

1 **Total Atmospheric Mercury Deposition in Forested Areas in Korea**

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Abstract

34 In this study, mercury (Hg) was sampled weekly in dry and wet deposition and
35 throughfall and monthly in litterfall, and as it was volatilized from soil from August 2008 to
36 February 2010 to identify the factors influencing the amount of atmospheric Hg deposited to
37 forested areas in a temperate deciduous forest in Korea. For this location there was no
38 significant correlation between the estimated monthly dry deposition flux (litterfall +
39 throughfall – wet deposition) ($6.7 \mu\text{g m}^{-2} \text{yr}^{-1}$) and directly measured dry deposition ($9.9 \mu\text{g}$
40 $\text{m}^{-2} \text{yr}^{-1}$) likely due primarily to Hg losses from the litterfall collector. Dry deposition fluxes
41 in cold seasons (fall and winter) were lower than in warmer seasons (spring and summer).
42 The volume-weighted mean (VWM) Hg concentrations in both precipitation and throughfall
43 were highest in winter likely due to increased scavenging by snow events. Since Korea
44 experiences abundant rainfall in summer, VWM Hg concentrations in summer were lower
45 than in other seasons. Litterfall fluxes were highest in the late fall to early winter when leaves
46 were dropped from the trees (September to November). The cumulative annual Hg emission
47 flux from soil was $6.8 \mu\text{g m}^{-2} \text{yr}^{-1}$. Based on these data, the yearly deposition fluxes of Hg
48 calculated using two input approaches (wet deposition + dry deposition or throughfall +
49 litterfall) were 6.8 and $3.6 \mu\text{g m}^{-2} \text{yr}^{-1}$ respectively. This is the first reported study which
50 measured the amount of atmospheric Hg deposited to forested areas in Korea and thus our
51 results provide useful information to compare against data related to Hg fate and transport in
52 this part of the world.

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54

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

57

58 1. Introduction

59 Mercury (Hg) is a highly toxic pollutant and a threat to human health and ecosystems
60 due to its ability to bioaccumulate and biomagnify through the food chain after it is
61 methylated (Lindqvist et al., 1991; Schroeder and Munthe, 1998). It is classified as a
62 persistent bioaccumulative and toxic (PBT) chemical (U.S.EPA, 1997a). Atmospheric Hg
63 exists in three different forms with different chemical and physical properties; gaseous
64 elemental mercury (GEM, Hg^0), gaseous oxidized mercury (GOM, Hg^{2+}), and particulate
65 bound mercury (PBM, Hg_p). GEM is the major form of Hg in the atmosphere and is relatively
66 water insoluble and very stable with a long residence time of 0.5 - 2 years (Carpi and
67 Lindberg, 1997; Cohen et al., 2004; Schroeder and Munthe, 1998; Zhu et al., 2014). GOM is
68 water soluble, with relatively strong adhesion properties (Han et al., 2005) and can be
69 scavenged by rain within precipitating and below clouds (Blackwell and Driscoll, 2015; Lin
70 and Pehkonen, 1999). The dry deposition velocity is similar to HNO_3 ($1\sim 5 \text{ cm sec}^{-1}$) if it is
71 assumed that all GOM is in the form of HgCl_2 (Petersen et al., 1995). PBM is formed by
72 GEM or GOM adsorbing to a particle (Lai et al., 2011). Atmospheric PBM transport is
73 significantly affected by its particle size distribution and may contribute to both wet and dry
74 deposition (Lynam and Keeler, 2002).

75 Wet and dry deposition of atmospheric Hg is an important input to the aquatic and
76 terrestrial ecosystems (Buehler and Hites, 2002; Fitzgerald et al., 1998; Landis and Keeler,
77 2002; Lindberg et al., 1998; Miller et al., 2005; Rolfhus et al., 2003; Selvendiran et al., 2008;
78 Shanley et al., 2015). Hg deposited from the atmosphere can be transformed to methyl
79 mercury (MeHg) which bio-accumulates in aquatic food chains, resulting in adverse health
80 and ecological effects (Ma et al., 2013; Lindberg et al., 2007; Rolfhus et al., 2003; Selin et al.,
81 2007; Weiss-Penzias et al., 2016; Zhu et al., 2014). Atmospheric Hg deposition to forests
82 includes direct dry deposition, throughfall, and litterfall. Dry deposition to leaves
83 compromises a large proportion of litterfall (Grigal, 2002; St. Louis et al., 2001). Previous
84 investigations (Fu et al., 2009) estimated dry deposition to forested areas as litterfall +
85 throughfall – wet deposition. However, there are many variables that can adversely influence
86 this technique including reemitted Hg from beneath the canopy and sampling artifacts.
87 Directly measuring dry deposition with a surrogate surface is an alternative approach,
88 although there is no universally accepted method on how to make these measurements.

