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Global Observations and Modeling of Atmosphere-Surface Exchange of Elemental Mercury – A Critical Review

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Abstract

Reliable quantification of air-surfaces flux of elemental Hg vapor (Hg^0) is crucial for understanding mercury (Hg) global biogeochemical cycles. There have been extensive measurements and modeling efforts devoting to estimating the exchange fluxes between the atmosphere and various surfaces (e.g., soil, canopies, water, snow, etc.) in past three decades. However, large uncertainty remains due to the complexity of Hg^0 bi-directional exchange, limitations of flux quantification techniques and challenges in model parameterization. In this study, we provide a comprehensive review on the state of science in the atmosphere-surface exchange of Hg^0. Specifically, the advancement of flux quantification techniques, mechanisms in driving the air-surfaces Hg exchange, and modeling efforts are presented. Due to the semi-volatile nature of Hg^0 and redox transformation of Hg in environmental media, Hg deposition and evasion are influenced by multiple environmental variables including seasonality, vegetative coverage and its life cycle, temperature, light, moisture, atmospheric turbulence, presence of reactants (e.g., O_3, radicals, etc.) that drives the physicochemical process of Hg in the media where Hg^0 exchange occurs. However, effects of these processes on flux have not been fundamentally and quantitatively determined, which limits the accuracy of flux modeling.

In this study, we compile an up-to-date global observational flux database and discuss the implication of flux data on global Hg budget. Mean Hg^0 flux obtained by micrometeorological measurement did not appear to be significantly greater than the flux measured by dynamic flux chamber methods over unpolluted surfaces (p=0.16, one-tailed, Mann-Whitney U test). The spatio-temporal coverage of existing Hg^0 flux measurements is highly heterogeneous with large data gaps existing in multiple continents (Africa, South Asia, Middle East, South America and Australia). The magnitude of evasion flux is strongly enhanced by human activities, particularly at contaminated sites. Hg^0 flux observations in East Asia are comparatively larger in magnitude than the rest of the world, suggesting substantial reemission of previously deposited mercury from anthropogenic sources. Hg^0 exchange over pristine surfaces (e.g., background soil and water) and vegetation need better constrains for global analysis of atmospheric Hg budget. The existing knowledge gap and the associated research needs for future measurements and modeling efforts for the air-surface exchange of Hg^0 are discussed.

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1. Introduction

Mercury (Hg) is a global pollutant of broad concerns due to its toxicity, bioaccumulation characteristics and adverse health effects (Driscoll et al., 2013), especially in its methylated forms such as monomethyl-mercury (CH_3Hg) species and dimethyl-mercury ($(CH_3)_2Hg$) (Clarkson and Magos, 2006). Fish consumption has been identified as the primary pathway for human exposure to CH_3Hg (Mergler et al., 2007; Mason et al., 2012), while the exposure through rice cultivated in areas with Hg pollution (e.g. mining and smelting areas) also poses a risk (Feng et al., 2008a; Zhang et al., 2010). To protect human health and the environment from the adverse effects of mercury, a global treaty "Minamata Convention for Mercury" that regulates Hg emission reduction from anthropogenic sources has been signed by 128 countries since October 2013 (UNEP Minamata Convention, 2014). Emission of Hg into the atmosphere occurs from both natural processes and human activities. The release of Hg from natural surfaces has been estimated to account for two thirds of global emissions (Fig. 1). However, this estimate is subject to large uncertainty because of the challenges in quantifying the flux and in understanding the mechanisms involved in the exchange process of elemental mercury vapor (Hg^0) (Selin, 2009; Zhang et al., 2009; Gustin, 2011; Zhang et al., 2012a).

Hg emitted from the anthropogenic sources include all atmospheric species: gaseous elemental Hg (Hg^0, GEM), gaseous oxidized Hg (GOM), and particulate bound Hg (PBM) (Pacyna et al., 2006; AMAP/UNEP, 2013), while evasion derived from the Earth's surfaces is dominated by GEM (Gustin, 2011). Owing to the high deposition velocity of GOM and PBM (~1-2 orders higher than GEM) (Zhang et al., 2009), GOM and PBM are readily deposited locally and regionally while GEM is subject to long-range transport (e.g., hemisphere scale) and can deposit remotely from the emission sources (Lindberg et al., 2007; Gustin and Jaffe, 2010). Atmospheric Hg continuously goes through the deposition and re-emission cycle while undergoing physical and chemical transformations (Lin and Pehkonen, 1999).

Extensive efforts have been devoted to understanding the spatial and temporal pattern of Hg^0 exchange flux. Geogenically Hg-enriched surfaces and anthropogenically polluted sites are strong Hg emission sources (Kocman et al., 2013). Emissions from natural sources and from previously deposited Hg^0 on substrate surfaces are not analytically distinguishable using current measurement techniques (cf. Section 2). Direct measurement of Hg^0 flux from the background surfaces is difficult due to small vertical Hg^0 concentration gradient (therefore low

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flux) (Zhu et al., 2015a). Since the first application of a stainless steel dynamic flux chamber for Hg^0 flux measurement over background lakes and soils in 1980s (Schroeder et al., 1989; Xiao et al., 1991), significant advancement in the experimental approaches (e.g., dynamic flux chamber, micrometeorological methods, $Hg^0/^{222}Rn$ flux ratio, enriched isotope tracer methods, open-path laser optical spectroscopic method, and Hg^0/CO ratio) have been made (Sommar et al., 2013a). However, a standard protocol for Hg^0 flux quantification does not exist (Gustin, 2011; Zhu et al., 2015b), which complicates the comparison and interpretation of flux data reported in the literature (cf. Section 4).

In this study, we present a comprehensive review on the global observation of Hg^0 flux in the peer-reviewed literatures, and provide a state-of-the-science assessment on the air-surface exchange of Hg^0. Specifically, the advancement of flux quantification techniques, physicochemical factors driving the exchange process, existing field data of Hg^0 flux, and modeling efforts for scaling up the measured flux for global assessment are synthesized. Furthermore, the spatial and temporal characteristics of Hg^0 flux, as well as the underlying influencing factors are investigated. Key knowledge gaps, future directions for field measurements, and development of new-generation air-surface exchange model for Hg^0 flux are discussed.

2. Advances in Hg^0 flux quantification methods

The theory and application of Hg^0 flux measurement techniques have been documented extensively (Zhang et al., 2009; Gustin, 2011; Sommar et al., 2013a). Here we focus on the developments, advantages and disadvantages, and comparability and uncertainties of different flux quantification techniques. DFCs, micrometeorological techniques (MM), and bulk methods (e.g., $Hg^0/^{222}Rn$ flux ratio, enriched isotope tracers) are the mostly widely applied approaches for surface-atmosphere Hg^0 flux quantification (Schroeder et al., 1989; Xiao et al., 1991; Kim and Lindberg, 1995; Kim et al., 1995; Cobos et al., 2002; Amyot et al., 2004; Olofsson et al., 2005; Obrist et al., 2006; Bash and Miller, 2008; Lin et al., 2012; Slemr et al., 2013; Zhu et al., 2013c), of which DFCs and MM techniques accounted for >95% of all observations documented to date (cf. Section 4). Open-path laser optical spectroscopic (LIDAR) method and Hg^0/CO ratio were applied to estimate Hg emission from area/regional sources (e.g. LIDAR: mining areas, industrial plants, geothermal sites; Hg^0/CO ratio: continental level atmospheric Hg transport) (Aldén et al., 1982; Edner et al., 1991; Sjöholm et al., 2004; Jaffe et

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al., 2005; Fu et al., 2015a). There has not been a standardized protocol for any of the techniques (e.g., instrumentation set-up, operation parameters) (Gustin, 2011; Zhu et al., 2015b). Recent collocated measurements and uncertainties analysis emphasized the importance of method standardization and processing of field data acquired by the measurement systems (Fritsche et al., 2008b; Converse et al., 2010; Zhu et al., 2015a). Application of appropriate flux measurement technique depends on the scalar detection accuracy, sensor response frequency and level of automation (Sutton et al., 2007). The traditional standard procedure of sampling ambient air Hg^0 is by enhancement collection onto traps containing gold (Fitzgerald and Gill, 1979; Slemr et al., 1979). A wide-spread continuous Hg^0 monitor is the automated dual channel, single amalgamation, cold vapor atomic fluorescence analyzer (Model 2537, Tekran Instruments Corp.), which relying on this principle. The certified detection limit is < 0.1 ng m^{-3}. However, the pre-concentration procedure takes ≥2.5 min and therefore real-time, high-frequency data acquisition is not possible (Gustin, 2011; Fu et al., 2012b; Gustin et al., 2013; Gustin et al., 2015). Monitoring ambient air Hg^0 with a higher frequency (≤ 1Hz) can be achieved by using Lumex RA-915+ Zeeman atomic absorption spectrometry (AAS) analyzer operating without trap pre-concentration. However, the instrument has a detection limit ~1 ng m^{-3} and therefore is preferred for industrial level studies but applicable under ambient Hg^0 concentration (Holland K., 2005). More recently, high frequency (25 Hz) cavity ring-down spectroscopy (CRDS) sensor has been deployed for Hg^0 concentration measurement, but it has a higher detection limit (> 0.35 ng m^{-3}) and suffers from sensor's baseline drifting and interferences with O_3 (Fain et al., 2010; Pierce et al., 2013). Another laser technique, laser-induced fluorescence sensor, has been designed and successfully applied for up to one day continuous measurement with improved detection limit (~15 pg m^{-3}) (Bauer et al., 2002; Bauer et al., 2014). However, both methods have not been yet proved to apply for long-term field measurement. The coupling with a commercial instrument (e.g. Tekran® 2537) renders continuous and unattended flux measurements by DFC or MM techniques to be accomplished and are most widely deployed over various surfaces (cf. Section 4). However, this implementation is associated with a significant cost, for which the expense of the Hg^0 analyzer is normally exciding that of the essential flux system.

2.1 Dynamic flux chambers

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The DFC method (footprint generally <0.1 m^2) is a frequently used Hg^0 flux measurement technique over soils, water surfaces, and low-stand grass due to its relatively low cost, portability, and versatility (Sommar et al., 2013a). DFCs operating under steady-state (Xiao et al., 1991; Carpi and Lindberg, 1998) and non-steady-state conditions (Rinklebe et al., 2009) are used in Hg research with the former configuration by far the most common. Dynamic flux bag (DFB) has been applied for flux measurement over tall grass and tree branches (Zhang et al., 2005; Graydon et al., 2006; Poissant et al., 2008). Laboratory mesocosms probing whole ecosystem Hg exchange have also been attempted; a 180×10^3 L chamber (7.3 × 5.5 × 4.5 m^3) was deployed for quantifying soil-plant-atmosphere flux (Gustin et al., 2004; Obrist et al., 2005; Stamenkovic and Gustin, 2007; Stamenkovic et al., 2008). Construction materials such as fluorinated ethylene propylene (FEP) films and quartz have been recommended for DFCs due to its high actinic light transmittance and low blank (Kim and Lindberg, 1995; Carpi et al., 2007; Lin et al., 2012). DFCs volumes and flushing flow rates reported ranged from 1 to 32 L and 1.5 to 20 L min^{-1}, resulting a turnover time (TOT) ranging from 0.1 to 14 min (Eckley et al., 2010; Zhu et al., 2011). Using DFCs, Hg^0 flux is calculated as:

$$F = \frac{Q(C_{out} - C_{in})}{A} \quad (1)$$

where F is Hg^0 flux (ng m^{-2} h^{-1}), Q is DFC internal flushing flow rate (m^{-3} h^{-1}), A is DFC footprint, C_{out} and C_{in} are the Hg^0 concentrations at the DFC outlet and inlet, respectively. Eq. (1) relies on mass balance calculation of two C_{out} and two C_{in} measurements alternately and assumes that the surface shear velocity over the DFC footprint is uniform and therefore results in a constant flux spatially over the wetted surface. Distinct Hg^0 fluxes have been observed using DFCs of different designed shapes under similar environmental conditions (Eckley et al., 2010). Lin et al. (2012) investigated the internal flow field and Hg^0 concentration distribution in two commonly designed DFC (i.e. rectangular and dome-shaped chambers) showed that the airstream inside the DFCs is not uniform and the surface shear flow is divergent over the footprint, resulting in a non-uniform Hg^0 concentration gradient over the substrate surface. Eckley et al. (2010) systematically investigated effects of fabrication material, footprint, chamber dimensions including port positions and flushing flow rates on the measured Hg^0 flux by DFCs. Consistent with previous studies, flushing flow rate is among the most influential

