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FOCUSED REVIEW

A Review of Dry Deposition Schemes for Speciated Atmospheric Mercury

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Abstract
This study reviewed the existing framework of dry deposition schemes for speciated atmospheric mercury. As the most commonly used methods for mercury dry deposition estimation, the big-leaf resistance scheme for gaseous oxidized mercury (GOM), the size distribution regarded resistance scheme for particulate bound mercury (PBM), and the bidirectional air–surface exchange scheme for gaseous elemental mercury (GEM) were introduced in detail. Sensitivity analysis were conducted to quantitatively identify the key parameters for the estimation of speciated mercury dry deposition velocities. The dry deposition velocity of GOM was found to be sensitive to the wind speed and some land use related parameters. The chemical forms of GOM could have a significant impact on the dry deposition velocity. The dry deposition velocity of PBM is sensitive to the mass fraction of PBM in coarse particles, while that of GEM is most sensitive to air temperature. Future research needs were proposed accordingly.

Keywords Atmospheric mercury · Dry deposition schemes · Speciation · Resistance model · Bidirectional exchange model

List of Symbols

F	Hg dry deposition flux (ng m^{-2} s^{-1})
C	Hg concentration at a reference height (ng m^{-3})
v_d	Dry deposition velocity (m s^{-1})
R_a, R_b, and R_c	Aerodynamic, quasi-laminar sublayer, and canopy resistances (s m^{-1})
z_r, z_0, and L	Reference height, surface roughness, and Monin–Obukhov length (m)
k	The von Karman constant
u_* and u_r	Friction velocity and wind speed at the reference height (m s^{-1})
z and d	Actual height and zero-plane displacement height (m)
υ	Kinematic viscosity of air (m^2 s^{-1})
D_a and D_{aw}	Molecular diffusivities of the pollutant and water vapor in air
T_a	Air temperature (K)
P	Atmospheric pressure (kPa)
M_a and M_x	Molecular weights of air and the compound (g mol^{-1})
V_a and V_x	Molecular volumes of air and the compound
W_{st}	Fraction of stomatal blocking under wet conditions
R_{st}, R_m, and R_{cut}	Stomatal, mesophyll, and cuticular resistances (s m^{-1})
R_{ac} and R_g	Resistances in the vegetative canopy and to uptake at the ground (s m^{-1})
SR and PAR	Solar radiation and photosynthetically active radiation (W m^{-2})
G_{st}	Unstressed canopy stomatal conductance
D	Water vapor pressure deficit (kPa)
T	Air temperature (℃)
Ψ	Leaf water potential (MPa)
f_D, f_T, and f_ψ	Functions of D, T, and ψ
$r_{st,\min}$	Minimum leaf stomatal resistance (s m^{-1})
b_{rs}	An empirical constant for G_{st} calculation (W m^{-2})

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F_{sun} and F_{shade}	Total sunlit and shaded leaf area indexes
LAI	Leaf area index of the canopy
θ	Solar zenith angle (°)
φ	Angle between the leaf and the sun (°)
a and b	Two power exponents for PAR calculation
R_{diff} and R_{dir}	Visible radiation fluxes from diffuse and direct-beam radiation (W m^{-2})
R_0	Average amount of PAR available at the top of the atmosphere (W m^{-2})
P/P_0	Ratio of actual to sea level pressure
b_{vpd}	A constant for D (kPa^{-1})
T_{opt}	Optimum temperature of maximum stomatal opening (°C)
T_{min} and T_{max}	Minimum and maximum temperatures for stomatal closure (°C)
ψ_{c1} and ψ_{c2}	Parameters which specify ψ dependency (MPa)
A	An empirical parameter for D
B	An empirical parameter for D (°C)
C	An empirical parameter for D (Pa)
ψ_0	An empirical parameter for ψ (MPa)
β_0	An empirical parameter for ψ
RH	Relative humidity
R_{ac0}	Reference value for in-canopy aerodynamic resistance (s m^{-1})
α and β	Two scaling factors for $R_{g/cut}$ calculation
R_{cutd0} and R_{cutw0}	Reference values for R_{cut} under dry and wet conditions (s m^{-1})
C_f and C_c	PBM concentrations in fine and coarse particles (pg m^{-3})
v_{df} and v_{dc}	Dry deposition velocities of fine and coarse particles (m s^{-1})
v_g	Gravitational settling velocity (m s^{-1})
R_s	Surface resistance (s m^{-1})
v_{dsf}	Surface deposition velocity for fine particles (m s^{-1})
v_{dsc}	Surface deposition velocity for coarse particles (m s^{-1})
a_1	An empirical coefficient for v_{dsf}
b_1, b_2, and b_3	Empirical coefficients for v_{dsc}
c_1, c_2, and c_3	Empirical coefficients for v_{dsc}
f	Mass fraction of PBM in coarse particles
χ_a and χ_c	GEM concentrations in the ambient air and at the canopy top (ng m^{-3})
χ_{st} and χ_g	Stomatal and ground compensation points (ng m^{-3})
T_{st} and T_g	Stomatal and ground temperatures (°C)
Γ_{st} and Γ_g	Stomatal and ground emission potentials
λ_1 and λ_2	Two constants for calculation of χ_{st} and χ_g

