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Total Atmospheric Mercury Deposition in Forest Areas in Korea

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Abstract

Atmospheric mercury dry and wet deposition, mercury in throughfall and litterfall, and mercury volatilization from soil were measured during August 2008 to February 2010 in a temperate deciduous forest in Korea. The yearly estimated mercury budget was calculated using two input approaches. For this location the annual mercury accumulation was estimated to be 6.8 μg m^{-2} yr^{-1} or 3.9 μg m^{-2} yr^{-1} depending on the approach used. Cumulative wet and throughfall fluxes were 4.3 and 6.7 μg m^{-2} yr^{-1}, respectively. The annual litterfall flux was 4.6 μg m^{-2} yr^{-1} and was highest from October to December due to the increased litter production during that period. The annual Hg emission flux from soil was 6.8 μg m^{-2} yr^{-1}. The overall ratio of wet deposition, throughfall, and litterfall was 1: 1.6: 1.1. Cumulative dry deposition fluxes of gaseous oxidized mercury (GOM) were highest in spring 2009 (10.0 ± 2.0 μg m^{-2} yr^{-1}), followed by summer 2009 (5.8 ± 4.2 μg m^{-2} yr^{-1}), winter 2008 (5.1 ± 5.0 μg m^{-2} yr^{-1}), winter 2009 (4.6 ± 5.7 μg m^{-2} yr^{-1}), fall 2008 (1.9 ± 1.0 μg m^{-2} yr^{-1}) and fall 2009 (1.2 ± 1.4 μg m^{-2} yr^{-1}) while dry deposition fluxes for particulate bound mercury (PBM) were highest in summer 2009 (9.6 ± 9.0 μg m^{-2} yr^{-1}), followed by winter 2009 (5.3 ± 5.9 μg m^{-2} yr^{-1}), winter 2008 (3.8 ± 2.0 μg m^{-2} yr^{-1}), spring 2009 (3.3 ± 2.6 μg m^{-2} yr^{-1}), fall 2008 (3.0 ± 1.7 μg m^{-2} yr^{-1}) and fall 2009 (1.2 ± 0.4 μg m^{-2} yr^{-1}). The VWM TM concentration in throughfall (14.4 ± 7.1 ng L^{-1}) was about two times higher than that in wet deposition (5.9 ± 3.8 ng L^{-1}). Wet deposition and throughfall fluxes were higher in summer than those in other seasons possibly due to a high precipitation depth.

Keywords: Dry deposition; Wet deposition; Throughfall; Litterfall; Gaseous oxidized mercury (GOM); Particulate bound mercury (PBM); Hg emission flux

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1. Introduction

Mercury (Hg) is a highly toxic pollutant and serious threat to human and ecosystem health. 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 mercury in the atmosphere and is relatively water insoluble and very stable with a long residence time of 0.5 - 2 year (Carpi and Lindberg, 1997; Cohen et al., 2004; Schroeder and Munthe, 1998).

GOM is water soluble, with relatively strong adhesion properties (Han et al., 2005) and can be scavenged by rain within precipitating and below clouds (Lin and Pehkonen, 1999). It has very high dry deposition velocity similar to HNO_3 (1~5 cm sec^{-1}) if it is assumed that all GOM is $HgCl_2$ (Petersen et al., 1995). PBM is strongly adsorbed to atmospheric particulate matter including soot, dust, ice crystals, sea salts (Lu and Schroeder, 2004). Atmospheric PBM transport is significantly affected by its particle size distribution and it is likely to be deposited at intermediate distances contributing to both wet and dry deposition (Lynam and Keeler, 2002). Atmospheric deposition via wet and dry processes is an important Hg input to the forest ecosystem (Buehler and Hites, 2002; Fitzgerald et al., 1998; Landis and Keeler, 2002; Lindberg et al., 1998; Miller et al., 2005; Rolfhus et al., 2003). Mercury 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; Rolfhus et al., 2003). Therefore, monitoring of the deposition flux as well as characterizing Hg deposition in forested areas is important for estimating environmental risks associated with Hg.

