

MODELING OF MERCURY EMISSION, TRANSPORT AND DEPOSITION IN NORTH-EASTERN NORTH AMERICA

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1. INTRODUCTION

Mercury (Hg) emission into the environment is a major concern because it is toxic, persistent and bio-accumulative, thus posing risks to human health. Hg is emitted into the atmosphere from both anthropogenic and natural sources. The latter also include previously deposited anthropogenic Hg.

After the Amendments to the 1990 U.S. Clean Air Act identified Hg as a hazardous air pollutant, models have been developed to understand its behaviour in the atmosphere (Petersen et al., 1998). Many of these, however, either ignore or oversimplify natural Hg emission. Recently, attempts have been made to develop detailed treatments of natural Hg emission from vegetation, water and soil. For example, Xu et al. (1999) developed a description of the bi-directional atmosphere-surface exchange of elemental Hg, which was then incorporated into the Sarmap Air Quality Model (SAQM). Also, Bullock and Brehme (2002) added Hg chemistry and transport processes to the US EPA's Community Multi-scale Air Quality (CMAQ) model (Byun and Ching 1999). The latter, however, did not consider natural Hg emission.

We have developed a natural Hg emission model, which was combined with anthropogenic emissions and then combined with the Bullock and Brehme CMAQ-Hg model, to simulate Hg behaviour in the north-eastern part of North America.

2. METEOROLOGY

The meteorology model used in this work is the version 3.6 of the PSU/NCAR MM5 model. The Land Surface Model (LSM) used with MM5 is the PX LSM model with indirect soil moisture nudging (Xiu and Pleim 2001). The PX LSM includes explicit simulation of soil moisture and temperature in two layers (surface - 1 cm and root zone - 1 m).

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3.0 DEVELOPMENT OF NATURAL MERCURY EMISSION MODEL

Mercury is emitted in three major forms: elemental Hg (Hg^0), reactive gaseous Hg (RGM) and particulate Hg (PHg). Naturally emitted Hg is predominantly Hg^0 . Natural Hg emissions were modelled for three major sources: vegetation, soil and water.

3.1 Emission from Vegetation

Mercury flux measurements over vegetation have indicated that foliar emission of Hg is more significant than emission from soil or water. Hg emissions from plants are considered to be transported through the transpiration stream. Hg has been collected in transpiration fluid (Khozhina et al. 2001). It has been suggested (Hanson et al. 1995; Leonard et al. 1998) and also observed that Hg emissions from vegetation are related to the transpiration rates (Lindberg 2002). Equation (1) is used to estimate Hg transpiration from vegetation canopy (Xu et al. 1999).

$$F_c = E_c C_s \quad (1)$$

where, F_c is the Hg^0 flux (units of $\text{ng m}^{-2} \text{s}^{-1}$), E_c is the canopy transpiration (m s^{-1}), and C_s is the concentration of Hg^0 in the surface soil solution (ng m^{-3}). E_c was calculated using a simplified canopy-atmosphere model (SCAM) (Raupach 1991) based on the Penman-Monteith equation (Monteith and Unsworth 1990). The SCAM model uses meteorological parameters (solar radiation, vapour pressure, wind speed) and canopy characteristics (height, albedo, and canopy resistance) to calculate the transpiration rate. In contrast to Xu et al. (1999) who treated canopy resistance as a function of soil moisture only, we used the approach found in Noilhan and Planton (1989), where canopy resistance (R_c), was calculated as,

$$R_c = \frac{R_{s\min}}{LAI} F_1 F_2^{-1} F_3^{-1} F_4^{-1} \quad (2)$$

F_1 is the effect of photosynthetically active radiation. It is given by

$$F_1 = \frac{1 + 0.55 \frac{R_G}{R_{GL}} \frac{2}{LAI}}{0.55 \frac{R_G}{R_{GL}} \frac{2}{LAI} + \frac{R_{smin}}{R_{smax}}} \quad (3)$$

R_{smin} is the minimum stomatal resistance, R_G is the solar radiation, R_{GL} has a value of 30 W m^{-2} for a forest and 100 W m^{-2} for a crop. R_{smax} is taken as 5000 s m^{-1} . LAI is leaf area index.

