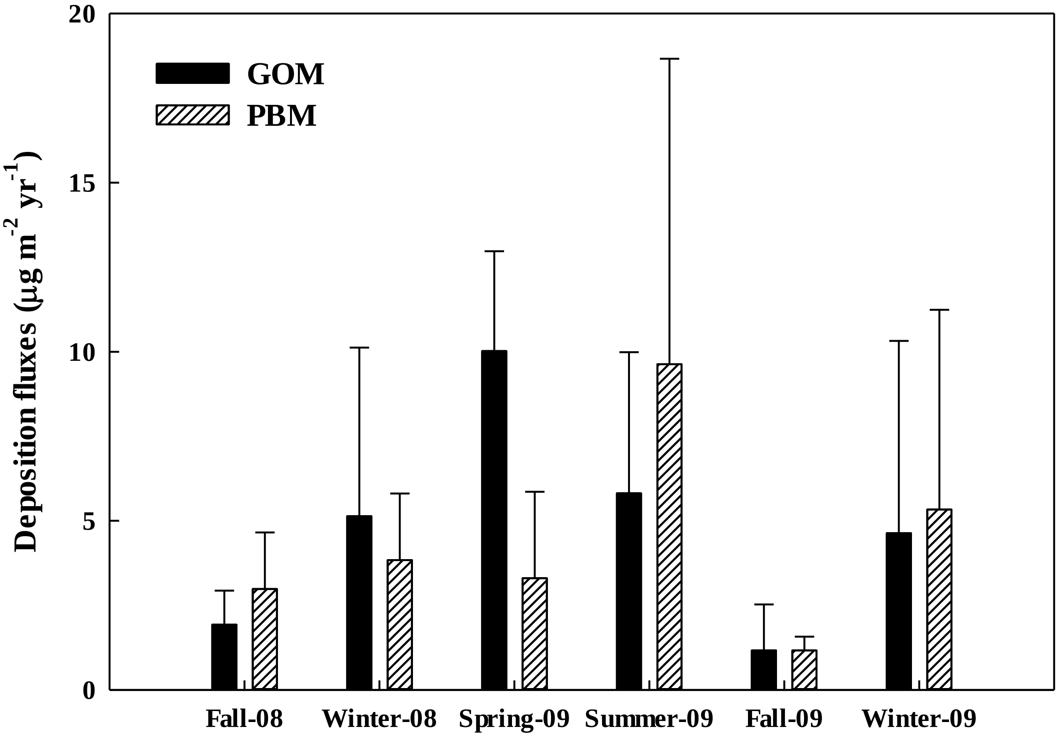

Fig. 2. Seasonal variation in dry deposition flux for GOM and PBM under the deciduous forest.