The deposition processes of Hg in the forest ecosystem are very complicated because of various interactions between atmospheric Hg and the canopy, such as oxidation of mercury on leaf surfaces (Iverfeldt, 1991), deposition of GOM and PBM on leaf surfaces (St. Louis et al., 2001), stomatal uptake of atmospheric Hg^0 (Iverfeldt, 1991; Lindberg et al., 1991; St. Louis et al., 2001), uptake via roots of dissolved Hg in soil and soil water (Cocking et al., 1995), and stomatal uptake of Hg^0 emitted from soils (Bishop et al., 1998).

Atmospheric Hg deposition to forests can follow several different pathways, such as dry deposition, throughfall, and litterfall. Dry deposition is the deposition of pollutants, including gases and particulate matter, onto surfaces including plant tissues. Hg deposited

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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 mercury in forest systems (St. Louis et al., 2001).

The objectives of this study were to characterize total atmospheric mercury deposition in a temperate deciduous forested area in Korea by measuring mercury dry deposition, wet deposition, throughfall, litterfall and volatilization from soils. Based on these data, the annual mercury fluxes were estimated.

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 TM in soil samples were determined in a deciduous forest (Elevation 60 m, N37°32´, E127°20´) (site B in Fig. 1). Since this area contains rivers, a flood plain, agricultural land, residential areas and forests, the study sites are appropriate for identifying the transport and transformation of Hg, as well as in/out flow of Hg in a forested ecosystem typical for this part of the world.

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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) in a deciduous forest dominated by chestnut.

2.2.1. Dry deposition for GOM and PBM

Similar to previous studies (Lai et al., 2011; Yi et al., 1996), the dry deposition sampler was equipped with a knife-edge surrogate surface (KSS) sampler using quartz filter for PBM deposition and KCl-coated quartz filter for GOM 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 ℃. The filters were then placed on a filter holder base, and clamped with a retaining ring before the filter holder was deployed in the KSS.

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 a depths of 6 (A horizons) and 15 cm (B horizons) in deciduous forest.

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

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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 2337A 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 DFC (3.78L) were placed 2cm under the soil. The types of DFCs were glass and polycarbonate which may block some UV light.

2.3. Analytical method

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 ℃, PBM: 900 ℃) and zero air passed through until the Hg concentration was zero. 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.

2.3.2. TM in wet deposition and throughfall

Total mercury (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

Total mercury 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

Relative percent difference (RPD) analyses for replicate GOM and PBM measurements were 19.4% and 22.9%, respectively. Recovery (%) of the Tekran 2537 measured by direct injection was 87~107% ($r^2 > 0.9995$). The MDL was 0.04 ng L^{-1}, the same as reported in EPA Method 1631. Relative Standard Deviation (RSD) measured by injecting mercury vapor standards in the same concentration seven times averaged 2 ~ 5%, within EPA Method 1631 requirements (± 25%). The average field blank (n = 4) concentration was 0.36 ng L^{-1} and the average lab blank (n = 44) concentration was 0.2 ng L^{-1}.

2.4.2. TM in wet deposition and throughfall

The method detection limit (MDL) for TM in wet deposition and throughfall calculated as three times the standard deviation of seven sequential regent blanks was 0.05 ng L^{-1}. Initial Precision Recovery (IPR) and On-going Precision Recovery (OPR) measured every 15 samples at the start of the analysis ranged from 80 ~ 107% (92.2 ± 7.0 % in average) and 81 ~ 117% (96.9 ± 13.7 % in average), respectively. The analysis of matrix spikes (MS) and matrix spike duplicates (MSD) measured every 10 samples to assess accuracy and precision ranged from 80 ~ 123% and relative percent difference (RPD) was 3 ~ 13%.

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 uL 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}.