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factor that if varied may induce up to one order of magnitude differences in the observed fluxes (Gustin et al., 1999; Wallschläger et al., 1999; Gillis and Miller, 2000a; Lindberg et al., 2002c; Zhang et al., 2002). Computational fluid dynamic modeling of DFC mass transfer indicated that smaller diffusion resistance at higher flushing flow rate yielded higher measured flux. However, due to the non-uniform internal Hg^0 concentration gradient, measured Hg^0 flux from substrates may change unpredictably when flushing flow rate varies (Eckley et al., 2010; Lin et al., 2012), which should be taken into consideration when flux obtained by DFCs of different designs and flushing flow rates cannot be directly compared. Another limitation of DFCs is the isolation of chamber internal surfaces from ambient condition. This excludes the effect of atmospheric turbulence and therefore may cause a large uncertainty when using DFC data as in-put for scale-up estimation. Lin et al. (2012) proposed an aerodynamic designed chamber (NDFC) which enables producing a uniform surface friction velocity to link with ambient shear condition to rescale to the ambient flux using Eq. (2), which allows to utilize ambient surface shear condition rather than artificial steady flushing flow rate to calculate flux:

$$F = \frac{Q(C_{out} - C_{in})}{A} \cdot \frac{k_{mass(a)}}{k_{mass(DFC)}} \quad (2)$$

where $k_{mass(a)}$ is the overall mass transfer coefficient under ambient condition, and $k_{mass(DFC)}$ is overall mass transfer coefficient in the DFC measurement area.

In addition to the uncertainties caused by varying flushing flow rates, altered short and long wave radiation balance within DFCs resulting in a modified micro-environment were found to bias the observed flux (Zhu et al., 2015a). DFC flux is measured through intermittent sampling of ambient and chamber air for Hg^0 analysis using a single detector (Lindberg et al., 2002c), which assumed that ambient Hg^0 variability was negligible during air sampling. At locations where significant variation in Hg^0 concentration exist (e.g., sites with anthropogenic emission sources), Eckley et al. (2011a) proposed a data assimilation protocol: $|\Delta C_{oi}| > |\Delta C_{ii}|$ should be valid for each calculated flux, otherwise the flux should be rejected (ΔC_{oi} is the difference between C_{out} and the average of two C_{in} which before and after taking C_{out}, while ΔC_{ii} is the difference between above two C_{in}). The concern about influencing plant physiology restricts the deployment of small DFCs to short term field

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measurements over the same vegetated plot. Given the small footprint and that Hg^0 fluxes over terrestrial surfaces are profoundly variable in space and time, replication DFC measurements are thus preferred but often not carried out.

2.2 Micrometeorological methods

MM methods differ in measurement principles and spatial scale of flux footprint compared to DFCs and have the capability of measuring ecosystem-scale (typically hectare scale) flux under undisturbed conditions and represent a preferred flux quantification techniques over vegetated landscapes. MM techniques for background Hg^0 flux measurements currently comprises of relaxed eddy accumulation method (REA), aerodynamic gradient method (AGM), and modified Bowen-ratio method (MBR). The preferred MM technique, eddy covariance (EC), a direct flux measurement method without any applications of empirical constants, requires a fast response (~10 Hz) gas analyzer, and has not been realized for regular Hg^0 flux measurements (Aubinet et al., 2012). Recently, Pierce et al. (2015) reported the first field trial of CRDS-EC flux measurement over Hg enriched soils with a minimum flux detection limit of 32 ng m^{-2} h^{-1}, insufficient for Hg^0 flux measurement at most, if not all, background sites. Sommar et al. (2013a) and Zhu et al. (2015b) detailed the theory, computation, and existing MM approaches for measuring Hg^0 fluxes. Gradient methods rely on quantifying the vertical concentration gradient (two or more heights sampling), turbulent parameters (AGM) or scalar concentration gradient (MBR), and scalar EC-fluxes. A major advantage of REA method is that REA up- and down-draft sampling conducted at one height, which overcomes the uncertainties associated with: (1) footprint differences due to two heights sampling in gradient methods, and (2) possible oxidation/reduction introduced forming or loss of Hg^0 between the two heights. On the other hand, the analytical requirement for REA is more stringent than for the gradient methods, especially under windy conditions, increasing the demand on the precision of the sampling and chemical analysis (Zhu et al., 2015a).

REA method has been deployed for flux measurement for agricultural lands, forest canopies, wetlands, and urban settings (Cobos et al., 2002; Olofsson et al., 2005; Bash and Miller, 2009; Osterwalder et al., 2015; Sommar et al., 2013b). AGM method has been used over grasslands, agricultural lands, saltmarsh, landfills, and snow (Lee et al., 2000; Kim et al., 2001; Kim et al., 2003; Cobbett et al., 2007; Cobbett and Van Heyst, 2007;

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Fritsche et al., 2008c; Fritsche et al., 2008b; Baya and Van Heyst, 2010). MBR method has been set up in grasslands, forest floor, agricultural lands, lakes, wetlands, and snow (Lindberg et al., 1992; Lindberg et al., 1995b; Lindberg et al., 1998; Lindberg and Meyers, 2001; Lindberg et al., 2002b; Brooks et al., 2006; Fritsche et al., 2008b; Converse et al., 2010). The theoretical and application requirement of micrometeorology is less restricted for large areas of uniform vegetation (or soil) in flat landscapes, where an atmospheric surface layer develops and the horizontal flux variability is low in the absence of pollution plumes and the flux above the surface remains constant with height (Wesely and Hicks, 2000). Under these turbulent exchange conditions, the flux acquired at the measurement height resembles the actual flux at the surfaces under measurement. There are several potential causes that can invalidate the above assumptions. For instance, the advection of Hg^0 from the nearby sources to the measurement site may occur. It is known that local point sources of Hg^0 can affect MM measurements downwind (Bash and Miller, 2007). Loubet et al. (2009) estimated such advection errors in NH_3 gradient flux to result in 2.1% to 52% of vertical flux at a monitoring site at 810m downwind of NH_3 source (a farm building) implying a significant error contribution from advection. Large variation of Hg^0 fluxes measured by MBR methods were also reported at nighttime as a result of advection in Nevada STORM project, however, the error have not been quantified (Gustin et al., 1999). For Hg^0 flux over forest canopies, the influence of within-canopy source and sink terms on net ecosystem flux has not been evaluated. A multiple heights gradients/REA measurements is needed to resolve the true flux. Since there is not a reliable sensitive Hg^0 sensor at high measurement frequency, an empirical multiplication factor or proxy scalar is required for computing all MM-Hg^0 flux (e.g., relaxation coefficient β derived from a selected proxy scalar for REA, eddy diffusivity K_H derived from sensible heat for AGM, and proxy scalar such as sensible heat, CO_2, and H_2O flux for MBR) (Lindberg et al., 1995a; Edwards et al., 2005; Baya and Van Heyst, 2010; Zhu et al., 2015b). These empirical factors may introduce uncertainties when the proxy scalar value is small, which frequently occur during dawn and dusk and under the condition of low atmospheric turbulence. Proxy scalar inferred relaxation coefficient (β_{CO_2}, β_{T_s}, β_{H_2O}) is typically not significantly different (~0.56) during a campaign above wheat agricultural land, while all β values were highly variable when the corresponding scalar flux was close to zero (Gronholm et al., 2008; Sommar et al., 2013b). Converse et al. (2010) reported Hg^0 flux over a wetland meadow using

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collocated AGM and MBR methods for four campaigns during an entire year. They found comparable fluxes in summer, while source/sink characteristics reversed between the two methods in fall and winter. Zhu et al. (2015b) found that AGM and MBR observed similar Hg^0 fluxes when absolute sensible heat flux was >20 W m^{-2}; and the agreement is not satisfactory when the absolute sensible heat flux was <20 W m^{-2}. Rejecting flux data collected under low turbulence conditions can bias the integrated flux over time (Mauder and Foken, 2004); and adequate data rejection and correction approaches need to be developed (Aubinet et al., 2012).

2.3 Comparability of flux measured by micrometeorological and chamber methods

Limited efforts have been devoted to understand the flux disparity caused by different flux measurement techniques. The Nevada STORMS project was the first attempt using eleven collocated measurements (7 DFC methods and 4 gradient-based MM methods) to simultaneously quantify Hg^0 flux from Hg-enriched bare soils in September 1997 (Gustin et al., 1999; Lindberg et al., 1999; Poissant et al., 1999; Wallschläger et al., 1999). In the campaign, the mean fluxes obtained using MM methods were three times greater than those obtained by DFCs (Fig. 2a). One possible reason for the low observed flux by DFC was the small flushing flow rates (corresponding TOT: 1.1-24 min) that were not sufficient to eliminate the accumulated Hg^0 in the DFC and subsequently suppressed Hg^0 evasion. Later, Gustin and coworkers extended the study at the same site using a 1-L polycarbonate DFC (TOT: 0.2 min) (Engle et al., 2001) and a MBR method (Gustin et al., 1999) in October 1998 (Gustin, 2011). Although MBR show substantial flux variability, DFC and MM fluxes were not significantly different (p>0.05) for dry and wet diel flux cycles (Fig. 2b). Two challenges in comparing MM and DFCs fluxes in these studies were the site heterogeneity (1.2-14.6 μg Hg g^{-1} in soil) and the footprint differences. The footprint of MM methods was estimated to be 40-70 m upwind the sampling sites (50-200 m^2) while DFC covered only 0.12-0.3 m^2 (Gustin et al., 1999). Recently, an integrated field Hg^0 flux methods intercomparison project measured Hg^0 flux from a background homogenized agricultural field (~45 ng Hg g^{-1}) using REA, AGM, MBR, a polycarbonate NDFC (TOT: 0.47 min), and a traditional quartz DFC (TDFC, TOT: 0.32 min) (Fu et al., 2008a; Zhu et al., 2015a, b). Overall, MM fluxes showed highly dynamic temporal variability while DFCs followed a gradual diel cycle similar to those temperature and solar irradiance. REA observed a broader flux distribution similar to NH_3 and CH_4 fluxes observed by MM techniques (Beverland et al., 1996; Moncrieff et al.,

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253 1998; Nemitz et al., 2001). The median fluxes obtained by REA, AGM, and MBR were not significantly
254 different (Friedman two-way analysis, $\chi^2 = 1.29 < \chi^2_{p=0.05} = 5.99$). Over a three-week period, NDFC obtained a
255 comparable mean flux with AGM and MBR which are approximately three times of the TDFC flux, implying
256 that NDFC potentially reduced uncertainty using real atmospheric boundary shear condition to rescale (Lin et al.,
257 2012). However, the correlation between NDFC/TDFC and MBR flux are weak because of high variability of
258 MM flux (Fig. 2c). Pierce et al. (2015) observed comparable mean flux from simultaneous measurement using
259 CRDS-EC, MBR, and DFC (849 ng m^{-2} h^{-1}, 1309 ng m^{-2} h^{-1}, and 1105 ng m^{-2} h^{-1}, respectively) over Hg-enriched
260 soils, similar flux patterns were recorded from CRDS-EC and MBR.