89 Hg deposited onto plant surfaces can be volatilized, incorporated into tissue or
90 washed off by precipitation (which is deemed throughfall) which often results in throughfall
91 having higher Hg concentrations than precipitation (Iverfeldt, 1991; Kolka et al., 1999;
92 Munthe et al., 1995; Choi et al., 2008; Grigal et al., 2000; Schwesig and Matzner, 2000).
93 Litterfall is dead plant material such as leaves, bark, needles and twigs that has fallen to the
94 ground. Litterfall carries new Hg inputs from the atmosphere to the forest floor and also Hg
95 recycled from volatilization from soils and other surfaces. Throughfall and litterfall
96 contribute to the biochemical recycling of atmospheric Hg in forest systems (St. Louis et al.,
97 2001) and are important Hg inputs that result in Hg accumulation in forest systems
98 (Blackwell and Driscoll, 2015).

99 The deposition of Hg in the forest ecosystem is complicated because of complex
100 interactions between atmospheric Hg and the canopy, including oxidation of Hg on leaf
101 surfaces (Blackwell and Driscoll, 2015; Iverfeldt, 1991), deposition of GOM and PBM on
102 leaf surfaces (Blackwell and Driscoll, 2015; Blackwell et al., 2014; St. Louis et al., 2001),
103 stomatal uptake of atmospheric GEM (Fu et al., 2010; Iverfeldt, 1991; Lindberg et al., 1991;
104 St. Louis et al., 2001), root uptake of dissolved Hg in soil and soil water and stomatal uptake
105 of GEM that was volatilized from soils (Bishop et al., 1998; Cocking et al., 1995; Ma et al.,
106 2015; St. Louis et al., 2001). Also, the Hg in forest canopies can be emitted and reemitted
107 from beneath the canopy (Risch et al., 2012). The Hg mass in litterfall have originated from a
108 large portion of dry deposition (Risch et al., 2012; St. Louis et al., 2001).

109 To date there have been few studies (Blackwell et al., 2014; Choi et al., 2008; Rea et
110 al., 2001) that have estimated atmospheric Hg deposition to forested areas and none in Korea.
111 Fully characterizing Hg deposition in forested areas is important for estimating
112 environmental risks associated with Hg. Thus, the objectives of this study were to
113 characterize total atmospheric Hg deposition in a temperate deciduous forested area in Korea
114 by measuring Hg dry deposition, wet deposition, throughfall, litterfall and volatilization from
115 soils and comparing directly measured and estimated dry deposition. Based on the collected
116 data the annual Hg flux was estimated using two approaches to determine inputs (wet
117 deposition + dry deposition, throughfall + litterfall) minus volatilization from soil.

118

119 **2. Materials and methods**

120

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 km² (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 km² (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

153 measure GOM + PBM deposition. The quartz filter and KCl-coated quartz filter (soaked in
154 KCl solution for 12h and dried on clean bench) were pre-baked in a quartz container at 900
155 °C for PBM and 525 °C for GOM + PBM. Before weekly sampling, the filters were placed on
156 a filter holder base and held in place with a retaining ring and then were placed on the KSS.
157 Filter exposed to the atmosphere from approximately one week and two side-by-side samples
158 were deployed during each dry day.

159

160 2.2.2. TM in wet deposition and throughfall

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

165

166 2.2.3. TM in soil and litterfall

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

170 Litterfall samples was collected every month from December 2008 to November
171 2010, except January 2010. Ten nylon-mesh-lined baskets (1.09 m² each) were acid cleaned
172 and randomly placed under the canopy. All litter and soil samples were freeze-dried, sorted
173 by tree species, weighed, and then homogenized by crushing manually prior to analysis.

174

175 2.2.4. Volatilization from soils

176 The gaseous mercury emission flux from soil was measured using a dynamic flux
177 chamber (DFC) connected to the Tekran 2537A (Tekran Inc., Toronto, Canada) and Tekran
178 1110 dual sampling unit (allows alternate sampling from inlet and outlet) (Choi and Holsen,
179 2009b) under the deciduous forest area once a month. Daily automated calibrations were
180 performed for the Tekran 2537A using an internal permeation source. Manual injections were
181 used to evaluate these calibrations using a saturated mercury vapor standard. The flowrate
182 was approximately 5 L min⁻¹. Four 1 cm diameter inlet holes were evenly placed around the
183 chamber ensuring it was well mixed. The bottom 2 cm of DFCs (3.78L) were covered by soil.