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3. Results and Discussion

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

The average dry deposition fluxes for GOM and PBM were 5.4 μg m^{-2} yr^{-1} (range: 0.4 ~ 14.4 μg m^{-2} yr^{-1}) and 0.5 ng m^{-2} h^{-1} (range: 0.8 ~ 19.4 μg m^{-2} yr^{-1}), respectively (Fig. S1). The dry deposition fluxes for GOM were highest in spring 2009 (10.0 ± 2.0 μg m^{-2} yr^{-1}), followed by summer 2009 (5.8 ± 4.2 μg m^{-2} yr^{-1}), winter 2008 (5.1 ± 5.0 μg m^{-2} yr^{-1}), winter 2009 (4.6 ± 5.7 μg m^{-2} yr^{-1}), fall 2008 (1.9 ± 1.0 μg m^{-2} yr^{-1}) and 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}), followed by winter 2009 (5.3 ± 5.9 μg m^{-2} yr^{-1}), winter 2008 (3.8 ± 2.0 μg m^{-2} yr^{-1}), spring 2009 (3.3 ± 2.6 μg m^{-2} yr^{-1}), fall 2008 (3.0 ± 1.7 μg m^{-2} yr^{-1}) and fall 2009 (1.2 ± 0.4 μg m^{-2} yr^{-1}) (Fig. 2). Nonparametric Mann-Whitney 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 season 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 contributes to the measured dry deposition (GOM, PBM) (Zhang et al., 2012).

Previous studies reported that the Hg species were dry deposited to leaf surfaces through oxidation, adsorption (Munthe et al., 1995) and uptake by stomata (Lindberg et al., 1992). As will be discussed later, the observed Hg dry deposition fluxes were also compared with the estimated Hg dry deposition fluxes using litterfall, throughfall and wet deposition.

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

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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 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). 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 TM concentrations in precipitation and throughfall in winter were associated with the combined effects of reduced mixing heights (Kim et al., 2009; Seo et al., 2015), and 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 November 24, 2015)). Another possible reason for the high TM concentration in precipitation and throughfall in winter was due to snow events. 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 an open area. 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

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ozone and subsequent wash off (Graydon et al., 2008). Other possible sources of Hg in throughfall are leaching and mechanical weathering of Hg from foliage. Some of the deposited Hg can be washed off by rainfall and reemitted to the atmosphere (Rea et al., 2001). Therefore, all of the Hg deposited on the foliar surfaces is not in the throughfall.

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. S2) and throughfall ($r^2 = 0.19$) ($p < 0.05$) (Fig. S3) due to dilution during the later stage of a precipitation event. This negative correlation has been also 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 variations in local and regional sources and other mechanisms involved in biogeochemical cycling for example dry deposition (St. Louis et al., 2001). There was a statistically significant positive correlation between rainfall depth and TM deposition flux in precipitation ($r^2 = 0.34$) ($p < 0.05$), suggesting that the TM deposition flux increased during large events even though continuous rain diluted the TM mass, similar to previous studies (Choi et al., 2008; Wang et al., 2014). 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 (deciduous trees) (average 8.1 ng L^{-1}) were higher than that in precipitation (average 5.4 ng L^{-1}) and 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 moderately 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

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branches that collected mercury due to dry deposition during dry periods that was subsequently collected by the sampler after being blown off by wind or after it melted.

The 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. The cumulative Hg fluxes in throughfall (leaf on: 7.0 μ*g* Hg m^{-2}, leaf off: 3.1 μ*g* Hg m^{-2}) were higher than in precipitation (leaf on: 4.9 μ*g* Hg m^{-2}, leaf off: 0.6 μ*g* 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} for the deciduous forest (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} in the deciduous forest (ranged from 0.01 to 1.9 μg m^{-2}). TM litterfall fluxes were different 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 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}) deciduous forest stand. 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, 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 a previous study 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 previous study. Choi and Holsen (2009) reported that during leaf-off periods, Hg emission flux were correlated with temperature and solar radiation. The cumulative annual Hg emission fluxes 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 the month before and after.

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 μg m^{-2} yr^{-1}) was lower than measured dry deposition (9.9 μg 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. Another reasons for these differences could be deposition to all media such as leaves, tree branch, soils and land types surrounding the sites (Zhang et al., 2012).