261 Fig. 3 showed the comparisons of Hg^0 fluxes measured by MM methods and DFCs from relative
262 homogeneous landscapes reported in the literature (cf. Section 4, substrate total Hg < 0.3 μg Hg g^{-1}). MM
263 methods yield a broader Hg^0 flux range compared to DFCs methods, consistent with the field campaigns using
264 collocated measurements (Zhu et al., 2015b). MM mean flux is higher than DFCs flux by a factor of two
265 approximately, which may be a result by the fact that a large fraction of DFC measurements utilized a relative
266 low TOT underestimating surface flux. However, Mann-Whitney *U* test indicated that the differences between
267 the two methods are not significant (p=0.16, one-tailed). Probability of the two data sets showed positive
268 skewness (4.2 and 3.9 for MM and DFCs, respectively) and kurtosis (19.6 and 27.2) caused by those high flux
269 observations, likely resulting from asymmetrical data distribution as well as the differences in measurement site
270 and periods. The flux data of MM methods in Fig. 3 were mostly obtained from agricultural fields (33%) and
271 grasslands (36%) while the data of DFC methods were mainly from background sites (68%); and MM
272 measurement generally covered a longer period (weeks to year) compared DFC measurements lasted a much
273 shorter period (hours, days to a few weeks). Typically, significant Hg^0 evasion is observed during daytime, while
274 deposition, bi-directional exchange, or mild emission occurs at nighttime (cf. Section 4). Agnan et al. (2015)
275 summarized MM and DFC fluxes observed in laboratory and during field campaigns over terrestrial substrates,
276 and found that observed the median MM flux (-0.01 ng m^{-2} h^{-1}, n=51) was statistically smaller than the median
277 DFC flux (0.5 ng m^{-2} h^{-1} and 1.75 ng m^{-2} h^{-1} for flushing flow rate ≤ 2 L min^{-1} and > 2 L min^{-1}, $p < 0.05$). They
278 suggest elevated flushing flow rate generated partial vacuum inside DFC created artificial Hg^0 flux from soil
279 even at <2 L min^{-1}, although this is not supported by the large Hg^0 concentration gradient (inside and outside

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DFC) formed at low flushing flow rate (Zhang et al., 2002; Eckley et al., 2010). An alternative explanation is that MM measurements were predominantly deployed for background vegetated surfaces while DFC were mainly applied for soil surfaces, the difference in the source/sink characteristics over vegetation and bare soils may cause the difference in median fluxes.

3. Factors influencing air-surface Hg^0 exchange

3.1 Air-soil Hg exchange

Meteorological parameters (solar radiation, soil/air temperature, atmospheric turbulence), soil substrate characteristics (e.g. Hg content, soil moisture, organic matters, porosity, and microbial activity), and ambient air characteristics (e.g. Hg^0 and O_3 concentration) can influence the air-surface exchange of Hg^0. Changes of these factors force two controlling processes: (1) formation of evaporable Hg^0, and (2) mass transfer of Hg^0. Solar radiation has been found highly positively correlated with soil Hg^0 flux (Carpi and Lindberg, 1997; Boudala et al., 2000; Zhang et al., 2001; Gustin et al., 2002; Poissant et al., 2004a; Bahlmann et al., 2006), which is generally regarded as enhancing Hg^{II} reduction and therefore facilitating Hg^0 evasion (Gustin et al., 2002). Actinic light spectral analysis suggested UV-B can reduce Hg^{II} to Hg^0 over soil, while UV-A and visible light have a much lower enhancement (Moore and Carpi, 2005; Choi and Holsen, 2009b). Temperature is an important factor that promotes Hg^0 evasion, typically described by Arrhenius equation (Carpi and Lindberg, 1997; Poissant and Casimir, 1998; Gustin et al., 2002). However, Arrhenius relationship cannot explain Hg^0 flux spikes at sub-zero temperatures, implying other mechanisms such as the expansion and contraction of liquid fraction in soil substrates occurred (Corbett-Hains et al., 2012). Atmospheric turbulence (i.e. wind, surface friction velocity) is another factor in driving the Hg^0 release from soil (Lindberg et al., 1999; Wallschläger et al., 1999). Increased turbulence enhances Hg^0 mass transfer and promotes Hg^0 desorption from soil (Gustin et al., 1997; Lindberg et al., 2002c; Zhang et al., 2002; Eckley et al., 2010; Lin et al., 2012).

Soil types, soil moisture and Hg content in soil are also important factors influencing observed Hg^0 flux (Xu et al., 1999; Kocman and Horvat, 2010; Lin et al., 2010a). Lindberg et al. (1999) observed that rainfall and irrigation enhances soil Hg^0 emission by an order of magnitude. Subsequent studies supported that adding water to dry soil promotes Hg reduction and that water molecular likely replaces soil Hg^0 binding sites and facilitates

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307 Hg^0 emission. In saturated soil, Hg emission is suppressed because the soil pore space is filled with water, which
308 hampers Hg mass transfer (Gillis and Miller, 2000b; Gustin and Stamenkovic, 2005). Pannu et al. (2014)
309 investigated Hg^0 flux over boreal soil by manipulating soil moisture, maximum flux was observed at 60% soil
310 moisture (water filled pore space), whereas flux become inhibited at 80%. Repeated rewetting experiments
311 showed smaller increase in emission, implying "volatizable" Hg^0 needs to be resupplied by means of reduction
312 and dry deposition after a wetting event (Gustin and Stamenkovic, 2005; Song and Van Heyst, 2005; Eckley et al.,
313 2011b). Soil organic matter (SOM) have a strong affinity with Hg^0 and form stable complexes with Hg^{II} (Grigal,
314 2003; Skyllberg et al., 2006), and therefore diminish soil Hg^0 efflux (Yang et al., 2007). Mauclair et al. (2008)
315 measured Hg^0 flux from sand (0.5 μg Hg g^{-1}) spiked with humic substances; and found that Hg^0 flux decreased
316 sharply by incremental addition of up to 0.1% of humic matter. Higher soil porosity has also been suggested to
317 facilitate Hg^{II} reduction and Hg^0 transfer from soil (Fu et al., 2012a). Microbial induced reduction can enhance
318 Hg^0 evasion but to a less extent (Fritsche et al., 2008a; Choi and Holsen, 2009b). Higher flux has also been
319 observed by increasing soil pH value (Yang et al., 2007).

320 Elevated ambient Hg^0 concentration has been found to suppress Hg^0 flux by reducing Hg^0 concentration
321 gradient at the interfacial surfaces (Xin and Gustin, 2007). At locations where ambient Hg concentration is high
322 (e.g., mining sites, landfills), deposition is predominately observed despite of the influence of meteorological
323 factors (Bash and Miller, 2007; Wang et al., 2007b; Zhu et al., 2013c). Atmospheric O_3 was found to induce
324 not-yet-understood chemical processes that enhance Hg^0 emission from soil in the dark (Zhang et al., 2008).
325 Laboratory experiments showed that Hg^0 flux from soils with Hg^{II} as the dominant species can be enhanced by
326 1.7 to 51 times in the presence of O_3 (50-70 ppb), and be decreased by >75% over Hg^0-amended soils (Engle et
327 al., 2005). Environmental factors interacts naturally (e.g., irradiation and temperature), which can impose
328 synergistic and antagonistic effects on forcing Hg^0 flux changes (Gustin and Stamenkovic, 2005). Fig. 4 shows
329 the individual effects and synergism between solar radiation, air temperature, and water content on Hg^0 flux from
330 a typical low organic content soil (~1.5 wt %) (Lin et al., 2010a). All three individual factors enhance flux by
331 90%-140%, while two-factor synergetic effect accounts for 20%-30% enhancement.
332

333 **3.2 Air-vegetation Hg^0 exchange**

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Vegetation alters air-ecosystem Hg^0 flux through (1) changing environmental variables at ground surfaces (e.g., reducing solar radiation, temperature, and friction velocity) (Gustin et al., 2004), and (2) provide active surface for Hg uptake. Carpi et al. (2014) reported forest floor soil fluxes of -0.73±1.84 and 0.33±0.09 ng m^{-2} h^{-1} from intact New England and Amazon forest floors, respectively. Substantial emission fluxes at 9.13±2.08, 21.2±0.35 ng m^{-2} h^{-1} were observed after deforestation suggested forest coverage effectively reduced ground floor Hg^0 emission. More importantly, air-plant interaction increases the complexity of air-terrestrial Hg exchanges; and the role of vegetation as a source or a sink of atmospheric Hg has been in debates in the literature. Lindberg et al. (1998) observed a significant Hg^0 emission from forest canopies in Tennessee and Sweden (10-300 and 1-4 ng m^{-2} h^{-1}); estimated annual Hg^0 emission from global forest to be 800-2000 tons; and emphasized the need for a re-assessment on this potentially important source. Based on the observed Hg presence in xylem sap (Bishop et al., 1998), plant has been hypothesized as a conduit for releasing geospheric Hg to the atmosphere (Leonard et al., 1998a, b). Subsequent models simply treated plant emission as a function of evapotranspiration rate (Xu et al., 1999; Bash et al., 2004; Gbor et al., 2006; Shetty et al., 2008). However, recent measurement suggested that air-surface exchange of Hg^0 is largely bidirectional between air and plant and that growing plants act as a net sink (Ericksen et al., 2003; Stamenkovic et al., 2008; Hartman et al., 2009). Stable Hg isotope tracer studies have shown that Hg in soils cannot be translocated from roots to leaf due to the transport barrier at the root zone (Rutter et al., 2011b; Cui et al., 2014), suggesting that the source of Hg in leaf is of atmospheric origin.

Hg concentration in foliage is generally influenced by the level of air Hg^0 present in air Hg^0 (Ericksen et al., 2003; Frescholtz et al., 2003; Ericksen and Gustin, 2004; Millhollen et al., 2006a; Fay and Gustin, 2007a; Niu et al., 2011). Climate factors (e.g., solar irradiation, temperature), biological factors (e.g., leaf age, plant species), and ambient air components (e.g., CO_2) also significantly influence on foliar Hg^0 flux (Rea et al., 2002; Millhollen et al., 2006a; Millhollen et al., 2006b; Fay and Gustin, 2007a; Bushey et al., 2008; Stamenkovic and Gustin, 2009; Rutter et al., 2011a). For instance, higher Hg concentration found at the bottom aged leaf suggest the influence of longer exposure time (Bushey et al., 2008) over an immediate source from soil (Frescholtz et al., 2003). Stomatal and non-stomatal (e.g., cuticle) processes are both viable pathways for bidirectional Hg exchange (Stamenkovic and Gustin, 2009). Stomatal process may play a predominant role as Hg accumulated on

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361 cuticle surface was generally <10% of total Hg content in leaf (Rutter et al., 2011a; Laacouri et al., 2013). Solar
362 radiation, temperature, and CO_2 concentrations regulating plant stomatal activity may therefore affect Hg uptake
363 and gas exchange. For instance, high air-vegetation Hg^0 flux observed during daytime show deposition, opposite
364 to daytime evasion observed over other terrestrial surfaces (cf. Section 4.3) (Stamenkovic et al., 2008). In
365 addition, Hg in leaf has been shown to be assimilated into leaf biomass during the growing stage (Bash and
366 Miller, 2009), suggesting Hg uptake occurs with plant assimilation metabolism.