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

186

187 **2.3. Analytical methods**

188

189 2.3.1. Dry deposition for GOM and PBM

190 The dry deposition samples for GOM and PBM samples were analyzed using a tube
191 furnace connected to a Tekran 2537. The tube furnace was pre-heated (GOM: 525 °C, PBM:
192 900 °C) and zero air passed through until the Hg concentration was zero (Kim et al., 2009;
193 Kim et al., 2012). After samples were placed inside the tube furnace, the tube furnace was
194 purged with zero air until Hg level was again zero. The mass of Hg desorbed from the sample
195 was determined using the product of concentration and flowrate (5 L min⁻¹). The system
196 recovery was measured by injecting mercury vapor standards (0, 10, 20, 30, 50 µL) manually.
197 It was assumed that GOM deposition was equal to the flux measured by the KCl-coated
198 quartz filter minus the flux measured by the quartz filter. However, recent studies (Lyman et
199 al., 2010) reported potential sampling artifacts in the presence of O₃.

200

201 2.3.2. TM in wet deposition and throughfall

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

206

207 2.3.3. TM in soil and litterfall

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

212

213 **2.4. QA/QC**

214 2.4.1 Dry deposition for GOM and PBM

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

221

222 2.4.2. TM in wet deposition and throughfall

223 Quality assurance and quality control were based on the U.S. EPA Methods 1631
224 version E (U.S.EPA, 2002) and LMMBMC (U.S.EPA, 1997b). The MDL (three times the
225 standard deviation of seven sequential reagent blanks) for TM in wet deposition and
226 throughfall was 0.05 ng L^{-1} . The standard curve was acceptable when r^2 was greater than
227 0.9995 (linear). More additional information is described SI.

228

229 2.4.3. TM in litterfall and soil

230 TM in litterfall and soil was reported on a dry-weight basis. Recovery (%) of
231 standard reference materials (SRMs) (MESS3, marine sediment) purchased from the National
232 Research Council of Canada and analyzed every 10 samples at the start of experiments was
233 $104 \pm 4\%$.

234

235 2.4.4. Volatilization from soil

236 The DFC was connected to the Tekran 2537A through Tekran 1110 sampling unit.
237 Ten μL of vapor phase Hg was injected into the DFC ($n = 10$) before deployment in the field.
238 Recovery was $86 \sim 110\%$ and averaged 101% at a flow rate of 5 L min^{-1} . Before flux
239 chamber measurements automated calibration was performed using the internal permeation
240 source connected to the Tekran 2537A and Tekran 1110 dual sampling unit. External
241 calibration and MDLs for this instrument are described above.

242

243

244 3. Results and Discussion

245

246 3.1. Monthly and seasonal variations in dry deposition fluxes of GOM and PBM

247 Weekly samples were collected using quartz filters (PBM) and KCl coated quartz
 248 filters (GOM). The average dry deposition fluxes for GOM (Table S1) and PBM (Table S2)
 249 were $5.4 \mu\text{g m}^{-2} \text{yr}^{-1}$ (range: $0.4 \sim 14.4 \mu\text{g m}^{-2} \text{yr}^{-1}$) and $4.3 \mu\text{g m}^{-2} \text{yr}^{-1}$ (range: $0.8 \sim 19.4 \mu\text{g}$
 250 $\text{m}^{-2} \text{yr}^{-1}$), respectively. The dry deposition fluxes for GOM were highest in spring 2009 (10.0
 251 $\pm 2.0 \mu\text{g m}^{-2} \text{yr}^{-1}$), lowest in fall 2009 ($1.2 \pm 1.4 \mu\text{g m}^{-2} \text{yr}^{-1}$) while the dry deposition fluxes
 252 for PBM were highest in summer 2009 ($9.6 \pm 9.0 \mu\text{g m}^{-2} \text{yr}^{-1}$), lowest in fall 2009 (1.2 ± 0.4
 253 $\mu\text{g m}^{-2} \text{yr}^{-1}$) (Fig. 2). Nonparametric Mann-Whitney U tests indicated that there were
 254 statistically significant differences in the dry deposition fluxes for GOM between spring 2009,
 255 fall 2008, and fall 2009 ($p < 0.05$) and there were statistically significant differences in the
 256 dry deposition flux for PBM between summer 2009 and fall 2009 ($p < 0.05$).

257 Zhang et al. (2012) reported that in eastern and central North America the GEM
 258 concentration in the colder seasons were generally higher than in warmer seasons. However,
 259 the dry deposition fluxes for GOM and PBM in spring and summer (warmer seasons) were
 260 higher than in the fall and winter (cold seasons) following the same pattern as average GEM
 261 concentrations (summer 2009: $2.7 \pm 0.9 \text{ ng m}^{-3}$, spring 2009: $2.4 \pm 0.6 \text{ ng m}^{-3}$, fall 2009: 2.3
 262 $\pm 0.7 \text{ ng m}^{-3}$, winter 2008: $1.2 \pm 0.2 \text{ ng m}^{-3}$) in Han River Environment Research Center
 263 (located approximately 2 km away).