Atmospheric deposition is a dominant pathway for mercury (Hg) to enter ecosystems and subsequently human bodies (Lyman et al. 2020). Over all the terrestrial regions, Hg dry deposition plays a more critical role than wet deposition (Wright et al. 2016). The three operationally defined forms of atmospheric Hg include gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate bound mercury (PBM), the residence times of which vary significantly (Lindberg et al. 2007; Fu et al. 2012; Gustin et al. 2021). Accurate estimation of local, regional and global Hg dry deposition fluxes helps to better quantify the source–sink relationship of atmospheric Hg, which is key to the effectiveness evaluation for implementation of the Minamata Convention on Mercury (Giang et al. 2015).

Large uncertainties exist in both observations and simulations of speciated Hg dry depositions to the terrestrial surfaces (Zhu et al. 2016; Zhang et al. 2019). The global monitoring network has not been established yet due to the technical challenges of Hg dry deposition flux measurements (Zhang et al. 2009, 2019). In chemical transport models (CTMs), Hg dry deposition is commonly calculated using resistance schemes for speciated atmospheric Hg or the bidirectional exchange scheme for GEM (Lin et al. 2006; Selin et al. 2007; Zhang et al. 2009; Wright et al. 2016; Zhu et al. 2016). However, most of the schemes in CTMs are highly simplified, and the validation of the schemes is based on data from field observation the uncertainties of which are also high (±(60%–200%) for speciated Hg dry deposition) (Zhang et al. 2019).

Critical reviews on Hg deposition have been conducted focusing on different aspects. Zhang et al. (2009) reviewed Hg dry deposition measurement methods and worldwide measurements of speciated Hg using these approaches, and summarized dry deposition schemes briefly. Wright et al. (2016) made an overview of Hg dry deposition, litterfall, and throughfall including methodology for measurements and comparison of different types of deposition. Zhu et al. (2016) provided a critical review on global observations and modeling work of atmosphere–surface GEM exchange. Our previous review work (Zhang et al. 2019) estimated the uncertainties in observations and simulations of Hg deposition over land surfaces. Although several review efforts on Hg deposition have been made in the recent decade, key parameters in Hg dry deposition schemes have not yet been systemically investigated, and their contributions to the deposition flux have not been quantitatively evaluated.

This study provides a detailed review of current knowledge regarding dry deposition schemes for speciated atmospheric Hg used in CTMs. Recent advances in estimating the key parameters were investigated, and sensitivity analysis was performed. Origins of uncertainties are quantitatively linked to the parameterization schemes, and future research needs to reduce the overall uncertainty of Hg dry deposition estimation have been proposed in this review work.

Overall Methodology for Hg Dry Deposition Estimation

In the commonly used modeling schemes, Hg dry deposition flux is the product of the dry deposition velocity and the atmospheric Hg concentration, as shown in Eq. (1) (Zhang et al. 2009):

$$F = C \cdot v_d \tag{1}$$

where F is the Hg dry deposition flux (ng m^{-2} s^{-1}); C is the Hg concentration at a reference height (ng m^{-3}); and v_d is the dry deposition velocity (m s^{-1}).

The speciated Hg concentrations (GEM, GOM, and PBM) are measurable, usually by the Tekran continuous monitoring system in the global monitoring network (Landis et al. 2002; Sprovieri et al. 2016). The concentration of GOM measured by the Tekran system has been reported to be biased low with the interference of ozone and specific humidity (Lyman et al. 2010; McClure et al. 2014; Gustin et al. 2015). A correction factor ranging from 1.56 to 3 has been applied in numerous studies (Huang and Gustin 2015; Huang et al. 2017; Saiz-Lopez et al. 2020) for GOM dry deposition simulations based on intercomparison of different GOM concentration monitoring methods (Gustin et al. 2013; Huang et al. 2013; Cheng and Zhang 2017; Marusczak et al. 2017).

Except for the concentration correction of GOM, the uncertainty of Hg dry deposition flux estimation lies mostly in the calculation schemes for Hg dry deposition velocities (Zhang et al. 2019). The following three sections present details on the dry deposition schemes for GOM, PBM, and GEM dry deposition velocities, respectively.