367 It has been proposed that Hg in leaf can be classified as two forms: (1) exchangeable Hg which can be
368 re-emitted back to the atmosphere, and (2) biological assimilated Hg retained in leaf (Rutter et al., 2011a).
369 However, whether or not Hg^0 can be oxidized after uptake into tissue, and the possibility of assimilated Hg being
370 reemitted from leaf (e.g., reduction of leaf retained Hg^{II} or un-oxidized Hg^0 originally from ambient air) remain
371 unclear. Many studies observed a so-called "compensation point" denoting the interfacial concentration of Hg
372 that drive the concentration gradient for bi-directional air-vegetation exchange of Hg^0 (Hanson et al., 1995;
373 Poissant et al., 2008; Bash and Miller, 2009). However, the hypothesis of compensation point does not explain
374 the accumulation of Hg in vegetation pool. Recent Hg isotopic fractionation studies show promise for exploring
375 air-leaf Hg exchange mechanism. Demers et al. (2013) reported a kinetic mass dependent fractionation (MDF,
376 δ^{202}Hg) of -2.89‰ during air-leaf Hg exchange from air to leaf. The result indicated that uptake of atmospheric
377 Hg by leaf occurs, and the deposited Hg is likely to be chemically bonded in leaf with sulfur and nitrogen
378 functional groups in enzymes within stomatal cavities (Rutter et al., 2011a), rather than with carboxylic ligands
379 on leaf surface. Another important finding is the negative mass independent fractionation (MIF, Δ^{199}Hg) of Hg of
380 -0.19‰ to -0.29‰, correlated well with Hg^{II} photochemical reduction by low molecular mass organic matter
381 with sulfur-containing ligands (Zheng and Hintelmann, 2010). This implies that the Hg reemission may result
382 from revolatilization of chemical bounded Hg in leaf. However, they did not rule out the potential influence of
383 PBM and GOM that deposit on the leaf, which may undergo partial uptake by plant with the remaining being
384 reemitted back to the atmosphere.
385
386 **3.3 Air-water Hg exchange**
387 Bulk method, DFC and MM methods have been utilized in air-water Hg^0 flux measurement. Bulk methods

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388 is the most widely utilized approach for oceanic surface (>80% of the field data, Table 1). Sommar et al. (2013a)
389 summarized the methodologies of the bulk method, which generally controlled by both kinetic (overall mass
390 transfer coefficient, *k*) and thermodynamic (partial pressure related concentration gradients) forcing
391 (Wanninkhof, 1992; Wanninkhof et al., 2009; Kuss et al., 2009; Kuss, 2014):

392 $$F = k \times \left(DGM - GEM/H_T^{'} \right) = 0.31 \times U_{10}^2 \times \left(\frac{v}{600 \times D_{Hg^0}} \right)^{-0.5} \times \left(DGM - GEM/H_T^{'} \right) \quad (3)$$

393 where DGM is dissolved gaseous Hg concentration in the surface water film, GEM is near surface gas Hg^0
394 concentration, $H_T^{'}$ is dimensions Henry's law constant, U_{10} is wind speed at 10m, v is the water kinematic
395 viscosity, and D_{Hg^0} is Hg^0 diffusion coefficient in water. Fig. 5 shows air-surface exchange processes and
396 transformation of DGM in water phase. From a kinetic point of view, the overall mass transfer coefficient of Hg^0
397 is described by a molecular diffusivity in the water and gas film. Since the mass transfer boundary layer of water
398 has much higher resistance than the gaseous layer for sparingly soluble Hg^0, the overall mass transfer coefficient
399 is limited by water transfer velocity (Eq. 5) (Kim and Fitzgerald, 1986). Surface wind speed is an important
400 driving force enhancing the mass transfer coefficient in water (Qureshi et al., 2011b), D_{Hg^0} has been
401 experimentally determined as a function of temperature (*T*, Kelvin) for freshwater ($D_{Hg^0}^{fresh} = 0.0335e^{-18.63/RT}$, *R*
402 represents gas constant) and seawater ($D_{Hg^0}^{sea} = 0.0011e^{-11.06/RT}$) (Kuss, 2014).

403 Processes controlled the concentration of DGM in surface water directly regulated air-water Hg^0 flux.
404 Photochemically induced Hg^{II} reduction is the predominant pathway of DGM formation in surface water (Amyot
405 et al., 1994; Amyot et al., 1997a; Amyot et al., 1997b; Costa and Liss, 1999; Lalonde et al., 2001; Zhang and
406 Lindberg, 2001; Feng et al., 2004). Zhang (2006) summarized Hg photochemical redox chemical process. Eq. (6)
407 resembling a simplified scheme of gross photo-reactions governing the DGM pool in surface waters (O'Driscoll
408 et al., 2006; O'Driscoll et al., 2008; Qureshi et al., 2010):

409 $$Hg_{reducible} + photoreductants \rightleftharpoons DGM + photooxidants \quad (4)$$

410 Fe^{III} has been reported to enhance sunlit photo-reduction in natural water (Lin and Pehkonen, 1997; Zhang and

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411 Lindberg, 2001). Complexes of Fe^{III}-natural organic ligands was hypothesized to undergo photolysis to form
412 reactive intermediates (e.g., organic free radicals) capable of reducing Hg^{II}. Dissolved organic matter (DOM)
413 serving as electron donor and complexation agent in the natural water is the most important precursor for
414 formation of photo-reductants (Ravichandran, 2004; Vost et al., 2011; Zhang et al., 2011). Similarly, irradiation
415 derived photo-oxidant may oxidize DGM simultaneously and reduce Hg evasion from water. Reactive radicals
416 (e.g., $\cdot O_2$, $\cdot OH$) produced through DOM, NO_3^- photolysis have been identified as possible oxidants (Lin and
417 Pehkonen, 1997; Zhang and Lindberg, 2001; Zhang et al., 2012b). In addition, Cl^- was reported to enhance
418 photo-oxidation by stabilizing the oxidative products ($HgCl_n^{2-n}$) and facilitating oxidation via formation of
419 highly oxidizing ligand ($Cl_2^{\cdot}$) (Yamamoto, 1996; Lalonde et al., 2001; Sun et al., 2014). Secondary radicals (e.g.,
420 $CO_3^{\cdot -}$) can sometimes act as a photo-oxidant (He et al., 2014). Field studies also observed DGM and Hg^0 flux
421 peaks in the nighttime, suggesting the importance of dark reduction (O'Driscoll et al., 2003; Zhang et al., 2006b;
422 Fu et al., 2013b). Dark abiotic redox transformation is the most important pathway (Fig. 5). Although dark
423 abiotic reduction takes place mainly in the anoxic environment (Gu et al., 2011; Zheng et al., 2012), it also occurs
424 in the oxic condition at a lower reaction rate (Allard and Arsenie, 1991). Natural organic matter shows reducing,
425 oxidizing, and complexing properties with Hg in the anoxic environment due to its diversity functional groups
426 (e.g., thiols group, quinones and non-quinoid structures, carboxyl group) (Gu et al., 2011; Zheng et al., 2012;
427 Zheng et al., 2013). Although aqueous liquid Hg droplet can be rapidly oxidized in oxygenated chloric water,
428 DGM is unable to be oxidized under such conditions (Amyot et al., 2005).

429 Biological redox transformation is another important DGM cycling pathway. Ariya et al. (2015) reviewed
430 the biological processes in Hg redox transformation, which contains phototrophic and chemotrophic Hg redox
431 processes. Aquatic algae, cyanobacteria, and diatoms involved phototrophic Hg reduction was positively
432 correlated with photosynthetic activities, which is likely a bio-detoxification process (Ben-Bassat and Mayer,
433 1975; Kuss et al., 2015). In addition, photo-reactivation of DOM and Fe^{III} facilitates Hg^{II} reduction through algae
434 (Deng et al., 2009). Kuss et al. (2015) reported that cyanobacteria-light synergetic and photochemical
435 transformation equally contributed to ~30% DGM production in Baltic Sea, while low-light production
436 contributed ~40%, highlighting the importance of biotic reduction. Two pathways have been identified for Hg^{II}

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reduction by bacteria. The first is reduction by Hg-resistant microorganisms where Hg^{II} is reduced in cell's cytoplasm by mercuric reductase and transported out as Hg^0 (Barkay et al., 2003); the other is Hg^{II} reduced by Hg-sensitive dissimilatory metal-reducing bacteria utilizing iron and/or manganese as terminal electron acceptor during respiration (Wiatrowski et al., 2006). Intracellular oxidation was supposed to be mediated by oxidase (Siciliano et al., 2002), while extracellular thiol functional groups on cell membrane also shows capability to oxidize Hg^0 under anoxic environment (Colombo et al., 2013; Hu et al., 2013). A review of genetic-based microbial Hg redox transformation can be found in Lin et al. (2011).

3.4 Air-snow Hg exchange

Schroeder et al. (1998) reported episodes of unexpected low Hg^0 concentrations in the Arctic air during spring time, so-called atmospheric mercury depletion events (AMDEs), through an arrays of photochemically initiated oxidation by halogens (Lindberg et al., 2002a; Sommar et al., 2007; Moore et al., 2014). The phenomena was finally confirmed widespread in the coastal Polar Regions. During AMDEs, a large amount of surface layer Hg^0 is oxidized and deposited in snowpack via GOM and PBM dry deposition (Steffen et al., 2008). The deposited Hg onto snow can be rapidly re-volatilized back to the atmosphere via photochemical Hg^{II} reduction on snow or in melted snow (Dommergue et al., 2003; Faïn et al., 2007; Kirk et al., 2006). Photo-reduction is the predominant pathway for Hg reemission from snow as inferred by Hg isotope fractionation signatures (Sherman et al., 2010). The reduction rate was found to be linearly correlated with UV intensity (Lalonde et al., 2002; Mann et al., 2015b), while Cl^- showed an inhibiting effect on the photo-reduction (Section 3.3) (Steffen et al., 2013). Oxidation and reemission of Hg^0 occurred simultaneously with the presence of oxidants (e.g., $\cdot OH$, Cl, and Br) formed through photolysis (Poulain et al., 2004). Nighttime elevated GEM in snow air was observed at Station Nord, Greenland, likely a result from dark formation of reducing radicals (e.g., $HO_2\cdot$) (Ferrari et al., 2004). Temperature is another factor enhancing Hg emission from snow by changing the solid and liquid water ratio (Mann et al., 2015a). Hg^0 flux from snow surface in the temperate regions has rarely been investigated (Faïn et al., 2007). Field data collected in Ontario and Northern New York confirmed that photo-reduction is the predominant pathway in enhancing Hg^0 emission (Lalonde et al., 2003; Maxwell et al., 2013). A positive correlation between Hg^0 fluxes and temperature has also been found (Maxwell et al., 2013).

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Hg^0 flux over snow cover under forest canopy was found to be smaller compared to those found in open field, possibly caused by lower light under canopy (Poulain et al., 2007).

