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Overview of mercury dry deposition, litterfall, and throughfall studies

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Abstract. The current knowledge concerning mercury dry deposition is reviewed, including dry deposition algorithms used in chemical transport models (CTMs) and at monitoring sites and related deposition calculations, measurement methods and studies for quantifying dry deposition of gaseous oxidized mercury (GOM) and particulate bound mercury (PBM), and measurement studies of litterfall and throughfall mercury. Measured median GOM plus PBM dry deposition in Asia (10.7 μg m^{-2} yr^{-1}) almost double that in North America (6.1 μg m^{-2} yr^{-1}) due to the higher anthropogenic emissions in Asia. Measured median litterfall and throughfall mercury are 22.3 and 56.5 μg m^{-2} yr^{-1}, respectively, in Asia, 12.8 and 16.3 μg m^{-2} yr^{-1} in Europe, and 11.9 and 7.0 μg m^{-2} yr^{-1} in North America. The much higher litterfall mercury than GOM plus PBM dry deposition suggests the important contribution of gaseous elemental mercy (GEM) to mercury dry deposition to vegetated canopies. Over all the regions, including the Amazon, dry deposition, estimated as the sum of litterfall and throughfall minus open-field wet deposition, is more dominant than wet deposition for Hg deposition. Regardless of the measurement or modelling method used, a factor of two or larger uncertainties in GOM plus PBM dry deposition need to be kept in mind when using these numbers for mercury impact studies.

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1. Introduction

Atmospheric mercury (Hg) exists in three operationally defined forms - gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate bound mercury (PBM). Quantification of atmospheric deposition of the three forms of Hg to various underlying surfaces is needed to assess Hg effects on sensitive ecosystems and subsequent human health impact. Wet deposition of Hg can be quantified through analysis of precipitation chemistry (Prestbo and Gay, 2009). While the direct measurement of Hg dry deposition is technically challenging, a number of methods have been developed for approximate Hg dry deposition, such as micrometeorological, surrogate surface, litterfall, and throughfall measurements (Cobbett and Van Heyst, 2007; Marsik et al., 2007; Graydon et al., 2008; Huang and Gustin, 2015; Risch et al., 2012; Ma et al., 2016).

The approaches used by the above methods to measure mercury dry deposition vary considerably. Efforts are now underway to obtain a better understanding of the variability of estimates from these methods, in an effort to provide a constraint of measurement uncertainties (Marsik et al., 2009; Gustin et al., 2015). The relationships between some of these methods were briefly discussed in Zhang et al. (2012b) and are further illustrated below. Mercury dry deposited to a forest canopy-soil system includes absorption of Hg by leaf stomata and cuticle, tree bark, and underlying soil. Some of the deposited Hg may emit back into the atmosphere. Mercury in litterfall includes a portion of the dry deposited Hg as well as capture of Hg emitted from the soil. Mercury in throughfall includes wet deposited Hg above the canopy and a portion of dry deposited Hg washed off from the canopy. Thus, litterfall Hg likely represents the low-end of Hg dry deposition if Hg emission from the underlying soil is small, although it can be higher than

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the actual dry deposition above the canopy due to the interception of emitted Hg by forest leaves if soil Hg emissions are high and the ambient Hg concentrations above the forests are low. The difference between throughfall and open-area wet deposition, with the former collected inside and the latter outside a forest, should also represent a portion of the dry deposition. Thus, on annual basis, dry deposition can be approximated as the sum of litterfall and througfall Hg minus wet deposited Hg.

In chemical transport models (CTMs) and at monitoring sites, Hg dry deposition is commonly calculated using the inferential method, where it is the product of the dry deposition velocity and the atmospheric Hg concentration (Fulkerson, 2006; Lyman et al., 2007; Marsik et al., 2007; Engle et al., 2010; Huang et al., 2012; Zhang et al., 2012b), or using the bi-directional exchange scheme for GEM (Xu et al., 1999; Bash, 2010; Wang et al., 2014; Wright and Zhang, 2015). Development and validation of these schemes need field-measured Hg dry deposition data, which unfortunately have larger uncertainties. The magnitudes of uncertainties are expected to be similar between measurement and model estimates (Zhang et al., 2009; Fang et al., 2012b).

The present study provides a detailed review of current knowledge concerning Hg dry deposition including numerical schemes used in CTMs and at monitoring sites, available field measurements on Hg dry deposition, and litterfall and throughfall Hg measurements. Knowledge gained from this study provides guidance for future research directions.

2. Dry deposition algorithms and estimation

2.1 In chemical transport models

There are several global and regional chemical transport models from Canada, the United States, Europe, Russia, and Asia that include algorithms for the dry deposition of mercury. A

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summary of the various models and their algorithms is provided in Table S1. In chemical transport models, the approach for the calculation of the dry deposition velocities of GEM, GOM, and PBM varies between models. For example, in GRAHM (Dastoor et al., 2015), GEOS-Chem (Song et al., 2015), ECHMERIT (De Simone et al., 2014), and GNAQPMS-Hg (Chen et al., 2015), the dry deposition velocity for GEM is calculated using the multiple resistance analogy approach described in Wesely (1989), Zhang et al. (2003) or Kerkweg et al. (2006). Due to uncertainties presented in Zhang et al. (2009), ECHMERIT sets a maximum allowed V_d for GEM of 0.03 cm s^{-1} equal to the annual mean GEM deposition velocity from Selin et al. (2008). Assumed values of 0.01 cm s^{-1} over land and 0 cm s^{-1} over the ocean for the dry deposition velocity of GEM have been implemented in CTM-Hg (Seigneur et al., 2004). In the case of many regional models, GEM is still not considered in the simulations under the assumption that the dry deposition of GEM is not important considering it is also emitted from the surface, for example WRF/Chem-Hg (Gencarelli et al., 2015), TEAM (Seigneur et al., 2006), REMSAD (Bullock et al., 2008), and CAMx (De Foy et al., 2014). CMAQ has implemented the bi-directional scheme of Bash (2010) for its treatment of GEM (Bash et al., 2014).

A similar resistance analogy for GEM is used to calculate GOM, for example in GRAHM, GEOS-Chem, and many regional models. In other models, such as WRF/Chem-Hg and CTM-Hg, the dry deposition velocity of GOM is assumed equal to HNO_3 due to their similar solubilities. A number of modelling studies have calculated the dry deposition velocity of PBM using the size-segregated particle dry deposition model described in Zhang et al. (2001b) or an earlier dry deposition and gravitational approach by Slinn and Slinn (1980), including Han et al. (2008); Zhang et al. (2012a); De Simone et al. (2014); and Dastoor et al. (2015). Two other

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approaches are to set the deposition velocity equal to the deposition velocity of the relatively non-reactive sulphate (Bullock and Brehme, 2002; Christensen et al., 2004; Chen et al., 2015) or to assume specific values over land (0.1 cm s^{-1}) and water (0.01 cm s^{-1}) (Seigneur et al., 2001; 2004).