The annual input flux calculated by summing wet deposition plus dry deposition (14.3 μg m^{-2} yr^{-1}) was higher than the input flux calculated by summing throughfall + litterfall (12.8 μg m^{-2} yr^{-1}) (Fig. 6). Nonparametric Mann-Whitney tests indicated that there

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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 mass balance of mercury was calculated using both input approaches described above. Input to the forest canopy (wet deposition in an open area: 4.3 μg m^{-2} yr^{-1}, dry deposition in the forested area: 9.9 μg m^{-2} yr^{-1}) with output (emissions from soil 6.8 μg m^{-2} yr^{-1}, TM in soil: 0.6 μg m^{-2} yr^{-1}) was estimated to be 6.8 μg m^{-2} yr^{-1}. The alternative method with input (throughfall: 6.7 μg m^{-2} yr^{-1}, litterfall: 4.6 μg m^{-2} yr^{-1}) with output (emissions from soil 6.8 μg m^{-2} yr^{-1}, TM in soil: 0.6 μg m^{-2} yr^{-1}) results in a net mercury flux of 3.9 μg m^{-2} yr^{-1}.

This result is similar to previous studies. At the Lehstenbach catchment in Germany the estimated fluxes was 6.8 μg m^{-2} yr^{-1} (Schwesig and Matzner, 2000). 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.

There are several few uncertainties associated with this study. 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 or and Hg can be lost from the collected litter due to rainfall due to relatively long sampling periods (Blackwell et al., 2014) and approximately half of the GEM stored in the leaf may be released to back to the atmosphere (Zhang et al., 2012).

DFCs can alter fluxes because they cover the soil potentially blocking some UV light. In addition several months of measurements were missed. Grab samples for TM in soil

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may not capture the true variability in the forest. Therefore, further investigations are required to elucidate exactly the mercury budget Additional work should focus on better quantifying dry deposition, TM in soil water, overflow rate and biogeochemically recycling within forest.

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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, Biogeochemistry, 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, Biogeochemistry, 119, 215-228, 2014.

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

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.

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.

Gabriel, M. C., Williamson, D. G., Zhang, H., Brooks, S., and Lindberg, S.: Diurnal and seasonal trends in total gaseous mercury flux from three urban ground surfaces, Atmos. Environ., 40, 4269-4284, 2006.

Graydon, J. A., St. Louis, V. L., Hintelmann, H., Lindberg, S. E., Sandilands, K. A., Rudd, J. W., Kelly, C. A., Hall, B. D., and Mowat, L. D.: Long-term wet and dry deposition of total and methyl mercury in the remote boreal ecoregion of Canada, Environ. Sci. Technol., 42, 8345-8351, 2008.

Grigal, D., Kolka, R. K., Fleck, J., and Nater, E.: Mercury budget of an upland-peatland watershed, Biogeochemistry, 50, 95-109, 2000.

Guo, Y., Feng, X., Li, Z., He, T., Yan, H., Meng, B., Zhang, J., and Qiu, G.: Distribution and wet deposition fluxes of total and methyl mercury in Wujiang River Basin, Guizhou, China, Atmos. Environ., 42, 7096-7103, 2008.