264
 265

266 **3.2. Monthly and seasonal variations of TM wet deposition and throughfall flux**

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

273 The high VWM Hg concentrations in precipitation and throughfall in winter were
 274 likely associated with the combined effects of reduced mixing heights (Blanchard et al.,
 275 2002) which increases atmospheric concentrations (Kim et al., 2009; Seo et al., 2015), low
 276 rainfall depth (11.7% of total rainfall depth) which is a typical pattern in Yangpyung, Korea
 277 (KMA,
 278 http://www.kma.go.kr/weather/climate/average_30years.jsp?yy_st&tnqh_x003D;2011&

279 stn&tnqh_x003D;108&norm&tnqh_x003D;M&obs&tnqh_x003D;0&mm&tn
280 qh_x003D;5&dd&tnqh_x003D;25&x&tnqh_x003D;25&y&tnqh_x003D;5
281 (accessed May 5, 2016) and the inclusion of snow events since scavenging by snow is more
282 efficient than by rain due to the larger surface area of snow (snow: 700 cm²/g, rain: 60 cm²/g)
283 (Kerbrat et al., 2008). While, Sigler et al. (2009) reported that GOM is scavenged less
284 efficiently during snow events.

285 Previous studies reported that rainfall depth in forested areas were approximately
286 8~24% smaller than that in an open area (Choi et al., 2008; Deguchi et al., 2006; Keim et al.,
287 2005; Price and Carlyle-Moses, 2003) due to capture by the foliage and subsequent
288 evaporation. In this study, rainfall depth in the forest was approximately 8% smaller than that
289 in the open area. Regression analysis revealed that the TM concentration in throughfall was
290 higher than in precipitation (statistically significant differences ($r^2 = 0.20$) ($p < 0.05$)) due to
291 wash off of previously deposited Hg from the foliage (Grigal et al., 2000; Iverfeldt, 1991;
292 Kolka et al., 1999; Schwesig and Matzner, 2000) and oxidation of Hg⁰ to Hg²⁺ on the wet
293 foliage surface by ozone and subsequent wash off (Graydon et al., 2008). Other possible
294 sources of Hg in throughfall are leaching and biogeochemical recycling of Hg from foliage
295 (St. Louis et al., 2001). Some of the deposited Hg can be washed off by rainfall and reemitted
296 as GEM to the atmosphere (Jiskra et al., 2015; Rea et al., 2001). Therefore, all of the Hg
297 deposited on the foliar surfaces is not in the throughfall. Throughfall also incorporates GOM
298 and PBM that is adsorbed from the atmosphere by leaves since GOM is soluble and it is
299 likely readily washed off during rain events (Blackwell and Driscoll, 2015).

300

301

302 **3.3 Relationship between rainfall depth, VWM TM concentration, TM wet deposition** 303 **and throughfall flux**

304

305 There was a statistically significant negative correlation between rainfall depth and
306 VWM TM concentrations in precipitation ($r^2 = 0.13$) ($p < 0.05$) (Fig. S1) and throughfall ($r^2 =$
307 0.19) ($p < 0.05$) (Fig. S2) due to dilution during the later stage of a precipitation event. This
308 negative correlation has also been found in previous studies (Guo et al., 2008; Landis and
309 Keeler, 2002; Seo et al., 2012; Seo et al., 2015; Wallschläger et al., 2000). About 19% of
310 throughfall and 13% of precipitation variation in VWM concentration are explained by

311 precipitation depth. The rest of the variation is likely due to meteorological parameters that
312 differ between events (Gratz et al., 2009), for example temperature (Table S3) and
313 precipitation type (Rain, Snow, Mixed) and variations in ambient Hg speciation and PBM
314 particle size distributions due to differing impacts of local and regional sources (Blackwell
315 and Driscoll, 2015). There was a statistically significant positive correlation between rainfall
316 depth and TM deposition flux in precipitation ($r^2 = 0.34$) ($p < 0.05$), similar to what was
317 found in previous studies (Choi et al., 2008; Gratz et al., 2009; Shanley et al., 2015; Wang et
318 al., 2014), suggesting that the TM deposition flux increased during large events even though
319 continuous rain diluted the TM mass. However, a large rainfall depth does not affect wet
320 deposition fluxes significantly if GOM and PBM concentrations are low (Zhang et al., 2012).