F_2 takes into account the effect of water stress

$$\begin{aligned} F_2 &= 1, & \text{if } q > q_{cr} \\ F_2 &= \frac{q - q_{wilt}}{q_{cr} - q_{wilt}} & \text{if } q_{wilt} \leq q \leq q_{cr} \\ F_2 &= 0 & \text{if } q < q_{wilt} \end{aligned} \quad (4)$$

θ_{cr} is the moisture content (θ) below which transpiration is stressed by soil moisture. This is assumed to be 0.75 times the saturated soil moisture (θ_{sat}), which is set as 0.4. The wilting point (θ_{wilt}) is set to 0.1. Xu et al. (1999) used constant soil moisture for the whole domain but we used the values obtained from MM5 simulations.

F_3 represents the effect of the vapour pressure deficit (δq) and is given by

$$F_3 = 1 - 0.12(\delta q) \quad (5)$$

F_4 represents the effect of air temperature (T_a) and is given by

$$F_4 = 1 - 0.0016(298 - T_a)^2 \quad (6)$$

In contrast to the work of Xu et al. (1999), where transpiration (or Hg^0 emission) was assumed to be zero when there is rain, we multiplied the transpiration rate (E_c) by a factor α given by (Mo et al. 2004)

$$\alpha = 1 - W_{fr} \quad (7)$$

W_{fr} (the wetted fraction of the canopy) is given by

$$W_{fr} = \left(\frac{(1 - \exp(-0.5LAI))p}{0.2LAI} \right)^{2/3} \quad (8)$$

where, p (mm) is the precipitation above the canopy.

The concentration of Hg^0 in soil water was assumed to be constant in any location in the work of Xu et al. (1999). Lin and Tao (2003), however, based the concentration on the closeness of that location to anthropogenic RGM and PHg emission sources. We assumed the Hg^0 in the transpiration stream to be dependent on the total Hg concentration in the soil. We obtained data on soil Hg concentration measured at 20 cm, or the B horizon for the United States from Boerngen and Shacklette (1981). For Canada, we assigned a value to various locations in our domain to produce a data density similar to that of the US. The value assigned corresponded to the median of Hg measurements done by the Geological Survey of Canada for Southern Ontario. The data were gridded over our domain to produce a Hg distribution similar to that reported in Gustavsson et al. (2001). We then

obtained total Hg soil water concentration from soil Hg concentration using a soil–water partition coefficient of 0.25 g/L calculated from data in Lyon et al. (1997). The total concentration of Hg in soil water was used as the concentration of Hg in the transpiration stream, since plants are known to reduce dissolved oxidized Hg species (Rugh et al. 2000). Laboratory experiments by Leonard et al (1998) showed that about 70 % of Hg taken up by roots was emitted into the atmosphere. Recent experiments by Schwesig and Krebs (2003) indicated that 70 to 94% of Hg loss from the soil of potted plants was due to volatilization from both soil and plant, but the contribution from each source was unknown.

3.2 Emission from Soil

Hg emission from soil can be classified into emission from bare soil and emission from soil under vegetation canopy.

For emission from bare soil, we extended the common flux-temperature relationship to include Hg concentration in soil. The Hg flux from soil (F_s) can be expressed as:

$$F_s = k[\text{Hg}]_s^n \quad (9)$$

where, k is a rate constant and $[\text{Hg}]_s$ is Hg soil concentration. Equation (9) can be simplified to obtain:

$$\ln F_s = -\frac{\beta}{T_s} + n \ln[\text{Hg}]_s + g \quad (10)$$

where, β and γ are constants and T_s is the soil temperature. β is a measure of the activation energy. We obtained a value of $12,589 \text{ K}^{-1}$ for this from Xu et al. (1999). Using additional data on Hg flux for different $[\text{Hg}]_s$ (Carpi and Lindberg 1998; Frescholtz and Gustin 2004), we obtained n as 1.0 and γ as 38.67.