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Hall, B. D., and St. Louis, V. L.: Methylmercury and total mercury in plant litter decomposing in upland forests and flooded landscapes, Environ. Sci. Technol., 38, 5010-5021, 2004.
Han, Y.-J., Holsen, T. M., Hopke, P. K., and Yi, S.-M.: Comparison between back-trajectory based modeling and Lagrangian backward dispersion modeling for locating sources of reactive gaseous mercury, Environ. Sci. Technol., 39, 1715-1723, 2005.
Iverfeldt, Å .: Mercury in forest canopy throughfall water and its relation to atmospheric deposition, Water Air Soil Pollut., 56, 553-564, 1991.
Keim, R. F., Skaugset, A. E., and Weiler, M.: Temporal persistence of spatial patterns in throughfall, J. Hydrol. , 314, 263-274, 2005.
Kerbrat, M., Pinzer, B., Huthwelker, T., Gäggeler, H., Ammann, M., and Schneebeli, M.: Measuring the specific surface area of snow with X-ray tomography and gas adsorption: comparison and implications for surface smoothness, Atmos. Chem. Phys. , 8, 1261-1275, 2008.
Kim, S.-H., Han, Y.-J., Holsen, T. M., and Yi, S.-M.: Characteristics of atmospheric speciated mercury concentrations (TGM, Hg (II) and Hg (p)) in Seoul, Korea, Atmos. Environ., 43, 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., 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., Owens, J., and Stratton, W.: Application of throughfall methods to estimate dry deposition of mercury, Oak Ridge National Lab., TN (United States), 1992.
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.
Lu, J. Y., and Schroeder, W. H.: Annual time-series of total filterable atmospheric mercury concentrations in the Arctic, Tellus B, 56, 213-222, 2004.
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.

© Author(s) 2016. CC-BY 3.0 License.

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, Ecotoxicology, 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.

Petersen, G., Iverfeldt, Å., and Munthe, J.: Atmospheric mercury species over central and Northern Europe. Model calculations and nordic air and precipitation network for 1987 and 1988, Atmos. Environ., 29, 47-67, 1995.

Price, A., and Carlyle-Moses, D.: Measurement and modelling of growing-season canopy water fluxes in a mature mixed deciduous forest stand, southern Ontario, Canada, Agric. For. Meteorol., 119, 69-85, 2003.

Rea, A. W., Lindberg, S. E., and Keeler, G. J.: Dry deposition and foliar leaching of mercury and selected trace elements in deciduous forest throughfall, Atmos. Environ., 35, 3453-3462, 2001.

Rolfhus, K., Sakamoto, H., Cleckner, L., Stoor, R., Babiarz, C., Back, R., Manolopoulos, H., and Hurley, J.: Distribution and fluxes of total and methylmercury in Lake Superior, Environ. Sci. Technol., 37, 865-872, 2003.

Schroeder, W. H., and Munthe, J.: Atmospheric mercury—an overview, Atmos. Environ., 32, 809-822, 1998.

Schwesig, D., and Matzner, E.: Pools and fluxes of mercury and methylmercury in two forested catchments in Germany, Sci. Total Environ., 260, 213-223, 2000.

Seo, Y.-S., Han, Y.-J., Choi, H.-D., Holsen, T. M., and Yi, S.-M.: Characteristics of total mercury (TM) wet deposition: scavenging of atmospheric mercury species, Atmos. Environ., 49, 69-76, 2012.

Seo, Y.-S., Han, Y.-J., Holsen, T. M., Choi, E., Zoh, K.-D., and Yi, S.-M.: Source identification of total mercury (TM) wet deposition using a Lagrangian particle dispersion model (LPDM), Atmos. Environ., 104, 102-111, 2015.

St. Louis, V. L., Rudd, J. W., Kelly, C. A., Hall, B. D., Rolfhus, K. R., Scott, K. J., Lindberg, S. E., and Dong, W.: Importance of the forest canopy to fluxes of methyl mercury and total mercury to boreal ecosystems, Environ. Sci. Technol., 35, 3089-3098, 2001.

U.S.EPA: Persistent, bioaccumulative and toxic chemical program. http://www.epa.gov/pbt, 1997a.

U.S.EPA: U.S. EPA Lake Michigan Mass Balance Methods Compendium. http://nepis.epa.gov/, 1997b.

U.S.EPA: Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, 2002.

Wallschläger, D., Herbert Kock, H., Schroeder, W. H., Lindberg, S. E., Ebinghaus, R., and Wilken, R.-D.: Mechanism and significance of mercury volatilization from contaminated floodplains of the German river Elbe, Atmos. Environ., 34, 3745-3755, 2000.