321

322

323 **3.4. Leaf-on vs. Leaf-off**

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

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

339

340

341 **3.5. TM in litterfall and soil**

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

353 Soil samples were collected from the near-surface A-horizon following the removal
354 of any rock fragments and the B-horizon. The mean soil TM concentrations were higher
355 within the A-horizon ($66.9 \pm 20.3 \text{ ng g}^{-1}$) than within the B-horizon ($46.1 \pm 17.5 \text{ ng g}^{-1}$). TM
356 concentration in soil collected in this study was similar to TM concentration found in soil
357 collected from uncontaminated baseline sites which ranged from 30 to 50 ng g^{-1} (Gray et al.,
358 2015).

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360

361 **3.6. Volatilization from soils**

362 Hg emission fluxes were estimated from directly measured soil volatilization of
363 gaseous elemental mercury (GEM) using a dynamic flux chamber (DFC). The measured
364 fluxes were the highest in June and the lowest in November. Emission fluxes were positively
365 correlated with ambient air temperature however, they were not influenced by precipitation.
366 For example, the ambient air temperature was higher in summer than other seasons, but were
367 not higher in July, a period of several severe rain storms nor were they lower in August which
368 had very little rain. This result may be because the relative humidity was high enough that the
369 soil remained moist. This result is similar to previous studies that found that Hg emission
370 fluxes were positively correlated with soil surface temperature and negatively correlated with
371 humidity (Choi and Holsen, 2009b; Gabriel et al., 2006; Wallschläger et al., 2000; Wang et al.,
372 2005). Hg emission fluxes during leaf-on periods (March to November) ($0.65 \pm 2.25 \text{ ng m}^{-2}$
373 hr^{-1} , 16.9 °C) were higher than leaf-off periods (December) ($0.02 \pm 2.13 \text{ ng m}^{-2} \text{ hr}^{-1}$, -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 $6.8 \mu\text{g m}^{-2} \text{yr}^{-1}$ (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 $4.8 \mu\text{g m}^{-2} \text{y}^{-1}$ 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 ($6.7 \mu\text{g m}^{-2} \text{yr}^{-1}$)
386 was lower than measured dry deposition ($9.9 \mu\text{g m}^{-2} \text{yr}^{-1}$) 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 ($14.2 \mu\text{g m}^{-2} \text{yr}^{-1}$) was higher than the input flux calculated by summing
398 throughfall + litterfall ($11.0 \mu\text{g m}^{-2} \text{yr}^{-1}$) (Fig. 6). This difference is likely, at least in part, due
399 to the fact that no Hg is reemitted from wet and dry deposition as happens for litterfall.
400 Nonparametric Mann-Whitney U tests indicated that there were not statistically significant
401 differences ($r^2 = 0.14$) ($p = 0.98$). In general, wet + dry deposition was larger than throughfall
402 plus litterfall except during fall when leaves were being actively dropped from the trees. The
403 largest difference was in July during a period of significant precipitation (about 26.3 % of the
404 total amount in 2009). This difference is most likely due to the many reactions and

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

407

408

409 **3.8. Mercury budget**

410 The yearly estimated budget of Hg in this study site was calculated using both input
411 approaches (Total input = wet deposition + dry deposition or Total input = throughfall +
412 litterfall) as follows. 1) Input to the forest canopy (wet deposition in an open area: $4.3 \mu\text{g m}^{-2}$
413 yr^{-1} plus dry deposition in the forested area: $9.9 \mu\text{g m}^{-2} \text{yr}^{-1}$) minus output (emissions from
414 soil $6.8 \mu\text{g m}^{-2} \text{yr}^{-1}$ plus accumulation in the soil $0.6 \mu\text{g m}^{-2} \text{yr}^{-1}$) resulting in a net flux of 6.8
415 $\mu\text{g m}^{-2} \text{yr}^{-1}$. 2) The alternative method yields input (throughfall: $6.4 \mu\text{g m}^{-2} \text{yr}^{-1}$ plus litterfall:
416 $4.6 \mu\text{g m}^{-2} \text{yr}^{-1}$) minus output (emissions from soil: $6.8 \mu\text{g m}^{-2} \text{yr}^{-1}$ plus accumulation in the
417 soil: $0.6 \mu\text{g m}^{-2} \text{yr}^{-1}$) resulting in a net flux of $3.6 \mu\text{g m}^{-2} \text{yr}^{-1}$. For comparison at the
418 Lehstenbach catchment in Germany, the estimated net fluxes were similar: $6.8 \mu\text{g m}^{-2} \text{yr}^{-1}$
419 (Schwesig and Matzner, 2000) and in the Experimental Lakes Area (ELA) watersheds in
420 Canada, the flux was $3 \sim 4 \mu\text{g m}^{-2} \text{yr}^{-1}$ (St. Louis et al., 2001). However, for the Lake
421 Langtjern spruce forest in southeast Norway ($20.1 \mu\text{g m}^{-2} \text{yr}^{-1}$) (Larssen et al., 2008) and
422 Huntington Wildlife forest ($15.9 \mu\text{g m}^{-2} \text{yr}^{-1}$ in deciduous, $26.8 \mu\text{g m}^{-2} \text{yr}^{-1}$ in conifer)
423 (Blackwell et al., 2014), the estimated fluxes were higher than in this study.