Dry Deposition Scheme for GOM

The resistance approach, also known as the big-leaf model, is the most commonly used scheme for GOM dry deposition (Zhang et al. 2003). A schematic diagram for this scheme is shown as Fig. S1 in the supporting information (SI). The primary resistances for GOM against the terrestrial surfaces are the aerodynamic resistance (R_a), the quasi-laminar sublayer resistance above the canopy (R_b), and the overall canopy resistance (R_c), based on which the dry deposition velocity can be defined as Eq. (2):

$$v_d = \frac{1}{R_a + R_b + R_c} \tag{2}$$

Aerodynamic Resistance

The aerodynamic resistance is related to atmospheric stability and surface roughness, and can be calculated by Eqs. (3) and (4) (Wesely et al. 2002).

For atmospherically stable and neutral conditions ($L \geq 0$), R_a is estimated as follows (Wesely et al. 2002):

$$R_a = \frac{\ln\left(z_r/z_0\right) + 5z_r/L}{ku_*} \tag{3}$$

where z_r is the reference height (m); z_0 is the surface roughness length scale (m); L is the Monin–Obukhov length scale reflecting the atmospheric stability (m), which can be calculated based on the Pasquill stability classification method as demonstrated in detail in Seinfeld and Pandis (2016); k is the von Karman constant (0.4); and u_* is the friction velocity (m s^{-1}).

For unstable conditions ($L < 0$), Eq. (4) is applied (Wesely et al. 2002):

$$R_a = \frac{\ln\left(z_r/z_0\right) - 2\ln\left(\left(1+\sqrt{1-16z_r/L}\right)/2\right) + 2\ln\left(\left(1+\sqrt{1-16z_0/L}\right)/2\right)}{ku_*} \tag{4}$$

The friction velocity can be further calculated with the following equation (Seinfeld and Pandis 2016):

$$u_* = \frac{ku_r}{\ln\left(z_r/z_0\right)} \tag{5}$$

where u_r is the wind speed measured at the reference height (m s^{-1}).

As a result, R_a is determined by z_r, z_0, and L. Among these three parameters, L is determined by the Pasquill stability classification method (Seinfeld and Pandis 2016), which is linked to meteorological factors, including wind speed, solar radiation, and cloud cover, with a relatively low uncertainty. The term z_r represents the height above the zero-plane displacement height d:

$$z_r = z - d \tag{6}$$

where z is the actual height (m). The term d can be determined by different methods. Brook et al. (1999) listed the d values by land use category (LUC). Wesley et al. (2002) suggested an estimate as 2/3 of the average vegetation height h, while Matsuda et al. (2010) set d to be 0.8 h. The term z_0 is usually determined by LUC (Wesely et al. 2002; Zhang et al. 2003).

The GOM deposition velocity is sensitive to the selection of z_r and z_0 through both R_a and R_b, and is more sensitive to the wind speed u_r, which will be further discussed in a latter section.

Quasi-Laminar Sublayer Resistance

The quasi-laminar sublayer resistance is mainly associated with the friction velocity u_* which is also linked to surface roughness (Wesely et al. 2002):

$$R_b = \frac{2.2\left(\upsilon/D_a\right)^{2/3}}{ku_*} \tag{7}$$

where υ is the kinematic viscosity of air (approximately 0.1505×10^{-4} m^2 s^{-1}); and D_a is the diffusivity of the gas of interest in air, which is calculated as follows:

$$D_a = \frac{0.143T_a^{1.75}\left(\left(1/M_a + 1/M_x\right)/2\right)^{0.5}}{P\left(V_a^{0.33} + V_x^{0.33}\right)^2} \tag{8}$$

where T_a is the air temperature (K); P is the atmospheric pressure (kPa); M_a and M_x are molecular weights of air (28.966 g mol^{-1}) and the compound (g mol^{-1}), respectively; and V_a and V_x are molecular volumes of air (19.7) and the compound, respectively.

Although different GOM species have different molecular weights and volumes, the GOM deposition velocity is not sensitive to these basic parameters.

Canopy Resistance

The canopy resistance is a more comprehensive term, which can be parameterized as follows (Zhang et al. 2003):

$$R_c = \left(\frac{1 - W_{st}}{R_{st} + R_m} + \frac{1}{R_{ac} + R_g} + \frac{1}{R_{cut}}\right)^{-1} \tag{9}$$

where W_{st} is the fraction of stomatal blocking under wet conditions; R_{st} is the stomatal resistance (s m^{-1}); R_m is the mesophyll resistance (0 for GOM) (Zhang et al. 2012); R_{ac} is the gas-phase resistance in the vegetative canopy (s m^{-1}); R_g is the resistance to uptake at the ground (s m^{-1}); and R_{cut} is the cuticular resistance (s m^{-1}).