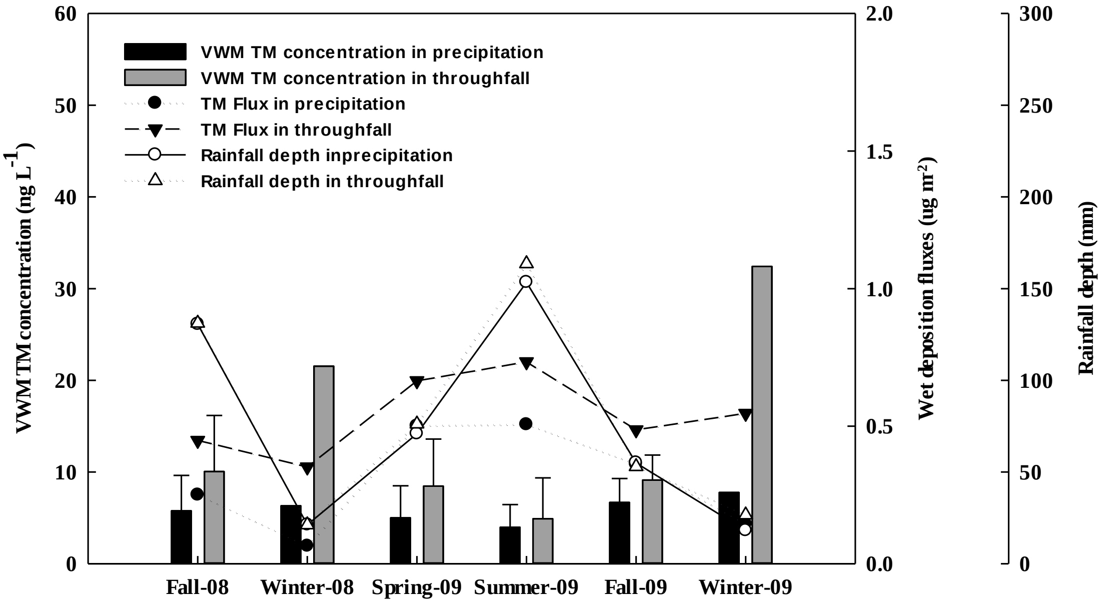

Fig. 3. Seasonal variation in VWM TM concentration, rainfall depth and TM flux in precipitation and throughfall.

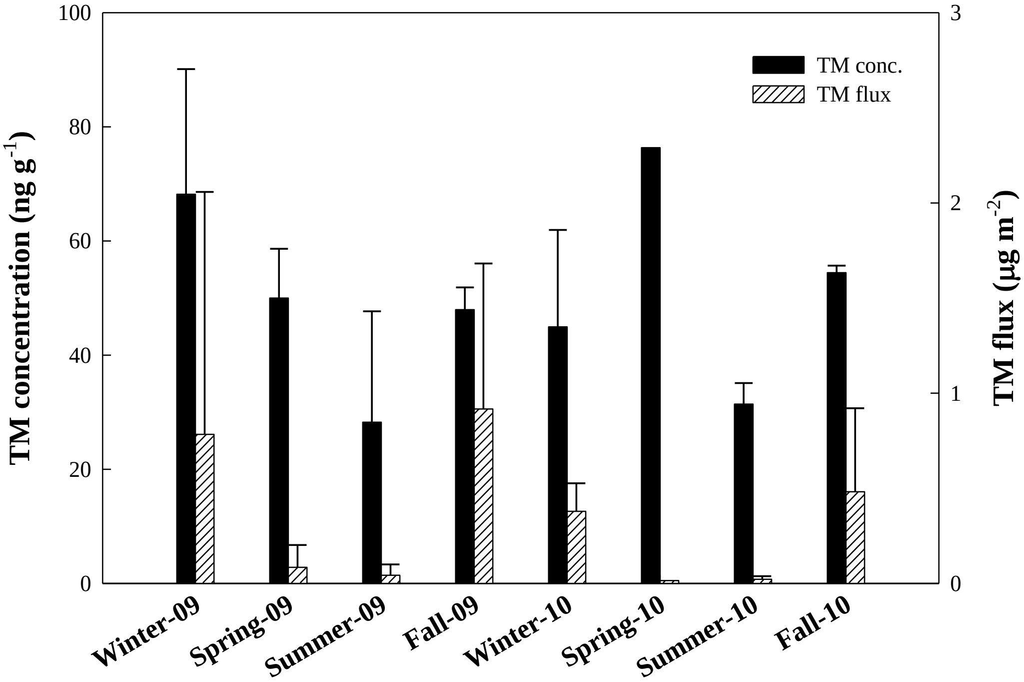

Fig. 4. Seasonal variation in TM concentration and flux in a deciduous.