424

425 **4. Conclusions**

426 Hg in dry and wet deposition, throughfall and litterfall and Hg volatilization from
427 soil were measured from August 2008 to February 2010 to identify the factors influencing the
428 amount of atmospheric Hg deposited to forested areas in a temperate deciduous forest in
429 Korea. In addition measured and theoretical dry deposition were compared. The GOM fluxes
430 were low in fall and increased towards the spring. PBM fluxes were lowest in fall and peaked
431 in summer. The estimated and directly measured deposition fluxes were not significantly
432 correlated likely due to loss of litter samples by wind or wash-off by rainfall and the fact that
433 accumulation in leaf stomata was not characterized in the direct dry deposition measurement
434 technique. The average VWM Hg concentration in throughfall was approximately 2.4 times
435 higher than in precipitation due to wash off of previously deposited Hg from the foliage. Both

436 were higher in winter due to increased concentrations in snow events relative to rain events
437 likely due to enhanced scavenging of GOM and PBM. TM in litterfall fluxes were highest in
438 fall when the leaves were dropped and lowest in summer from June to August. Hg emission
439 fluxes from soil resulted in a cumulative annual volatilization of $6.8 \mu\text{g m}^{-2} \text{yr}^{-1}$ of GEM.

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

455
456

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462

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464 **References**

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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.

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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

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688

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

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

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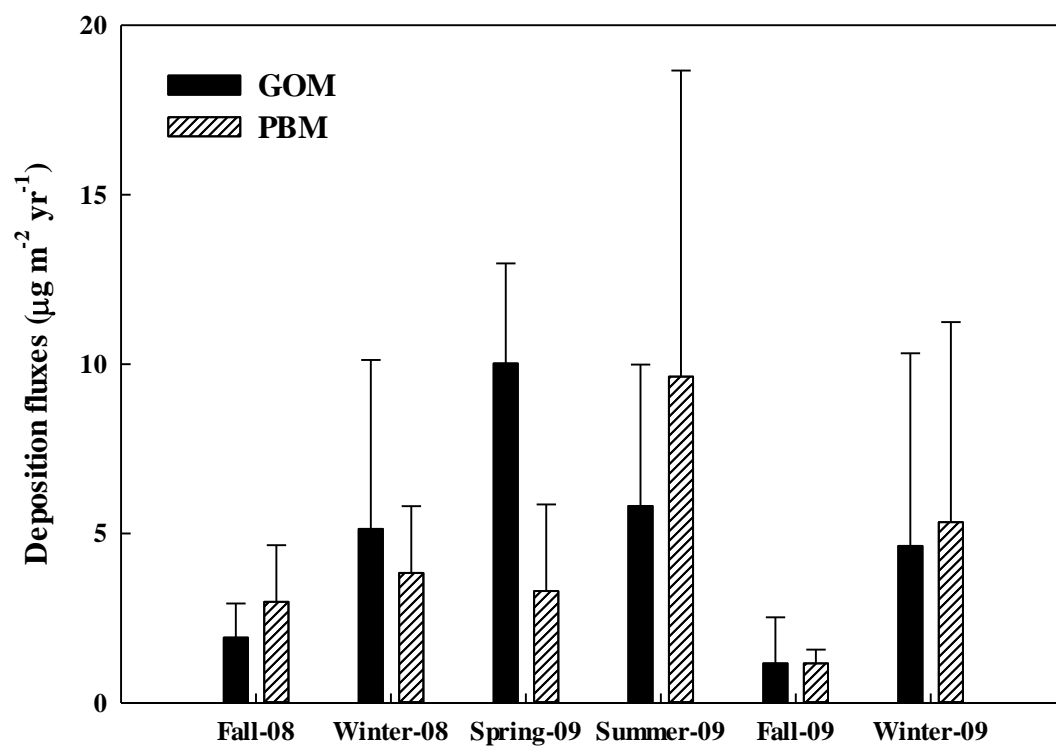


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695 **Fig. 1. The locations of the sampling sites used in this study (Yangsu-ri, Korea).**

