Supporting Information for Estimation of Dry Deposition of Atmospheric Mercury in Nevada by Direct and Indirect Methods

Seth N. Lyman, Mae Sexauer Gustin, Eric M. Prestbo, Frank J. Marsik

6 pages of text, no figures, no tables

Detailed Site Descriptions.

NV02- Soil is loam with mercury concentrations of $56 \pm 53 \,\mu g \, kg^{-1}$ (mean \pm standard deviation). Concentrations of atmospheric mercury species were measured at 3 m during the spring, summer, and fall field campaigns and at 1.5 m during the winter field campaign due to a change in field equipment availability. Wind measurements were collected at 3 m.

NV99- Soil is loam to sandy loam with mercury concentrations of $32 \pm 13 \,\mu g \,kg^{-1}$. Concentrations of mercury species were measured at 1.5 m, and wind measurements were collected at 3 m.

DRI- Soil is stony loam with a mean mercury concentration of 78 μg kg⁻¹ (average of two samples). Measurements of mercury species were collected atop a 20 m tower on the western edge of the DRI building complex. Wind measurements were collected at a developed weather station at 15 m on a rooftop at the east end of the building complex.

Details of Speciation System Operation and Quality Control Procedures. The flow rate into the Tekran Model 2537A analyzer was 1 L min⁻¹, and the total flow through the denuder and quartz filter assembly was 7 L min⁻¹. These flow rates were lower than suggested by Landis et al. (15), and were applied at the recommendation of Tekran personnel to adjust for altitude effects on instrument mass flows. The lower flow rate does not affect denuder performance, but it does increase the aerodynamic diameter cut point of the impactor from 2.5 to 3.0 μ m (26). Sampling time was 5 minutes for Hg⁰ and 2 hours for RGM and Hg_p. The system inlet, tubing, glassware, and other components

were cleaned or replaced regularly. Quartz annular denuders were cleaned and coated with KCl as described in Landis et al. (15), and fresh denuders were installed at the beginning of each field campaign at NV02 and NV99 and every three weeks at DRI. Particulate filter assemblies were packed with new quartz filter disks on the same schedule. The Model 2537A was set to automatically calibrate every 24 hours using its internal mercury permeation source. Calibration checks were performed at the beginning and end of each field campaign and at least once per week at DRI by injecting a known amount of gaseous mercury into ambient air being sampled by the Model 2537A.

The 2537A analyzer quantifies total gaseous mercury (TGM) and operationally defined Hg⁰, RGM, and Hg_p when the unit is operated with the speciation system, and has a detection limit of <0.1 ng m⁻³ (27, 28). Mercury collected by in the denuder or particulate assembly is transported into the 2537A unit in mercury free air. During summer months (June through September), the detection limit, calculated as three times the standard deviation of the speciation system blank measured before and after each RGM and Hg_p analysis, was 5 pg m⁻³. During all other months the blank measurements were 0 pg m⁻³. It is thought that the seasonal difference in blanks is due to high temperatures in the summer, which may have caused mercury to be mobilized from the sampling/analytical line. Thus the level of quantitation, or that constituent concentration that produces a signal sufficiently greater than the blank (29), varies according to operating and atmospheric conditions. Detection limits reported for two recent studies were 0.88 and 1.6 pg m⁻³ (30 and 31, respectively).

Before and after each simultaneous deployment of mercury speciation systems, both systems were operated at the same location and set to sample the same air for several days to determine inter-system precision. TGM was measured during each of the comparative experiments, and Hg^0 , RGM, and Hg_p were measured in October and January. The Model 2537A used for mercury soil flux was also collocated and sampled the same air during these periods. Based on these experiments, relative instrument drift from the beginning to the end of field campaigns was quantified, and field data were adjusted using the percent change over this time. Average TGM relative percent difference among instruments during all comparative experiments was $7.0 \pm 5.3\%$. RGM and Hg_p were both below instrument detection limits during the January comparative experiments, but in October relative percent difference was $7.2 \pm 37.7\%$ and $41.4 \pm 62.1\%$, respectively (n = 19 two hour measurements). The discrepancy between replicate Hg_p measurements was possibly due to the low concentrations in air. In a separate comparative experiment at DRI, relative percent difference between systems for RGM was $6.1 \pm 28.1\%$ (n = 10).

Model Details.