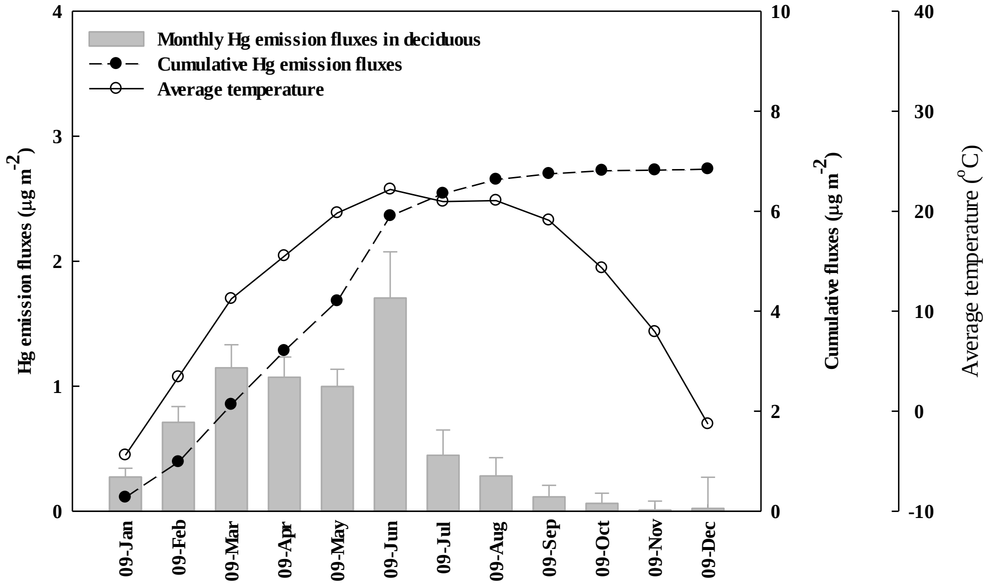

Fig. 5. The estimated annual Hg emission fluxes in 2009 from soil.

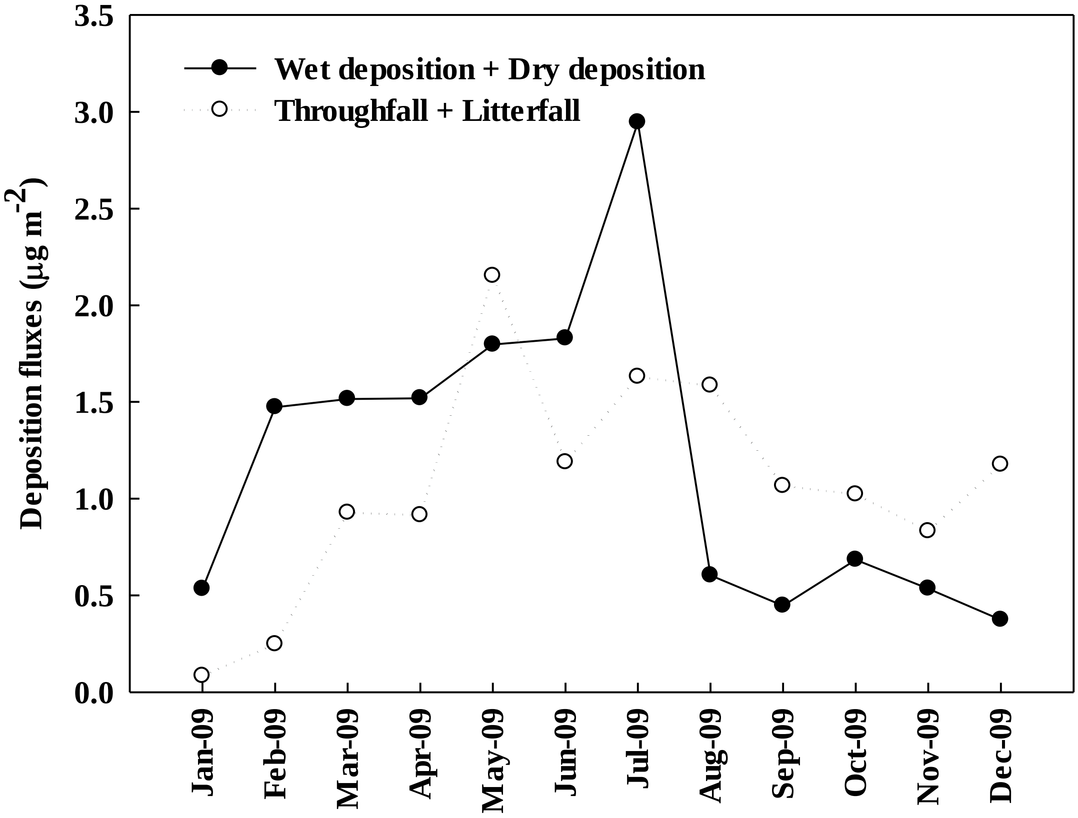

Fig. 6. Comparison of deposition flux calculated by summing wet deposition + dry deposition and throughfall + litterfall