Wang, S., Feng, X., Qiu, G., Wei, Z., and Xiao, T.: Mercury emission to atmosphere from Lanmuchang Hg–Tl mining area, southwestern Guizhou, China, Atmos. Environ., 39, 7459-7473, 2005.

Wang, Y., Peng, Y., Wang, D., and Zhang, C.: Wet deposition fluxes of total mercury and methylmercury in core urban areas, Chongqing, China, Atmos. Environ., 92, 87-96, 2014.

Yi, S.-M., Holsen, T. M., and Noll, K. E.: Comparison of dry deposition predicted from models and measured with a water surface sampler, Environ. Sci. Technol., 31, 272-278, 1996.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-7, 2016
Manuscript under review for journal Atmos. Chem. Phys.
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Zhang, L., Blanchard, P., Gay, D., Prestbo, E., Risch, M., Johnson, D., Narayan, J., Zsolway, R., Holsen, T., and Miller, E.: Estimation of speciated and total mercury dry deposition at monitoring locations in eastern and central North America, Atmospheric Chemistry and Physics, 12, 4327-4340, 2012.

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Table List

Figure List

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-7, 2016
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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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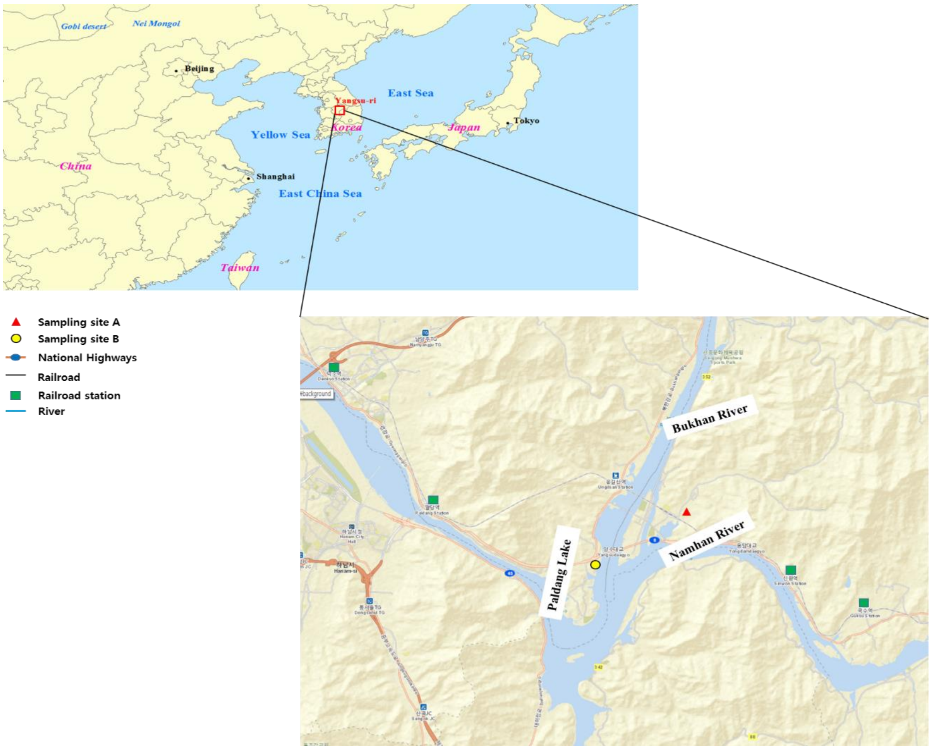

Fig. 1. The locations of the sampling sites used in this study (Yangsu-ri, Korea).