Emission from soil under a canopy was neglected in previous work. Since a large part of our domain is forested, we included emission from beneath the canopy, based on a Hg flux-solar radiation relationship, since solar radiation was found to correlate better with Hg flux from soils under a canopy (F_{sc}) than temperature. From Carpi and Lindberg (1998),

$$\log F_{sc} = 0.0013R_{Gc} + 0.3 \quad (11)$$

R_{Gc} , the solar radiation reaching the soil under the canopy, is given as:

$$R_{Gc} = R_G e^{-\lambda LAI} \quad (12)$$

The value for λ is taken to be 0.65 (Monteith and Unsworth 1990).

3.3 Emission from Water

Emission flux of Hg^0 from water (F_w) is given by

$$F_w = K_w C_w \quad (13)$$

where, K_w is the mass transfer coefficient and C_w is the concentration of dissolved gaseous mercury (DGM) in the water. We used the approach shown in Lin and

Tao (2003) to calculate K_w . In Xu et al. (1999), one value was used for C_w . A number of reports indicate that the concentration of DGM in water follows a diurnal pattern. The concentration of DGM (C_w , pg L^{-1}) has been found to correlate with time-shifted solar radiation (R_G , kW m^{-2}) (Driscoll et al. 2003).

$$C_w = aR_{G(t \text{ min prior})} + b \quad (14)$$

The optimum time, t was found to be 75 minutes ($R = 0.9$). We used a time of 60 minutes since we have 60 minute meteorology time steps and also the correlation observed by the authors was good for $t = 60$ minutes ($R = 0.85$). Measurements indicate that concentration of DGM in the great lakes is usually higher ($20\text{-}130 \text{ pg L}^{-1}$) than that in the ocean ($10\text{-}50 \text{ pg L}^{-1}$). Therefore, for lakes we used $a = 13$ and $b = 82$ (Driscoll et al. 2003) and for the ocean we used $a = 10$ and $b = 40$.

4. ANTHROPOGENIC MERCURY EMISSIONS

Anthropogenic Hg emission data for US and Canada for 1995/96 were obtained from the Ontario Ministry of the Environment. The US data was already speciated into Hg^0 , RGM and PHg. The Canadian point source emission data was speciated using speciation profiles in Pacyna and Pacyna (2002), according to the source category. For the area and mobile source emissions, an average speciation profile was used. The anthropogenic emissions were processed using SMOKE1.4 to generate gridded emission for CMAQ 4.2.

5. SIMULATION CONDITIONS

Our modeling domain (Fig. 1) is 50×42 grid squares with a grid size of 36 km and 15 vertical layers. For this trial simulation, the modeling period covers June 17 to July 18, 1995. We first ran MM5, followed by MCIP. We included the natural emission algorithms into MCIP to generate the natural Hg emissions. The natural and anthropogenic emissions were merged using SMOKE. The CMAQ-Hg model used, including the initial and boundary conditions is the same as that given by Bullock and Brehme (2002), except for the dry deposition velocity of Hg^0 and RGM which was calculated by incorporating the physical properties of the Hg species into MCIP. We modeled the following scenarios: (S1) - omitting natural emissions; (S2/S3) - varying natural emissions by $\pm 50\%$; (S4) - reducing anthropogenic emissions by 50% and (S5) - turning off Canadian anthropogenic Hg emissions.

6. RESULTS AND DISCUSSION

The average natural Hg emission for the simulation period is shown in Figure 1. The distribution is dependent on meteorology and soil Hg. The Hg flux from vegetation ranged between 0 and $40 \text{ ng m}^{-2} \text{ h}^{-1}$ depending on the location and time. The maximum emission flux from water and soil was generally less than $10 \text{ ng m}^{-2} \text{ h}^{-1}$. The range of emission fluxes

obtained is reasonable when compared with field measurements. The natural Hg emission for the simulation period was about 55% of the total emission.

Modeled Hg air concentration and wet deposition values were similar to measurements as shown in Figure 2.