The term W_{st} is set to be 0 when solar radiation (SR, W m^{-2}) is low or the canopy is dry, and given a value other than 0 only when SR is relatively strong (following Eq. (10)) and the canopy is wet (when rain or dew occurs).

$$W_{st} = \begin{cases} 0 & SR \le 200 \\ \frac{SR-200}{800} & 200 < SR \le 600 \\ 0.5 & SR > 600 \end{cases} \tag{10}$$

The wet canopy condition can be determined by rain and dew monitoring or through an empirical method described in Brook et al. (1999).

The stomatal resistance can be described as a comprehensive function of foliar and meteorological parameters, following Eq. (11) (Zhang et al. 2002).

$$R_{st} = \frac{1}{G_{st} f_D f_T f_\psi D_a / D_{aw}} \tag{11}$$

where G_{st} is the unstressed canopy stomatal conductance which is a function of the photosynthetically active radiation (PAR, W m^{-2}); f_D, f_T, and f_ψ are functions of water vapor pressure deficit (D, kPa), air temperature (T, °C), and leaf water potential (ψ, MPa), respectively; and D_a and D_{aw} are the molecular diffusivities of the pollutant and water vapor in air, respectively, which can be calculated by Eq. (8).

The term G_{st} is further parameterized as follows (Zhang et al. 2002):

$$G_{st} = \frac{1}{r_{st,\min}}\left(\frac{F_{sun}}{1 + b_{rs}/PAR_{sun}} + \frac{F_{shade}}{1 + b_{rs}/PAR_{shade}}\right) \tag{12}$$

where $r_{st,\min}$ and b_{rs} are the minimum leaf stomatal resistance (s m^{-1}) and an empirical constant (W m^{-2}), respectively, both of which are dependent on LUC and can be found by LUC in Zhang et al. (2003); F_{sun} and F_{shade} are the total sunlit and shaded leaf area indexes (LAIs), respectively; and PAR_{sun} and PAR_{shade} are PAR received by sunlit and shaded leaves, respectively. The latter four parameters can be calculated as follows:

$$F_{sun} = 2\cos\theta(1 - \exp(-0.5LAI/\cos\theta)) \tag{13}$$

$$F_{shade} = LAI - F_{sun} \tag{14}$$

$$PAR_{sun} = R_{dir}^a \cos\varphi / \cos\theta + PAR_{shade} \tag{15}$$

$$PAR_{shade} = R_{diff}\exp\left(-0.5LAI^b\right) + 0.07R_{dir} (1.1 - 0.1LAI)\exp(-\cos\theta) \tag{16}$$

where LAI is the leaf area index of the canopy, the profile of which can be adapted from Zhang et al. (2003); θ is the solar zenith angle, which can be obtained from a solar position algorithm (Reda and Andreas 2004); φ is the angle between the leaf and the sun (60° for a canopy); a and b are two power exponents, which are set to 1.0 and 0.7, respectively, when $LAI < 2.5$ or $SR < 200$ W m^{-2}, and set to 0.8 and 0.8, respectively, otherwise (Zhang et al. 2002); and R_{diff} and R_{dir} are the downward visible radiation fluxes above the canopy from diffuse and direct-beam radiation, respectively, which can be further calculated as follows (Weiss and Norman 1985):

$$R_{dir} = R_0\exp\left(-0.185\left(P/P_0\right)(\cos\theta)^{-1}\right)\cos\theta \tag{17}$$

$$R_{diff} = 0.4\left(R_0 - R_{dir}\right)\cos\theta \tag{18}$$

where R_0 is the average amount of *PAR* available at the top of the atmosphere (600 W m^{-2}); and P/P_0 is the ratio of actual to sea level (101.325 kPa) pressure.

The other functions in Eq. (11) are calculated as follows:

$$f_D = 1 - b_{vpd}D \tag{19}$$

$$f_T = \frac{T - T_{min}}{T_{opt} - T_{min}}\left(\frac{T_{max} - T}{T_{max} - T_{opt}}\right)^{\frac{T_{max}-T_{opt}}{T_{opt}-T_{min}}} \tag{20}$$

$$f_\psi = \frac{\psi - \psi_{c2}}{\psi_{c1} - \psi_{c2}} \tag{21}$$

where b_{vpd} is a constant (kPa^{-1}) for D; T_{opt} is an optimum temperature that indicates the critical temperature (°C) of maximum stomatal opening; T_{min} and T_{max} are minimum and maximum temperatures that indicate the critical temperatures (°C) below and above which complete stomatal closure occurs; and ψ_{c1} and ψ_{c2} are parameters (MPa) which specify ψ dependency ($f_\psi = 1.0$ when $\psi > \psi_{c1}$). All of the parameters here are dependent on LUC and can be found by LUC in Zhang et al. (2003).