4. Global observation of atmosphere-biosphere Hg exchange

4.1 Data sources, extraction and processing

A comprehensive database of global observation of Hg^0 flux over terrestrial and oceanic surfaces is compiled from the field observed data reported in peer-reviewed literatures; and the fluxes over water surfaces calculated using two-film gas exchange model based on *in-situ* measured DGM are also included. For those studies that measured TGM (Hg^0 + GOM) got flux calculation, the measured flux is regarded as Hg^0 flux because of the small fraction of GOM in TGM measurement (GOM/GEM < 2% in general, Gustin and Jaffe, 2010, Sprovieri et al., 2010; Fu et al., 2015), therefore Hg^0 and TGM are not discriminable for Hg vapor analyzer during a typical concentration measurement period (5 mins sampling, 1.0-1.5 L min^{-1}) in flux sampling. As complete time-series flux datasets are not available in literature, each data point included in the database corresponds to the arithmetic mean of the flux observed during each campaign, with the campaign period lasting up to one year. For those studies periodically (e.g. weekly) measured seasonal flux at the same site, the average fluxes of all campaigns was used. A summary of Hg^0 flux data documented in a total of 172 peer reviewed articles are presented in Table 1, which were obtained using DFCs (85.6%), MM (7.9%), $Hg^0/^{222}Rn$ flux ratio (0.3%), and enriched isotope tracers (0.1%), or estimated using two-film gas exchange model (6.1%). Based on the landscapes characteristics and surface Hg contents, the flux datasets are assigned into 11 categories. Classification of background soils (e.g., open field bare soil and forest ground soils with little perturbation by human activities) follows the corresponding literature definition. Soil Hg content of ≤ 0.3 μg g^{-1} was applied as the threshold for background soil in case no classification was assigned in the original article. Hg contaminated sites are divided into natural enriched and anthropogenic contaminated sites based on the Hg sources. The remaining flux data were categorized into 9 classes according to the land uses and ecosystem types (Table 1). It is important to recognize that the Hg^0 fluxes represent the experimental and modeling results using diverse methodologies with campaign periods of different durations. Given the reasonably large flux sample sizes, the flux statistics (e.g., mean, median) from multiple studies for different landscapes are compared. It should be

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491 noted that flux reported in laboratory controlled and field manipulated experimental studies utilizing
492 treated/untreated substrates are *not* included in the database. Instead, the implications of those studies are
493 discussed in terms of the environmental effects of Hg^0 exchange mechanisms (cf. Section 3).
494
495 **4.2 Global database of earth surfaces-atmosphere Hg^0 flux**
496 Table 1 summarizes the statistics of Hg^0 fluxes measured to date. The site characteristics where Hg^0 flux
497 measurements were performed are highly diverse. Most studies were devoted to flux investigation over natural
498 Hg-enriched sites (~38.2%) and background surfaces (~18.4%). Direct field measurements over terrestrial
499 surfaces accounts for 94.1% (n=811) of the data, only 5.9% (n=51) of the data represents oceanic fluxes. In terms
500 of substrate Hg contents, measurements at contaminated sites (natural Hg-enriched and anthropogenic polluted)
501 consisted of 44.9% of the datasets, motivated by extensive emission at these sites caused by local and regional
502 atmospheric pollution. For unpolluted terrestrial surfaces, most measurements were carried out over background
503 soils (37%, n=159), while only a few studies directed to the forest foliage and above canopy flux (n=8). DFC
504 methods are suitable for bare soil and low vegetated surface, covering 97% of the data over background soils.
505 The remaining datasets are observations of ecosystem flux using MM methods, which require relatively more
506 complex instrumentation and experimental efforts in the field (Gustin, 2011; Aubinet et al., 2012; Sommar et al.,
507 2013a).
508 Fig. 6 shows the box and whisker plots of Hg^0 fluxes. As seen, the categorized data exhibit substantial data
509 variability and positive skewness. Many campaigns focus only on daytime flux (cf. Section 4.3.2) and therefore
510 the median of mean flux in each category is a more appropriate statistics for comparison. The medians of Hg^0
511 fluxes for the 11 site categories follow the order: grasslands < forest foliage & canopy level < background soils <
512 wetlands < seawater < snow < freshwater < urban settings < agricultural fields < anthropogenically contaminated
513 surfaces < natural Hg-enriched surfaces (Table 1). A clear increase in flux from background to contaminated
514 sites suggests the strong influence of substrate Hg contents on Hg^0 flux. Median fluxes from contaminated sites
515 are two orders of magnitude greater than those over other surfaces; such source strength significantly enhances
516 local and regional atmospheric Hg concentration. Fluxes over vegetative surfaces (grasslands, forest foliage and
517 canopy level), mixed vegetated waters (wetlands) are lower than those over background soils and open water

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(freshwater and seawater), supporting that vegetation reduces Hg emission by masking ground floor evasion and/or plant uptake. The fluxes at human perturbed urban settings and over agricultural fields were higher than the flux over undisturbed earth surfaces, likely a result of reemission of legacy Hg deposition. Most surfaces showed net Hg^0 emission; approximately 25% of measurements over vegetated surfaces showed net Hg deposition (Fig. 6).

Results of frequency analysis of the mean Hg^0 fluxes for each land cover are presented in Fig. 7. While the mean Hg^0 flux from background soils have a large range (-51.7 – 33.3 ng m^{-2} h^{-1}), ~90% of the flux data ranges from -5 to 10 ng m^{-2} h^{-1}. Similar patterns are also evident for freshwater, oceans, grasslands, and wetlands. The occasional high emission and deposition fluxes are mainly due to short sampling duration (e.g. mid-day flux) or extreme atmospheric Hg^0 concentration events caused by local/regional sources. Comparatively, fluxes over agricultural fields and in urban settings show a much larger range and a lower kurtosis. Strong Hg^0 evasion was observed at contaminated sites (>97% of total observations showed evasion), although extremely high deposition also occurred in the presence of high ambient Hg^0 and atmospheric subsidence (Bash and Miller, 2007; Zhu et al., 2013c). Most measurements over snow (87%) show evasions; these studies were carried out in the Polar Regions and focused on Hg reemission from snow after AMDEs. The distribution of Hg^0 fluxes of air-foliage and canopy level exchange showed that half of the measurements (n=4) gave a net emission, while the mean flux is not significantly different from zero (p=0.24, ANOVA).

4.3 Spatial distribution and temporal variation of global Hg^0 flux data

4.3.1 Spatial distribution

Fig. 8 shows the box and whisker plots of Hg^0 flux from four relatively homogenized surfaces (background soils, agricultural fields, grasslands, and freshwater) observed in different regions. Worldwide flux measurement was unevenly distributed, most studies were conducted in North American and East Asia, which limits global representativeness. Hg^0 flux observed in East Asia is consistently higher compared to those measured in Europe, North and South America, Australia, and South Africa ($p < 0.05$, ANOVA, except freshwater). This can be explained by the greater anthropogenic emission and re-emission of Hg deposition (Selin et al., 2007; Selin et al., 2008; Lin et al., 2010b; Smith-Downey et al., 2010). The flux over freshwater in Europe is somewhat higher than

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those measured in East Asia (6.5 vs. 4.6 ng m^{-2} h^{-1}, p=0.40, ANOVA). These data were obtained mostly prior to 2002 (n=9) or during summer time and daytime (n=8) (Schroeder et al., 1989; Xiao et al., 1991; Lindberg et al., 1995b; Gårdfeldt et al., 2001; Feng et al., 2002), which could have yielded higher fluxes.

4.3.2 Diurnal and seasonal patterns

Fig. 9 displays the general diel variation of Hg^0 flux measured by DFC and DFB methods. Fluxes were typically higher during daytime and lower at nighttime from soil, mine, water and snow surfaces, where Hg^0 can be formed through photo-reduction. As discussed in Section 3, the observed diel variations are in agreement with results from laboratory controlled studies: higher irradiance and temperature promoted Hg^0 reduction and evasion at daytime, which formed a "dome-shaped" diel flux pattern from most earth surfaces (e.g., soils, mine, water, and snow). On the contrary, greater deposition during daytime and evasion/near-zero-flux at nighttime have been frequently observed from foliage, possibly facilitated by the uptake through stomata that exhibit higher stomatal conductivity during daytime.

Seasonally, higher evasion flux occurs in warm season and smaller exchange is observed in cold season. For example, seasonal data from Choi and Holsen (2009a) showed a higher evasion from forest floor soil in Adirondack Mountain (New York, USA) in summer (1.46 ng m^{-2} h^{-1}) shifted to insignificant exchange in winter (0.19 ng m^{-2} h^{-1}). Similar trends were also found in agricultural soils, freshwater, and mine surfaces (Fu et al., 2010a; Eckley et al., 2011b; Zhu et al., 2011). Observed diurnal and seasonal patterns may also be influenced by vegetative surface changes and meteorological characteristics. For example, Sommar et al. (2015) reported seasonal flux observation over a wheat-corn rotation cropland using REA measurement, an unexpected low flux was observed in summer during corn growing stage (median: -6.1 ng m^{-2} h^{-1}) due to the uptake by corn leaf (leaf area index 2.7-3.6), which is similar to the flux (-6.7 ng m^{-2} h^{-1}) observed in winter and much lower than the wheat canopy flux (13.4 ng m^{-2} h^{-1}) in early spring. The limited availability of seasonal data in peer-reviewed literature does not allow a thorough assessment of seasonal characteristics of different terrestrial surfaces. It is important to recognize that the modified landscapes and vegetative biomass growing cycle caused by seasonal changes (e.g., change of LAI in deciduous forest, growing season of forest ecosystem, etc.) may significantly modify the flux characteristics. More data, especially measurements using consistent quantification techniques

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over a longer campaign period (e.g., 1 year or longer), are needed for addressing the seasonal variability of Hg^0 exchange flux and better estimating the annual exchange from vegetative surfaces. To accomplish such measurements, automation of flux quantification apparatus is also required.

4.4 Source and sink characteristics of natural surfaces in the context of global Hg budget

4.4.1 Background soils and water are important diffuse sources of Hg^0

Although Hg^0 flux observed over background soil (1.3 ng m^{-2} h^{-1}) and unpolluted water bodies (2.8 and 2.5 ng m^{-2} h^{-1} for fresh and seawater) may appear mild (Table 1), the annual emission from these two types surfaces accounted for 64% of total atmospheric Hg emission because of their large areal coverage globally (Pirrone et al., 2010). For example, it has been estimated that bare soil releases ~550 Mg yr^{-1} (Selin et al., 2008; Pirrone et al., 2010) and surface ocean releases 2000-2900 Mg yr^{-1} of Hg^0 globally (Fig. 1) (Mason et al., 2012; AMAP/UNEP, 2013). Constraining the uncertainties on Hg^0 emission from these diffuse sources will greatly improve the accuracy of global Hg budget. Global Hg^0 evasion from soil is mainly based on empirical relationship between flux, temperature and irradiation (cf., Section 5), which needs mechanistic refinement. Air-seawater exchange estimated by global models is subject to the uncertainty in (1) mechanisms of aqueous redox transformation and the associated kinetic parameters, and (2) Hg^0 mass transfer rates as determined by surface fiction velocity (Qureshi et al., 2011a). Kinetic parameters of these processes largely rely on limited field data without experimental verification (AMAP/UNEP, 2013) and require further investigation. Parameterization of Hg^0 flux using field data and redox transformation rate constants in soil and water are critical to reduce the uncertainty in future studies.

4.4.2 Contaminated surfaces are intensive local Hg^0 sources

Hg evasion from contaminated surfaces (Fig. 6 and Fig. 7) has been recognized as an important input contributing to regional atmospheric Hg budget (Ferrara et al., 1998b; Kotnik et al., 2005). Hg^0 flux from contaminated point sources have been extensively investigated by using LIDAR technique, which is by far the most effective experimental approach to spatially resolve the Hg^0 air-surface exchange at contaminated sites. Ferrara et al. (1998a) measured the spatial distribution TGM concentration and TGM flux from the world's

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largest Hg mine, Almadén Hg mine, in Spain. TGM concentration and flux were estimated to be 0.1 – 5 μg m^{-3}, 600 – 1200 g h^{-1} in fall, 1993, above the village of Almadén. Several attempts have been made to quantitatively estimate atmospheric Hg input in mining areas. Gustin et al. (2003) and Wang et al., (2005) applied a log-linear correlation between the flux and substrate Hg contents and solar irradiance. Eckley et al. (2011b) computed annual Hg emission from two active gold mines (up to 109 kg $year^{-1}$) using flux measurement of flux and statistically derived the empirical relationship between flux and meteorological variables based on Geographical Information System (GIS) data. Similarly, Kocman and Horvat (2011) obtained ~51 kg $year^{-1}$ emission from Idrijca River catchment, a former Hg mine, using field measurement and GIS data. In total, annual Hg emission from global contaminated surfaces was estimated to be ~82 Mg via modeling of flux from more than 3000 Hg contaminated sites comprising Hg mining, non-ferrous metal production, precious metal processing, and various polluted industrial sites (Kocman et al., 2013), which is emitted from a very limited surface areas thus can pose a strong environmental impact to the local area surrounding the contaminated sites.