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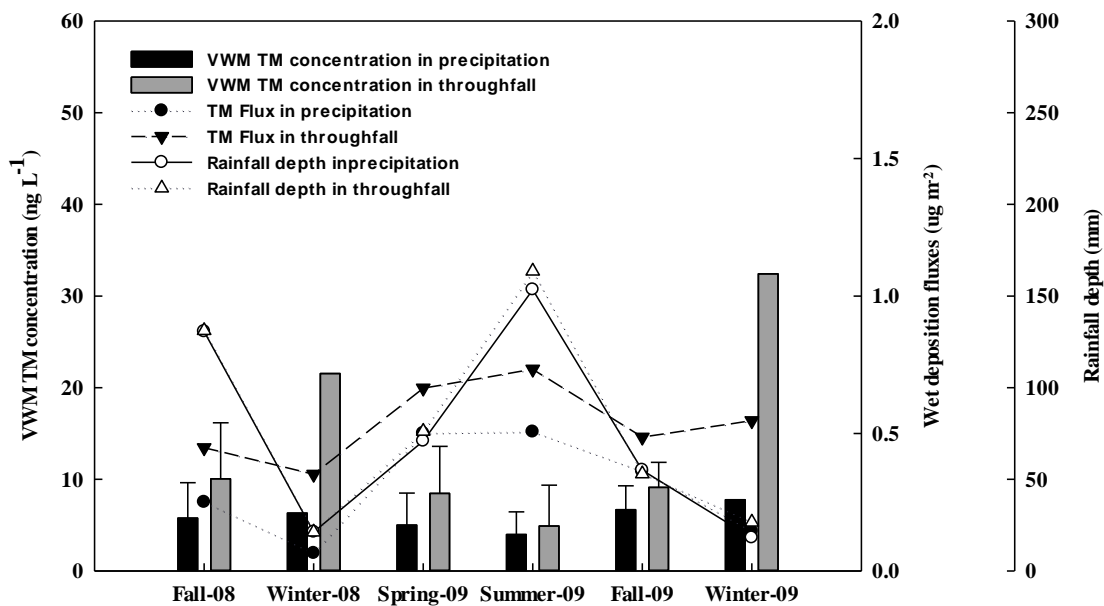


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699 **Fig. 2. Seasonal variation in dry deposition flux for GOM and PBM under the**
700 **deciduous forest.**

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

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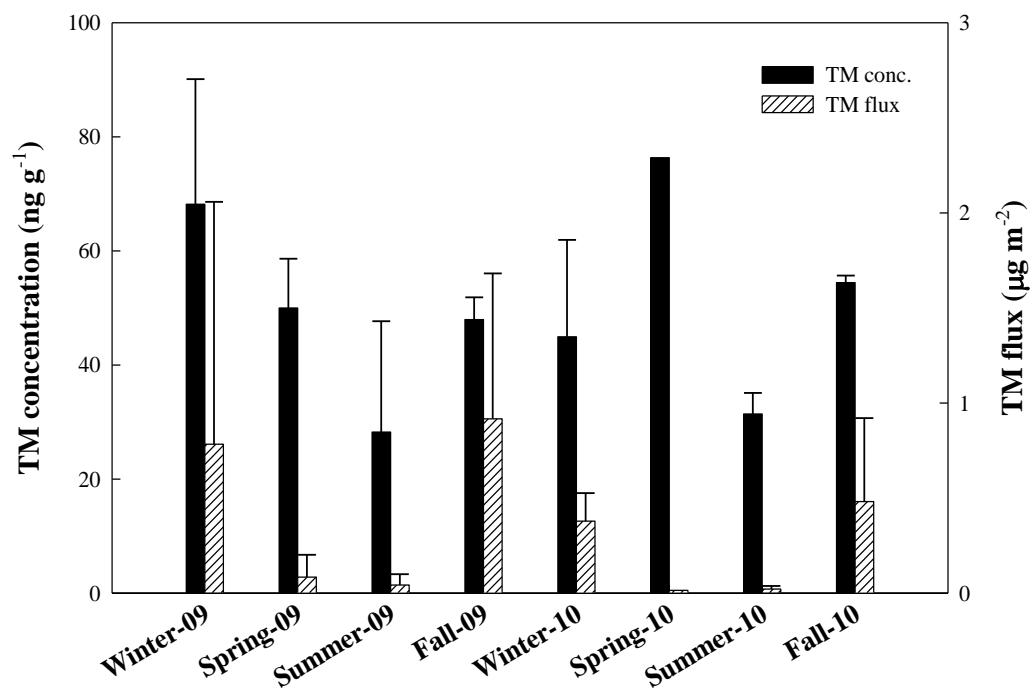


Fig. 4. Seasonal variation in TM concentration and flux in a deciduous.