The water vapor pressure deficit and the leaf water potential can be estimated using the following equations (Zhang et al. 2003; Lawrence 2005):

$$D = C\exp\left(A/(B+T)\right)(1 - RH) \tag{22}$$

$$\psi = \psi_0 - \beta_0 \cdot SR \tag{23}$$

where A, B, C, ψ_0, and β_0 are all empirical parameters, which are valued as 17.625, 243.04°C, 610.94 Pa, −0.72 MPa, and 0.0013, respectively.

The term R_{ac} in the canopy resistance can be calculated as follows:

$$R_{ac} = \frac{R_{ac0}LAI^{1/4}}{u_*^2} \tag{24}$$

where R_{ac0} is the reference value for in-canopy aerodynamic resistance, which is dependent on LUC and can be found by LUC in Zhang et al. (2003).

The terms R_g and R_{cut} in the canopy resistance are calculated for SO_2 and O_3 and then scaled for other gaseous species following Eq. (25):

$$R_{g/cut} = \frac{\alpha}{R_{g/cut}(SO_2)} + \frac{\beta}{R_{g/cut}(O_3)} \tag{25}$$

where α and β are two scaling factors based on the solubility and half-redox reactivity of the chemical species, which have aroused most controversies in previous studies. A number of studies (Marsik et al. 2007; Castro et al 2012; Zhang et al. 2012; Yu et al. 2013) set both α and β to be 10 as the solubility and reactivity of GOM were believed to be similar as HNO_3. However, Lyman et al. (2007) calculated the effective Henry's Law constant (H^*) and the negative log of electron activity for half-redox reactions in neutral aqueous solutions (pe^0) for $HgCl_2$ and $Hg(OH)_2$, and found HONO to be a more suitable analogue with both α and β to be 2. Huang and Gustin (2015) found that the values of α and β could vary over time depending on the chemical form of GOM. The sensitivity of the GOM deposition velocity to these two scale factors are high, which will be further discussed in a latter section.

The value of R_g for O_3 is taken as 2000s m^{-1} for water, snow, and ice surfaces, 200 s m^{-1} for all vegetated surfaces, and 500 s m^{-1} for non-vegetated surfaces or surfaces with wet ground (Zhang et al. 2003). The value of R_g for SO_2 is also dependent on LUC and can be found by LUC in Zhang et al. (2003).

The term R_{cut} is calculated for dry and wet conditions separately following Eqs. (26) and (27), respectively:

$$R_{cutd} = \frac{R_{cutd0}}{e^{0.03RH}LAI^{1/4}u_*} \tag{26}$$

$$R_{cutw} = \frac{R_{cutw0}}{LAI^{1/2}u_*} \tag{27}$$

where R_{cutd0} and R_{cutw0} are reference values for R_{cut} under dry and wet conditions, respectively. Values of R_{cutd0} and R_{cutw0} for O_3 and values of R_{cutd0} for SO_2 are dependent on LUC and can be found by LUC in Zhang et al. (2003), while the value of R_{cutw0} for SO_2 is 50 and 100 s m^{-1} for rain and dew conditions, respectively. It should be noted that a lower limit of 100 s m^{-1} is suggested for dry canopies and 20 s m^{-1} for wet canopies for SO_2. When the air temperature is below −1°C, R_{gd} and R_{cutd} are increased by as much as double their original values, and need adjustment (Zhang et al. 2003):

$$R^*_{gd/cutd} = R_{gd/cutd}\exp\left(0.2(-1 - T)\right) \tag{28}$$

Dry Deposition Scheme for PBM

The resistance approach is applicable for PBM dry deposition with the gravitational settling velocity considered and contributions from fine, coarse and giant (if applicable) particles considered separately (Zhang et al. 2001, 2016; Zhang and He 2014):

$$F_{\mathrm{PBM}} = C_f v_{df} + C_c v_{dc} \tag{29}$$

where C_f and C_c are the PBM concentrations (pg m^{-3}) in fine and coarse particles, respectively; and v_{df} and v_{dc} are the corresponding dry deposition velocities (m s^{-1}).

It should be noted that particles can also be divided into three groups (Zhang and He 2014): $PM_{2.5}$, $PM_{2.5–10}$, and PM_{10+}. However, information on PBM size distribution is very limited, and Zhang et al. (2016) simplified the calculation of F_{PBM} as Eq. (29). If more information is available, the estimation could be more accurate.

The particle dry deposition velocity is expressed as follows (Zhang et al. 2001):

$$v_d = v_g + \frac{1}{R_a + R_s} \tag{30}$$

where v_g is the gravitational settling velocity (m s^{-1}); R_a is the aerodynamic resistance above the canopy (s m^{-1}), the estimation method of which is the same as the one for GOM, Eq. (3); and R_s is the surface resistance (s m^{-1}).