The largest major inter-model comparison study, the Intercomparison Study of Numerical Models for Long-Range Atmospheric Transport of Mercury, involved eight regional, hemispheric, and global models that compared both short and long term simulations over Europe. This inter-comparison took place between 2000 and 2005 and was conducted in three phases. The first was an examination of the physical and chemical schemes of Hg (Ryaboshapko et al., 2002); the second phase compared short-term simulations (Ryaboshapko et al., 2007a); and the third phase included simulations over an entire year (Ryaboshapko et al., 2007b). In this latter study, the annual model results conducted over the full year (1999) of the dry deposition of Hg were within ±50% of the observations; however, the range of the monthly modelled dry deposition results were up to ±100% of the observations. The large discrepancies observed were attributed to two factors noted earlier, that not all of the models included the dry deposition of GEM and that some models used a fixed deposition velocity over forests for GOM (Ryabshapko et al., 2007b).

The North American Mercury Model Intercomparison Study involved three regional-scale models (CMAQ, REMSAD, and TEAM) running simulations over North America using the same initial/boundary conditions (Bullock et al., 2008; 2009). In this study, the dry deposition results varied between the models by close to a factor of ten, with REMSAD producing the smallest dry deposition fluxes. Only TEAM simulated dry deposition of GEM,

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105 however the GEM results were not reported due to the assumption that most of the GEM dry
106 deposited was re-emitted back to the atmosphere (Bullock et al., 2008).

107 More recently, the Hemispheric Transport of Air Pollution (HTAP) modelling
108 experiment, included inter-comparisons between GRAHM, GEOS-Chem, GLEMOS, CMAQ-
109 Hg, and ECHMERIT (Travnikov et al., 2010). Hg dry deposition varied between the models,
110 with GEOS-Chem simulating dry deposition fluxes between ~5 μg m^{-2} yr^{-1} over the Arctic to
111 almost 30 μg m^{-2} yr^{-1} over East Asia. Over all of the regions, GLEMOS produced the smallest
112 dry deposition fluxes ranging between ~1 μg m^{-2} yr^{-1} over the Pacific to ~8 μg m^{-2} yr^{-1} over East
113 Asia. In this study, mercury deposition results reflected the different model parameterizations.
114 For example, GRAHM simulated higher mercury deposition in the Polar Regions due to the
115 inclusion of AMDE events, whereas the incorporation of sea salt aerosol scavenging resulted in
116 higher deposition by GEOS-Chem over oceans (Travnikov et al., 2010). The dry deposition
117 varied by more than an order of magnitude over Europe/North Africa, North America, East Asia,
118 and South Asia. Therefore, Travnikov et al. (2010) recommends the need for more measurements
119 of dry deposition in these regions.

120 In a regional model study by Zhang et al. (2012a), speciated mercury was modeled over
121 the Great Lakes using CMAQ2002, CMAQ2005, and GRAHM2005. The differences between
122 the estimations of dry deposition of GOM and PBM in the CMAQ models and GRAHM at the
123 regional scale were significant (up to a factor of two). For all three models, the differences
124 between modelled and measured GOM and PBM concentrations were between factors of two
125 and ten, whereas the GEM concentrations were within 30%.

126 As part of the Global Mercury Assessment (GMA), in 2013, three models (GLEMOS,

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GEOS-Chem, and GMHG) were used to explore global mercury deposition (Travnikov et al., 2015). These models simulated higher deposition fluxes over industrial sites and regions with higher emissions, similar to trends observed in measurements over China (Fu et al., 2010a). The largest contributions to dry deposition fluxes of GOM and PBM were over South Asia, East Asia, and Europe. All three models included AMDE events where the highest dry deposition fluxes in the Arctic were produced in the spring months. The focus of Travnikov et al. (2015)'s study was more to use the three models as an ensemble to examine the global circulation of mercury so the discussion was not on the differences between the models. However, individual results from each model were included in the report. Examples of differences between the models include the relative contribution of domestic and foreign anthropogenic sources to mercury deposition over different regions for 2013. All three models produced the highest contributions in East Asia from domestic anthropogenic sources and in the Arctic from foreign anthropogenic sources. Differences between the models were observed for predicted deposition in Europe, where GLEMOS and GEOS-Chem attributed the largest contribution to domestic sources (>30% and 20%, respectively), whereas GMHG had foreign sources as the major contributor. The other region with differences was South Asia, where again GLEMOS and GEOS-Chem had domestic sources as the larger contributor and GMHG had foreign sources as the major contributor.

Challenges still exist in modelling speciated mercury deposition in chemical transport models. These uncertainties come from uncertainties in model-simulated GOM and PBM concentrations (Baker and Bash, 2012; Holloway et al., 2012; Zhang et al., 2012a, Kos et al., 2013), uncertainties in existing dry deposition algorithms for GOM and PBM, and the lack of

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proper dry deposition algorithms for GEM. A better treatment of some of the processes simulated in these models, based on new knowledge generated from analysis of large data sets of recently collected speciated atmospheric data (Cheng et al., 2014; 2015), may improve model performance in simulating GOM and PBM concentrations. For example, the fixed gas-particle partitioning of oxidized Hg in some models (e.g., GRAHM) can be replaced with temperature-dependant parameterizations described in Cheng et al. (2014). The coarse PBM fraction neglected in many models (Zhang et al., 2012a) should also be addressed since coarse PBM contributes significantly to Hg dry and wet deposition budget (Fang et al., 2012b; Cheng et al., 2015). Validation and implementation of updated bi-directional air-surface exchange schemes into chemistry transport models, such as the one for GEM by Wang et al. (2014) will be beneficial in reducing these uncertainties.

The limited amount of measurement data inhibits the development and improvement of chemical transport models. While speciated mercury data has been increasing rapidly in the recent decade through enhanced monitoring networks (Gay et al., 2013) and increases in field studies (Lindberg and Stratton, 1998; Kim et al., 2009; Maestas et al., 2011; Fu et al., 2015; Lee et al., 2016), there is no practical way for direct dry deposition measurement as further illustrated in Section 3. Besides, the monitored oxidized Hg concentration data, especially GOM, likely have large uncertainties (Jaffe et al., 2014; Gustin et al., 2015) and caution should be made when applying this data for model evaluation (Kos et al., 2013).

2.2 At monitoring networks/sites

An increase in the monitoring of speciated atmospheric Hg in the past decade has led to an increase in the number of dry deposition estimations using the inferential method. There are

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several monitoring networks that have been established to monitor speciated atmospheric Hg. The largest network to date is the National Atmospheric Deposition (NADP)/Atmospheric Mercury Network (AMNet), which includes more than 30 sites mostly in the United States (Gay et al., 2013). Other networks include the European Monitoring and Evaluation Programme (EMEP) (Travnikov and Ilyin, 2009), the Arctic Monitoring and Assessment Program (AMAP) (Travnikov et al., 2015), and the Global Mercury Observation System (GMOS) (Sprovieri et al., 2013). There have been several monitoring sites which have performed year-long measurement campaigns of Hg dry deposition of GOM and PBM, such as over ten sites in Japan (Sakata and Marumoto, 2004; 2005; Sakata and Asakura, 2008) and a number in Taiwan (Fang et al.. 2012a, b; 2013; 2014; 2016). A comprehensive review of atmospheric GEM and TGM mercury measurements, sites, and trends across the globe can be found in the literature (e.g. Sprovieri et al., 2010). The majority of the Hg dry deposition studies using the inferential approach and speciated ambient concentrations (referred to as modelled deposition below) were conducted for GOM and PBM (Lindberg and Stratton, 1998; Fulkerson, 2006; Lyman et al., 2007, 2009; Marsik et al., 2007; Han et al., 2008; Engle et al., 2010; Lombard et al., 2011; Castro et al., 2012; Huang et al., 2012; Petersen et al., 2012; Sather et al., 2013; Huang and Gustin, 2015; Fang et al., 2016), while a few studies also included GEM (Rea et al., 2001; Miller et al., 2005; Caldwell et al., 2006; Holmes et al., 2011; Zhang et al., 2012b; Bieser et al., 2014; Enrico et al., 2016). A summary of estimated dry deposition fluxes for GOM and PBM estimated using the data from the various monitoring networks and other field campaigns is provided in Table S2.