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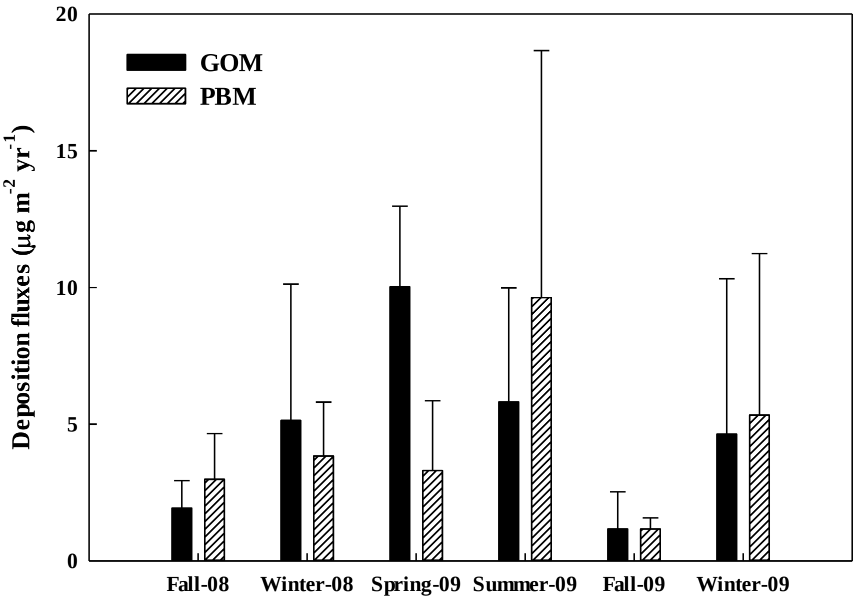

586
587 **Fig. 2. Seasonal variation in dry deposition flux for GOM and PBM under the**
588 **deciduous forest.**
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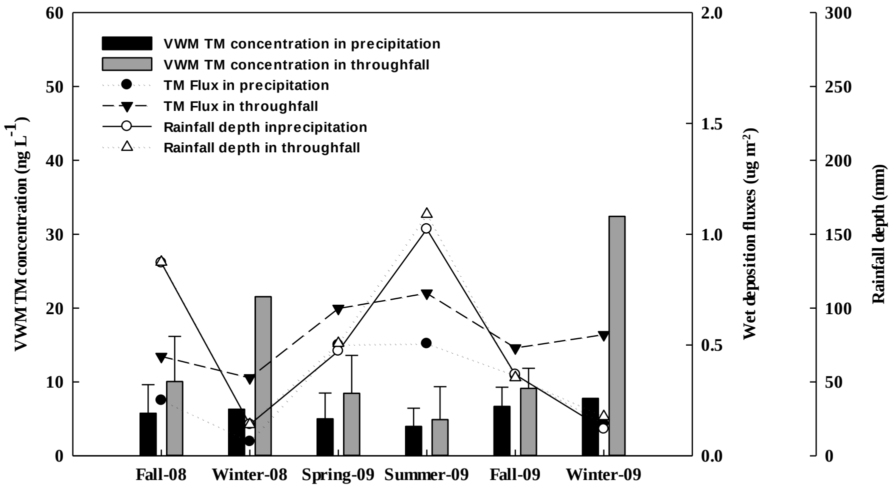

Fig. 3. Seasonal variation in VWM TM concentration, rainfall depth and TM flux in precipitation and throughfall.

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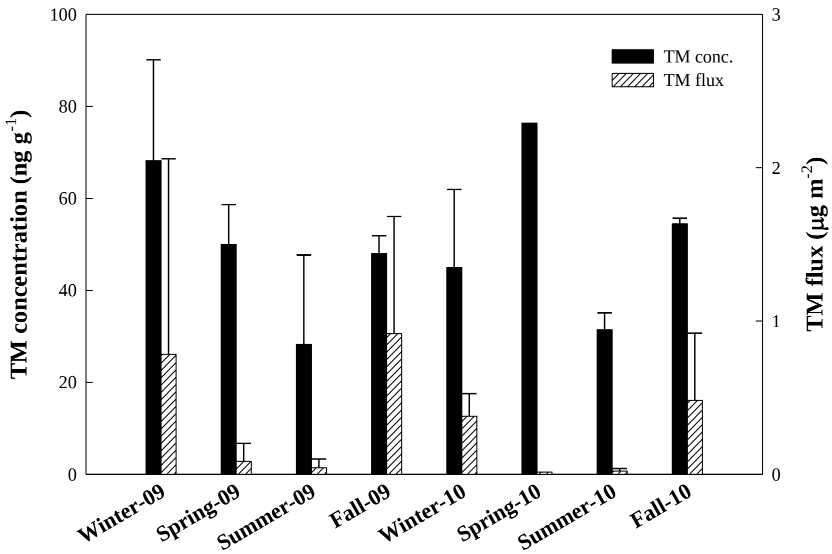

Fig. 4. Seasonal variation in TM concentration and flux in a deciduous.