The term v_g was estimated by Zhang and He (2014) to be 3.7×10^{-5}, 1.8×10^{-3}, and 3.4×10^{-2} m s^{-1} for $PM_{2.5}$, $PM_{2.5–10}$, and PM_{10+}, respectively. The term R_s is the inverse of the surface deposition velocity (v_{ds}), which is calculated for fine and coarse particles separately using the following equations:

$$v_{dsf} = a_1 u_* \tag{31}$$

$$v_{dsc} = \left(b_1 u_* + b_2 u_*^2 + b_3 u_*^3\right) \exp \left(\left(c_1 u_* + c_2 u_*^2 + c_3 u_*^3\right)\left(\frac{LAI}{LAI_{max}} - 1\right)\right) \tag{32}$$

All the empirical coefficients, including a_1, b_1, b_2, b_3, c_1, c_2, and c_3, are dependent on LUC and can be found by LUC in Zhang and He (2014). The parameterization schemes for u_* and LAI are the same as those for GOM.

The PBM concentration of fine particles (C_f) can be obtained directly by observation of the Tekran system which has an impactor to remove $PM_{2.5+}$ (Landis et al. 2002). However, the term C_c is estimated based on Hg mass distribution between fine and coarse particles:

$$C_c = \frac{f}{1-f} C_f \tag{33}$$

where f is the mass fraction of PBM in coarse particles. The value of f was taken as 0.3 in Zhang et al. (2016). The value was close to the range (approximately 0.2–0.4) in a few recent observational studies in China (Han et al. 2018; Tang et al. 2019; Wang et al. 2021). However, large f values (approximately 0.4–0.6) also occurred in a number of early studies (Xiu et al. 2009; Feddersen et al. 2012; Zhu et al. 2014). The PBM deposition velocity is most sensitive to the parameter f, which will be further discussed in a latter section.

Dry Deposition Scheme for GEM

Early studies (Zhang et al. 2003; Selin et al. 2008) used the resistance approach for the calculation of GEM dry deposition flux as well, and estimated the upward flux of GEM for natural and legacy emissions separately. However, in fact the downward and upward fluxes are significantly coupled. Therefore, the bidirectional exchange scheme exhibited better performance (Wright and Zhang 2015). A schematic diagram for this scheme is shown as Fig. S2 in the SI. The community multiscale air quality model (CMAQ) has a bidirectional air–surface exchange module, but requires information on historical deposition budget (Bash 2010; Wang et al. 2014). Here we mainly focus on the bidirectional exchange scheme for GEM.

Wright and Zhang (2015) proposed a bidirectional air–surface exchange model for GEM based on the big-leaf model (Zhang et al. 2003). In the bidirectional scheme, the net GEM dry deposition flux is calculated as follows (Zhang et al. 2019):

$$F_{\mathrm{GEM}} = \frac{\chi_a - \chi_c}{R_a + R_b} \tag{34}$$

where χ_a and χ_c are the GEM concentrations (ng m^{-3}) in the ambient air and at the top of the canopy, respectively; and R_a and R_b are the aerodynamic and quasi-laminar resistances (s m^{-1}), respectively, the estimation methods of which are the same as those for GOM dry deposition (using the molecular property for GEM).

The term χ_c can be comprehensively calculated as follows (Wright and Zhang 2015; Zhang et al. 2016):

$$\chi_c = \left(\frac{\chi_a}{R_a + R_b} + \frac{\chi_{st}}{R_{st}} + \frac{\chi_g}{R_{ac} + R_g}\right) \left(\frac{1}{R_a + R_b} + \frac{1}{R_{st}} + \frac{1}{R_{ac} + R_g} + \frac{1}{R_{cut}}\right)^{-1} \tag{35}$$

where R_{st}, R_{ac}, R_g, and R_{cut} are the stomatal, in-canopy aerodynamic, ground, and cuticular resistance (s m^{-1}), respectively, the estimation methods of which are the same as for GOM dry deposition (using the molecular property for GEM) and the values of the two scaling factors α and β for the estimation of R_g and R_{cut} for GEM are taken as 0 and 0.1, respectively (Zhang et al. 2012); and χ_{st} and χ_g are the stomatal and ground compensation points (ng m^{-3}), respectively,

Table 1 Responses of GOM, PBM, and GEM dry deposition velocities to the changes of key parameters (LUC is set to be urban)