Dry deposition flux estimations of GOM in North America range from 0.02 ng m^{-2} hr^{-1} to 5.91 ng m^{-2} hr^{-1} with one exception in August, Georgia, where the maximum estimated GOM dry

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193 deposition flux was 36.3 ng m^{-2} hr^{-1} over vents of a mercury chlor-alkali plant (Landis et al.,
194 2004). In China, the estimation is higher at 20.4 ng m^{-2} hr^{-1} (Huang et al., 2012). Dry deposition
195 flux estimations of PBM range from 0.003 ng m^{-2} hr^{-1} to 4.54 ng m^{-2} hr^{-1} in North America and
196 from 0.43 ng m^{-2} hr^{-1} to 46.46 ng m^{-2} hr^{-1} in East Asia. In Europe, the median of estimated
197 GOM+PBM dry deposition fluxes is 0.34 ng m^{-2} hr^{-1}. In most studies, dry deposition of GOM
198 has been estimated to be much higher than PBM due to the much higher deposition velocities of
199 GOM than PBM (Han et al., 2008; Engle et al., 2010; Huang et al., 2012; Zhang et al., 2012b).
200 Another reason that needs to be emphasized is the exclusion of coarse PBM concentration in the
201 monitoring process in many studies (e.g., Zhang et al., 2012b). Differences between the
202 modelled and measured fluxes are typically at a factor of 2 or larger due to measurement
203 uncertainties and choice of model parameters (Lyman et al.; 2007; Marsik et al., 2007; Huang
204 and Gustin, 2015), although some studies obtained very close model-measurement values (Miller
205 et al., 2005; Lyman et al., 2009; Zhang et al., 2012b).
206 Dry deposition is often assumed to be less important than wet deposition since earlier studies
207 only estimated GOM and PBM dry deposition. Using speciated Hg data at 19 monitoring sites in
208 North America, Zhang et al. (2012b) estimated speciated and total Hg dry deposition and also
209 used litterfall Hg measurements at the regional scale as a constraint for model estimation. In
210 thestudy of Zhang et al. (2012b), GEM was demonstrated to contribute much more than
211 GOM+PBM to the total dry deposition over vegetated surface. Thus, total dry deposition, when
212 including GEM, was much higher than wet deposition at the majority of the sites, a conclusion
213 that can be supported from litterfall (Risch et al., 2012) and somewhat by throughfall
214 measurements (see more discussion in Sections 5 and 6).

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3. Deposition (flux), litterfall, and throughfall measurement methodologies

3.1. Micrometeorological approaches

The most common micrometeorological approach employed for the measurement of the air-surface exchange of mercury is the flux-gradient approach. In a common application, time-averaged fluxes of speciated mercury (typically reported in either nanograms (or pictograms) per meter squared per hour) are obtained using the relation:

$$F_{Hg,i} = -K_Z \frac{\Delta C_i}{\Delta Z}$$

where $F_{Hg,i}$ is the flux of a given mercury species, i, K_Z is the vertical eddy-transfer coefficient and $\frac{\Delta C_i}{\Delta Z}$ is the time-averaged vertical gradient of the mercury species, in question. Several approaches have been used to determine the values of the stability-dependent eddy-transfer coefficient K_Z, including the aerodynamic approach (e.g., Edwards, 2005; Marsik et al., 2005; Fritsche et al., 2008) and the modified Bowen-ratio approach (e.g., Kim et al., 1995; Lindberg et al., 1995; Meyers et al., 1996; Poissant et al. 2004; Fritsche et al., 2008). In each case, the assumption is made that all scalar quantities are mixed in a similar fashion within the atmospheric surface layer, and thus the vertical eddy-transfer coefficient for heat (or other tracers, such as CO_2 or H_2O_v) can be used as a surrogate for the vertical eddy-transfer coefficient for mercury.

The vertical gradient of mercury has been measured using either: (a) manual approaches (such as gold-bead traps for GEM, KCl-coated denuders for GOM and quartz filters for PBM) or (b) automated sampling systems (such as a Tekran® Model 2537A Mercury Vapor Analyzer combined with a Tekran® Model 1110 Synchronized Two-Port Sampling Unit for GEM, a Tekran® Model 1130 Mercury Speciation Unit for GOM, combined with a Tekran® Model

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1135 Particulate Mercury Unit for PBM).

3.2. Dynamic gas flux chambers

Dynamic gas chambers, which have been used to study the flux of a number of gaseous species from a variety of emitting surfaces, including leaves, soil and water, have been successfully employed for use in the measurement of the air-surface exchange of GEM (e.g., Poissant and Casimir, 1998; Zhang et al., 2001a; Wallschläger et al., 2002; Marsik et al., 2005; Eckley et al., 2011; Edwards and Howard, 2013). In a typical configuration for the measurement of the air-surface exchange of GEM from soil or water surfaces, a polycarbonate flux chamber (DFC) is placed on the emitting surface to be measured. Ambient air is drawn by vacuum through the DFC at a constant flow rate, nominally 1.5 LPM. The concentration of GEM is measured at both the inlet and outlet of the DFC, typically using an automated system, such as a Tekran® Model 2537A Mercury Vapor Analyzer combined with a Tekran® Model 1110 Synchronized Two-Port Sampling Unit, though initial approaches used manual gold bead traps. The resulting GEM flux (typically reported in nanograms per meter squared per hour) is calculated using the relation:

$$F_{GEM} = \left[\frac{(C_O - C_i) \cdot Q}{A}\right]$$

where C_O is the concentration of GEM at the outlet, C_i is the concentration of GEM at the inlet, Q is the volume flow rate through the DFC and A is the area of the footprint of the DFC on the surface in question. As with other approaches, the final flux is determined using the above equation, subtracting a sample blank value from measured value. Typically, DFC blanks are obtained at the start and completion of a given sampling period by placing the DFC over a clean, inert surface (e.g., Aluminum foil).

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3.3. Surrogate surface approaches

A number of studies considered in this manuscript have utilized surrogate surface measurement approaches to provide a direct measurement of mercury to the Earth's surface. The designs of the various surrogate surfaces tend to favor the quantification of one form of mercury over the others, while not being able to totally rule out a contribution from one of the other forms. Intercomparison studies have suggested that the different approaches provide relatively consistent results (Marsik, 2009; Gustin et al., 2015), though care must be taken when interpreting surrogate surface results due to the differences in surrogate surface designs.