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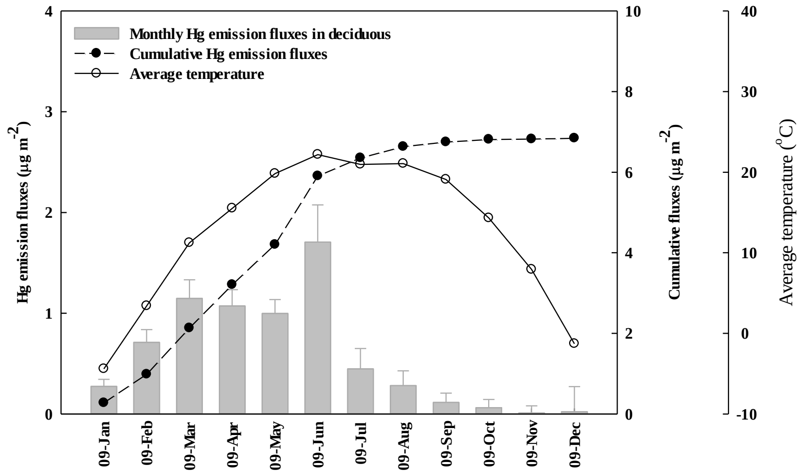

604
605
606 **Fig. 5. The estimated annual Hg emission fluxes in 2009 from soil.**
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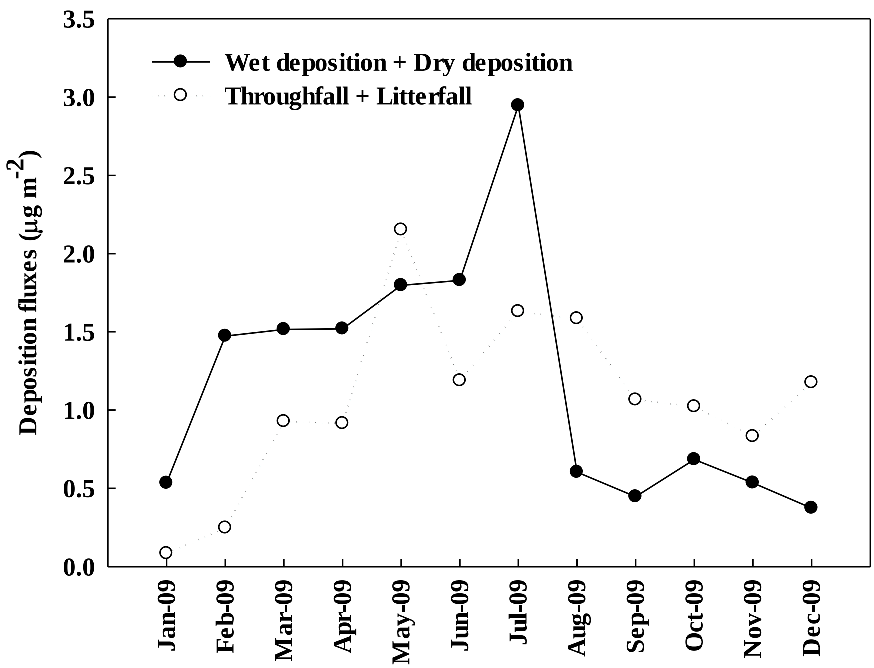

Fig. 6. Comparison of Deposition flux calculated by summing wet deposition + dry deposition and throughfall + litterfall