When natural Hg emissions are neglected (S1), air concentrations are significantly under predicted (Fig. 3). A decrease in the natural emission estimate by 50% (S3) caused more decrease in the air concentration than a 50% decrease in anthropogenic emissions (S4).

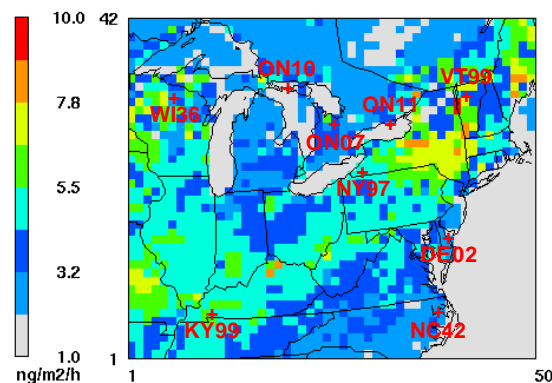


Fig. 1. Average natural Hg emission flux from June 17 to July 18, 1995 in our domain. Monitoring sites used for model comparison with measurements are indicated.

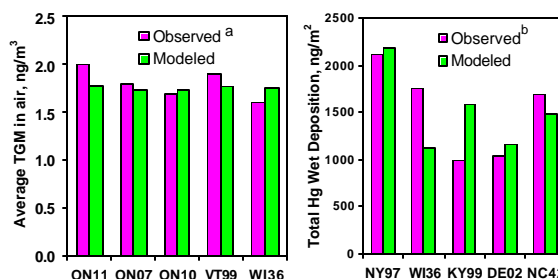


Fig. 2. Measured and modeled average Total Gaseous Mercury (TGM) and wet deposited Hg from June 20 to July 18, 1995. (a) long-term averaged values compiled by Lin and Tao (2003), (b) mercury deposition network.

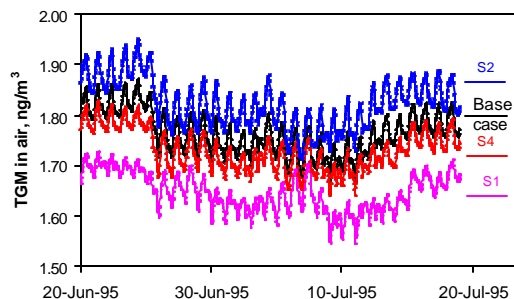


Fig. 3. Hourly mercury concentration averaged over the whole domain for different scenarios.

However, S4 led to a greater decrease in wet deposition than S3. These results are due to the speciation differences between natural and anthropogenic Hg emissions. S5 did not result in any significant change in Ontario air concentrations, which are dominated by long range transport and high natural Hg emissions.

7. CONCLUSION

We have incorporated a detailed natural emission model into the CMAQ-Hg model and used it to study Hg behaviour in the north-eastern US. Modeled natural Hg emission rates, air concentration and wet deposition values were close to measurements. Exclusion of natural emission was found to underestimate Hg air concentrations and dry deposition, but did not lead to a significant decrease in wet deposition.

The model is limited by current information on Hg, especially with respect to natural Hg emissions.