There are a variety of surrogate surface approaches that have been used to directly measure the dry deposition of mercury. The general classes of approaches can be categorized in the following manner: (a) water/solution-based surfaces, (b) filter-based surfaces, (c) membrane-based surfaces and (d) turf-based surrogate surfaces. A brief discussion of each of these approaches is presented below.

a. Water/solution-based surfaces

Water- or solution-based surrogate surfaces have been used by a number of groups (Sakata and Marumoto, 2005; Marsik et al., 2007; Lai et al., 2011) for the quantification of the dry deposition of mercury. In general, these approaches deploy a given volume of ultra-pure water in a reservoir that is part of an aerodynamic sampler design. Following a specified period of deployment, the sample solutions are retrieved and the amount of mercury within the sample solution is quantified. In most cases, the final results are "bias-corrected", meaning that the average amount of mercury found in a subset of unexposed solutions is subtracted from the exposed solution to obtain a net amount of mercury which is assumed to be due to that dry

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283 deposited to the exposed solution. Some approaches utilize a static amount of solution which is
284 deployed in a fixed reservoir within the sample holder (Marsik et al., 2007; Lai et al., 2011).
285 Other water/solution-based systems approaches use a more dynamic approach for the
286 measurement of the dry deposition of mercury and other species, in which the sample solution is
287 continuously-circulated through the sampling apparatus, with the exposed surface area remaining
288 constant through the sample period (e.g., Sakata and Marumoto, 2004).

289 In general, surrogate water surface approaches using "ultra-pure" water are considered to
290 collect both GOM and PBM, with limited uptake expected from GEM due to the relatively
291 insolubility of this latter species. In most cases, the resultant deposition flux of mercury (in
292 picograms per square meter per hour) is determined by

293

$$Deposition\ flux = \left[\frac{(Hg_{Sample} - Hg_{Blank})}{A \cdot T}\right]$$

294

295 where $\boldsymbol{Hg_{Sample}}$ is the amount of mercury in the sample solution, $\boldsymbol{Hg_{Blank}}$ is the amount of
296 mercury in the sample blank, $\boldsymbol{A}$ is the exposed surface area of the solution and $\boldsymbol{T}$ is the length of
297 time over which the sample was exposed to the ambient air.

298 It should be noted that some approaches use slightly acidified solutions for the purpose of
299 "fixing" deposited mercury to avoid volatilization after deposition to the exposed solution. It is
300 possible that such dilute-acid solutions may lead to an enhanced uptake of GEM due to the
301 fixation of any GEM which may even temporarily become dissolved in the solution.

302 **b. Filter-based surfaces**
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304 A number of filter-based approaches have been used in the collection of mercury dry-
305 deposition (Lai et al., 2011). The general concept of this approach is that the three-dimensional
306 structure of the filters will lead to a capture of GOM and PBM. Like the water/solution-based
307 approaches, the filter surfaces are exposed for a given amount of time and then returned to the
308 analytical laboratory at the end of the sampler period, with subsequent quantification of the
309 amount of mercury deposited to the surface, followed by a bias-correction for the average
310 amount of mercury found in a subset of unexposed filters. As before, the mercury dry-deposition
311 flux is quantified as:
312

$$Deposition\ flux = \left[\frac{(Hg_{Sample} - Hg_{Blank})}{A \cdot T}\right]$$

313

314 where $\boldsymbol{Hg_{Sample}}$ is the amount of mercury on the exposed sample filter, $\boldsymbol{Hg_{Blank}}$ is the amount of
315 mercury on the sample filter blank, $\boldsymbol{A}$ is the exposed surface area of the filter and $\boldsymbol{T}$ is the length
316 of time over which the sample was exposed to the ambient air.
317 While some of the filter-based approaches utilize the filter surfaces as received from the
318 manufacturer, some approaches coat the filter surfaces either with a solution (that is subsequently
319 allowed to dry) or, in some cases, with a fine film of gold. In these latter cases, the goal is to
320 enhance the collection of GEM mercury that would otherwise be missed by the other filter-based
321 approaches.

322 **c. Membrane-based surfaces**
323
324 One of the more recently developed approaches uses cation exchange membranes as the
325 exposed deposition surfaces (e.g., Lyman et al., 2007; Castro et al., 2012; Sather et al., 2013;

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Huang and Gustin, 2015). These membranes have been designed to specifically favor the uptake of GOM over either GEM or PBM, using the assumption that the deposition of mercury is dominated by the former species. This class of filters is typically deployed facing downward, which serves to reduce contamination by large particles and by precipitation. An example of one such filter (Pall Corporation, P/N ICD45S3R) was employed by Lyman *et al*. (2007) and is constructed out of negatively-charged polysulfane on one side, with a non-woven polyester backing on the other. As before, the resultant deposition flux of mercury (in picograms per square meter per hour) is determined by

$$Deposition\ flux = \left[\frac{(Hg_{Sample} - Hg_{Blank})}{A \cdot T}\right]$$

where $\boldsymbol{Hg_{Sample}}$ is the amount of mercury on the exposed sample filter, $\boldsymbol{Hg_{Blank}}$ is the amount of mercury on the sample filter blank, $\boldsymbol{A}$ is the exposed surface area of the filter and $\boldsymbol{T}$ is the length of time over which the sample was exposed to the ambient air. The inverted sampler design employed with cation exchange membrane samplers protects the membranes from contamination by rainfall, thus allowing these samplers to be deployed for long periods of time and thus providing a long-term integrated measure of Hg dry deposition.

d. Turf Surrogate Samplers

Much in the way that cation-exchange membrane surfaces were developed in a way that protects them from contamination by rainfall, the turf surrogate samples (TSS) approach was developed to allow for dry deposition measurements to be performed in such a way that the samplers could remain deployed during both dry- and precipitating-periods (Marsik et al., 2009;

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Lynam et al., 2015), thus allowing its application for long-term (days to week) quantification of Hg dry deposition. In addition to reducing the amount of person-hours required to cover surrogate surfaces in the advent of precipitation, this approach also sought to characterize dry-deposition to wetted surfaces which can occur following instances of dewfall or rainfall. TSS utilize circular disks of artificial turf (e.g., polyethylene Astro Turf®, GrassWorx, LLC, St. Louis, MO), which serve as three-dimensional deposition surfaces. The turf has approximately 2-cm high polyethylene "blades of grass" which are placed into a Teflon well-style insert (such as that used in the surrogate water-based samplers noted above) that is part of an aerodynamic airfoil. The backing of the turf has a lattice-like construction which allows precipitation to flow through the turf surface into a "throughfall" sample bottle which is included as part of the sample train.

For the period over which the TSS was exposed to ambient air, the estimated dry deposition of mercury is calculated as:

$$Dry\ Deposition\ Flux = Hg\ flux_{TSS} + Hg\ flux_{TF} - Hg\ flux_{WO}$$

where $Hg\ flux_{TSS}$ is the flux of mercury to the TSS over the period of exposure, $Hg\ flux_{TF}$ is the flux of mercury captured within the throughfall bottle and $Hg\ flux_{WO}$ is the flux of mercury captured with a collocated wet-only precipitation sampler. In this case, the wet-only measurement is used to remove the wet-deposited mercury flux from the throughfall measurement, which would contain a combination of both wet- and dry-deposited mercury. All components of the TSS system are acid-cleaned prior to deployment, with field blanks collected

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for the circular pieces of turf, the throughfall samples and the wet-only precipitation samples. The appropriate corrections are then made to the data in the determination of the final estimation of the measured flux.