Type of parameter	Parameter	Value			Response of v_d for GOM (%)		Response of v_d for PBM (%)		Response of v_d for GEM (%)	
		Min	Typical	Max	To min	To max	To min	To max	To min	To max
Meteorology related	u_r (m s^{-1})	0	3.3	6	−95	77	−94	94	−54	11
	SR (W m^{-2})	0	480	900	−5	−1	−12	0	0	−11
	T (℃)	−5	15	40	−32	−1			−59	−130
	RH	0.2	0.7	1	−35	49			−24	25
Land cover related	z_0	0.1	1	2.5	−58	76	−62	128	−11	9
	z_r	5	10	20	50	−27	72	−29	6	−4
	$\cos\theta$	0	0.6	1	−3	0			−59	0
	LAI	0.1	0.5	1	−4	6			−46	30
	Γ_{st}	5	15	25					10	−10
	Γ_g	5	15	22					5	−3
Hg species related	α and β (GOM)	2	5	10	−38	39				
	f	0	0.3	0.6			−83	83		

following the Clausius–Clapeyron equation for temperature dependence (Wright and Zhang 2015):

$$\chi_{st/g} = \frac{\lambda_1}{T_{st/g}}\Gamma_{st/g} \exp\left(-\frac{\lambda_2}{T_{st/g}}\right) \tag{36}$$

where T_{st} and T_g are the stomatal and ground temperatures (°C), respectively; Γ_{st} and Γ_g are the stomatal and ground emission potentials, respectively, which are dependent on LUC and can be found by LUC in Wright and Zhang (2015); and λ_1 and λ_2 are two constants valued at 7.3675×10^{13} and 8353.8, respectively.

Sensitivities of Dry Deposition Velocities to Key Parameters

Among the numerous parameters in the dry deposition schemes mentioned above, the dry deposition velocities for speciated atmospheric Hg are sensitive to a number of key ones. Sensitivity analysis was performed in this study based on the responses of GOM, PBM, and GEM dry deposition velocities to the changes of key parameters from typical values to the common variation ranges (from minimum to maximum). More details on the methods and quality control for the sensitivity analysis are available in Section S2 in the SI. The contribution of key parameters to v_d can be identified. Results of the sensitivity analysis are shown in Table 1. It should be noted that the sensitivities of v_d to key parameters are not equivalent to the uncertainties of v_d since the variation ranges of the parameters are not the same as the uncertainty ranges of them.

The dry deposition velocity of GOM is most sensitive to the wind speed (u_r) through its impact on u_* and consequently R_a, R_b, R_{ac}, and R_{cut}. The parameter u_r is an indicator of the turbulence condition of atmosphere. Strong atmospheric turbulence favors dry deposition of gaseous substances since they are more easily transported to the surface. This is consistent with a previous observational study at two sites in North America where GOM dry deposition fluxes was found to be the highest in spring with the highest mean wind speeds (Gustin et al. 2012). For land use related parameters, v_d for GOM is also quite sensitive to z_0 and z_r through the same influencing pathway as u_r. Among all the meteorological factors, RH is another important parameter for GOM dry deposition velocity besides wind speed, while air temperature causes considerable sensitivity only when it is below zero. The stomatal resistance was affected by RH through the function of water vapor pressure deficit (f_D) using an empirical equation (Brook et al. 1999). High RH leads to low R_c. Air temperature is the key parameter for f_T which indicates the conductance-reducing effects of T. Complete stomatal closure occurs if T was below 0°C or above 45°C (Zhang et al. 2003), and R_{st} would then substantially increase. The two scaling factors (α and β) are highly uncertain, which could cause approximately ±40% variation in the estimation of GOM dry deposition velocity according to the sensitivity analysis. These two parameters are probably the main source of uncertainty in the estimation of v_d for GOM.

The dry deposition velocity of PBM is most sensitive to u_r, z_0, and z_r through their impacts on u_* and consequently R_a and R_s. The friction velocity u_* is crucial to both R_a and R_s, which leads to the much more important role in the calculation of v_d for PBM than for GOM. The PBM dry deposition velocity is also significantly sensitive to the mass fraction of PBM in coarse particles (f), which is probably the main source of uncertainty in the estimation of v_d for PBM since f is usually unknown during model simulation.

Table 2 Variations of dry deposition velocities for speciated Hg by LUC compared to the median values of v_d for all the land use types

LUC	Value of v_d (cm s^{-1})			Variation of v_d (%)		
	GOM	PBM	GEM	GOM	PBM	GEM
Evergreen broadleaf trees	1.63	2.64	0.083	70	126	4
Evergreen needleleaf trees	1.35	1.41	0.079	41	20	−1
Deciduous broadleaf trees	0.96	1.22	0.080	0	4	0
Deciduous needleleaf trees	1.19	1.17	0.077	24	0	−3
Tropical broadleaf trees	1.89	3.43	0.086	97	192	7
Drought deciduous trees	0.65	1.13	0.062	−32	−4	−23
Evergreen broadleaf shrubs	0.76	0.72	0.076	−21	−39	−6
Deciduous shrubs	0.72	0.61	0.087	−25	−48	9
Thorn shrubs	0.81	0.72	0.066	−15	−39	−17
Short grass and forbs	0.72	0.45	0.072	−25	−61	−10
Urban	1.26	1.50	0.080	31	28	0
Tundra	0.93	0.42	0.036	−3	−64	−54
Swamp	0.83	0.58	0.086	−13	−51	7
Mixed wood forests	1.16	1.27	0.092	20	8	15
Transitional forest	1.15	1.27	0.089	20	8	11
Median values[a]	0.96	1.17	0.080			