4.4.3 Areas impacted by human activities exhibit elevated Hg^0 reemission

The median evasion flux over human urban settings and agricultural fields is 5-10 times higher than the value over background soils (Table 1). Direct anthropogenic Hg input and atmospheric Hg deposition explain the enhanced reemission. Natural surfaces nearby the anthropogenic point sources (e.g. power plant, Pb-Zn smelter, chlor-alkali plant) generally showed higher soil Hg content due to atmospheric Hg deposition (Lodenius and Tulisalo, 1984; Li et al., 2011; Zheng et al., 2011; Guédron et al., 2013). A fraction of these deposited Hg can be swiftly reemitted back to the atmosphere (Fu et al., 2012a; Eckley et al., 2015). Newly deposited Hg to soil, aquatic system and snow pack in the Polar Regions can also be readily converted to Hg^0 and reemitted (Amyot et al., 2004; Poulain et al., 2004; Ericksen et al., 2005). Eckley et al. (2015) observed soil Hg^0 flux near a large base-metal smelter (Flin Flon, Manitoba, Canada) and reported a net deposition during operation (-3.8 ng m^{-2} h^{-1}) and elevated emission (108 ng m^{-2} h^{-1}) after operation ceased. To date, the source and sink characteristics of surfaces impacted by human activities have not been adequately investigated. Future investigation should be coordinated toward spatially resolving the Hg^0 exchange over human impacted surfaces for better quantifying the emission budget of legacy Hg.

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627 *4.4.4 Flux over vegetated surfaces likely a sink but large uncertainties remains*

628 Data of Hg^0 flux over foliage and forest canopy showed a small net emission (median: 0.7 ng m^{-2} h^{-1}) with
629 substantial variability (Figs. 6 and 7). There have been conflicting reports regarding the role of forest ecosystems
630 as Hg source or sink at global scale (Lindqvist et al., 1991; Lindberg et al., 1998; Frescholtz and Gustin, 2004;
631 Fay and Gustin, 2007a; Fay and Gustin, 2007b; Hartman et al., 2009; Cui et al., 2014). Laboratory studies
632 suggested that plant is a net sink atmospheric Hg through leaf assimilation (Millhollen et al., 2006a;
633 Stamenkovic and Gustin, 2009; Rutter et al., 2011b; Cui et al., 2014). Using Hg concentration in plant tissues and
634 net primary productivity as a proxy for atmospheric Hg deposition, Obrist (2007) estimated plants remove
635 ~1024.2 Mg yr^{-1} Hg globally (foliage contributed 237.6 Mg/yr). Fu et al. (2015b) estimated that global litterfall
636 contributes to 1232 Mg yr^{-1} of Hg deposition, throughfall contributes to 1338 yr^{-1} of Hg deposition, and forest
637 floor evades ~381 Mg yr^{-1} of Hg into the atmosphere. Hg content in forest soil is comparatively higher than the
638 concentration found in bare soil due to the input via litterfall and wet Hg deposition (Blackwell and Driscoll,
639 2015a, b; Obrist et al., 2011); and ~90% boreal forest soil Hg was believed to be originated from litterfall input
640 (Jiskra et al., 2015). These studies suggested forest ecosystem is likely a large atmospheric Hg sink, although
641 these bulk proxy methods are not sufficiently sophisticated to resolve the global Hg mass balances.
642 Synchronized, long-term observation of air canopy flux and litterfall/throughfall deposition is useful to
643 understand the source and sink characteristics of forest.

644

645 **5. Modeling of air-surface Hg^0 exchange flux**

646 A summary of recent modeling efforts on estimating natural emission was presented in Table 2. For
647 air-foliage Hg^0 exchange, earlier parameterization (S1, Table 2) calculates the flux as a function of the
648 evapotranspiration rate based on soil-root-stem-foliage transpiration stream. It is assumed that Hg passed
649 through the soil-root interface and then is transferred into foliage in as complexes with organic ligands (Moreno
650 et al., 2005a; Moreno et al., 2005b; Wang et al., 2012). However, root uptake is unlikely to occur (Cui et al.,
651 2014). Hg isotopic signatures between air and foliage (Demers et al., 2013; Yin et al., 2013), and air-foliage flux
652 measurements (Graydon et al., 2006; Gustin et al., 2008) suggest that: (1) the exchange is bi-directional, and (2)

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653 atmospheric Hg uptake by foliage is the major pathway for Hg accumulation. Therefore, a bidirectional flux
654 scheme building on the compensation point (S2, Table 2) is perhaps more scientifically sound and
655 mathematically robust. For air-soil Hg^0 exchange, in addition to the bidirectional resistance scheme (S3),
656 statistical relationships have been developed based on measured flux and observed environmental factors such as
657 air/soil temperature, solar radiation, soil moisture and soil Hg content (S1-S2, Table 2), which tends to be
658 site-specific and oversimplifies the influence of environmental factors (Wang et al., 2014). For air-water flux
659 simulation, the two-film diffusion model is widely used by incorporating surface storage and aqueous Hg redox
660 chemistry (Bash et al., 2007; Strode et al., 2007). Bash (2010) suggested a pseudo-first kinetic water photo-redox
661 scheme in CMAQ simulation with bidirectional Hg exchange. Strode et al. (2007) parameterized the reduction
662 rate as the product of local shortwave solar radiation, net primary productivity, and a scaling parameter in
663 GEOS-Chem. Soerensen et al. (2010) updated the surface ocean redox reactions in GEOS-Chem, and added a
664 term for dark oxidation, and suggested new linear relationships between the total solar radiation, net primary
665 productivity, and photo-oxidation rate coefficient, photoreduction coefficient, and biotic reduction coefficient.

666 Using the S1 scheme (Table 2), the range of simulated air-foliage fluxes were 0 to 5 ng m^{-2} h^{-1} in North
667 America (Bash et al., 2004) and 0 to 80 ng m^{-2} h^{-1} in East Asia (Shetty et al., 2008). Change the modeling
668 approach to resistance based models with compensation point assumption (S2 scheme), the range was -2.2 to
669 -0.7 ng m^{-2} h^{-1} (Wang et al., 2014). Zhang et al. (2012a) reported the annual Hg^0 uptake by foliage was 5-33 μg
670 m^{-2} with the S2 scheme, similar to the litterfall Hg flux measured at Mercury Deposition Network Sites. For
671 air-soil exchange, model-estimated fluxes ranged from 0 to 25 ng m^{-2} h^{-1} using the S1 and S2 scheme (Bash et al.,
672 2004; Gbor et al., 2006; Shetty et al., 2008; Kikuchi et al., 2013), comparable to the 0-20 ng m^{-2} h^{-1} using the S3
673 scheme (Wang et al., 2014). For air-water exchange, the model-estimated flux was 1-12 ng m^{-2} h^{-1}, consistent
674 with measured fluxes (Bash et al., 2004; Shetty et al., 2008; Bash, 2010; Wang et al., 2014).

675 Future development of Hg^0 flux model requires mechanistic understanding of air-surface exchange
676 processes. Presently, bidirectional resistance scheme, the stomatal compensation point is treated as a constant
677 value (Bash, 2010; Wang et al., 2014) or calculated as following in Wright and Zhang (2015):

678 $$\chi_{st} = 8.204 \frac{8.9803 \times 10^9}{T} \cdot \Gamma_{st} \cdot e^{-\frac{8353.8}{T}} \quad (5)$$

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where T is the temperature of stomata/surface, and Γ_{st} is the emission potential of the stomata. Γ_{st} is an empirical input value and suggested in 5-25 ng m^{-3} depending on the specific land use. Battke et al., 2005; Heaton et al., 2005; and Battke et al., 2008 reported that plants have the ability to reduce the Hg^{II} to Hg^0 in foliar cell through reducing ligands (e.g., NADPH). To propose a more physically robust modeling scheme, the redox processes in foliage and the role of ligands on Hg uptake need to be better understood. The finding that Hg^0 can pass through the soil-root interface under artificial laboratory conditions (Moreno et al., 2005b) needs to be carefully verified in the field.

Another area that requires advancement is the determination of Hg^{II} reduction rate (Scholtz et al., 2003;Bash, 2010;Wang et al., 2014) and the hypothetical parameter Γ_{st} (Wright and Zhang, 2015) in soil. It is well known that Hg^{II} can be reduced by natural organic acids via biotic/abiotic reduction (Zhang and Lindberg, 1999; Zheng et al., 2012). Experimental investigations showed that O_3 is important in controlling Hg emissions from substrates (Engle et al., 2005). However, the kinetic description of these process is fundamentally unknown. The pseudo-first reduction rate constant of Hg^{II} has been assumed to be in the range of 10^{-11} to 10^{-10} s^{-1} (Scholtz et al., 2003; Qureshi et al., 2011a). Under laboratory conditions at 100 W m^{-2} and 32±7 °C, the pseudo-first reduction rate was estimated to be 2-8×10^{-10} m^2 s^{-1} w^{-1} basing on 2 mm soil depth (the maximum depth for light penetration in soil) (Quinones and Carpi, 2011). Si and Ariya (2015) reported a photo-reduction rate of Hg^{II} in presence of alkanethiols to be 3-9×10^{-9} m^2 s^{-1} w^{-1}. Other than these kinetic information, kinetic measurements for Hg^{II} reduction in the absence of light will enable additional mechanistic parameterization of Hg evasion model for soil and vegetative surface.

6. Conclusions and future perspectives

Understanding in the air-surface exchange of Hg^0 has been steadily advancing since mid-1980s. Substantial amount of data exists, but with large uncertainty and data gaps in Africa, South and Central Asia, Middle East, South America and Australia. Fundamentally, flux measurement approaches (e.g., MM and DFCs) are different and individual flux measurement data are not directly comparable. The Hg^0 flux data compiled in this study represent the current state of understanding that requires continuous updates. Hg^0 flux in East Asia is statistically higher than the values observed in other world regions, suggesting reemission of atmospheric deposition or

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strong anthropogenic influence. Hg^0 exchange over weak diffuse sources (e.g., background soil and water) and vegetation need better constrains for global analysis of atmospheric Hg budget through extensive on-site measurement and fundamental mechanical studies (e.g., redox transformation rate constant, mass transfer diffusivity). Although predominate factors in controlling Hg^0 flux have been identified, the effects of those factors on flux have not been fundamentally and quantitatively determined for different surfaces, which limited the accuracy of flux modeling. Based on the data synthesis in this study, the following knowledge gaps need to be addressed:

(1) Improving temporal resolution and sensitivity of Hg^0 flux measurements. Insufficient temporal resolution and sensitivity in the detection of ambient Hg has limited our capability in accurately determining the air-surface exchange of Hg^0. Development of high temporal resolution and sensitive sensor for determining Hg^0 concentration gradient is of prime importance to improve flux data quality and to reduce uncertainty in the global assessment of Hg budget. Such advancement will also open up new opportunities to explore fundamental exchange mechanism in response to the changes in environmental factors.