3.4. Litterfall and throughfall-based approaches

There are several methods for collecting litterfall: manual sampling of leaves using gloves (Roulet et al., 1998; 1999; Kalicin et al., 2008; Michelazzo et al., 2010; Ding et al., 2011; Juillerat et al., 2012; Obrist et al., 2011; 2012; Melendez-Perez et al., 2014; Jiskra et al., 2015); nylon nets attached to aluminium frames placed a certain distance from the ground (Iverfeldt et al., 1991; Munthe et al., 1995; Lee et al., 2000; Nóvoa-Muñoz et al., 2008; da Silva et al., 2009; Wang et al., 2009; Fisher and Wolfe, 2012); litterfall traps/collectors (Rea et al., 1996; Grigal et al., 2000; St. Louis et al., 2001; Johnson, 2002; Sheehan et al., 2006; Silva-Filho et al., 2006; Bushey et al., 2008; Graydon et al., 2008; Larssen et al., 2008; Selvendiran et al., 2008; Fu et al., 2010a; Risch et al., 2012; Zhou et al., 2013); funnel and net combinations (Schwesig and Matzner 2000; 2001); and the use of litterbags (Hall and St. Louis, 2004; Demers et al., 2007; Pokharel and Obrist, 2011). Fresh foliage was cut directly from trees and shrubs manually from inside branches and outside branches (McLaughlin et al., 2008); from the crowns of the trees (Mélières et al., 2003; Michelazzo et al., 2010; Blackwell and Driscoll, 2015b; Fostier et al., 2015; Luo et al., 2015); middle branches (Rasmussen et al., 1991; 1995; Rea et al., 2002; Richardson and Friedland, 2015); lower tree branches (Michelazzo et al., 2010; Obrist et al., 2012; Gong et al., 2014; Hutnik et al., 2014; Fostier et al., 2015); or shot down with a pellet gun (Bushey et al., 2008; Blackwell and Driscoll, 2015a).

Mercury that is dry deposited to leaves, needle surfaces, branches, and trunks gets

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washed off during precipitation events. This Hg-enriched rain then lands on the surface and becomes throughfall (Rea et al., 2000; 2001; Mélières et al., 2003; da Silva et al., 2009; Risch et al., 2012). The Hg in the throughfall is then either adsorbed by the litter or forest floor or re-volatized (Demers et al., 2007). In addition to dry deposition to the leaf/needle surface, foliar leaching was thought to be a possible source of Hg in throughfall but was found to be negligible (Rea et al., 2001). Throughfall Hg is calculated by multiplying the volume-mean-weighted Hg concentration in throughfall by the total throughfall volume. In throughfall field studies, sampler are collected weekly (Choi et al., 2008; Wang et al., 2009; Fu et al., 2010a; 2010b; Luo et al., 2015), bi-weekly (Kolka et al., 1999; Grigal et al., 2000; Schwesig and Matzner, 2000; Witt et al., 2009; Åkerblom et al., 2015); monthly (Munthle et al., 1995; Fostier et al., 2000; Lee et al., 2000; Larssen et al., 2008); on an event basis (Rea et al., 2001; Demers et al., 2007; Kalicin et al., 2008); or the funnels are covered during precipitation events to avoid contamination by dry deposition of Hg on the funnels (Rea et al., 1996). Lengths of campaign measurements vary between a single growing season (Munthe et al., 1995; Rea et al., 1996; 2001; Fostier et al., 2000) to up to a five-year period (Lee et al., 2000; Porvari and Verta, 2003), with the current majority of throughfall studies having been for a one-year length (Larssen et al., 2008; Wang et al., 2009; Fu et al., 2010a; 2010b; Fisher and Wolfe, 2012; Åkerblom et al., 2015; Blackwell and Driscoll, 2015b; Luo et al., 2015).

4. Oxidized mercury flux measurements

Measurements of GEM flux have been reviewed in Zhu et al. (2016) so this section only focuses on GOM and PBM. The majority of the dry deposition flux measurement campaigns for GOM and PBM (88%) have used surrogate surface techniques, with 67% of them being at sites

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412 in North America and 33% of them at sites in Asia. These measurement studies have included
413 several long-term campaigns of up to three years in length in both Asia (Sakata and Asakura,
414 2008; Fang et al., 2016; Han et al., 2016) and North America (Lyman et al., 2009; Castro et al.,
415 2012; Peterson et al., 2012; Weiss-Penzias et al., 2012; Sather et al., 2013; 2014; Wright et al.,
416 2014; Huang and Gustin, 2015). Dry deposition fluxes of GOM+PBM are the highest in Asia
417 where median and mean values are 10.7 and 22.7 μg m^{-2} yr^{-1}, with a range between 2.4 and 463
418 μg m^{-2} yr^{-1}. In North America, the median and mean values are 6.1 and 30.8 μg m^{-2} yr^{-1} with a
419 range between 0.26 and 520 μg m^{-2} yr^{-1}. Long term studies have shown a stronger dependence on
420 GOM dry deposition (40-57%) to the total Hg deposition over arid regions, such as the Four
421 Corners and Nevada (Caldwell et al., 2006; Lyman et al., 2007; Sather et al., 2014) than in more
422 humid regions such as Texas and Oklahoma (5-27%) and Florida (Lyman et al., 2007; Marsik et
423 al., 2007; Peterson and Gustin, 2008; Weiss-Penzias et al., 2011; 2012; Sather et al., 2014).
424 Current knowledge on particle size distribution of PBM, although limited, has started to be
425 studied in more depth in recent years (Keeler et al., 1995; Ames et al., 1998; Feddersen et al.,
426 2012; Kim et al., 2012). Although PBM mass distributes more in fine ($PM_{2.5}$) than coarse
427 particles (>2.5 μm), dry deposition from fine and coarse PBM are equally important due to the
428 faster deposition velocity of coarse particles (Fang et al., 2012a). An increase in North American
429 PBM studies would be beneficial in further exploration of these trends. For a detailed summary
430 of the measured dry deposition fluxes of GOM and PBM (ng m^{-2} hr^{-1}), as well as the measured
431 concentrations of GOM and PBM (pg m^{-3}), see Table S3.

432 GOM and PBM concentrations and dry deposition fluxes have been observed to be up to
433 five times greater at urban and industrial sites due to the close proximity to, or downwind from,

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point source emissions (Sakata and Marumoto, 2005; Liu et al., 2007; Sakata and Asakura, 2008; Fang et al., 2012a; Huang et al., 2012; Sather et al., 2014) than at rural sites (Sakata and Marumoto, 2005; Sakata and Asakura, 2008; Castro et al., 2012; Sather et al., 2014). GOM concentration and dry deposition have shown positive correlations to wind speed (Lyman et al., 2010; Gustin et al., 2012; Sather et al., 2014; Huang and Gustin, 2015) and higher elevations (Huang and Gustin, 2015). Diel trends in GOM and PBM have shown higher concentrations in the morning and afternoon (Lindberg and Stratton, 1998; Poissant et al., 2004; Liu et al., 2007; Peterson and Gustin, 2008; Lai et al., 2011; Weiss-Penzias et al., 2011; Gustin et al., 2012; Fang et al., 2013; Fu et al., 2016) and then a decrease at night, potentially due to a reduction in photochemical production of GOM at night (Weiss-Penzias et al., 2011) or due to nighttime inversion (Huang and Gustin, 2015).