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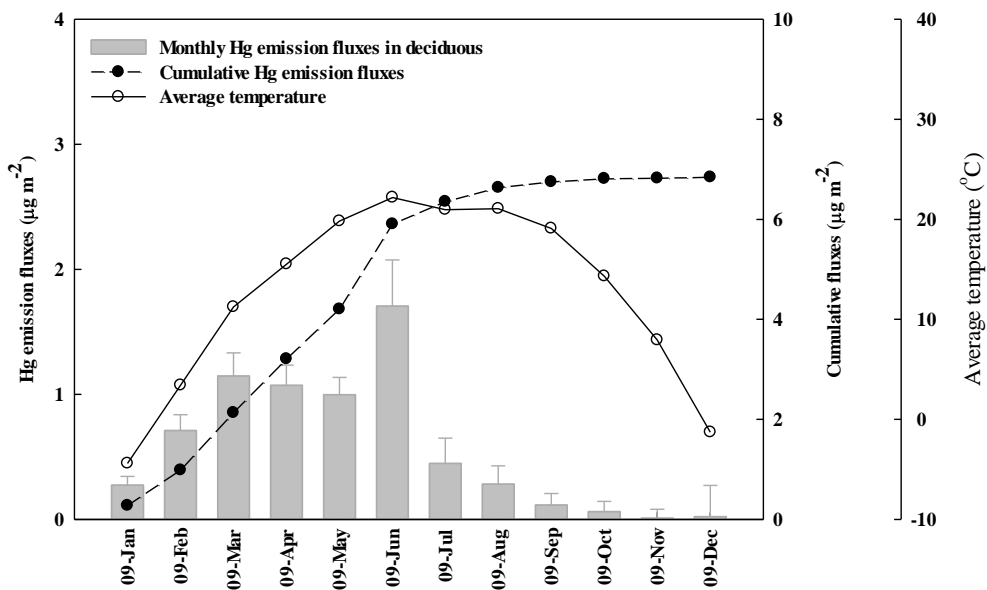
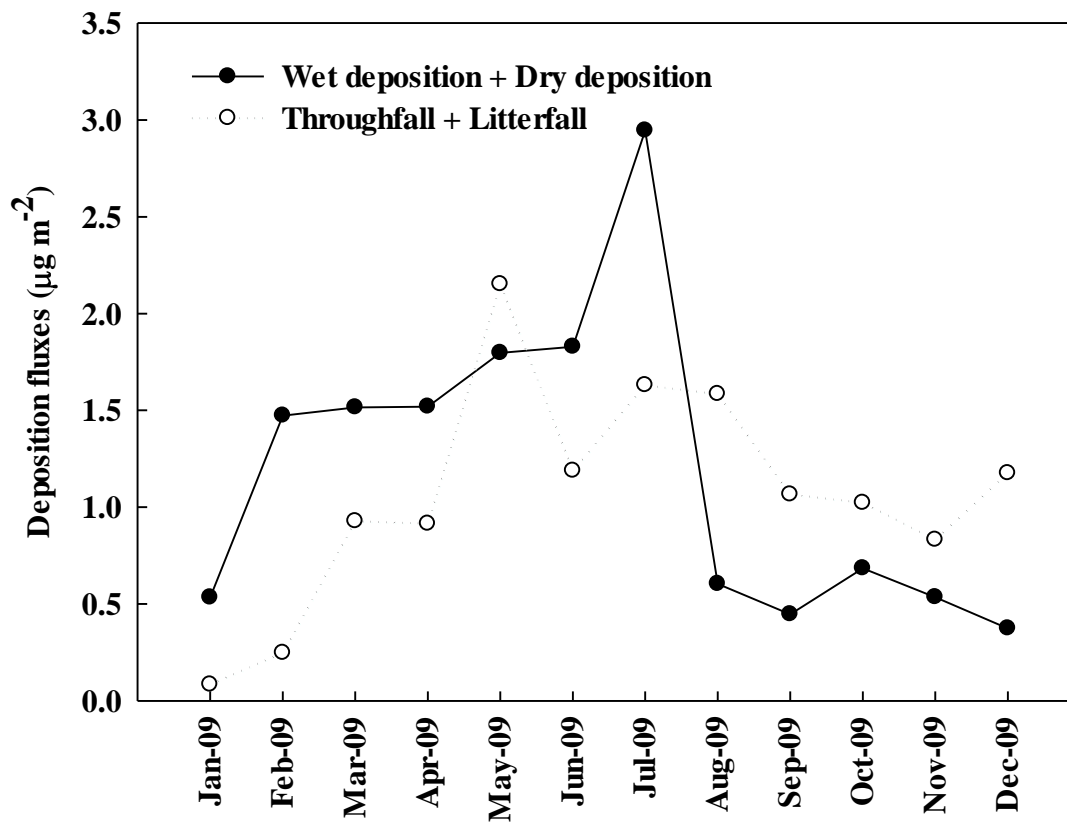


Fig. 5. The estimated annual Hg emission fluxes in 2009 from soil.

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