(2) Standardization of Hg^0 flux measurement techniques and establish data comparison strategy. Hg^0 flux measurement uncertainties from using different techniques remains large, standardized method is useful to compare flux obtained from various techniques. Fundamental study is needed to compare current Hg^0 flux quantification methods, synchronized measuring flux from various methods using varied operation parameters is suggested to build potential empirical data comparison strategy and correction methods, this will largely reduce the gross uncertainty in the Hg budget estimation and greatly improve comparability of flux data reported by different research groups.

(3) Fundamental investigation on the environmental processes driving Hg exchange. Although flux response to environmental parameters (e.g., irradiance, precipitation, temperature rising) are qualitatively defined in statistical sense, the processes driving Hg^0 exchange need to be understood fundamentally. Recent advancement on isotopic tracing techniques (e.g., enriched Hg isotope tracers and stable Hg isotopic fractionation data) may offer mechanistic insights and new data should be incorporated into new modeling analysis.

(4) Long-term measurement of Hg^0 flux at representative sites. There is a substantial data gap in the current

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733 Hg^0 flux database in terms of geographical coverage and land use type. Forest is most likely an overlooked sink
734 for atmospheric Hg^0, however, few field campaigns have been conducted at forest sites. In addition, current flux
735 database are mainly from short-term campaigns. It is presently unclear how global changes (e.g. climate change,
736 global anthropogenic Hg reduction) will force Hg^0 flux changes over different surfaces. There is presently no
737 network of flux measurements at global monitoring sites. Continuous observation of flux is also useful for
738 providing better database for scale-up estimation.

739 **(5) Development and improvement of air-surface exchange models for Hg.** The present state of development
740 of air-surface exchange model does not allow appropriate process analysis due to a lack of fundamental
741 understanding in the chemical and mass transfer processes of evasion and deposition. Existing air-surface Hg^0
742 flux schemes incorporate over-simplified chemical schemes with not-yet verified kinetic parameters. In addition,
743 the interactions between Hg^{II} and organic matters in the natural environment, as well as the interfacial transfer of
744 different Hg species over various surfaces, have significant knowledge gaps. Studies address these gaps are
745 critically needed and will benefits not only the measurement approaches but also the model parameterization in
746 estimating the global air-surface exchange of Hg.

747

748 **Acknowledgements**

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752 **Table 1:** A statistical summary of field *in situ* observed Hg^0 flux reported in the literatures.

753

Landscapes	Hg^0 flux (ng m^{-2} h^{-1})				*N*	References[b]
	Mean	Median	Min (*min*)[a]	Max (*max*)[a]		
Background soil	2.1	1.3	-51.7 (*-51.7*)	33.3 (*97.8*)	159	*(1)*
Urban settings	16.4	6.2	0.2 (*-318*)	129.5 (*437*)	29	*(2)*
Agricultural fields	25.1	15.3	-4.1 (*-1051*)	183 (*1071*)	59	*(3)*
Forest foliage & canopy level	6.3	0.7	-9.6 (*-4111*)	37.0 (*1000*)	8	*(4)*
Grasslands	5.5	0.4	-18.7 (*-989.6*)	41.5 (*870*)	38	*(5)*
Wetlands	12.5	1.4	-0.3 (*-375*)	85 (*677*)	23	*(6)*
Freshwater	4.0	2.8	-0.3 (*-18.2*)	74.0 (*88.9*)	93	*(7)*
Sea water	5.9	2.5	0.1 (*-2.7*)	40.5 (*46.0*)	51	*(8)*
Snow	5.7	2.7	-10.8 (*-2160*)	40 (*720*)	15	*(9)*
Natural enriched surfaces	5618	226	-5493 (*-9434*)	239200 (*420000*)	329	*(10)*
Anthropogenically contaminated surfaces	595	184	-1.4 (*-286.2*)	13700 (*13700*)	58	*(11)*

754 Notes: [a]. Min/Max are campaign/site-based average flux, while *(min)/(max)* represent lowest/largest instantaneous flux; [b] References: see **Appendix A**.

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757 **Table 2:** A comparison of natural surface mercury flux models

	General models	Description	References
Foliage	S1: F = ECs	E: transpiration rate (g m^{-2} s^{-1}) Cs: Hg^0 in soil water (ng g^{-1})	Xu et al., 1999; Bash et al., 2004; Shetty et al., 2008; Gbor et al., 2006
	S2: $F_{st/cu} = \frac{\chi_{st/cu} - \chi_c}{R_{st/cu}}$	$\chi_{st/cu}$: stomatal/cuticular compensation point (ng m^{-3}) $F_{st/cu}$: air-cuticular/stomatal flux (ng m^{-2} s^{-1}) χ_c: compensation point at the air-canopy (ng m^{-3}) $R_{st/cu}$: resistance between air-cuticular/stomatal (m s^{-1})	Zhang et al., 2009;Bash, 2010;Wang et al., 2014;Wright and Zhang, 2015
Soil	S1: $\log F = -\frac{\alpha}{T} + \beta \log(C) + \gamma R + \varepsilon$	T: soil temperature (°) C: soil Hg concentration (ng g^{-1}) R: solar radiation (W m^{-2})	Xu et al., 1999; Bash et al., 2004; Gbor et al., 2006; Shetty et al., 2008; Selin et al., 2008
	S2: $\frac{F}{C} = \alpha T + \beta R + \delta\Theta + \delta TR + \cdots$	T: soil temperature (°) C: soil Hg concentration (ng g^{-1}) R: solar radiation (W m^{-2}) Θ: soil moisture (%)	Lin et al., 2010a; Kikuchi et al., 2013
	S3: $F = \frac{\chi_s - \chi_c}{R_g + R_{ac}}$	χ_s: soil compensation point (ng m^{-3}) χ_c: compensation point at the air-soil (ng m^{-3}) R_g: resistance between air-soil (m s^{-1}) R_{ac}: In-canopy aerodynamic resistance (m s^{-1})	Zhang et al., 2009; Bash, 2010; Wang et al., 2014; Wright and Zhang, 2015
Water	$F = \frac{\chi_w - \chi_c}{R_w + R_a}$	χ_w: water compensation point (ng m^{-3}) χ_c: air Hg^0 concentration (ng m^{-3}) R_w: liquid side resistance (m s^{-1}) R_a: air side resistance (m s^{-1})	Xu et al., 1999; Bash et al., 2004; Gbor et al., 2006; Shetty et al., 2008; Bash, 2010; Wang et al., 2014

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761 **Fig. 1.** The most recent Hg reservoirs and global atmosphere Hg inventory illustrating the exchange flux
762 between atmosphere and earth surfaces. Adapted from Selin, 2009; Gustin and Jaffe, 2010; Soerensen et al.,
763 2010; Corbitt et al., 2011; Mason et al., 2012; AMAP/UNEP, 2013.
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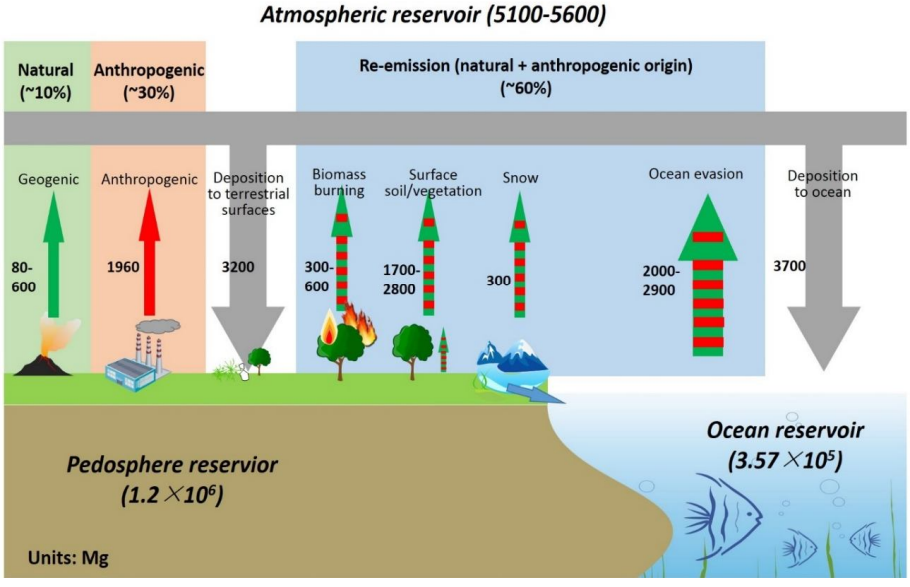

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768 **Fig. 2.** Field collocated DFCs and MM techniques observed fluxes from two intercomparison studies: (a).
769 Inlaid scatter plot of averaged 4-MM flux vs. averaged 7-DFC flux (TOT: 1.1-24 min) in Hg-enriched
770 Nevada STORMS site in September, 1997 (Gustin et al., 1999); (b). Diel evolution of Hg^0 flux measured
771 using a 1L polycarbonate-DFC (TOT: 0.2 min) and MBR method at same Nevada STORMS site in October,
772 1998 (Gustin, 2011); (b). Scatter plot of DFC with traditional/novel designs (TDFC/NDFC) vs. MBR Hg^0
773 flux obtained in Yucheng Intercomparision project (Zhu et al., 2015b).
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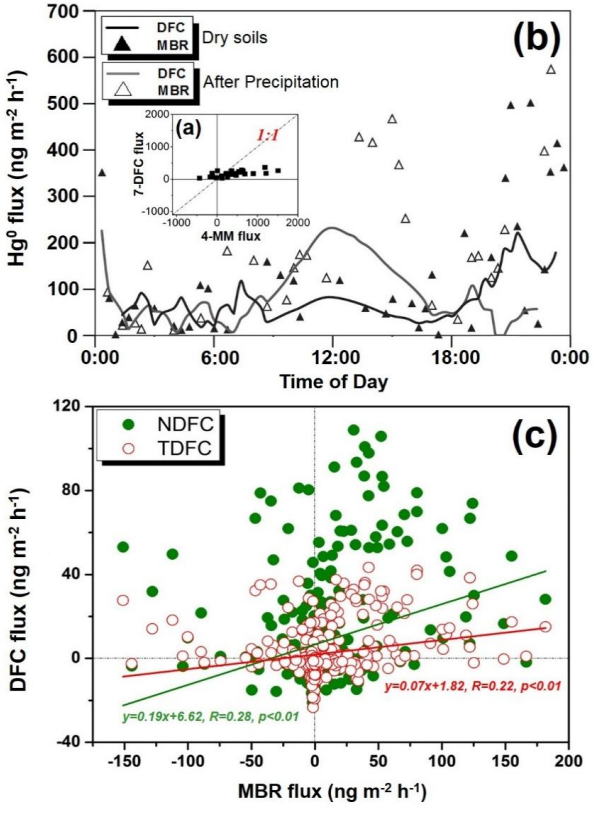

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778 **Fig 3.** Box and whisker plots of Hg^0 fluxes measured by MM methods and DFC methods. (Flux data
779 including measurements from background soils, agricultural fields, grasslands, and wetlands at substrate
780 total Hg lower than 0.3 µg Hg g^{-1}, data source: Table 1. The two box horizontal border lines indicate 25th and
781 75th percentiles, whiskers represent 10th and 90th percentiles, and outliers (green circles) indicate 5th and
782 95th percentiles from bottom to top. Red line and black line indicate mean and median flux).
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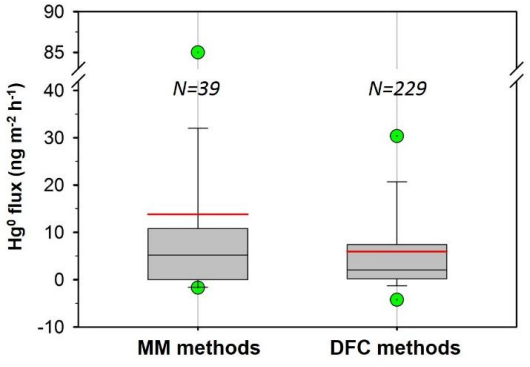

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787 **Fig. 4.** 4-D graphical visualization of the effect of air temperature, soil water content, and solar radiation on

788 the measured Hg^0 flux from soil (Lin et al., 2010a).