The seasonal changes in the fluxes depend on geography and site characteristics, where in general, the fluctuations in the GOM and PBM dry deposition seasonal variations have been observed to be more pronounced in arid regions. Higher GOM deposition has been observed in the spring due to GOM events and long-range transport (Liu et al., 2007; Lyman et al., 2009; Weiss-Penzias et al., 2011; Castro et al., 2012; Gustin et al., 2012; Peterson et al., 2012; Sather et al., 2013; Huang and Gustin, 2015; Han et al., 2016). At three sites in Taiwan, PBM concentrations were highest in November and December and in the summer due to industry, such as coal-fired power plants, and GOM events (Lindberg and Stratton, 1998; Fu et al., 2016). Higher PBM has been measured in the winter due to increases in the winter in the use of vehicles, biomass burning, electricity consumption such as home heating, or due to an accumulation in PBM because of lower temperatures and solar radiation (Liu et al., 2007; Sakata

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and Asakura, 2008; Fang et al., 2012a; Fu et al., 2016; Han et al., 2016).

There are some physical aspects of the various measurement techniques that have been observed to affect measured values. The direction that the filter in the cation-exchange membrane is facing can alter amount of deposited particles, with lower measured dry deposition fluxes of GOM and PBM in downward facing membranes (Lyman et al., 2007; 2009; Weiss-Penzias et al., 2011; Gustin et al., 2012; Huang et al., 2012; Peterson et al., 2012; Sather et al., 2013; 2014; Huang and Gustin, 2015) than upward facing (Huang et al., 2012). In addition to direction of the membrane, higher deposition rates have been observed for rectangular mounts than aerodynamic mounts, possibly due to artificial turbulence created by the rectangular mounts (Lyman et al., 2009). The length of deployment times for surrogate surfaces is under debate, with recommendations that a minimum sampling time of two weeks be implemented at rural sites (Huang et al., 2012; Huang and Gustin, 2015) and for passive samplers (Lyman et al., 2010). Improvements and changes in sampling techniques continue. For example, the ICE 450 passive sampler, used in several GOM studies (e.g. Castro et al., 2012; Huang et al., 2012; Sather et al., 2013; 2014), was replaced in July 2013 with the Mustang S passive sampler (Huang and Gustin, 2015), where fortunately no significant differences in the measurement results from the two samplers have been observed (Huang and Gustin, 2015). Clearly, surrogate surfaces may differ significantly from the real-world natural surfaces, and choices of surrogate surfaces and instrument setup can both affect the measured deposition values.

5. Litterfall measurements

Litterfall Hg represents Hg collected by and retained in leaves. It has been observed in recent years to be an important pathway for Hg input from the atmosphere to the floor of forest

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ecosystems via plant litter. Litterfall is comprised of senesced leaves and needles, twigs, and branches, and other plant tissues. Litterfall Hg can be transmitted to the soil as the litter decomposes. Litterfall Hg is related to the concentration of Hg in the leaf litter (Rea et al., 1996; Sheehan et al., 2006; Silva-Filho et al., 2006; Wang et al., 2009; Niu et al., 2011). Another method for estimating litterfall Hg has been to multiply the Hg concentration in fresh foliage by 1.5 under the assumption that the Hg accumulates in the leaf linearly over an average six month growing season (Fu et al., 2010b; Gong et al., 2014). Litterfall measurement campaigns have ranged from the growing season (Rea et al., 1996; 2002; Fostier et al., 2003; Larssen et al., 2008; Ding et al., 2011; Fisher and Wolfe, 2012) to long-term studies of a year (Schwesig and Matzner , 2000; 2001; St. Louis et al., 2001; de Oliveira et al., 2006; Silva-Filho et al., 2006; Sheehan et al., 2006; da Silva et al., 2009; Wang et al., 2009; Fu et al., 2010a; Teixeira et al., 2012; Zhou et al., 2013; Lang, 2014; Luo et al., 2015) to two years or more (Xiao et al., 1998; Lee et al., 2000; Hall and St. Louis, 2004; Graydon et al., 2008; Selvendiran et al., 2008; Obrist et al., 2011; Risch et al., 2012; Hutnik et al., 2014; Blackwell and Driscoll, 2015b; Richardson and Friedland, 2015). A summary of available measurements of Hg concentrations in leaves and litter (ng g^{-1}) and litterfall Hg (μg m^{-2} yr^{-1}) is provided in Table S4.

Litterfall Hg measurements are highest in Asia, where the median and mean values (22.3 and 26.7 μg m^{-2} yr^{-1}, respectively) are approximately two times higher than the measured litterfall Hg in Europe (12.8 and 14.2 μg m^{-2} yr^{-1}, respectively) and North America (11.9 and 12.9 μg m^{-2} yr^{-1}, respectively). Litterfall Hg range from 4.2 – 70.6 μg m^{-2} yr^{-1} in Asia to 0.05 – 42 μg m^{-2} yr^{-1} in Europe. In South America, litterfall Hg ranges between 43 and 184 μg m^{-2} yr^{-1}, respectively. Measurements of litterfall Hg in the Amazonian rainforest have been reviewed in

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detail by Fostier et al. (2015). Atmospheric Hg concentrations affect the levels of Hg concentrations in foliage and leaf litter with higher litterfall Hg in urban forests than remote forests (Fostier et al., 2003; Wang et al., 2009; Fu et al., 2010a; 2010b; Gong et al., 2014); higher Hg concentrations in close proximity to degassing vents and during eruption activity of volcanoes (Martin et al., 2012); and higher Hg concentrations at intermediate altitudinal mountain zones (Szopka et al., 2011). In Europe, a decrease in litterfall Hg has been associated with the decrease in Hg emissions in recent years (Larssen et al., 2008).

Due to coniferous needles remaining on trees for longer periods than deciduous trees (years vs. one season), needle litter tend to have higher Hg concentrations than leaf litter (Grigal et al., 2000; Sheehan et al., 2006; Niu et al., 2011; Blackwell and Driscoll, 2015b; Fisher and Wolfe, 2012; Obrist et al., 2012). This, however, does not translate directly to higher litterfall Hg in coniferous forests due to the contribution from the higher mass of leaf litter than needle litter.As a result, litterfall Hg in deciduous forests has been found to be higher than in coniferous forests (Schwesig and Matzner, 2000; Demers et al., 2007; Kalicin et al., 2008; Fisher and Wolfe, 2012; Obrist et al., 2012; Richardson and Friedland, 2015).