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REFERENCES

- Boerngen, J. G. and Shacklette, H. T., 1981: Chemical analyses of soils and other surficial materials of the conterminous United States. *U.S.G.S. Open-File Report 81-197*, 143 p.
- Bullock, O. R. and Brehme, K. A., 2002: Atmospheric mercury simulation using the CMAQ model: formulation description and analysis of wet deposition results. *Atmos. Environ.*, **36**, 2135-2146.
- Byun, D. W. and Ching, J. K. S., 1999: Science algorithms of the EPA models -3 community multiscale air quality (CMAQ) modeling system, *EPA-600/R-99-030*, US Environmental Protection Agency.
- Carpi, A. and Lindberg, S., 1998: Application of a Teflon dynamic flux chamber for quantifying soil mercury flux: Tests and results over background soil. *Atmos. Environ.*, **32**, 873-882.
- Driscoll, N., Beauchamp, S., Siciliano, S., Rencz, A. and Lean, D., 2003: Continuous analysis of dissolved gaseous mercury (DGM) and mercury flux in two freshwater Lakes in Kejimikujik Park, Nova Scotia: Evaluating mercury flux models with quantitative data. *Environ. Sci. Technol.*, **37**, 2226-2235.
- Frescholtz, T. and Gustin, M., 2004: Soil and foliar mercury emission as a function of soil concentration. *Water, Air, and Soil Pollution*, **155**, 223-237
- Gustavsson, N., Bølviken, B., Smith, D. B. and Severson, R. C., 2001: Geochemical landscapes of the conterminous United States. New map presentations for 22 elements. *U.S.G.S. Professional Paper 1648*, 38 p.
- Hanson, P.J., Lindberg, S.E., Taberer, T.A., Owens, J.G., and Kim, K.-H., 1995: Foliar exchange of mercury vapor: evidence for a compensational point. *Water, Air and Soil Pollution*, **80**, 373-382.
- Khozina, E. I., Paleskii, S. V. and Saprykin, A. I., 2001: Migration of heavy metals into the atmosphere in the process of transpiration. *Atmos. Oceanic Opt.*, **14**, 553-556.
- Leonard, T.L., Taylor Jr., G.E., Gustin, M.-S. and Fernandez, G.C.J., 1998: Mercury and plants in contaminated soils: 1. Uptake, partitioning, and Emission to the Atmosphere. *Environmental Toxicology and Chemistry*, **17**, 2062-2071.
- Lin, X. and Tao, Y., 2003: A numerical modelling study on regional mercury budget for eastern North America, *Atmos. Chem. Phys.*, **3**, 535-548.
- Lindberga, S. E., Donga, W., and Meyers, T., 2002: Transpiration of gaseous elemental mercury through vegetation in a subtropical wetland in Florida. *Atmos. Environ.*, **36** 5207-5219.
- Lyon, B., Ambrose, R., Rice, G. and Maxwell, C., 1997: Calculation of soil-water and benthic sediment partition coefficients for mercury, *Chemosphere*, **35** 791-808.
- Mo, X., Liu, S., Lin, Z., and Zhao, W., 2004: Simulating temporal and spatial variation of evapotranspiration over the Lushi basin. *Journal of Hydrology*, **285**, 125-142.
- Monteith, J. L. and Unsworth, M. H., 1990: *Principles of Environmental Physics*. Edward Arnold, London.
- Noilhan, J. and Planton, S., 1989: A simple parameterization surface processes for meteorological models. *Monthly Review*, **117**, 536-549.
- Pacyna, E. and Pacyna, J., 2002: Global emission of mercury from anthropogenic sources in 1995. *Water, Air, and Soil Pollution*, **137**, 149-165.
- Petersen, G., Munthe, J., Pleijel, K., Bloxam, R. and Kumar, A., 1998: A comprehensive Eulerian modeling framework for airborne mercury species: Development and testing of the Tropospheric Chemistry Module (TCM). *Atmos. Environ.*, **32**, 829-843.
- Raupach, M. R., 1991: Vegetation-atmosphere interaction in homogeneous and heterogeneous terrain: some implication of mixed-layer dynamics. *Vegetatio*, **91**, 105-120.
- Rugh, C., Bizily, S. and Meagher, R., 2000: Phytoreduction of environmental mercury Pollution, in, *Phytoremediation of Toxic metals: Using Plants to Clean up the Environment*, by Raskin I. and Ensley B. (eds.), John Wiley and Sons, NY.
- Schwesig, D. and Krebs, O., 2003: The role of ground vegetation in the uptake of mercury and methylmercury in a forest ecosystem. *Plant and Soil*, **253**, 445-455.
- Xiu, A. J. and Pleim, J. E., 2001: Development of a land surface model. Part I: Application in a mesoscale meteorological model. *J. Appl. Meteor.*, **40**, 192-209.
- Xu, X., Yang, X., Miller, D. R., Helble, J. J. and Carley, R. J., 1999: Formulation of bi-directional atmosphere-surface exchanges of elemental mercury. *Atmos. Environ.*, **33**, 4345-4355.