[a]To prevent the influence of high values, median values were used as the baseline instead of arithmetic mean values

The dry deposition velocity of GEM is most sensitive to air temperature. Responses of v_d for GEM to the minimum and maximum values of the common variation range both go negative because the impact of T takes effect through f_T and consequently R_{st}. Stomatal closure occurs at both high and low temperatures. The dominant influence of T on GEM dry deposition velocity needs extra attention, especially in high-temperature conditions. GEM would turn from deposition to reemission when T approaches 40°C. With more frequent extreme temperatures occur in the future because of global climate change, GEM dry deposition as an important sink of Hg would decrease, and the global Hg cycling would change gradually. Among the meteorological factors, RH and u_r are important parameters for GEM dry deposition velocity besides air temperature. The solar zenith angle (θ) and LAI also have considerable impacts on GEM dry deposition velocity. The temporal profile of LAI is probably the main source of uncertainty in the estimation of v_d for GEM. However, it should be noted that v_d for GEM could be quite sensitive to the emission potentials Γ_{st} and Γ_g when the net GEM dry deposition flux is close to zero (Zhang et al. 2019).

Besides the land cover related parameters, LUC itself also has a significantly impact on the dry deposition velocities for speciated Hg. Table 2 shows the variations of GOM, PBM, and GEM dry deposition velocities by LUC compared to the median values of v_d for all the land use categories. The v_d values for GOM are close to the common range summarized by Wright et al. (2016) but much lower than those reported by Zhang et al. (2009), which is due to the choice of typical wind speed and scaling factors (α and β) for GOM. The v_d values for PBM are much higher than those reported by Wright et al. (2016) because the contribution of Hg on coarse particles was considered in this study. The v_d values for GEM are close to the common range reported by Zhang et al. (2009). Tropical and evergreen broadleaf trees have significantly higher values of v_d for PBM and GOM than the average levels. The impact of LUC on v_d for PBM takes effect mainly through the surface roughness length scale (z_0), while the impact of LUC on v_d for GOM is highly related to the parameter R_{ac0} according to sensitivity analysis. The dry deposition velocity of GEM is not sensitive to LUC except for tundra where leaf water potential (ψ) plays a key role. Mixed wood forests have the highest v_d for GEM, which is also related to the values of ψ. LUC change is an important strategy to cope with climate change. Concerns on the change of land use should be raised for Hg dry deposition estimation.

Summary and Research Needs

This study summarized the detailed methodology for the estimation of speciated Hg dry deposition fluxes, and performed sensitivity analysis to identify the key parameters and pivotal sources of uncertainties for speciated Hg dry deposition velocities. Uncertainty of the GOM dry deposition flux mainly originates from the bias in GOM concentration measurements by the Tekran system and the choice of two scaling factors (α and β) for the dry deposition velocity of GOM. The dry deposition velocity of PBM is sensitive to meteorological factors, but the main source of uncertainty in the estimation of v_d for PBM is the mass fraction of PBM in coarse particles (*f*). The dry deposition velocity of GEM is most sensitive to air temperature. The uncertainty of the GEM dry deposition flux grows fast when it gets close to zero.

Based on this review work, future research needs are recommended as follows:

(1) More comprehensive correction methods for GOM concentration measurements by the Tekran system need to be developed for better estimation of GOM dry deposition fluxes. Different chemical forms of GOM could have distinguishing scaling factors (α and β) for the estimation of v_d for GOM (Lyman et al. 2007). Experimental studies on the quantification of the two scaling factors for different GOM species are in need.

(2) Since the mass fraction of PBM in coarse particles contributes most uncertainty to the estimation of v_d for PBM, the size-resolved Hg concentration on particles and its influencing factors need to be further investigated. Dynamic values of v_d for PBM are recommended with particle size distribution considered.

(3) GEM dry deposition flux is sensitive to air temperature, and the relationship is subject to other meteorological factors (e.g., solar radiation) and land cover parameters (e.g., soil moisture) (Zhu et al. 2016). More observational studies on the dry deposition flux of GEM are needed to improve the bidirectional air–surface exchange scheme for the estimation of GEM dry deposition velocity.

(4) CTMs could be improved using new parameterization schemes for estimation of dry deposition velocities for speciated Hg and other air pollutants, and uncertainties of deposition flux simulation in CTMs could be evaluated based on sensitivity analysis as conducted in this study.

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