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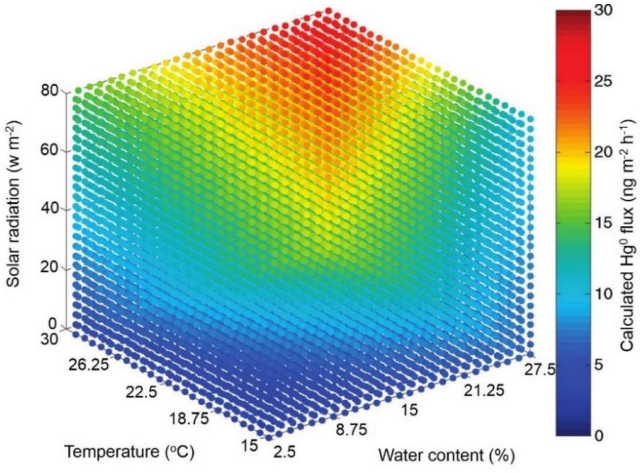

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793 **Fig. 5.** Conceptual view of DGM cycling in water and mass transfer process across the atmosphere-water

794 interface.

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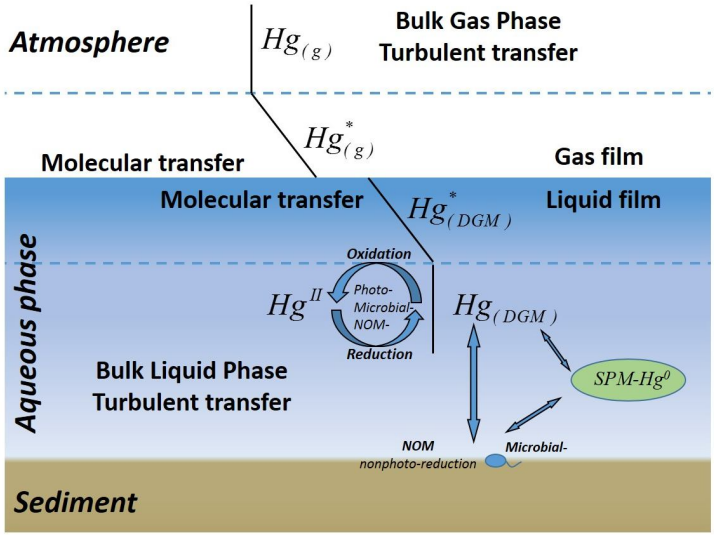

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799 Fig. 6. Box and whisker plots of global field observed Hg^0 flux obtained from various landscapes. (Data
800 Source: Table 1. Red line and black line indicate mean and median flux).
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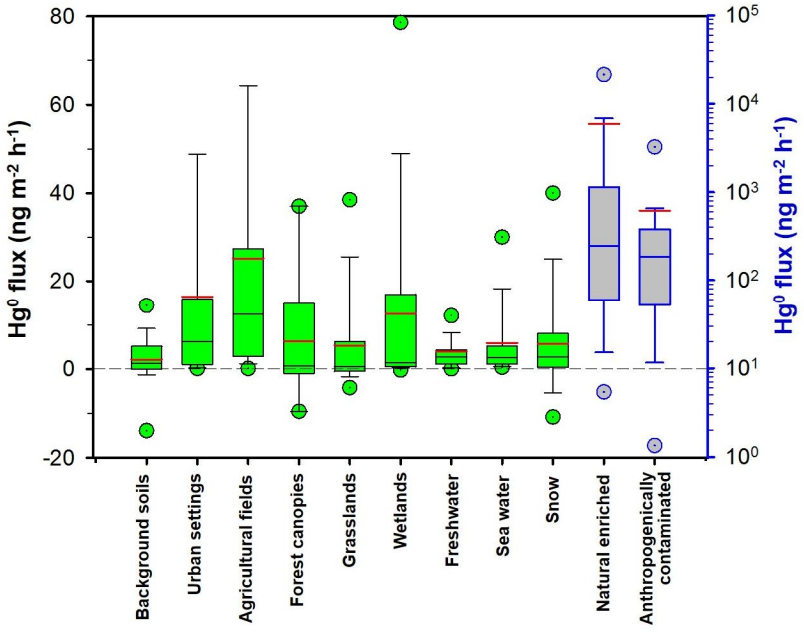

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805 **Fig. 7.** Histograms of Hg^0 flux frequency distribution obtained from various earth surfaces. (Data source:

806 Table 1).

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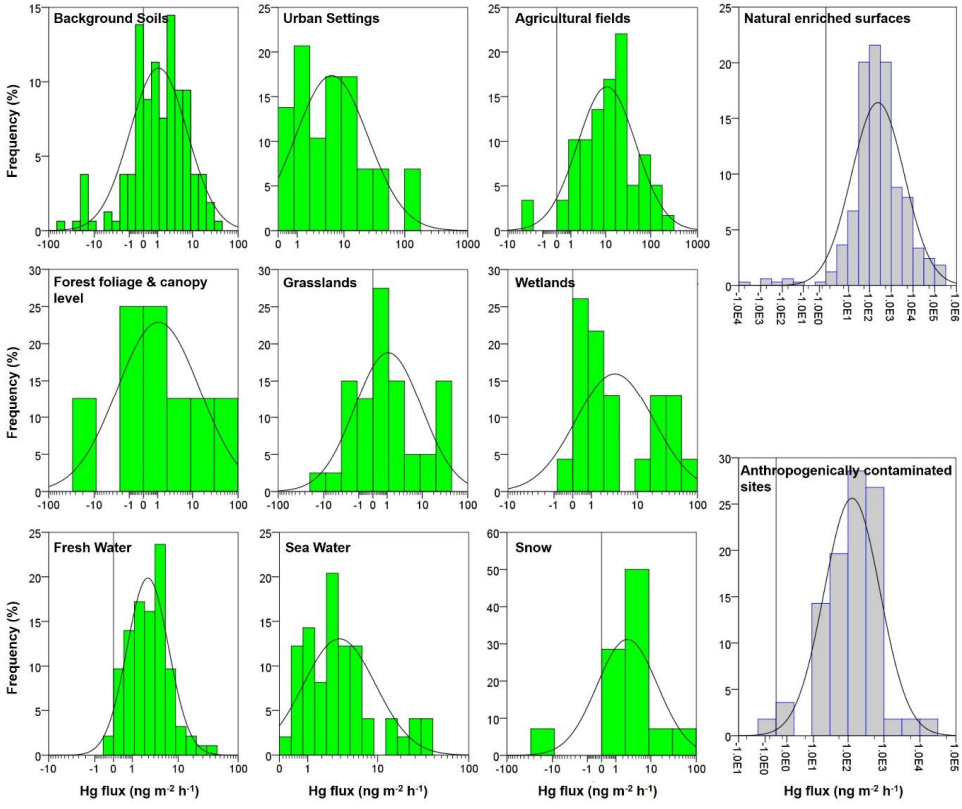

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811 **Fig. 8.** Box and whisker plots of continents segregated Hg^0 flux obtained from four homogeneous surfaces
812 (Background soils, agricultural fields, grasslands, and freshwater. Filled square block and horizontal line in
813 box indicate mean and median flux).
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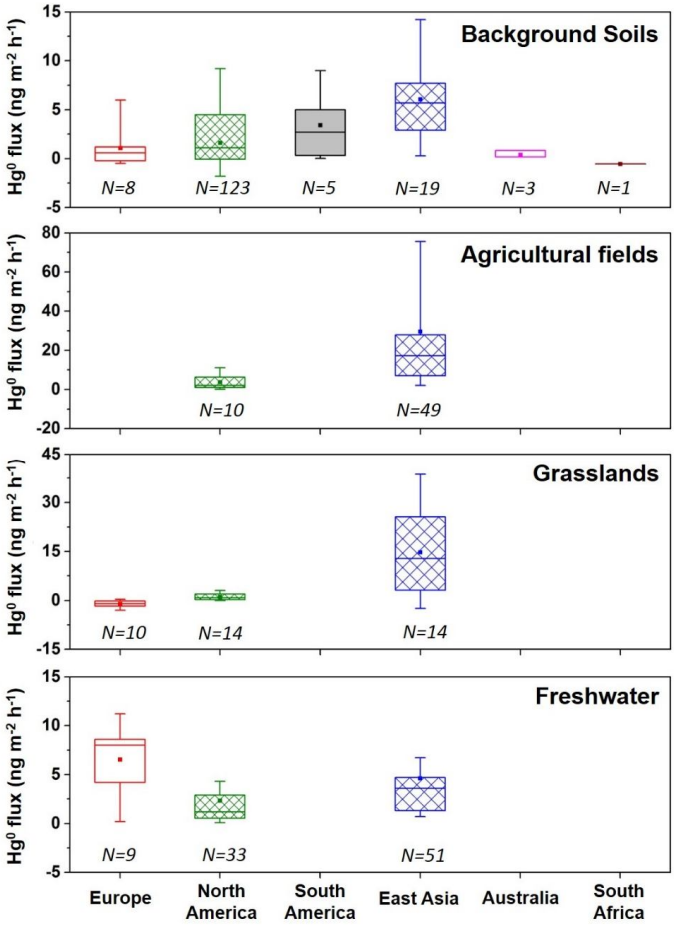

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818 **Fig. 9.** Diurnal patterns of Hg^0 flux from various environmental compartments (soil, mine, freshwater, forb
819 leaf, growing broad leaf, and snow) measured using DFC methods. (Data obtained from soil: Zhu et al.,
820 2015b; mine: Eckley et al., 2011a; fresh water: O'Driscoll et al., 2003; forb leaf: Stamenkovic et al., 2008;
821 growing broad leaf: Fu et al., 2015c; and snow: Maxwell et al., 2013)
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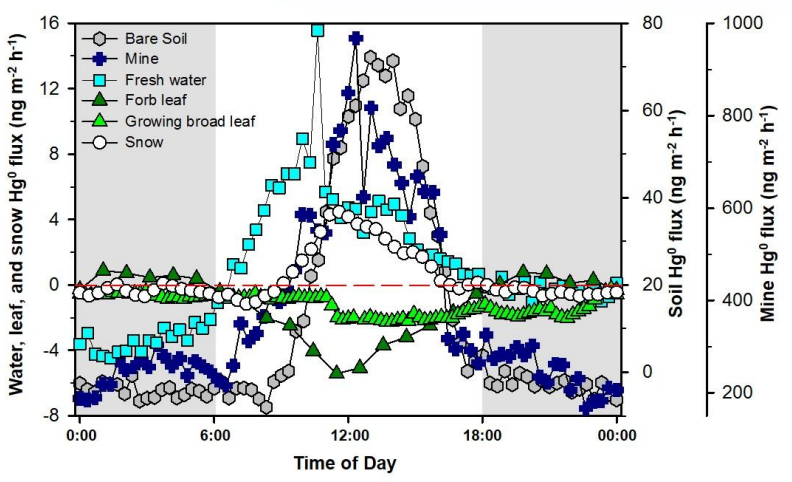

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Appendix A: References for Table 1

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