RGM Dry Deposition Model- RGM was modeled using the method of Zhang et al. (20), which does not explicitly outline a technique for calculating R_a (aerodynamic resistance) or R_b (quasi-laminar sublayer resistance). In this study, R_a was calculated from measurements of wind speed and standard deviation of wind direction by the equations $R_a = 4/[u\sigma_\theta^2] \text{ (neutral and stable conditions)}$ and

 $R_a = 9/[u\sigma_\theta^2]$ (unstable conditions)

where u is wind speed and σ_{θ} is standard deviation of wind direction (32). As suggested by Meyers et al. (33), the atmosphere was assumed to be unstable when global radiation exceeded 100 W m⁻². Standard deviation of wind direction was calculated by the equation

$$\sigma_\theta = sin^{\text{-}1}(\epsilon)[1.0 + 0.1547\epsilon^3]$$

where

$$\varepsilon^2 = 1 - (s_a^2 + c_a^2),$$

 s_a is the average sine of wind direction, and c_a is the average cosine of wind direction (34). R_b was calculated by the equation

$$R_b = (2/ku*)(Sc/Pr)^{2/3}$$

where k is the von Karman constant (0.4), u_* is the friction velocity, Sc is the Schmidt number, and Pr is the Prandtl number for air (0.72) (32). The Schmidt number is the kinematic viscosity of air divided by the diffusivity of a gas of interest. The diffusivity of RGM was estimated from the square root of the ratio of the molecular weights of water and HgCl₂ as outlined by Wesely (35). Friction velocity (u_*) was calculated from the equation

$$\mathbf{u} * = \left(u / \mathbf{R}_{\mathbf{a}} \right)^{1/2}$$

as inferred from Hicks et al. (32).

 R_c was calculated as described in Zhang et al. (20). Land use category 10 (evergreen broadleaf shrubs) was chosen because all study sites consisted predominantly of sage, rabbitbrush, and other evergreen shrub species. Leaf area index was estimated at 0.75 for NV99 and 0.50 for NV02 and DRI(36). Leaf angle distribution was assumed to be spherical. The model calculates R_c from the equation

$$1/R_c = (1 - W_{st})/(R_{st} + R_m) + 1/R_{ns}$$

where

$$1/R_{\rm ns} = 1/(R_{\rm ac} + R_{\rm g}) + 1/R_{\rm cut}$$

and W_{st} is a stomatal wetness parameter, R_{st} is stomatal resistance, R_m is mesophyll resistance, R_{ns} is non-stomatal resistance, R_{ac} is in-canopy aerodynamic resistance, R_g is ground resistance, and R_{cut} is cuticle resistance. R_m was given a value of zero for RGM, as suggested in Zhang et al. (23) for species with high solubility. R_g and R_{cut} are scaled from land use category-dependent values for O_3 and SO_2 by the equation

$$1/[R_x(i)] = \alpha(i)/[R_x(SO_2)] + \beta(i)/[R_x(O_3)]$$

where $R_x(i)$ is R_g or R_{cut} for gaseous species i, $R_x(SO_2)$ is R_g or R_{cut} for SO_2 , $R_x(O_3)$ is R_g or R_{cut} for O_3 , and $\alpha(i)$ and $\beta(i)$ are scaling parameters for species i. Because of their contrasting chemical properties, O_3 and SO_2 are convenient compounds from which to scale resistances of other species (23, 35). The scaling parameters α and β depend on the species being modeled, and Zhang et al. (23) provide scaling parameters for a number of gaseous species. They also outline a method for choosing scaling parameters for any chemical species of interest based on the effective Henry's Law constant (H*) and the negative log of electron activity for half-redox reactions in neutral solutions [pe⁰(W)]. In this study, H* for HgCl₂ and Hg(OH)₂ were calculated using available data (5, 37). For calculation of H* for HgCl₂, [ClT] was assumed to be 0.2 mg L⁻¹, a typical value for continental rainwater (38). pe⁰(W) was calculated for the half-redox reaction

$$Hg^{2+}_{aq} + 2e^{-} \leftrightarrow Hg^{0}_{l}$$

using the equation

$$Pe^{0}(W) = (1/n)[\log_{10}(K)] - 7n_{H}$$

given in Zhang et al. (23), where n is the number of electrons in the half-reaction, K is the equilibrium constant of the reduction half-reaction, and n_H is the number of protons exchanged per electron in the half-reaction. K was calculated from values of Gibbs free energy of formation (39). The calculated values for H* and pe⁰(W) were used to compare RGM to gaseous species listed in Zhang et al. (23), and, based on evident similarity, the scaling parameters listed for nitrous acid (HONO) were used to scale R_g and R_{cut} for RGM ($\alpha = \beta = 2$).

 Hg_p Dry Deposition Model- The model described in Zhang et al. (14) was used to infer Hg_p deposition. R_a and u_* were calculated as described above, and land use category 10 (shrubs and interrupted woodlands) was used. A particle diameter of 0.68 μ m (13) and a density of 1.5 g cm⁻³ were assumed.