Correlations between Hg concentrations and age of the foliage have been observed with concentrations increasing with age (Barghigiani et al., 1991; Roulet et al., 1999; Ericksen et al., 2003; Larssen et al., 2008; Ding et al., 2011; Martin et al., 2012) and higher in litter than foliage (Iverfeldt, 1991; Bushey et al., 2008; Michelazzo et al., 2010; Ding et al., 2011; Melendez-Perez et al., 2014; Luo et al., 2015).

In Asia, annual litterfall Hg deposition can account for up to 75% of the total Hg input fluxes to urban forests (Wang et al., 2009). The contribution of Hg from litterfall has been found

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to be three times the amount from throughfall (Fu et al., 2010a) and anywhere from two times up to 14 times the contribution from wet deposition (Wang et al., 2009; Fu et al., 2010a; Zhou et al., 2013). In Europe, litterfall Hg has been found to represent between 27% and 90% to the total deposited Hg (Schwesig and Matzner, 2000; 2001; Jiskra et al., 2015), from equal to 1.5 times the deposited throughfall Hg and two times the open-field precipitation (Iverfeldt et al., 1991; Munthe et al., 1995; Lee et al., 2000). In the Amazonian rainforest, litterfall Hg has been observed to be twice the contribution from wet deposition (da Silva et al., 2009) and more than doubled during the dry season (Silva-Filho et al., 2006). In North America, some studies have found contributions to the deposition flux from litterfall and throughfall equal (Iverfeldt et al., 1991; Rea et al., 1996; Grigal et al., 2000; Lee et al., 2000), whereas in other studies, litterfall has contributed up to two times more Hg than throughfall (St. Louis et al., 2001; Johnson, 2002; Fisher and Wolfe, 2012).

Median litterfall deposition of 12.3 μg m^{-2} yr^{-1} accounted for 55% of the Hg deposition to deciduous forest floors at 23 sites in eastern USA (Risch et al., 2012). In this study that spanned 15 states over three years, litterfall Hg ranged between 3.5 and 23.4 μg m^{-2} yr^{-1}. Litterfall Hg was found to be more correlated to the amount of litter collected (i.e. the sample catch) than Hg wet deposition, with the highest median litterfall Hg deposition (14.7 μg m^{-2} yr^{-1}) found in deciduous forests. Mixed forests and coniferous forests had the same median litterfall Hg concentration (38.6 ng g^{-1}) but the mixed forest litterfall Hg was higher (9.3 vs. 7.0 μg m^{-2} yr^{-1}) due to the higher sample catch. Of the deciduous sites, oak-hickory forests had higher litterfall Hg than maple-beech-birch forests and aspen-birch forests. Litterfall Hg deposition was more dependent on the forest cover type than geographical region. Intraseasonal variations were observed with

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544 higher litterfall Hg concentrations in the first autumn sampling than the second. Interannual
545 variations were observed for the sample catch but were not significant for litterfall Hg
546 concentrations.

547 **6. Throughfall measurements**

548 Factors that affect throughfall Hg deposition include: canopy type, with higher
549 concentrations in coniferous canopies than deciduous canopies due to a combination of higher
550 Hg scavenging efficiency in coniferous forests over deciduous forests and larger surface areas
551 (Kolka et al., 1999; Rea et al., 1996; Grigal et al., 2000; Schwesig and Matzner, 2000; 2001;
552 Johnson, 2002; Demers et al., 2007; Wang et al., 2009; Fu et al., 2010a; 2010b; Fisher and
553 Wolfe, 2012; Åkerblom et al., 2015; Luo et al., 2015); canopy density, with Hg throughfall
554 concentrations increasing with canopy density (Grigal et al., 2000; Witt et al., 2009);
555 meteorology, with higher throughfall concentrations under drier conditions, resulting from
556 increased dry deposition to the foliage (Blackwell and Driscoll, 2015b); and location, with higher
557 concentrations in regions with high atmospheric Hg emissions or close to point sources, such as
558 urban forests (Wang et al., 2009; Luo et al., 2015). A summary of available measurements Hg
559 concentrations in throughfall (ng L^{-1}) and throughfall Hg (μg m^{-2} yr^{-1}) is provided in Table S5.

560 In Asia, median and mean throughfall Hg for this region are 56.5 and 47.1 μg m^{-2} yr^{-1},
561 respectively, with a range in the means between 10.5 and 71.3 μg m^{-2} yr^{-1}. These median and
562 mean are more than two to three times the European values (16.3 and 19.0 μg m^{-2} yr^{-1} for the
563 median and mean, respectively), where the range is between 12.0 and 40.1 μg m^{-2} yr^{-1}. In North
564 America, the median and mean values are the lowest at 7.0 and 9.3 μg m^{-2} yr^{-1}, respectively,
565 with a range between 2.1 and 26.6 μg m^{-2} yr^{-1}. The only throughfall Hg measurement in South

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America is an estimate of 72.0 μg m^{-2} yr^{-1} in the Brazilian Amazon (Fostier et al., 2000), which has been suggested to be an overestimation. Without any other Amazonian throughfall studies, it is not known whether this is a typical value for this rainforest or if the high value was related to the monthly collection. In Asia and Europe, Hg contributions from throughfall are higher than from wet deposition, with throughfall ranging from approximately two to four times the wet deposition (Munthe et al., 1995, Lee et al., 2000; Fu et al., 2010a; 2010b; Wang et al., 2009). In North America, the throughfall-precipitation ratio has been found to differ with forest type, where based upon throughfall measurements, dry deposition was found to be less than wet deposition in deciduous forests (Demers et al., 2007; Kalicin et al., 2008; Blackwell and Driscoll, 2015b) and greater than precipitation in coniferous forests (Demers et al., 2007; Kalicin et al., 2008; Witt et al., 2009) and over watersheds (Lindberg et al., 1994; Rea et al., 1996; 2001; Grigal et al., 2000; Graydon et al., 2008).

7. A brief comparison of dry, litterfall, throughfall and wet deposition

The annual contributions to Hg deposition from wet deposition, throughfall, litterfall, and dry deposition (μg m^{-2} yr^{-1}) are shown in Figure 1 for various sites in (a) Asia, (b) Europe, (c) North American deciduous forests, and (d) North American coniferous forests. In these figures, the wet deposition represents open-field wet deposition measurements, with the exception of the measurements at Whiteface Mountain, in the Adirondack Park, NY (Blackwell et al., 2015b), where the wet deposition at this site is from cloud water. The estimated dry deposition shown in this Figure is the sum of the litterfall Hg and throughfall Hg minus the wet deposited Hg.

In China, dry deposition accounted for between 25% up to 90% of the total Hg deposited to subtropical forested catchments. Litterfall Hg was the dominant pathway in these forests

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588 contributing between 53 and 90% of the dry deposition to these forests. In forested watersheds in
589 Germany, wet deposition played a stronger role, accounting for 78% of the total Hg deposition in
590 Steinkreuz and almost twice as much at Lehstenbach. At the other European sites, wet deposition
591 only represented between 9 and 45% of the total Hg deposition. At all of the European sites,
592 litterfall Hg was the dominant pathway at 64 to 98% of the dry deposited Hg, with the exception
593 of Buskerud, Norway where wet deposition was not reported, preventing an accurate estimate of
594 dry deposition. In North America, the dry deposition of Hg ranged between 13 and 83% of the
595 total deposited Hg over deciduous forests and 15 and 70% over coniferous forests. Exceptions to
596 these values were at Whiteface Mountain, as mentioned above, where wet deposition is reported
597 as high elevation cloudwater Hg rather than open-field precipitation. The contributions from net
598 throughfall Hg (throughfall Hg – wet deposition) were higher in the coniferous forests than the
599 deciduous forests. In the deciduous forests, litterfall Hg accounted for between 46 and 95% of
600 total deposited Hg.

601 **8. Summary and recommendations**

602 The modelling of GOM and PBM dry deposition on regional and global scales using
603 various chemical transport models shows inconsistencies between the models, up to a factor of
604 ten in some cases, which are caused by differences in model simulated GOM and PBM
605 concentrations and in selected dry deposition algorithms. Recent analysis of large data sets of
606 speciated atmospheric mercury has provided some needed knowledge for improving these
607 models. However, measurement uncertainties in ambient GOM and PBM concentrations, and
608 the significant lack of measurements over the oceans, the Polar Regions, the Southern
609 Hemisphere, Europe, and Asia are inhibiting further evaluation of the models. Progress has been

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made on the inferential estimation of speciated and total Hg dry deposition at monitoring sites or networks. GEM deposition to forest canopies is more important than previously assumed in chemical transport models. Further development of dry deposition algorithms, especially the bi-directional exchange for GEM, is still needed, but reliable Hg flux data is lacking in validating such models.

Surrogate surfaces are the current preferred method for measuring the dry deposition of GOM and PBM, with a new turf surrogate surface showing promise in extending the length of the sampling times to longer campaigns. Uncertainties in the measured GOM and PBM dry deposition associated with the selected surrogate surfaces and instrument setup are larger than a factor of two. Measurements of PBM dry deposition are very limited around the world due to the challenges associated with making these measurements. Measured GOM and PBM dry deposition are strongly correlated to emissions from local point sources due to their short lifetime in air. GOM deposition can play a significant role in total Hg deposition, contributing to more than half of Hg dry deposition in some regions, and having been found to be higher than wet deposition in some arid regions and lower in more humid regions due to the high solubility of GOM.

There has been a large increase in the number of field campaigns measuring litterfall and throughfall mercury in Asia, Europe, the Amazon, and North America. Generally, litterfall and throughfall Hg are higher in urban regions of Asia as a result of the high levels of atmospheric Hg in Asia, followed by remote regions in Asia, then Europe, and North America. As can be seen in North American field studies, litterfall Hg is more dominant than throughfall Hg over deciduous canopies due to the larger amounts of litter under these canopies, whereas throughfall

632 is the primary pathway for mercury deposition over coniferous canopies. Net throughfall Hg is
633 the throughfall Hg minus the precipitation. This deposition, combined with the deposition of
634 litterfall Hg is higher than the precipitation Hg over all canopies and regions. A combination of
635 litterfall, throughfall and open-field precipitation Hg measurements and a comparison with
636 modelled Hg dry deposition is an effective way of improving our understanding of the
637 mechanisms involved in these transfers.

638
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Table 1: Summary of estimated and measured mercury dry deposition, and measured mercury in litterfall and throughfall in Asia, Europe and North America (converted to annual value in the unit of μg m^{-2} yr^{-1}).

	Asia		Europe		North America	
	Median, Mean	Range	Median, Mean	Range	Median, Mean	Range
Modelled GOM+PBM	34.5, 83.8	3.8 – 407	3.0, 3.8	0.1 – 17.5	2.6, 8.7	0.05 – 318
Measured GOM+PBM	10.7, 22.7	2.4 – 463			6.1, 30.8	0.26 – 520
Litterfall	22.3, 26.7	4.2 – 70.6	12.8, 14.2	0.05 – 42.0	11.9, 12.9	0.02 – 57.1
Throughfall	56.5, 47.1	10.5 – 71.3	16.3, 19.0	12 – 40.1	7.0, 9.3	2.1 – 26.6

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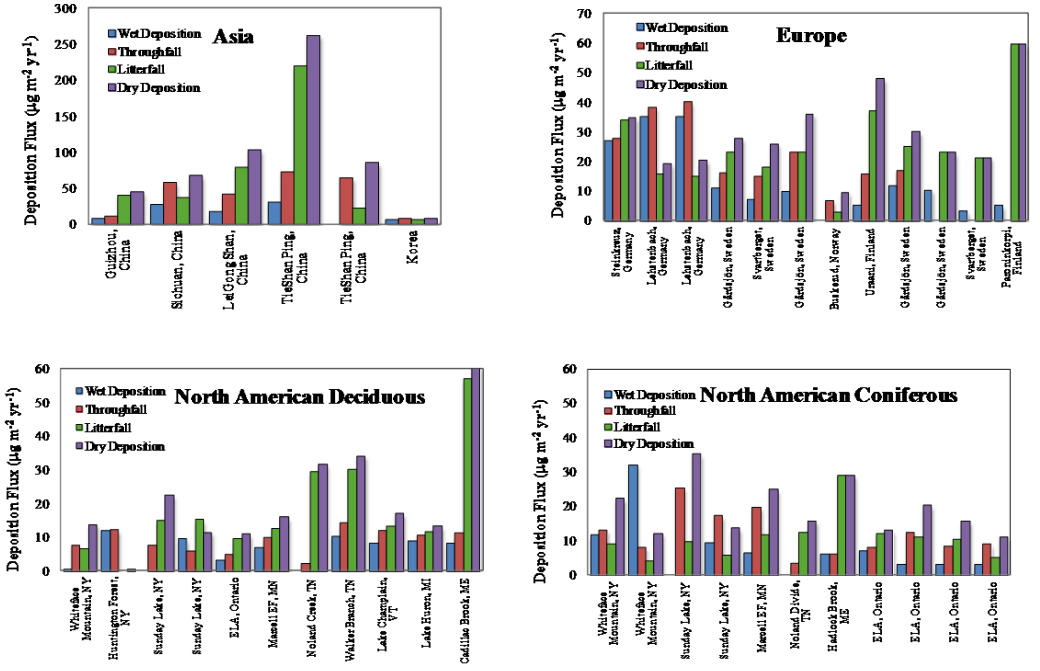

Figure 1: : Contributions to the mercury deposition flux (μg m^{-2} yr^{-1}) from wet deposition, throughfall Hg, litterfall Hg, and dry deposition in: **(a.)** Asia, **(b.)** Europe, **(c.)** North American deciduous forests, and **(d.)** North American coniferous forests. *(References in order of appearance: Fu et al., 2010a, b; Wang et al., 2009; Luo et al., 2015; Schwesig and Matzner, 2000, 2001; Hultberg et al., 1995; Lee et al., 2000; Larssen et al., 2008; orvari and Verta, 2003; Iverfeldt, 1991; Lee et al., 1998; Blackwell and Driscoll, 2015b; Choi et al., 2008; Demers et al., 2007; Kalicin et al., 2007;Graydon et al., 2008; Grigal et al, 2000; Fisher and Wolde, 2012; Lindberg et al., 1996; Rea et al., 1996, 2001; Johnson et al., 2007; St. Louis et al., 2001))*